Arabian Journal for Science and Engineering (2021) 46:7057–7085
https://doi.org/10.1007/s13369-021-05408-x

REVIEW-MECHANICAL ENGINEERING

Influence of Higher Alcohol Additives in Methanol–Gasoline Blends on the Performance and Emissions of an Unmodified Automotive SI Engine: A Review

Bhavin K. Bharath[1] · **V. Arul Mozhi Selvan**[1]

Received: 13 October 2020 / Accepted: 28 January 2021 / Published online: 23 February 2021

Abstract

More stringent emission norms are implemented all over the world to protect the environment from vehicular pollution. Biofuels are one of the best alternative solutions to reduce cost and environmental pollution. Among many alternate fuels, alcohol is a leading fuel used in automotive spark-ignition engines in pure or blended form. The capability of methanol to substitute gasoline has been known for a long time. This paper aims to systematically review methanol–gasoline blend with higher alcohol additives (ternary blends) as a transportation fuel in unmodified automotive spark-ignition engines. This review summarizes the previous research in methanol–gasoline blends with and without additives on spark-ignition engines' performance and emission characteristics. Many researchers found that methanol–gasoline blended fuels improve engine performance and emissions. Generally, alcohols burn very effectively and produce only fewer emissions compared to gasoline. Still, lower alcohol may cause some problems such as increased specific fuel consumption, phase separation and corrosion. These problems are further optimized using higher alcohol additives through improved energy content, kinematic viscosity, corrosion resistance, water tolerance and phase stability. Several research studies have been carried out in the past years, which focused mainly on single alcohol blended fuels for spark-ignition engines. Thus, a comprehensive survey of performance, combustion and emission characteristics of methanol–gasoline blended fuel with higher alcohol additives is necessary to show the potential of ternary blends in automotive engines.

Keywords Alcohol additives · Emission · Methanol–gasoline blend · Performance · Spark-ignition engine

Abbreviations

SI	Spark ignition
SFC	Specific fuel consumption
NO_x	Nitrogen oxides
SO_x	Sulfur oxides
PM	Particulate matter
DME	Dimethyl ether
BASF	Badische anilin und soda fabrik
ICI	Imperial chemical industries process
EU	European Union
CCS	Carbon capture and storage
CO_2	Carbon dioxide
CO	Carbon monoxide
H_2	Hydrogen
HC	Hydrocarbon
ATR	Autothermal reforming
SR	Steam reforming
MTBE	Methyl tertiary-butyl ether
GDI	Gasoline direct injection
MON	Motor octane number
RON	Research octane number
NITI	National Institution for Transforming India
ASTM	American Society for Testing and Materials
LHOV	Latent heat of vaporization
LHV	Lower heating value
PST	Phase separation temperature
TAME	Tert-amyl methyl ether
VOC	Volatile organic compounds
AIT	Autoignition temperature
IEO	International Energy Outlook
MT	Million tons
CH_3OH	Methanol

✉ V. Arul Mozhi Selvan
arulmozhi@nitt.edu

Bhavin K. Bharath
bhavin.bhavam@gmail.com

[1] Department of Mechanical Engineering, National Institute of Technology, Tiruchirapalli, India

MPFI	Multipoint fuel injection
iB	Isobutanol
nB	*n*-Butanol
BTDC	Before top dead center
M15	15% concentration of methanol
M100	100% concentration of methanol
nBE	*n*-Butanol–bioethanol–gasoline
iBM	Isobutanol–biomethanol–gasoline
UHC	Unburnt hydrocarbons
CR	Compression ratio
BTE	Brake thermal efficiency
EGT	Exhaust gas temperature
BSFC	Brake specific fuel consumption
η_{vol}	Volumetric efficiency
FP	Friction power
IP	Indicated power
BP	Brake power
IMEP	Indicated mean effective pressure
HRR	Heat release rate

1 Introduction

Fossil fuels are considered finite, and the world may run out of crude oil by the near future. The petroleum reserves may not sustain beyond 2050 globally [1]. Concerns over energy efficiency and energy security have sparked interest in using efficient and economical alternative fuels produced from renewable feedstock. The depletion of fossil fuel supply, increasing petroleum prices, and strict pollution regulations demand the synthesis of alternative renewable fuels for internal combustion engines [2–4]. At present, the transportation sector, mainly road transport, which uses petroleum fuel, accounts for most fuel and energy consumption and pollution around the world [5–8]. The aim to minimize the environmental effect of internal combustion (IC) engines has made many recent automotive industry changes. This is the right time to implement a sustainable development pathway to minimize its negative effect on nature. IC engines are considered obsolete, and EVs are emerging into the transport sector because they produce zero tailpipe emissions and are also expected to reduce dependence on petroleum fuels if electricity is produced from local or renewable resources [1, 9]. The present electricity generation capacity will not be sufficient to supply an entirely electric global fleet when considering the automobile transportation sector's electrification. Electric vehicles are not free from creating environmental problems. The existing conventional automobiles with IC engines will continue for the next 10–20 years; therefore, establishing alternative fuels suitable for existing automotive engines is very important to reduce the use of fossil fuel, energy consumption, exhaust emission and environmental pollution [9–11]. The main pollutants from internal combustion engine vehicles are hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_X) and particulate matters (PM) [12]. It is essential to have significant advances in the technology of alternative renewable fuels for economic and environmental sustainability [9]. Biofuels such as alcohols produced from renewable resources using any biological processes or chemical conversion biomass can be considered an attractive solution in this scenario [13–16]. The alcohol fuels can be used in present automobiles without much modification to the engine design because of the similar ignition and combustion characteristics of present fossil fuels [17, 18]. There are, however, several problems in the use of alcohol in compression ignition engines (CI). Low miscibility, high autoignition temperature, low amount of cetane, stability and weak lubricating properties are the key problems [19, 20]. So, alcohol fuels are more suitable for spark-ignition engines. Alcohols such as ethanol and methanol can improve spark-ignition engine performance with various properties such as high oxygen content, octane number, autoignition temperature, and knocking resistance [21]. Ethanol in small concentration (10% volume) is commonly used as a conventional gasoline additive for transportation fuel in the USA and many other countries [22]. Biomass-derived alcohols (bio-alcohols) are considered as future sustainable fuel for internal combustion engines [14, 23].

The automotive spark-ignition (SI) engine's performance and emissions depend on engine conditions and fuel properties. One of the main properties of the fuel which affects the engine efficiency is the octane rating. Octane rating is a degree of the fuel's resistance to knocking phenomena that lead to abnormal combustion. The alternative high octane rating fuels such as alcohols and ethers are the essential solution to improving energy efficiency and emission reduction of spark-ignition engines. Adding more oxygen to gasoline by adding oxygenate additives like alcohol allows complete combustion of the fuel and finally leads to decreased engine emissions like HC, CO, etc., and improved efficiency [24–28]. Methanol is an efficient fuel with an octane number of 100 (approximate value), which rejects lesser amounts of NO_x, sulfur oxides (SO_x), and PM [29, 30]. Manoj et al. [31] conducted a detailed study on the importance of methanol–gasoline blends in spark-ignition engines. They concluded that the methanol–gasoline blend has the potential to substitute gasoline in upcoming days.

The two main application areas of methanol are the transportation sector and industries where methanol is an alternative fuel for internal combustion engines and solvents in several processes, respectively [32]. China is the largest methanol producer globally and focuses more on methanol use in vehicles and the methanol economy [29, 33]. China is partially running its public transport vehicle in alcohol blended fuels, and they are looking toward a methanol economy. India is progressing on the development path, but the energy demand is anticipated to rise at a rate of 3.5% (Compounded Annual Growth Rate) up to 2040. According to the available data, India has imported 37% of its primary total energy demand in 2015–2016 [29]. Also, the import of crude oil and natural gas is increasing day by day. The rising imports can overcome by using methanol and its derivative dimethyl ether (DME) in different energy demand areas because methanol can be produced from various feedstock present abundantly in India. The government promotes methanol as a transport fuel, seeing the chances of converting methanol from abundant coal reserves in India and exploring biomethanol production from the available resources. The Indian government has recently implemented emission norm Bharat Stage (BS)-VI to protect the environment and human health. These emission norms encourage low-carbon fuels in the existing automobiles and various after-treatment systems [1]. The European Union (EU) members have decided to work toward the growth of renewable energy resources so that it must be able to bear 10% of transportation fuels and 20% of energy supply before 2020 [34–37]. Similarly, India has also fixed the target of decreasing the import of crude oil by 10% by 2022. Figure 1 shows the global energy demand growth in leading regions in terms of fuel.

Even though methanol is the right fuel for the SI engine, there are some drawbacks to using it as an alternative fuel. Lower carbon alcohols like methanol are useful in enhancing octane value, but they have low heating value, cold start, corrosion and hygroscopic nature [39]. A practical problem of using lower order alcohol-based fuels is the low energy content and lower volumetric efficiency [21]. These lower alcohols and their blends can produce more power when used near their stoichiometric air–fuel ratios, but they may reduce the fuel economy. Moreover, the higher latent heat of vaporization (LHOV) of methanol than gasoline may cause cold start problems and low kinematic viscosity and flash point causes wear and safety problems [40]. The high LHOV of methanol and the Lower Heating Value (LHV) are the main factors behind the lower flame temperature of methanol–gasoline blends [41, 42]. The methanol fuel may produce more NO_x emissions than gasoline because of the high laminar flame speed and faster combustion. Still, the NO_x emission rate may vary depending on the methanol concentration in blends and the operating conditions [43, 44]. Additives such as oxygenates and octane enhancers are added to minimize the drawbacks of methanol blends [38]. Adding a higher order of alcohol additives in methanol–gasoline blends (ternary blends) is considered as a suitable solution for these problems [40, 45].

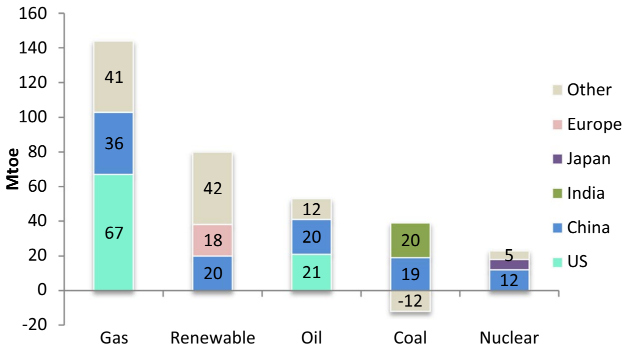

Fig. 1 Global primary energy demand growth by fuel and leading regions [38]

There exist other review works on methanol fuel and alcohol fuels: methanol as a fuel for IC engines [46]; overview of methanol as internal combustion engine fuel [47]; biomethanol as potential renewable energy [2]; methanol as a fuel for SI engines [48]; decomposed methanol as a fuel [49]; alcohol and ether as alternative fuels in SI engine [5]; and light alcohol fuels in diesel engine [50] overview of alcohol as alternative fuels [27]. However, most of these studies generally focus on alcohol fuel for internal combustion engines. At the same time, reviews on methanol–gasoline blended fuel and higher alcohol additives for methanol–gasoline blended fuels for unmodified spark ignition are very few. Hence, this paper focuses more on methanol–gasoline blended fuel and possible higher alcohol additive for unmodified SI engine based on the recent research studies. The primary structure of this paper is elaborated as follows:

The synthesis and applications of methanol for the basic understanding purpose are presented in Sect. 2. The usage of methanol as a transportation fuel with its advantages and disadvantages is explained in Sect. 3. The critical physicochemical properties of methanol as a fuel are explained in Sect. 4. The present methanol economy in India is briefly explained in Sect. 5. Methanol–gasoline blending is discussed in Sect. 6, followed by higher alcohol additives for methanol–gasoline blended fuel and important isobutanol higher alcohol additive in Sect. 7. The effects of methanol–gasoline blended fuel with and without additives on the SI engine's combustion, performance and emissions are discussed and compared through the Sects. 8–12. Finally, the conclusions and recommendations are presented in Sect. 13.

2 Synthesis of Methanol and Applications

Methanol is the simplest alcohol with various utilizations in the production of chemicals, and also it has a high potential to become an alternative fuel and a renewable energy carrier [51]. Methanol or wood alcohol consists of a methyl group (CH_3) linked with a hydroxyl group (OH). Methanol is a tasteless, colorless, and toxic alcohol with a very faint odor and biodegradable, clean-burning fuel. Methanol production offers a ‘future-proof’ transition to sustainable fuels and chemicals [52]. As mentioned earlier, the methanol is mainly manufactured from natural gas and fossil fuel or coal-based synthesis gas (syngas) [53–55]. Methanol has the advantage of ‘poly-generation’; that is, it can be manufactured from any feedstock, which is a source of synthesis gas which includes agricultural waste, municipal solid waste, biomass, CO_2, and some other feedstock [56]. Methanol can also be made from different sources such as wood, municipal solid wastes, CO_2 and even sewage [56]. Finding a suitable catalyst for the commercial production of methanol is the key focus of many researchers. The viable methanol production using different feedstock through innovative and efficient catalytic processes has got a lot of consideration nowadays [33, 57]. The synthesis of methanol from CO_2 using catalysts is getting the highest priority because it helps reduce greenhouse gases [33]. The world is looking toward carbon capture and storage (CCS) these days. Conversion of the captured CO_2 to methanol will help in avoiding carbon storage problems in CCS technology. The reduction of CO_2 and water with the help of renewable energy is another method for methanol production [58]. The methanol synthesis is generally carried out in three stages via the production of syngas, syngas to methanol conversion and the reactor effluent distillation [23, 56]. The technology known as gasification is used for the production of syngas. According to the data available in the methanol institute website [59], almost 138 billion liters or 36.6 billion gallons combined methanol production capacity is open from 90 methanol plants located in different countries. The data available with HIS revealed that the world methanol demand touched 75 million metric tons in 2015 and that 40% of methanol consumption was found in evolving energy applications. Approximately 200,000 tons of methanol is used as a transport fuel or chemical feedstock around the world every day [60]. Figures 2 and 3 show the worldwide methanol consumption and different forms of application of methanol.

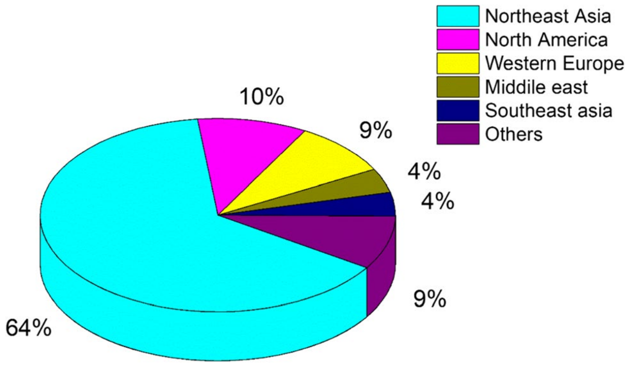

Fig. 2 Worldwide methanol consumption 2017 [61]

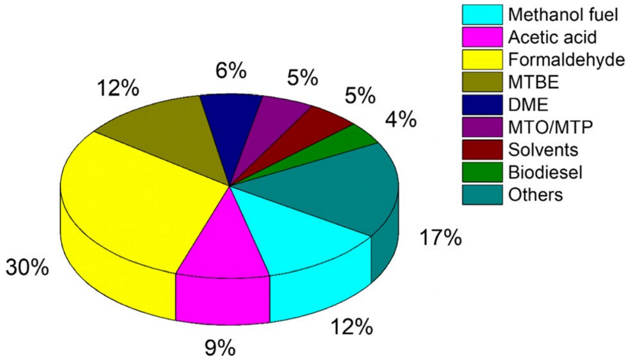

Fig. 3 Methanol Demand by derivative [59]

2.1 Methanol from Natural Gas

Natural gas is a combination of gases that are rich in hydrocarbons occurring naturally, and natural gas reserves are found deep inside the earth and near hydrocarbon’s beds like crude oil or coal. The main component of natural gas is methane (about 70% to 90%), and some amounts of other higher alkanes, hydrogen sulfide, nitrogen, carbon dioxide, etc., are also present. It has been reported that most of the methanol production around the world is by steam reforming of natural gas (NG) [48, 62]. The first step in the synthesis of methanol from natural gas is the syngas or synthesis gas (a mixture of mainly CO, CO_2 and H_2) production [63]. The next step is the conversion of the synthesis gas into crude methanol. The final step is to distill the crude methanol to attain the desired purity [50, 64]. Figure 4 describes the steps in the conventional method of methanol production.

The methods used for the conversion of natural gas to synthesis gas are steam methane reforming (SMR) and autothermal reforming (ATR), as shown in Eqs. (1.1), (1.2) and (1.3) [63].

The SMR consists of the steam methane reforming reaction and the water gas shift (WGS) reaction:

$$\mathrm{CH_4 + H_2O \rightleftarrows CO + 3H_2} \quad \mathrm{(SMR)} \quad \Delta H_\mathrm{R} = 206\,\mathrm{KJ/mol} \tag{1.1}$$

$$\mathrm{CO + H_2O \rightleftarrows CO_2 + H_2} \quad \mathrm{(Water\text{ - }gas\ shift)} \quad \Delta H_\mathrm{R} = -41.2\,\mathrm{KJ/mol} \tag{1.2}$$

In ATR, consists of lean combustion with the steam reforming reactions of Eqs. (1.1) and (1.2):

$$\mathrm{CH_4} + \frac{1}{2}O_2 \rightarrow \mathrm{CO + 2H_2} \quad \mathrm{(ATR)} \quad \Delta H_\mathrm{R} = -35.6\,\mathrm{KJ/mol} \tag{1.3}$$

ATR needed less water than SMR. A high-pressure equilibrium and the limited catalytic process were employed for the production of methanol through the methanol synthesis

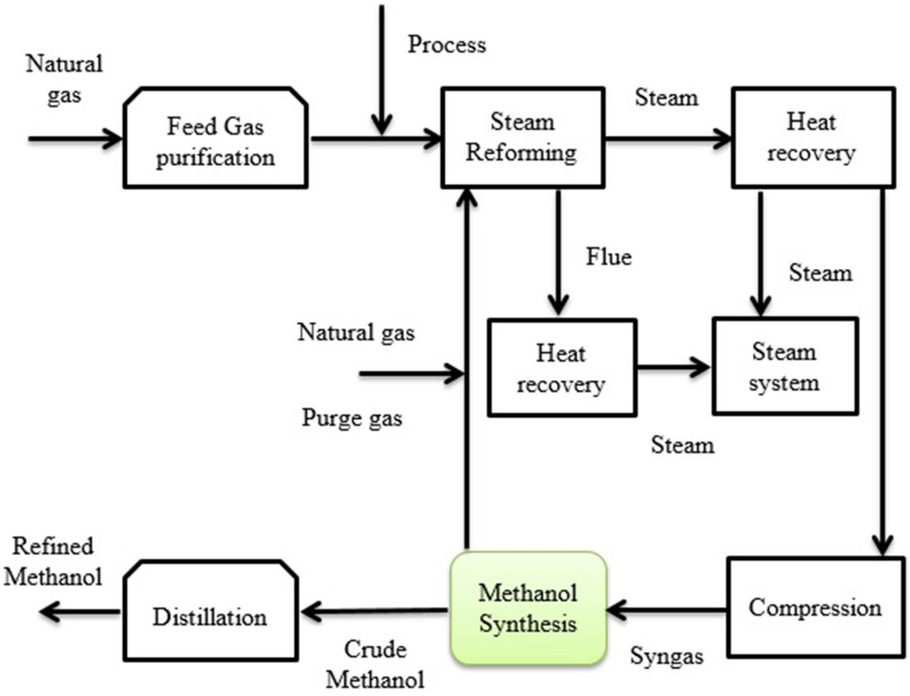

Fig. 4 Methanol production (conventional) from natural gas [64]

reaction and the reverse WGS reaction [60, 61]. The main reactions involved in methanol synthesis are shown in Eqs. (1.4) and (1.5).

Hydrogenation of CO_2 [63]:

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \quad \Delta H_R = -49.6\,\text{KJ/mol} \tag{1.4}$$

Hydrogenation of CO [62]:

$$CO + 2H_2 \rightleftarrows CH_3OH \quad \Delta H_R = -100.46\,\text{KJ/mol} \tag{1.5}$$

The composition of the syngas formed by methane reforming deviates from the stoichiometric composition of the syngas (i.e., $(H_2–CO_2)/(CO–CO_2)$ has an ideal value above 2), depending on the reforming technology and the operating parameters.

A methanol reactor operates at high pressure (50–100 bar) and comparatively low temperatures (200–300 ℃) [62]. The reaction requires a sturdy thermal sink to sustain constant temperature because it is highly exothermic [63]. Generally, higher conversion at equilibrium is achieved by lower temperatures but with slow kinetics [64]. The syngas conversion in thermodynamic equilibrium restricts the process to low per-pass conversion. Therefore, it involves a broad unconverted gas recycling process. The investment costs of this process segment are primarily dependent on the resulting recycling and cooling duty [62]. The synthesis is usually conducted at 200–300 ℃ and in this temperature range, the maximum theoretical once-through conversion, which is limited by the reaction equilibrium, is 55–75% [65]. Over the years, several solid catalysts and different methods such as BASF process (high-pressure method), ICI method (high-pressure method), Haldor-Topsoe methods, etc., have been developed in order to maximize methanol yield and selectivity and minimize by-product formation. It was reported that the BASF method could produce methanol at an approximate rate of 0.07896 t/day only. In contrast, Haldor-Topsoe and ICI methods can produce methanol at a rate of approximately 2400 t/day and 2500 t/day, respectively. As can be seen, the evolution of the processes from the high pressure (BASF) to the low pressure (ICI) led to an increase of 105 t/day. A world-scale methanol plant produces 5000 metric tons per day or 2.3 billion liters per year (600 million gallons/year) by natural gas steam reforming and converting the resulting synthesis gas [52].

2.2 Methanol from Coal

The processes used for methanol production from coal are the same as the processes used in natural gas to methanol production. The coal-based methanol production processes generally have four phases via generation of syngas, the purification of syngas, synthesis of methanol and rectification of methanol [66]. In the preliminary stage, the biomass is converted to gaseous products using gasifier equipment. The gaseous products comprise syngas, biogas (CH_4 and CO_2), alkaline gases and pure hydrogen. The thermochemical conversion technique, gasification, allows the conversion of solid biomass into gaseous mixtures with air, steam and flue gases. Equations (1.6), (1.2), (1.1), (1.7) and (1.8) are the reactions occurring in the conversion of gaseous products [6, 62].

$$C + H_2O \rightarrow CO + H_2 \quad \text{(Char gasification)} \quad \Delta H_R = 131.5\ \text{KJ/mol} \tag{1.6}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad \text{(Water - gas - shift)} \quad \Delta H_R = -41.2\text{KJ/mol} \tag{1.2}$$

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \quad \text{(SMR)} \quad \Delta H_R = 206\text{KJ/mol} \tag{1.1}$$

$$C + CO_2 \rightarrow 2CO \quad \text{(Boudouard reaction)} \quad \Delta H_R = 172\ \text{KJ/mol} \tag{1.7}$$

$$C + 2H_2 \rightarrow CH_4 \quad \text{(Methanation reaction)} \quad \Delta H_R = -74.8\ \text{KJ/mol} \tag{1.8}$$

2.3 Methanol from Biomass (Biomethanol)

Biomethanol is also known as 'wood alcohol' and is made from waste biomass such as old wood and biodegradable waste. Different methods are used for the production of biomethanol, such as biosynthesis, gasification, pyrolysis, photoelectrochemical processes and electrolysis [2, 67]. Biomethanol synthesis requires carbon-rich feedstock, H_2 and a catalyst (Al_2O_3/ZnO/Cu catalyst). The synthesis process consists of three main steps, the first step is the reforming of biomass to bio-syngas with an optimal ratio of 2, and the second and third steps are the conversion and distillation of bio-syngas to obtain methanol, respectively [14, 23]. The common feedstock used for biomethanol production is sawdust, Japanese cedar, rice bran, straw and husk, cow dung, banana peel, boiled rice, goats fed grass, soy pellets, plant biomass, forest residue, lignin, etc. The biomethanol production from biomass causes very low emissions because the alcohol carbon content is resulting from the carbon content, which was collected and stored during the growth phase of the bio-feedstock from the atmosphere. The same stored carbon in the bio-feedstock is rereleased into the atmosphere during the production of methanol [54, 68]. So, the biomass-derived fuels also do not increase the total global CO_2 because of combustion [56]. The biomethanol can also be made from crude glycerin. The main advantage of this method is the reduction of greenhouse gas by recycling the by-product of biodiesel. Ghasemzadeh et al. [64] have reported that methanol production from biomass is occurring in four basic ways. Figure 5 shows the schematic diagram of methanol synthesis from biomass.

The following are the steps involved in the biomethanol production from biomass.

i. The biomass is biochemically transformed into sugar by the help of microorganisms and enzymes.
ii. Utilizing heat energy and chemical catalysts, conversion of biomass to fuels (thermochemical conversion).
iii. Gasification of the biomass in an oxygen-starved environment with high temperature to produce synthesis gas [70].
iv. Pyrolysis process to boost the decomposition of biomass.

Yadav et al.[60] studied the environmental impact and cost assessment of methanol production from wood biomass with respect to both the conventional and novel methods. They found that both the novel and the conventional biomethanol production methods had much lower global warming potential (GWP) (48.2 and 63.1 kg CO_2, respectively) when compared to methanol production from fossil-based resources. The renewable methanol cuts CO_2 emissions by up to 95%, reduces NO_x emissions by up to 80% and completely eliminates SO_x and PM emissions compared to conventional fuels [71]. The cost of biomethanol will always be comparable to that of methanol derived from fossil fuels. This analogy is not optimistic at this time, but it is fair to conclude that it would be more favorable in the coming years due to the anticipated rise in the price of natural gas and the decreased supply of fossil fuels [56].

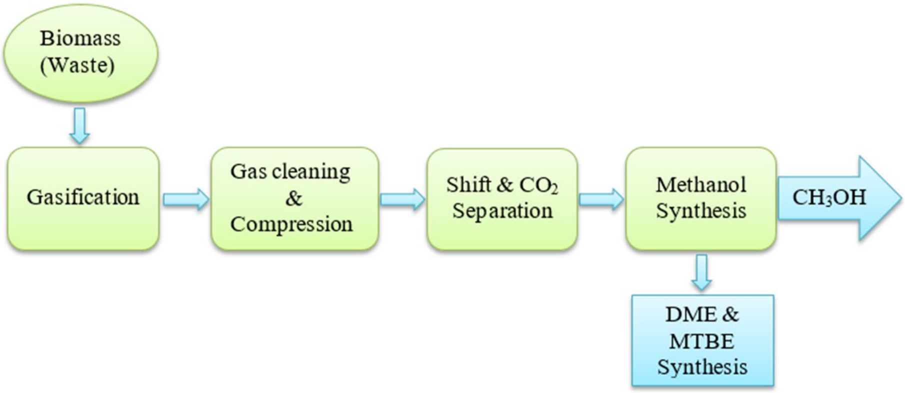

Fig. 5 Biomethanol synthesis from biomass [69]

2.4 Methanol Synthesis from Biogas

The low efficiency and toxic emissions are the main problems that restrict the direct use of biogas in IC engines. One alternative method of using biogas effectively in internal combustion engines is to convert biogas into alternative fuels like methanol. So, the synthesis of methanol from biogas is getting more importance these days [72]. Biogas is mainly comprised of methane (CH_4) and CO_2. The primary step in converting methanol from biogas is the production of syngas using tri-reforming or oxy-steam reforming. Tri-reforming combines the following processes (1) steam reforming, (2) dry reforming, and (3) partial oxidation either in autothermal or isothermal conditions. Tri-reforming process allows producing syngas from a mixture of CH_4, H_2O, CO_2, and O_2 [72, 73]. Some biological methods are also used for direct conversion of methanol from biogas using some aerobic bacteria like methanotrophs [74]. According to vita et al. [72], the steam reforming of biogas at $S/CH_4 = 1$ and $T = 700$ ℃ in the absence of carbon deposits and lower consumption of energy is the most suitable path for the production of syngas for direct methanol synthesis. This method avoids the steps such as WGS) and/or pressure swing adsorption (PSA) installed between reforming reactor and methanol synthesis reactor. So this method results in more compact design, lower operating and maintenance costs and lower investment than the conventional methanol synthesis process. Approximately, more than 80% CH_4 conversion was achieved using this method.

2.5 Methanol Synthesis from CO_2

The methanol production from atmospheric CO_2 is an efficient and environmentally friendly process. This method is considered to be one of the most significant research fields since the reaction helps prevent greenhouse gases and thus control global warming [56]. The industries such as power plants, steel industries, cement factories and distilleries generate more CO_2, which could be used as a source for methanol production. Carbon Recycling International takes 5600 metric tons of carbon dioxide every year, which is reacted with renewable hydrogen to synthesize 4000 metric tons of renewable methanol [71].

2.5.1 Methanol from Electrofuels

Electrofuels are future carbon-based fuels produced from CO_2 and water using water with electricity as the primary energy source. This fuel is also called synthetic fuel, and the process is called the power-to-fuels (P2F) process [75, 76]. This process begins with separating water (H_2O) into hydrogen (H_2) and oxygen (O_2) with the use of electricity. The produced hydrogen is then synthesized with co-feed CO_2 to form a range of liquid fuels (methanol, fuel oil, diesel, biodiesel, etc.) and gaseous fuels (CH_4, DME, LNG, etc.) [76]. Methanol from electrofuels is a new effective way to utilize CO_2 and to reduce GHG in the atmosphere or to achieving a neutral CO_2 balance across the entire mobility chain. Methanol is the simplest of all liquid energy carriers suitable as a transport fuel and having the highest hydrogen to carbon ratio (four hydrogens to each carbon atom).

2.5.2 CO_2 Hydrogenation

The concept of methanol economy and CO_2 hydrogenation to methanol depends on the combination of CCS with chemical recycling. Carbon dioxide is the main cause of global warming. Still, it can also be used as a potential source of carbon to produce other compounds such as alcohols, aldehydes and hydrocarbons [77]. Different reactions of CO_2 to methanol are the following: (1) direct methanol synthesis and (2) methanol synthesis from CO (hydrogenation of carbon monoxide), which is formed as a by-product of WGS reaction. Equation (1.9) shows the hydrogenation of carbon dioxide to methanol. Equations (1.10) and (1.11) show the WGS reaction and hydrogenation of carbon monoxide, respectively [62].

$$CO_2 + 3H_2 = CH_3OH + H_2O \quad \text{(Direct methanol synthesis)} \tag{1.9}$$

$$CO_2 + H_2 = CO + H_2O \quad \text{(Reverse water - gas - shift)} \tag{1.10}$$

$$CO + 2H_2 = CH_3OH \quad \text{(Hydrogenation of CO to methanol)} \tag{1.11}$$

The CO_2 capturing may be done from any industrial source, natural source, or air by absorption and human activities. The required hydrogen for the reaction is produced from water by electrolysis, reforming biomass-derived products, and biomass pyrolysis [78–80]. Blumberg et al. [81] reported that an inlet fraction of 10 mol% CO_2 is recommended for a Pareto-optimal operation with a high product yield and a large conversion rate for CO_2. The findings show, that a maximum methanol yield of 15.2 mol% in the product gas is obtained for a CO_2-fraction of 11 mol% decreasing with an increasing CO_2-inlet fraction. High CO_2 conversion of more than 80% are only achieved for CO_2-inlet fractions below 3 mol%. Bellotti et al. [82] carried out a low-carbon footprint production of methanol from CO_2. The technique involves CO_2 sequestration and utilization for mixing it with H_2 (produced by water electrolysis) to produce methanol.

2.5.3 Photoreduction of CO_2

The photoreduction of CO_2 in light irradiation and water with the help of different heterogeneous semiconductors is an attractive way to produce methanol. Photoreduction is a photocatalytic reaction that occurs once the catalyst is treated with suitable light energy such as visible or UV with charge carrier's formation [17]. The formed charge carriers are then separated on a semiconductor and reacted with the adsorbed molecules [28]. Artificial photosynthesis has reduced conversion effectiveness. The key issues with this technology are the low solubility of carbon dioxide in water and the poor separation performance of the catalyst, which uses only a small portion of the solar spectrum which is appropriate for semiconductor activation. Besides, the mechanism results in poor selectivity due to several reactions taking place concurrently in the photoreactor [83]. However, modern photoreactors are suitable for working under pressures up to 20 bar allowing a significant increase in the solubility of CO_2 in water, which increases the process's efficiency.

Owing to the competitive prices of methanol for fuel and affordable infrastructure, the methanol economy is entering other parts of the world [84]. The rate at which methanol is replacing oil is maintained due to the low prices of natural gas. However, a good basis for environmental pollution control can be provided by the use of CO_2 for methanol processing. In order to reduce global warming by recycling CO_2, methanol production from CO_2 using carbon capture technology and its use as fuel for automobiles are therefore of long-term significance.

2.6 Important Applications of Methanol

The important applications of methanol are described below [2, 49, 62, 85]. Figure 6 shows the main areas where it is used as energy sources.

- Methanol is a clean-burning fuel used in IC engines in pure form, blended form, or as an additive to increase engine performance and reduce emissions. It is one of the main components in the renewable biodiesel fuel production process.
- Dimethyl ether (DME), an integral derivative of methanol, can be successful as an alternative home heating fuel along with liquefied petroleum gas (LPG).
- Methanol plays a significant role in municipal and private waste treatment facilities to clean wastewater and eliminate 'dead zones' in waterways caused by dangerous nitrates.
- Methanol is very suitable for fuel cell-powered vehicles because it can be degraded to hydrogen and CO_2.
- Methanol is a useful carrier storage compound for organic liquid hydrogen.

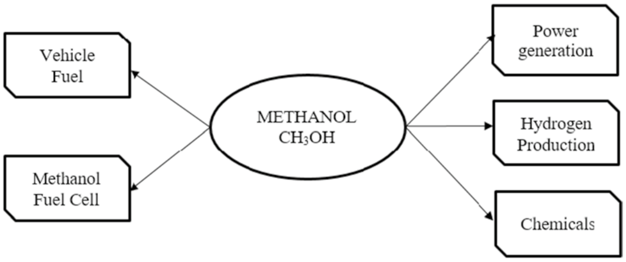

Fig. 6 The main uses of methanol as an energy source [86]

3 Methanol as a Renewable and Alternative Transportation Fuel

All over the world, methanol has found its use as a fuel for automotive engines in a blended form with motor spirit. Among alcohols, methanol is considered the most suitable blending agent for petrol and is a potential alternative fuel for transportation because of its excellent combustion properties [87–89]. Compared to gasoline, methanol has high oxygen content, supporting the efficient burning of fuel in automotive SI engines. High performance, lower regulated emissions, lesser risk of flammability, environmental and economic advantages are some of the good qualities of methanol fuel compared to gasoline [48, 90]. Soheil et al. [91] have studied the effect of oxygenated additives in a gasoline engine and concluded that the Reid vapor pressure (RVP) of gasoline increases with the addition of methanol. It also improves both MON and RON. Many countries like India are moving toward EVs; however, methanol-fueled vehicles seem to be an eco-friendly and economical solution compared to EVs because of the following reasons: (1) the existing electricity production capacity in India could not be able to afford large scale use of EVs in the transport sector, (2) absence of necessary resources for EVs production, (3) methanol can be produced in India economically and it helps in reducing petroleum import bill and (4) methanol blends can be used as an alternative fuel without any significant alterations in the existing engines [1].

Liu et al. [92] have concluded from their study that methanol in lower concentrations can be blended with gasoline to use as an alternative fuel for SI engines without any engine modifications. They found that the addition of methanol to gasoline improves the cold start emissions by considerably lowering CO and HC emissions. Nowadays, passenger cars are widely equipped with a gasoline direct-injection (GDI) engine because of its high power delivery and low fuel consumption. Due to nonhomogeneous air/fuel mixing, there could be more soot emission [93]. Liu et al. [94]

studied the soot formation of methanol–gasoline blend fuel and concluded that methanol significantly reduced the soot. Danaiah et al. [89] observed a reduction in CO, CO_2, HC, and NO_X emissions with the use of methanol in gasoline up to a concentration of M15.

As far as methanol consumption is concerned, India is the third-largest energy consumer and a significant importer of methanol. So, the Indian government promotes the production of biomethanol and bio-butanol for their application in the transport system from the surplus biomass availability [95]. Turner et al. [58] examined the effect of gasoline, ethanol, and methanol (GEM) blended in a flex-fuel vehicle and concluded that considering the low price of methanol, and using it as a ternary blend, could create an approach to economic and profitable fuel.

China has been focusing more on gasohol (low volume concentration less than or equal to 50% of methanol with gasoline). The gasohol can be used as fuel in existing IC engines without modifying the control unit and engine parts. It also helps in lowering the risks of carbonyl pollution and corrosion [85]. NITI Aayog (a policy-making body of India) promotes methanol as an alternative fuel because of its different qualities like easy availability, reduced pollution, and higher efficiency and electrical mobility. It will help in reducing India's dependence on fossil fuels. The world is moving toward electric vehicles that run on lithium-ion batteries. According to NITI, lithium is not an abundant resource, and the world will face the problem of scarcity if all shift over to lithium-ion batteries for running vehicles. In India, it requires much effort in setting up extensive infrastructure, primarily charging stations across the country, and it would put an additional burden on the already growing demand for electricity. Hence, electric vehicles are not a sustainable and cost-effective solution for fuel scarcity. Since road transport makes up almost two-thirds of overall transport emissions, widespread adoption of vehicles powered by renewable methanol would dramatically lower CO_2 emissions in transportation [71].

3.1 Advantages of Methanol Fuel

- Methanol can be produced from any carbon-based feedstock such as coal, biomass and natural gas so that methanol fuel will reduce dependence on imported petroleum.
- Higher combustion efficiency, lower sulfur, and aromatic content, renewability and biodegradability are the main features of methanol fuel [27, 68, 69, 96].
- Methanol has a high latent heat of vaporization (LHOV) and is combined with the low stoichiometric air to fuel ratio leading to high degrees of intake charge cooling [68, 97].
- Methanol has a high knock-resistant capacity, and the considerable cooling effect can be one reason for this. Its higher LHOV causes a lower mixture temperature and lower compression temperature near TDC, which suppresses knock [88, 94, 98].
- The use of methanol fuel improves power and efficiency by applying optimal spark timing and higher compression ratios [68, 97].
- Compared to gasoline, methanol is less flammable and safer than gasoline while transporting and storing [47, 96].
- Methanol fuel can improve engine thermal efficiency because of the advanced laminar flame propagation, which helps combustion to finish early [99, 100].
- Methanol offers better power and decent acceleration to any vehicle engine because of the high octane value [17, 48].
- The methanol fuel's higher octane number gives an improved antiknock performance to the internal combustion engine [88, 94, 101]
- Methanol fuel is considered economical in the sense that it could be reached at low prices compared to petroleum [29, 94].

Growing awareness of the danger faced by human-made climate change has inspired government agencies, industry and research to discover renewable fuels to power economic activity. In this sense, as a sustainable alternative to fossil fuels, renewable methanol has grown, providing a direct route to dramatically reducing pollution in power generation, overland transport, shipping and industry. Renewable methanol cuts carbon emissions by 65 to 95% compared to fossil fuels, depending on the feedstock and conversion process. It is one of the most considerable possible reductions for gasoline, diesel, coal, and methane to be substituted by any fuel currently being produced. Besides, no SO_x, and PM and low NO_x, emissions are created by the combustion of pure methanol. The roads will be packed not with methanol cars but with electric vehicles charged with clean energy in a perfect low-carbon environment. However, we are still well short of the target. In every country where they are sold, EVs today make up a tiny fraction of vehicles. Even under the most ambitious expectations, it could be midcentury until the bulk of vehicles on the road are all-electric. In the meantime, methanol is among the most promising options to reduce our vehicle's carbon footprint dramatically. The total carbon emitted into the environment is halved if a methanol plant is fueled using a green energy source and collects the CO_2 from the exhaust and converted into methanol. So even though burning methanol in a car's internal combustion engine does release CO_2, along with some water vapor, basically there is a carbon recycling happens (carbon capture and utilization) and extracting some useful work before it gets released. Even though EVs can solve climate problems, there are many hurdles related to EV technology in many countries. In this scenario, compared to EV's, methanol fuel is feasible. Methanol can be stored, transported, and distributed using the same necessary infrastructure used for petroleum fuels and there is no need to build an entirely new infrastructure from scratch.

Increasingly, methanol is being used worldwide in several innovative applications to meet the growing energy demand, particularly in transport. It is possible to mix low levels of methanol with gasoline and use it in the existing vehicles. Mid-level methanol blends as high octane fuels, substantially greater than traditional 25–30% gains from turbocharged diesel engines or hybrid vehicles, can provide potential performance gains of 40–45%, and at a much more affordable rate [102]. Neat methanol can also be used as a replacement for either gasoline or diesel fuel in both spark-ignition and combustion-ignition engines in modified automobiles.

3.2 Reformed Methanol Fuel for IC Engines

Fuel reforming is a conversion process in which fuels are converted to gases rich in hydrogen. Lower alcohols such as methanol, ethanol can be used for fuel reforming processes. Steam reforming, autothermal reforming, and partial oxidation are three different processes to convert alcohol fuels to hydrogen-rich gas [103]. Methanol can be used in fuel cells and as an alternative liquid fuel, which allows running the IC engine with gaseous H_2-rich reformate produced onboard by fuel reforming. The process of converting liquid fuels to hydrogen onboard a vehicle is 'onboard reforming' [104]. Methanol is an excellent primary fuel for thermochemical recuperation (TCR). It can be reformed at relatively low temperatures (250–300 °C) to produce hydrogen-rich reformate [104, 105]. Thus, the major issues such as H_2 fueling infrastructure and risk in the storage of H_2 onboard a vehicle can be reduced [103, 104, 106, 107]. The 'methanol reformate' helps improve the efficiency of internal combustion engine operation compared to gasoline, and a gain of 50% efficiency can be achieved at mid-load or city driving conditions [104]. About 30% of the fuel energy is wasted with the hot exhaust gas coming out of the IC engines [108]. Thus, reforming methods, which partially utilize this waste energy, may contribute significantly to the IC engine's overall efficiency and also known as waste heat recovery (WHR) methods. The experimental results of Tartakovsky et al. [106] showed that a reduction in pollutant emissions and improvement in energy efficiency could be achieved when an H_2-rich reformate like methanol is used as a fuel for ICE. In exhaust gas reforming, fuels are reformed catalytically by direct contact with the hot products of combustion a certain quantity of steam. The generated fuel gas contains quantities of hydrogen, carbon monoxide and nitrogen, and these components provide the potential for lean combustion leading to lower emissions and higher engine thermal efficiency than conventional fuel [109].

3.3 The Adverse Effect of Methanol as a Fuel

3.3.1 Phase Separation

The quantity of water that can congregate by gasoline is deficient because of the low water solubility. Low water content in gasoline will not affect the performance of the engine [110]. The major trouble with alcohol fuels is its hydrophilic nature and the phase separation tendency due to the solubility of the alcohol–water–gasoline blend system [17]. The phase separation may cause engine damage and engine functioning problems. Even though a small quantity of water present in a methanol–gasoline blend at lower temperature creates phase separation because of the direct hydrogen bonding between alcohol and water, the level of phase separation depends on the alcohol concentration in the blend, water contamination, the ambient temperature and the chemical composition of the base gasoline fuel (especially aromatic content) [5, 110, 111]. In phase-divided state, the lower phase consists of methanol, water and the aromatic components of gasoline, while the upper phase is rich in gasoline and contains paraffinic hydrocarbons. An important factor that is to be considered while selecting alcohol fuel is water tolerance, which is the percentage volume of water that fuel can bear at a certain temperature without any phase separation [112]. This phase separation may cause difficulties like low-quality fuel, damage to storage containers and metallic parts of the engine due to corrosion [111]. The phase separation temperature (PST) is one of the main parameters used for calculating methanol–gasoline blend stability. PST is the temperature at which an alcohol–gasoline divided into two phases. Suitable additives such as nonionic surfactants, higher alcohols like isomers of butanol, propanol and fusel oil can be used in gasoline–alcohol-blends fuels to avoid these problems [5, 113, 114]. The fusel oil is a by-product of alcohol manufacture via fermentation and distillation. It comprises iso-amyl (55–60%), n-propyl (15–20%), iso-butyl (6–8%) alcohol, and bits of n-butyl alcohol and ethanol [115, 116]. It is essential to note that the fusel oil cannot be used directly into the internal combustion engine because of the water content present. So, the fusel oil water content should be removed before use in IC engines [117]. Karaosmanoglu et al. [113] have introduced a novel, effective blending agent molasses fusel oil for methanol–gasoline blend fuel for reducing the phase separation problem. Lojkisek et al. [118] have found that methanol in gasoline blends increases the stability of the fuel blend. They proved that water tolerance increased after the addition of isobutanol to methanol–gasoline blend. The improvement is three times higher than the addition of methyl tert-butyl ether (MTBE) and tert-amyl methyl ether (TAME). Zhang et al. [119] have synthesized phase stabilizers and saturation vapor pressure depressors for methanol–gasoline blend fuels. They have concluded that tartaric esters are excellent bifunctional additive for reducing phase separation tendency.

3.3.2 Vapor Lock

The vapor lock occurs when the liquid fuel changes its state to gas while in the delivery system due to high vapor pressures and relatively low boiling points of methanol. This problem will affect engine performance adversely. The vapor lock problem increases, particularly on warm summer days and at high altitudes, because vapor pressure varies with seasons [27]. Vapor pressure is a critical property that affects the cold-start drivability, and the standard range of vapor pressure for fuel is 7–15 psi as per ASTM. Vapor lock and other hot fuel handling problems can be avoided by selecting low vapor pressure value fuels. On the other hand, the high values of vapor pressure result in improved cold-start engine performance, so we need to consider both conditions [69, 111]. The excessive volatility of the blended fuel could also result in a vapor lock in the fuel supply system [120]. Among the alcohols used in fuel applications, the butanol is least likely to cause vapor lock because of its low vapor pressure [121].

3.3.3 Corrosion

In all proportions, alcohols are completely miscible with water, but gasoline is immiscible with water. So the presence of water in the alcohol blended gasoline fuel may result in corrosion problems on the engine components made of aluminum, copper and brass [122]. The severity of the problem depends on the type of alcohol and the concentration of alcohol in the fuel, so it is better to avoid the materials mentioned above in the fuel delivery system to minimize this problem [7]. There is a chance that the higher concentration of alcohol in the blended fuel may react with rubber fuel pipe. But the use of fluorocarbon rubber avoids this problem [10]. There are rarely some chances of splitting the gasoline-methanol mixture into two phases at low temperatures due to the lower miscibility of alcohol with gasoline [123]. These problems can be avoided to certain extent by the use of higher alcohol blends.

3.3.4 Engine Modifications

Engine modification is needed to use 100% methanol fuel in automotive SI engines. Sometimes these engine modifications are needed to the higher volume percentage of methanol blend fuels. The main engine alterations include changes in the material of the fuel system and engine management system. Certain modifications are needed to convert the modern vehicle engines to run on pure or high-level methanol blends [5, 21, 27]. The following are some of the modifications.

- The intake manifold design should be modified to evaporate more by providing more heating facilit**ies** because alcohol does not evaporate readily as gasoline.
- The fuel pump and injector should be compatible methanol to handle higher flow rates.
- Use of improved compression ratios or turbochargers for better fuel efficiency and to have a smaller sized engine.
- The use of improved cold starting approaches needed to eliminate cold start problems.
- Use methanol-compatible material for the fuel tank and provide flame arrestors in the fill and vent tubes to prevent ignition by an external source. Teflon fuel hoses and stainless fuel lines also work well with alcohol.
- Use methanol-resistant potentiometers float level with a circuit that protects against corrosion.

3.3.5 Unregulated and Evaporative Emission

Conventional fossil fuels hardly produce unregulated emissions because of the compositional properties, but alternative fuels may produce unregulated pollutants. Many studies have done by the researchers in evaporative emissions or unregulated pollutants from alternative-fueled vehicles. The volatile organic compounds (VOCs) from evaporative emissions of engines contribute much to air pollution [124]. From the studies, it was clear that one of the main reasons for carbonyls emissions to the atmosphere is combustion in IC engines. The evaporative emissions are depending on many factors such as ambient temperature, fuel volatility, the material of fuel tank and fuel system, etc. [69, 125]. The carbonyls can be treated as toxic air contaminants, mutagens and carcinogens. Some of the research studies have reported that the most abundant carbonyls found in exhaust emissions are formaldehyde and can be produced from engines that work in methanol blended gasoline fuels [87, 126]. Among the HC emissions from methanol–gasoline blends, the carbonyls and the volatile organic compounds are harmful to human health [126, 127]. The methanol fuel is less reactive than gasoline in the atmosphere and produces the only one toxic component that is formaldehyde. Still, the emission of gasoline fuel contains lots of formaldehyde and carcinogenic components [128].

4 Physicochemical Properties of Methanol

The use of methanol in SI engines is advantageous because of the high oxygen mass percentage, higher octane value, high latent heat of vaporization and improved antiknock characteristics, etc. These properties lead to increased charge density, volumetric efficiency and sometimes improved torque and performance [3, 25, 129, 130]. The boiling point and storage stability of methanol are high compared to gasoline because of the formation of hydrogen bonds between molecules. The comparatively higher octane number of methanol fuel makes it usable in the engine with a higher compression ratio [131]. Table 1 shows the physicochemical properties of gasoline and methanol.

The octane number signifies the fuel's capability to resist knocking and characterizes the ignition quality of the fuel. The two categories of the specification of octane number are MON and RON [91]. Methanol has a higher octane number than so it is considered a functional alcohol additive used to improve the octane number of conventional gasoline fuel [42, 68]. The research and motor octane numbers of methanol–gasoline blends were found to rise with the increase in the concentration of methanol in the fuel blend. That way, engine performance is also improved by a higher level of methanol in the blended fuel [133]. Methanol is an excellent blending agent used for improving octane distribution in the base gasoline fuel, improving cold-start performance of the engine. Blending octane value (BOV) range of methanol is 97–104 and 129–134, respectively, for MON and RON. The actual blending value can be calculated using MON or RON values of methanol blend fuel and gasoline fuel using Eq. (1.12) [8, 134]:

$$\mathrm{BOV} = \left\{\mathrm{ON} - \left(\mathrm{ON}_{\mathrm{base}} \times (1 - Y)\right)\right\}\Big/Y \tag{1.12}$$

ON MON or RON of the gasoline blended fuel, $\mathrm{ON}_{\mathrm{base}}$ MON or RON of the base fuel gasoline, Y Blending component's volume fraction.

Table 1 Comparison of physicochemical properties gasoline and methanol [5, 46, 132]

Properties	Unit	Gasoline	Methanol
Chemical formula	–	Various	CH_3OH
Molecular weight	g/mol	95–120	32.04
Oxygen	mass%	0	49.93
Hydrogen	mass%	14	12.5
Carbon	mass%	87.5	37.5
Density	g/mL	0.737	0.792
Autoignition temperature	°C	257	423
Boiling point	°C	27–225	78
Freezing point	°C	−40	−97.5
Flashpoint	°C	−45 to −13	11
Reid vapor pressure	kPa	53–60	32.4
Motor octane no	–	82–92	88.6
Research octane no	–	90–100	108.7
Latent heat of vaporization	kJ/kg	349	920–1109
Low heating value	MJ/kg	44	20.1
Viscosity	mm^2/s	0.29	0.596
Stoichiometric AFR	kg/kg	14.7	6.5
Solubility in water at 25 °C	ml/100 ml H_2O	< 0.1	Fully miscible

Methanol has a higher LHOV compared to gasoline. It leads to a more cooling operating condition in the combustion chamber since more heat is required to vaporize the fuel [5, 17]. The heating value or calorific value of methanol is lower than gasoline, and the reason for the poor heating value of methanol is related to the high oxygen and less carbon content in the composition [5, 17]. The boiling point is connected to fuel volatility, the ability of the fluid to evaporate at a comparatively low temperature. Gasoline has a variable boiling point (27–225 °C), but methanol or, in general, alcohol has a single boiling point, which helps increase energy release. Methanol has a considerably lower single boiling point that evaporation becomes faster compared to gasoline, and spillage chances are less [5]. The autoignition temperature (423 °C) of methanol is almost two times higher than gasoline (221–257 °C). So, methanol is safer for storage and transportation [5]. Lan et al. [135] found that a binary mixture having different components shows a gradually increasing AIT trend with the increase in the higher AIT content and rapidly growing AIT trend corresponding to an improvement in the volume ratio of the component [135]. It has been reported that fuel blends with different autoignition tendencies can be used for knocking control [136]. Methanol and ethanol inhibit the autoignition reactivity of the blended fuels because of their high AIT [137].

The oxygen content in the methanol fuel helps in cleaner complete combustion and improved combustion and thermal efficiency [121, 138]. The addition of higher alcohols like butanol enhances the combustion utilizing more oxygen for combustion, and the effect is known as 'leaning effect' [121, 138, 139]. Because of the leaning effect, the chances of the reduction in CO emissions are high. But this extra oxygen for combustion will lead to an increase in the rate of complete combustion, and there may be an increase in the highest value of temperature in the combustion chamber. Since NO_x emission is mainly related to the higher temperature produced during combustion, there are chances of significant NO_x emission [140].

5 Methanol Economy in India

According to the current status, India is the sixth-highest consumer of fossil fuel around the world. It is anticipated that the country will become the third-largest consumer shortly. Currently, India needs approximately 2900 cr liters of petrol and 9000 cr liters of diesel per year. This large requirement accounts for the six lakh crore of crude oil imports in a year [141]. By careful planning and by adopting the right technology, India can produce methanol at a regular price of 19 rupees per liter (30% cheaper than fossil fuel) from local coal and other feedstock. By running the current SI engine vehicles on methanol–gasoline blended fuels, India can reduce the fuel cost by approximately 5000 cr/year annually. Figure 7 shows that methanol imports in India, from the year 2010–2011 to 2015–2016, were continuously increasing and became almost double in 2015–2016. India has been exporting methanol for a long time but only in small amounts compared to imports [29]. The consumption of gasoline in India in the year 2015–2016 was 22 MT; still, India has not yet started the use of methanol–gasoline blended fuel for transportation even though the country has enough potential for the production of methanol from plenty of feedstock available. Recently, Methanol Institute (MI) is supporting India's effort to increase the use of methanol as a vehicle fuel. MI is working with the Automotive Research Institute of India (ARAI) and Indian Institute of Petroleum to facilitate the rollout of methanol blends [142].

6 Methanol–Gasoline Blended Fuel

As explained earlier, almost all the vehicles manufactured today are not compatible with pure methanol (100%) fuel. So, the alcohol biofuels are used in the blended form with gasoline. Methanol–gasoline blends have been using successfully since 1980. Methanol blends are the best possible solutions to fight with the growing gasoline demand and to extend the gasoline supply by meeting all the environmental regulations [134]. The high blending octane value of methanol provides a cost-effective means of improving the low octane value of gasoline. Methanol is an efficient blendstock for all grades of gasoline. Blending vapor pressure is one of the factors which affect the fuel blend performance adversely. Methanol may form nonideal (azeotropic effect) blends with gasoline, and there are chances of the increasing Reid vapor pressure in the range 200–800 kPa. Higher alcohol added to the methanol–gasoline blends can reduce the increase in Reid vapor pressure. Methanol blends at 15 volume percent are successfully used in modern engines having fuel injectors with the feedback control system and the engine developing a satisfactory performance with the blend fuels.

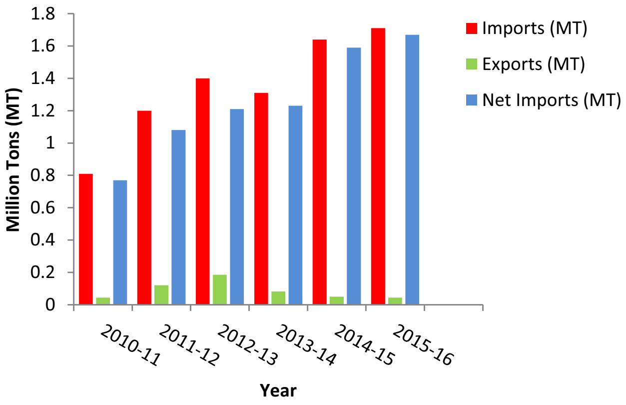

Fig. 7 Methanol import and export status in India [143]. Source: ministry of chemical and petrochemical

7 Higher Alcohol Additives for Methanol–Gasoline Blended Fuel

Generally, additives are added to blend fuel to reduce the adverse effects or drawbacks, thereby achieving emission reduction and performance improvement. The additives include oxygenates, corrosion inhibitors, octane enhancers, antiknock compounds, dyes and detergents [68]. Most issues by adding alcohol may be avoided by low amounts of alcohol or by using another cosolvent [144]. Higher alcohol (higher molecular and higher carbon alcohol) with specific chemical and physical properties is added to the methanol–gasoline blend to reduce its adverse effects. These three-component (alcohol + higher alcohol + gasoline) fuels are also known as ternary blend fuels. Alcohol with a higher carbon number, such as isobutanol, has high energy content and can displace more petroleum gasoline than methanol–gasoline blended fuel [121]. Factors such as oxygen content, heating value, flame speed and octane number affect combustion efficiency and increase these factors, which would help boost combustion and minimize engine emissions [145]. The dual alcohol blends of higher alcohol and lower alcohol are a viable option to alleviate the limitations associated with the volatilities of single alcohol–gasoline blends [22]. The combined properties of both methanol and higher alcohol can improve the blended fuel's performance because the disadvantages of methanol and higher alcohol would be limited mutually.

Alcohols such as pentanol, butanol and propanol have gained more attention in recent years because of their advantages over low-carbon alcohols. These alcohol fuels are called next-generation biofuels [146]. Shirazi et al. [147] found that dual alcohol blends could achieve RVP values near gasoline. Elfasakhany [148] has done an experimental study on the emissions and performance of both *n*-butanol–methanol–gasoline and isobutanol–biomethanol–gasoline blend fuels in an SI engine. They concluded that ternary blend fuels at a lower rate would decrease the performance and inversely affect the emissions. Still, a higher percentage of blended fuels will improve performance and reduce emissions. Geo et al. [149] investigated the effect of the addition of alcohol in the SI engine with

Table 2 Comparison of functionalities of methanol and isobutanol relevant to automobile application [132, 157, 158, 160–162]

Methanol	Isobutanol
Less carbon and hydrogen atom—Low energy content and higher fuel consumption	More carbon and hydrogen atom—High energy content and lower fuel consumption
High saturation pressure (Higher volatilities)—More chances of cavitation and vapor lock problems	Low saturation pressure (Lower volatilities)—fewer chances of cavitation and vapor lock problems
The high heat of vaporization—difficult engine starting in cold atmospheric conditions	Low heat of vaporization (half of methanol)—Relatively light engine starting in cold atmospheric conditions
Lower kinematic viscosity—It may become a source of wear problems in the fuel line	Higher kinematic viscosity—avoids potential wear problems in the fuel line
Corrosive in large doses	Less corrosive
Low flashpoint—unsafe while using in hot environmental conditions	High flash point—much safer fuel in hot environmental working conditions
Low Stoichiometric A/F ratio—comparatively less compatible with present automobile engine design	Relatively high Stoichiometric A/F ratio—more consistent with current automobile engine design
Low water tolerance—comparatively more chances of separation from base fuel	Comparatively high water tolerance—fewer chances of separation from base fuel
Toxic in large doses	Moderate toxic

a 10% volume of n-pentanol, *n*-butanol and isobutanol in gasoline. They found that all the oxygenate blends exhibited better performance except for *n*-butanol blends. Emissions also low compared to gasoline except for NO_x, which varied concerning the latent heat of vaporization. Geo et al. [150] have observed that the higher alcohol–gasoline blends' emission parameters were lower in higher load conditions and in-cylinder pressure. However, heat release rates were increased compared to gasoline.

Yilmaz et al. [151] studied the effects of hydrogen addition in methanol–gasoline blends on an SI engine's performance and emission characteristics. They found that the addition of H_2 improves the combustion process but caused increasing CO_2 and NO_x emission. On the other hand, CO and HC emissions were reduced due to the leaning effect caused by the methanol addition. Gong et al. [152] studied the influence of added hydrogen in methanol engines. They concluded that CO and HC emissions decrease by using H_2 at low engine speeds and various ignition timing but increases NO_x and soot emissions. Even though the hydrogen addition to the methanol–gasoline blend has some advantages, it is very costly and complicated to store and use onboard [153]. It needs some significant modifications to the engine design to use hydrogen in the existing SI engines. According to Hosseini et al. [107], internal combustion engines attain only 20–25% efficiency and low power output when using hydrogen fuel compared to fossil fuel. The running costs of hydrogen vehicles could be one-third higher than for existing gasoline vehicles because of the high price of hydrogen. Also, the hydrogen addition may increase NO_x emissions. So it is better and easy to use higher alcohol in methanol–gasoline blended fuel. Butanol is an excellent biofuel, and advancements in biotechnology applications can make butanol production cost less and easier [13].

7.1 Isobutanol (Isomer of Butanol) as Additives of Methanol–Gasoline Blended Fuel

Experimental studies on the use of methanol and butanol isomers in SI engines either as a pure form or as blended with gasoline have been reported in several articles. Still, the idea of ternary blends of these additives with gasoline has come recently [146, 154–157]. Generally, the butanol isomers help reduce emissions because of the low hydrocarbon fractions and high oxygen levels [154]. Most used butanol isomers are n-butanol (CH_3–CH_2–CH_2–CH_2OH) and isobutanol (CH_3 $(CH_2)_3OH$). Their production methods are more familiar than other isomers. Some of the research findings revealed that isobutanol is a suitable methanol–gasoline blendstock than *n*-butanol [158]. Isobutanol is consisting of four carbon atoms, which is also represented as i-BuOH with the IUPAC nomenclature of isobutanol is 2-methylpropan-1-ol. The other names of isobutanol are isobutyl alcohol, 2 methyl-1-propanol, 2-methylpropyl alcohol, and isopropyl carbinol. The energy content of isobutanol is high compared to methanol and is almost 80% of gasoline's energy content. It has low Reid vapor pressure compared to ethanol and methanol, making it a more suitable gasoline blendstock [159]. Table 2 shows the functionalities of methanol and isobutanol relevant to automobile applications. Table 3 shows the comparison of the physicochemical properties of isobutanol, *n*-butanol and methanol.

Recent researchers identified bio-butanol as promising next-generation eco-friendly alternative fuel because of its capability to reduce the amount of carbon escape to the atmosphere during combustion and which further reduces greenhouse gases and global warming [164]. Bio-butanol is mainly produced using an anaerobic biological process called ABE (acetone, butanol and ethanol) fermentation. It is the process of converting sugar to acetone, butanol and ethanol in the ratio of 3:6:1, respectively, with genus clostridia [160, 164–168]. Bio-butanol offers an alternative fuel for spark-ignition engines and has superior fuel properties than lower alcohols, which are conventionally used in fuel blends [169]. The butanol can be derived from fossil fuels known as petrobutanol. Both bio-butanol and petrobutanol have the same physical and chemical properties [170]. Elfasakhany [158] has done experiments on an unmodified SI engine with different ternary blend fuels. He observed that adding isobutanol to methanol–gasoline blended fuel can lead to a significant reduction in exhaust emissions. The performance is comparable to gasoline fuel and higher than n-butanol-added ethanol–gasoline blend fuels.

8 Combustion Characteristics of Alcohol Blended Fuels

The cylinder pressure and heat release rate (HRR) are essential combustion characteristics used to collect information about the engine's combustion behavior. Ignition, development of flame, propagation and termination of the flame are the main combustion processes [44]. The parameter flame speed is the most important among other combustion parameters since it influences the rate of fuel burning and combustion duration [171]. The physical and chemical properties of the fuel used in internal combustion engines are among the main parameters that affect HRR [172]. The alcohol–gasoline blends can improve the HRR with increasing alcohol concentration in the blended fuel. A high HRR indicates that the combustion is adequate. The addition of alcohols to gasoline increases the blended fuel's oxygen content, which makes the fuel burn more fully and the HRR increases [173]. Methanol is superior to ethanol and butanol in improving the HRR of the engine in the range of speeds 2000–2500 rpm; still, at higher engine speeds (greater than 2500 rpm), the HRR of methanol and ethanol blends begins to decrease.

On the other hand, butanol–gasoline blends can burn better and release more heat at high speeds and full-load operation. Butanol is more suitable for running at higher engine speeds and full-load conditions than methanol and ethanol [173]. Qi et al. [44] have observed increased peak cylinder pressure with the rise in methanol level in the blended fuel. But these peak cylinder pressures for all the test fuels were almost identical at lower engine loads. Eyidogan et al. [172] compared combustion characteristics of alcohol blended fuels and gasoline with cylinder gas pressure and HRR. They observed that the cylinder gas pressure using pure gasoline started increasing earlier than fuel blends and $P_{\max}$ of all the test fuels occurs near the top dead center (TDC). Because of the longer combustion duration, gasoline's cylinder gas pressure is wider than methanol–gasoline fuel blends. At the vehicle speed of 80 km/h, $P_{\max}$ was obtained from M10 at 5 kW, whereas with the use of pure gasoline, the same wheel power was obtained at 10 kW, 15 kW and 20 kW.

Agarwal et al. [174] examined an MPFI automotive engine's combustion characteristics using gasoline-methanol blends (gasohol). They observed that the combustion characteristics of methanol–gasoline blend were similar to gasoline. There was a decrease in combustion duration because

Table 3 Comparison of the physicochemical properties of isobutanol, n-butanol, and methanol [14, 146, 158, 163]

Properties	Unit	Isobutanol	*n*-butanol	Methanol
Chemical formula	–	C_4H_9OH	C_4H_9OH	CH_3OH
Molecular weight	g/mol	74.12	74.12	32.04
Oxygen	mass%	21.62	21.62	49.93
Hydrogen	mass%	13.5	13.5	12.5
Carbon	mass%	64.8	64.8	37.5
Density	g/ml	0.81	0.802	0.792
Autoignition temperature	°C	415.6	343	423
Boiling point	°C	108	117.7	78
Flashpoint	°C	28	37	11
Reid vapor pressure	kPa	2.3	2.27	32.4
Motor octane no	–	105	98	88.6
Latent heat of vaporization	kJ/kg	686.4	919.6	920–1109
Lower heating value	MJ/kg	33.1	33.19	20.1
Viscosity at 20 °C	mm^2/s	1.36	5.38	0.596
Stoichiometric AFR	kg/kg	11.20	11.20	6.5
Solubility in water at 25 °C	ml/100 ml H_2O	10.6	7.7	Miscible

of the faster combustion of gasoline-methanol blends. They concluded that methanol and gasohol could be used as good alternative fuel for unmodified engines. Gravalos et al. [175] have experimentally studied the influence of various alcohol–gasoline blended fuels in an SI engine. They found that the methanol–gasoline blend has achieved good combustion efficiency, and the high NO_x emissions can be regulated using a catalytic converter. Ozsezen et al. [176] investigated the combustion characteristics of methanol/ethanol–gasoline blends (E5, E10, M5, M10). They observed reduction in HC and CO emission when using alcohol blends than gasoline. Celik et al. [177] have done experiments on a single-cylinder, four-stroke SI engine using methanol and gasoline under different compression ratios 6:1–10:1 at an engine speed range of 1500–3500 rpm. They observed a knock phenomenon at CR of 8:1 when fuel was gasoline and no-knock when methanol was used at CRs of 8:1 and 10:1. So, methanol addition will surely reduce the knocking tendency.

From the literature studies, the authors observed the following effects of methanol–gasoline blends. Methanol–gasoline blends help to improve the overall combustion efficiency of the SI engine. Advances in laminar flame speed, decreased combustion duration, rise in peak cylinder pressure, higher HRR and reduced knock tendency. Many researchers found increased BSFC due to the addition of methanol in gasoline. The reason for this effect may be the low heating value of alcohol compared to gasoline.

9 Effect of Methanol–Gasoline Blended Fuels on SI Engine Performance

Methanol is coming up as a favorite alternative fuel all over the world because of the compatible properties. Methanol can be blended with gasoline easily, and researchers have done mixing up to a concentration of 85% [5, 178, 179]. Many researchers observed some significant positive engine performance changes, fuel economy and emissions when using blended methanol fuel compared to regular gasoline [139, 175, 180]. Methanol fuel can suppress knocking and improve the thermal efficiency of the engine [88, 93, 181].

Tian et al. [173] used GT-Power software to simulate the working of a turbocharged direct-injection four-cylinder engine. For achieving better convergence and reducing the simulation error, the simulation used 200 cycles. They observed that when the engine speed is between 2000 and 2500 rpm, alcohol fuels can significantly increase its brake torque (BT). Methanol can increase the BT of the engine than ethanol and butanol. An increase of 6.41% and 6.42% in BT is exhibited by M10 and M20, respectively, at 2000–2500 rpm. However, a higher BSFC can be observed by the methanol blends in the SI engine. The increased BSFC is mainly because of the relatively low LHV of methanol. They also observed that at a speed of 3000 rpm, the addition of alcohol fuels has little effect on engine torque, but the BSFC increases.

Eyidogan et al. [172] have examined the performance of alcohol blends methanol–gasoline and ethanol–gasoline in an MPFI SI engine using a chassis dynamometer setup at different speeds. They have found the following effects: (1) increased brake specific fuel consumption, (2) delay in rising cylinder gas pressure compared to gasoline fuel and (3) the lowest heat release rate attained by the gasoline fuel in all test conditions. M10 exhibited increased BTE of 4.7 and 2.5% at 100 km/h and 80 km/h, respectively, because of the better combustion due to more oxygen content of M10. BSFC of M10 is 1.2% higher than gasoline at 100 km/h; however, this increase is normal due to the lower energy content of alcohols. Elfasakhany [158] had done a comparative study among five different fuel blends via methanol (M), ethanol (E), isobutanol (iB), *n*-butanol (nB) and acetone (AC) in gasoline to find the best alternative fuel among them. He used an unmodified SI engine test setup and found that the methanol blend showed the maximum volumetric efficiency and increased output torque. Simeon Iliev [182] investigated a four-stroke SI engine's emission and performance using ethanol and methanol blends. He developed a one-dimensional model of a four-stroke SI engine for finding the effect of various fuel types on a four-stroke SI engine at different operating conditions. His study revealed that the usage of blend fuels causes decreased brake power and increased fuel consumption. Abu-Zaid et al. [101] have studied the impact of methanol–gasoline blends on an SI engine's performance. The tests were conducted under different engine speeds varying from 1000 to 2500 rpm and in the condition of wide-open throttle (WOT) using different methanol–gasoline blend fuels. The results showed increased BSFC for all blend fuels compared to pure gasoline. Danaiah et al. [89] have done experiments on the carburetor-type four-cylinder SI engine using gasoline–methanol blends (5% to 15% volume) and changing the ignition timing 10° to 30° BTDC. They observed an increased thermal efficiency and decreased BSFC for a 15% volume concentration of methanol (M15). Table 4 shows a brief description of research findings on the use of methanol–gasoline blended fuels without additives on unmodified SI engine performance and emission.

Li et al. [53] had done a comparative analysis on performance and emissions of butanol–gasoline, methanol–gasoline and ethanol–gasoline in the PFI engine. They concluded that the butanol, methanol and ethanol and gasoline blends showed improved combustion and increase with the rise in volume ratios of methanol, ethanol and butanol in blends due to the superior laminar flame speed of alcohols. When the volume ratio of butanol increased to 60%, the tendency was reversed due to the low vapor pressure and charge-cooling

Table 4 Research findings on the use of methanol–gasoline blended fuels without additives on unmodified SI engine performance and emission

Engine specification	Operating conditions	Fuel	Blend fuel compared to gasoline		General findings	References
			Performance	Emission		
1.4i Honda Civic, MPFI, four-cylinder, 16-valve	Steady-state conditions				The BSFC for methanol fuel was lower than that ethanol	
Compression ratio: 10.4:1, Capacity: 1398 cc Max O/P: 66 kW @ 5600 rpm Max torque: 130 N-m @ 4300 rpm	Wheel powers varied from 5–20 kW Vehicle speeds of 80 km/h and 100 km/h were used for tests Without engine modification	Gasoline E5 E10 M5 M10	BTE ↑ (≈0.4–2.5%) BSFC ↑ (≈0.6–3.3%) EGT ↓ (≈0.2–1.5%)	CO ↓ (≈0.6–3.3%) CO_2 ↓ (≈3–9.5%) HC ↓ (≈27–35%) NO*x* ↓ (≈1.3–15.5%)	As the volumetric efficiency increases, the BSFC decreases CO emission shows a varying trend for M10 and E5 between 15–20 kW at 100 km/h The CO emission shows a decreasing trend for M5 and E10 for all-wheel powers at100 km/h	Eyidogen, canakci et al. [139, 172]
Four-cylinder, four-stroke, water-cooled engine Multipoint port injection Max O/P: 55 kW @ 5000 rpm	Tests were performed at various speeds ranging from 1000 to 4000 rpm Without engine modification	Gasoline M10 E10 Bu10	EGT ↑ BTE ↑ (≈2.8–6.8%) BSFC ↑	CO ↓ CO_2 ↑ (≈5.8–7.15%) HC ↓ (≈13.4–18.4%) NO*x* ↓	The Bu10 is more effective than E10 and M10 in reducing HC emissions M10 is more effective in reducing CO emission	Varol et al. [183]
Four-cylinder, four-stroke Air-cooled engine Max O/P: 13 kW @1500 rpm	The ignition timing range 10–30° varied by 10°	Gasoline M5 M10 M15	BTE ↑ BSFC ↓	CO ↓ (≈3.2–3.98%) HC ↓ NO*x* ↓ (≈8.3%)	The methanol addition leads to better combustion, thereby lowering fuel consumption	Danaiah et al. [89]
Single-cylinder, Four-stroke Air-cooled capacity: 196 cc CR: 8.5:1	All the data were collected at each engine speed when exhaust emissions to become constant	Methanol Ethanol	BTE ↑ (≈3.65–4.51%) BMEP ↑ 5.25–10.5%) BSFC ↑ (≈30.22–58.9%)	CO ↓ 14.49–29.37%) CO_2 ↑ 1.46–2.19%) HC ↓ 22.79–28.22%) NO*x* ↑ 18.1–22.97%)	Engine torque decreased after it reached the maximum point, along with the increasing of engine speeds	Balki et al. [184]
Single-cylinder, Compression Ratio: 8.5:1 Air-cooled Capacity:163 cc Max O/P: 3.5 kW @ 3600 rpm	EPA six-mode cycle, 3600 rpm at five loads, and 1800 rpm (idling) under no-load Without engine modification	M15 M25	BSFC ↓ (≈5.9%)	CO ↓ (36.4–54.2%) HC ↓ (18–27.9%) NO*x* ↑ (≈60–71.4%)	Methanol–gasoline blended fuels resulted in an increase in the lambda and made the inducted fuel–air mixture leaner Blends cause higher levels of formaldehyde and acetaldehyde	Wang et al. [185]

Table 4 (continued)

Engine specification	Operating conditions	Fuel	Blend fuel compared to gasoline		General findings	References
			Performance	Emission		
Volkswagen Passat sedan, GDI In-line, Four-cylinder Capacity: 1800 cc	Tests were conducted in March 2014 at an altitude of 70 m	Gasoline M15 M25 M40	–	CO ↓ (9.4–33.2%) CO_2 ↓ (0.8–4.1%) HC ↓ (9.7–36.9%) NO*x* ↓	Emission reduction benefits and fuel-related costs Low-content gasohol required no modifications of the engine	Wang et al. [85]
Single cylinder, Four-stroke Air-cooled, CR:7:1	Speed range of 2600–3450 rpm and a load of 1.3–1.6 kW was used	Gasoline E3, E7, E10 M3, M7 M10 EM3, EM7 EM10		CO ↓ 17.7–55.5%) CO_2 ↑ (3–9.2%) HC ↓ (19.6–26%)	The methanol–gasoline blends (M) confirm the lowest emissions of CO and UHC among all test fuels Increasing methanol concentration in gasoline leads to reduced emissions	Elfasakhany [186]
Single-cylinder, four-stroke, multifuel research engine Water-cooled, research engine, Compression ratio: 10:1 Max O/P: 4.5 kW @ 1800 rpm	The engine speed range of 1200–1750 rpm A constant load of 8 kg at different throttle openings Without engine modification	E20 M20 Iso-Octane	Torque ↑ (≈1.39%) IP ↓ (≈4%) BP ↑ (≈4%) FP ↓ (≈3.33–32.2%) BSFC ↑ (≈33%)	–	Increased volumetric efficiency, cylinder pressure, temperature and improved combustion due to leaner operation Addition up to 20% of methanol and ethanol needs no modification of the modern engine	Kamboj et al. [129]
Single-cylinder, four-valve Capacity:147 cc, compression ratio: 7:1 Max O/P: 1.5 kW @ 3400 rpm	The engine was run on a full load from 2600 to 3400 rpm with an interval of 100 rpm	E10, E7, E3 M10, M7, M3 iB10, iB7, iB3 nB10, nB7, nB3	Torque ↑ (≈1.3–2.13%) BP ↑ (≈2.8–7.4%) η_{vol} ↑ (≈32%)	CO ↓ (7–32%) CO_2 ↑ (2.3–8%) HC ↓ (1.8–19.6%)	CO emissions vary with engine speeds The higher the rate of fuel blends in the mixture, the complete combustion, and less emission	Ashraf Elfasakhany [45]

effect. Wu et al. [187] have studied the impact of pure methanol on the emission and combustion performance of an SI engine working under idle conditions. The study results showed that methanol had played a useful role in refining engine economy and performance under lean-burn conditions. A higher indicated thermal efficiency value of 24.7% was obtained at lambda 1.4, which is comparatively higher than the value obtained when using gasoline in the same condition. It was found that methanol has improved combustion rate and has decreased flame development and flame propagation periods.

Only a few researchers observed a significant decrease in BSFC for a low dose of methanol blends. Most of the researchers observed higher volumetric and brake thermal efficiency (BTE) for methanol–gasoline blends. The brake torque (BT) showed an increasing trend, but the engine's brake power is decreasing by using methanol–gasoline blends. Suppose the alcohol cost is lower than the conventional fossil fuel and considering methanol as a renewable fuel. In that case, the adverse effect of higher brake specific fuel consumption (BSFC) can be neglected.

10 Effect of Methanol–Gasoline Blends with Higher Alcohol Additives on SI Engine Performance

Additives are generally used in methanol–gasoline blend fuels to improve the blends' properties, thereby enhancing engine performance. Higher alcohol can be used as a potential additive for this purpose as gasoline's miscibility is better than other additives like alkanes and hydrogen.

Elfasakhany [40] has studied the effect of ternary blends of n-butanol–bioethanol–gasoline (nBE) and isobutanol–biomethanol–gasoline (iBM) on the performance and emissions of an SI engine. The blended fuel showed a slight decrease in performance because of the lack of engine tuning. The engine performance of iBM was lower than gasoline as 2.6%, 0.43%, 2.4% and 2.5%, and for BP, Torque, VE, EGT, respectively, while the ICP of iBM was found to be higher by about 1.2%. He also found that the performance of iBM is better than nBM blends and is comparable to gasoline. In another study, Elfasakhany [154] performed experimental investigations in a spark-ignition engine using n-butanol/isobutanol dual alcohol–gasoline blends. He found that at a higher volume percentage of alcohols, the volumetric efficiency exceeds the gasoline value because the heat of evaporation starts to dominate the saturation pressure in higher concentrations. At all engine speeds, torque using dual alcohols/gasoline blends is decreased relative to that of the pure gasoline by about 3.6%, 4% and 2.1% for niB3, niB7 and niB1. The engine power also reduced by 5.9%, 7.2% and 4.6% for niB3, niB7 and niB10, respectively, compared to pure gasoline. The reduction in performance is due to the lower energy content of alcohols. However, the performance can be improved by proper selection of blends and concentrations. Elfasakhany [186] studied an SI engine's performance and emission characteristics using ethanol–methanol–gasoline blends. He observed an approximately 33% and 27% increase in volumetric efficiency for methanol and methanol ethanol blends than base gasoline because of the higher latent heat of vaporization of ethanol and methanol. Sharudin et al. [121] studied the isobutanol additive effect in the methanol–gasoline fuel of unmodified spark-ignition engines. They have used a lower ratio of methanol–gasoline blends (M5) with the isobutanol additive (5–15% with 5% increment) than base gasoline fuel. The results showed a 10.1% and 19.3% increase in BP and BTE achieved by M5B15 blended fuel compared to base fuel at 2500 rpm. Siwale et al. [179] compared the combustion, emission and performance characteristics of methanol–gasoline blend with methanol–*n*-butanol–gasoline blend with gasoline at steady state. The dual alcohol–gasoline blend (M53b17) was selected according to gasoline fuel's vapor pressure requirement. The use of M53b17 was preferred over M70 due to the lower EGT benefits, leading to improved volumetric efficiency and consequently reducing the compression work. Besides, its combustion efficiency also improved due to better energy content when using the M53b17 blend. Elfasakhany [155] has studied the effect of ternary blends of n-butanol–isobutanol–gasoline, isobutanol–ethanol–gasoline and ethanol–methanol–gasoline on a single-cylinder, four-stroke SI engine. The results showed betterment in brake power, torque and volumetric efficiency for ethanol–methanol–gasoline blends compared to other combinations. Yilmaz et al. [151] investigated the performance and emissions characteristics of a methanol–gasoline blend with the addition of hydrogen in an SI engine. They observed a decrease in thermal efficiency and an increase in the SI engine's brake specific fuel consumption due to the homogeneous air–fuel mixture and better combustion properties of hydrogen. Table 5 shows a brief description of research findings on the use of methanol–gasoline blended fuels with additives on unmodified SI engine performance and emission.

11 Effect of Methanol–Gasoline Blends on SI Engine Emission

The engine emission depends on many factors such as fuel, combustion characteristics, cylinder temperature, cylinder pressure, etc. Simeon Iliev [147] observed the following results during his experimental study. The CO and HC emissions decrease when methanol and ethanol concentration increases. The blends M50 show the lowest HC and CO

Table 5 Research findings on the use of methanol–gasoline blended fuels with additives on unmodified SI engine performance and emission

Engine specification	Operating conditions	Fuel	Blend fuel compared to gasoline Performance	Emission	General findings	References
Four-cylinder, four-stroke, water-cooled engine Capacity: 1598 cc, Compression ratio: 10:1 Max O/P: 85 kW @ 5800 rpm Max torque: 160 N-m @ 4000 rpm	Tests were carried out at an excess air ratio 1.40, with intake manifold absolute pressures of 93, 80 and 68 kPa for different rpm Tested at different engine speeds of 1200, 1800 and 2400 rpm The added H_2 volume fraction in the intake mixture was 0%, 3%, and 6%	Gasoline Methanol (0%, 3%, and 6% fraction of added hydrogen)	MEP ↓ HRR_{max} ↓ $P_{cyl,\,max}$ ↓ (at low speeds) IMEP ↑ HRR_{max} ↑ $P_{cyl,\,max}$ ↑ (at high speeds)	CO ↓ HC ↓ (Low speeds) NOx ↑ Soot ↑ (High speeds)	Postponing ignition timing causes IMEP, maximum cylinder pressure, ignition delay and NO_X and soot emissions to decrease with added hydrogen at high engine speeds	Gong et al. [152]
Ford MVH418 spark ignition Four-cylinder, four-stroke, Capacity: 1796 cc, Compression ratio: 10:1 Max O/P: 77 kW @ 5950 rpm Max torque: 153 N-m @ 4000 rpm	Tests were conducted with three engine load conditions (no-load, 50% and 100%) with a constant speed of 2000 rpm Without engine modification	G100 G95M5 G90M10 G85M15 (3, 6, 9, 12 and 15% fractions of hydrogen added)	BSFC ↓ η_{Th} ↑	CO ↓ CO_2 ↑ HC ↓ NO*x* ↑	By the addition of hydrogen to the methanol—gasoline mixtures, the BSFC decreased by 4%, and the thermal efficiency increased by 2% compared to the gasoline	Iyimaz et al. [151]
Single-cylinder, four-stroke, Air-cooled capacity: 1597 cc Compression ratio: 7:1 Max O/P: 1.5 kW @ 6000 rpm,	The tests are conducted by varying the engine speeds from 2600 to 3400 rpm with 100 rpm Without engine modification	Isobutanol–biomethanol–gasoline (iBM) n-butanol–bioethanol–gasoline (nBE)	Torque ↓ BP ↓ EGT ↓	CO ↓ (29–33%) CO_2 ↓ (16.7–21.9%) HC ↓ (30–34%)	The better engine performance is shown by iBM and which is very similar to the neat gasoline performance	Ashraf Elfasakhany [40]
Four-cylinder, Multipoint electric port fuel system Air-cooled engine Capacity:1596 cc, Compression ratio: 8.5:1 Max O/P: 78 kW @ 6000 rpm Max torque: 135 N-m @ 4000 rpm	Tests were conducted at constant full load with an engine speed range of 1000–2500 rpm with an increment of 500 rpm Without engine modification	Gasoline M5 M5B5 M5B10 M5B15	BP ↑ (3.9–10.1%) BTE ↑ (≈2%) BSFC ↑ (0.5–1.42%) EGT ↓ (1.3–4.5%)	CO ↓ (1.93–7.34%) CO_2 ↑ (≈12.9%) HC ↓ (0.5–2%) NO*x* ↑ (1.93–7.34%)	The effect of the isobutanol additive on methanol–gasoline blends improved the brake power by 10.1% than base fuel Blends cause higher levels of formaldehyde and acetaldehyde	Sharudin et al. [121]
Suzuki RS-416 Four-cylinder, DOHC Naturally aspired Capacity:1596 cc Compression Ratio: 11:1 Max O/P: 92 kW @ 4800 rpm Max torque: 148 N-m @ 4800 rpm	The spark timing was varied from 18 to 32°bTDC and speed was set to 2500 rpm Without engine modification	*n*-butanol M53b17	BTE ↑ BSFC ↑ EGT ↓ η_{vol} ↑	CO ↑ CO_2 ↑ HC ↓ NO*x* ↑	Due to the lower EGT of M53b17, the volumetric efficiency increases M53b17 blend shows improved combustion efficiency The vapor pressure of M53b17 is matching with gasoline	Siwale et al [180]

Table 5 (continued)

Engine specification	Operating conditions	Fuel	Blend fuel compared to gasoline		General findings	References
			Performance	Emission		
Four-cylinder, MPFI Capacity:1086 cc Max O/P: 48 kW @ 5500 rpm Max torque: 99 N-m @ 2500 rpm	Engine speed varied in the range (1000–2500 rpm) Without engine modification	Gasoline M10 M15 iBM 10 iBM15	–	CO ↓ (65–87%) HC ↓ (10–25%) NO*x* ↑ (68.02%)	The higher alcohol isobutanol has enhanced the emission characteristics unmodified automotive gasoline engine	Bharath et al. [8]

emissions, but there was a significant increase in NO*x* emissions when increasing the volume percentage of alcohols up to 30%, and then it decreases.

Canakci et al. [139] have done experiments on an SI engine fueled with methanol–gasoline fuel blends and pure gasoline. They observed a decrease in HC and CO at the vehicle speed of 80 km/h due to methanol–gasoline blends. Siwale et al. [180] studied the effects of blend fuel on combustion, performance and emission characteristics of single alcohol and dual alcohol–gasoline blends (methanol–gasoline and methanol–*n*-butanol–gasoline). The result revealed that M70 (70% methanol and 30% gasoline) produced low NOx emissions than ternary blends, and the NO_x emission increases with the increase in spark timing. The blend M20 (20% methanol and 80% gasoline) produced more NOx emissions. Liu et al. [88] have studied the engine emissions and cold-start performance with the methanol–gasoline blend in a three-cylinder SI engine with port fuel injection. They observed a reduction in CO emissions during the warming-up and cold start. Varol et al. [183] have experimentally proved that methanol–gasoline fuel (M10) can decrease CO emissions. Zervas et al. [188] have examined the effect of equivalence air–fuel ratio and fuel composition on NO_x emissions. They have concluded that blends of 2-propanol, methanol, ethanol and MTBE with gasoline (by 5% and 20% volume) could reduce NOx emission up to 60% at the stoichiometric condition. Tian et al. [173] studied the emission characteristics of methanol, ethanol and butanol in the TISI engine. They found that compared with ethanol and butanol, methanol can better increase engine BTE, but it also increases BSFC.

Li et al. [53] have observed an increased CO emission by adding ethanol, methanol and butanol, at stoichiometry and decreased CO emission at the rich condition. Unburned hydrocarbon emission was found to be increased for a methanol–gasoline blend while decreased for the butanol–gasoline blend. But methanol–gasoline blends showed a lesser NO_x emission compared to gasoline. Liu et al. [92] studied the effect of methanol–gasoline blend in a three-cylinder port fuel injection engine. They concluded that methanol reduces HC emissions throughout the cold-start and warming-up process at 5 °C. In the first few seconds, HC reduction was more than 50% and decreased to 30% in the final warming-up period. Also, there was a nearly 25% reduction in CO when using M30 fuel. Zhen et al. [189] have done numerical analysis on emissions in an SI engine and concluded that the CO emission could be reduced by increasing compression ratios and delaying spark timings. Still, there is a chance of increased CO emission in higher engine speeds. Zhao et al. [87] have examined the effect of methanol blend and 100% methanol fuel on passenger cars' emission characteristics. They concluded that methanol–gasoline blended fuels caused a 9–21% reduction in CO and a 1–55% reduction in THC emissions. They have observed four and two times higher formaldehyde emissions for M100 and M15, respectively, compared to gasoline. Tian et al. [173] observed that alcohol fuels to gasoline could reduce CO and CO_2 emissions, along with a slight increase in HC and NO_x emission. Adjusting the ignition time and flame kernel radius can efficiently enhance engine torque and reduce fuel consumption and exhaust emissions, especially NO_x emissions. Rifal et al. [190] found that methanol–gasoline fuel blend reduced HC and CO emissions by 45% and 33.25%, respectively; however, the CO_2 emissions increased by 10.3% for all engine speeds.

12 Effect of Methanol–Gasoline Blends with Higher Alcohol Additives on SI Engine Emission

The higher alcohol additives are generally added to methanol–gasoline blends to improve their blend properties and to enhance combustion, performance and emission characteristics. The methanol–gasoline blended fuel with higher alcohol additives is also called ternary blend fuels. The higher alcohols will work as a property enhancer for the methanol–gasoline blend fuels without any miscibility issues since the additives are also from the alcohol family.

Elfasakhany [40] has studied the effect of *n*-butanol–bioethanol–gasoline (nBE) and isobutanol–biomethanol–gasoline (iBM) on emissions of a SI engine. He found that all the fuel blends (iBM and nBE) showed low UHC, CO_2 and CO emissions than the regular gasoline and emissions decrease with an increase in the concentration of the additive in blends. Bharath et al. [8] studied the noise, vibration and emission characteristics of methanol-based ternary blends on a four-cylinder automotive SI engine. They observed significant reduction in HC and CO emissions without any modification to the engine. Sharudin et al. [121] have investigated the effect of volume percentages of isobutanol (B5, B10, and B15) on an unmodified SI engine fueled with methanol–gasoline blended fuel (M5). He proved that isobutanol–methanol–gasoline significantly improved the performance of the engine compared to the methanol–gasoline blend. Siwale et al. [180] studied the emissions of a spark-ignition engine using methanol (53%)–n-butanol (17%)–gasoline (30%) blended fuels and compared results with biomethanol (70%)–gasoline (30%), biomethanol (20%)–gasoline (80%) and neat gasoline. The results showed lower emissions and higher performance of blended fuels than those of neat gasoline and ternary blends showed lower UHC emission, more elevated CO, NO_x and CO_2 emissions and lower brake thermal efficiency than those of dual fuel blends. Elfasakhany [155] has observed reductions in CO and UHC emissions for the ternary blend of ethanol–methanol–gasoline, compared to other blends.

13 Conclusions and Recommendations

In this review, the authors enlightened the influence of higher alcohol additives in methanol–gasoline fuel (methanol-based ternary fuel) on an SI engine's performance and emissions. The paper explains the different methods used for the production of methanol and its applications. The benefits of using 'isobutanol' in methanol–gasoline blended fuel and its properties were discussed concerning automobile applications. The addition of higher alcohol could resolve some of the adverse effects of methanol blended fuel in an unmodified SI engine. Most of the test spark-ignition engines described in the literature review are without engine modifications, which shows that methanol can be a possible alternative fuel for existing gasoline engines. Methanol, as an alternative fuel, can considerably reduce fuel import and transportation costs since methanol can be produced from the locally available feedstock. The following are the general conclusions:

1. Many research studies have reported that alcohol as an alternative fuel has a more substantial part in satisfying the existing energy demand mainly in the transport sector and in fighting against the fossil fuel crisis because of the feasibility and its economic aspects. The methanol–gasoline blended fuel of optimum concentration can be used directly in SI engines without engine modifications.
2. The majority of researchers reported that methanol has specific chemical and physical characteristics, which increases the brake torque (BT), heat release rate (HRR) and overall brake thermal efficiency (BTE) of the engine and helps to reduce emissions of CO, HC, etc.
3. Performance studies using methanol–gasoline blended fuel indicated that increasing the dose of methanol will lead to higher BSFC compared to gasoline because of the low energy content. Still, the use of higher alcohol additives can control this adverse effect. Ignition time and flame kernel radius tuning can efficiently reduce fuel consumption and exhaust emissions, especially NOx, and also improve engine torque.
4. Studies revealed that higher alcohol additives such as isobutanol could be used with methanol–gasoline blended fuel to improve blend fuel properties. It also helps to avoid phase separation problems and enhance the stability of the blended fuel.
5. Production of methanol from CO_2 and electrofuels can reduce greenhouse gases and global warming. Waste biomass or even sewage can work as the feedstock for biomethanol. Conversion of biogas to methanol is also

significant because, through this process, the biogas can be effectively utilized in internal combustion engine operations.

6. Methanol in pure form (100%) can be used directly in modified spark-ignition engines. The increased compression ratio at higher blending concentration or methanol fuel in the pure form will increase the engine's power and torque because of the high octane rating of methanol.

Based on the study mentioned above, it can be concluded that a lot many researchers have made great attempts and efforts in exploring, understanding and experimenting methanol's ability to fight against the energy crisis. The researchers are also promoting it as a future alternative fuel, but there are still spaces for advancement in many countries like India. Further investigation is needed to determine methanol production from different biomass (biomethanol) and to find more easy production methods. The selection criteria and selection methods for higher alcohol additive to methanol–gasoline blended fuel should be explained well. The concentration of higher alcohol additives added to the methanol fuel needs optimization for economic aspects and efficient performance of the engine. The authors have a strong opinion that the researchers should focus more on bio-alcohol, production of electrofuels from CO_2 and conversion of the same to methanol to reduce carbon in the atmosphere. Other areas of focus should be on storage, stability and conveyance of methanol–gasoline blend fuel. Also, It is needed to concentrate more on the modification or conversion of the present automobiles in minimum efforts to work efficiently in higher percentage methanol blends and conform to the current emission standards.

References

1. Mustafi, N.N., Agarwal, A.K.: Future automotive powertrains for India: methanol versus electric vehicles. In: Akhilendra Pratap Singh, Y.C.S., Agarwal, N.N.M.A.K. (eds.) Altern. Fuels Their Util. Strateg. Intern. Combust. Engines, pp. 229–271 (2020). https://doi.org/10.1007/978-981-15-0418-1_13.
2. Shamsul, N.S.; Kamarudin, S.K.; Rahman, N.A.; Kofli, N.T.: An overview on the production of bio-methanol as potential renewable energy. Renew. Sustain. Energy Rev. **33**, 578–588 (2014). https://doi.org/10.1016/j.rser.2014.02.024
3. Masum, B.M.; Kalam, M.A.; Masjuki, H.H.; Palash, S.M.; Fattah, I.M.R.: Performance and emission analysis of a multi cylinder gasoline engine operating at different alcohol-gasoline blends. RSC Adv. **4**, 27898–27904 (2014). https://doi.org/10.1039/c4ra04580g
4. Rathinam, S.; Balan, K.N.; Subbiah, G.; Sajin, J.B.; Devarajan, Y.: Emission study of a diesel engine fueled with higher alcohol-biodiesel blended fuels. Int. J. Green Energy. **16**, 667–673 (2019). https://doi.org/10.1080/15435075.2019.1617001
5. Awad, O.I.; Mamat, R.; Ali, O.M.; Sidik, N.A.C.; Yusaf, T.; Kadirgama, K.; Kettner, M.: Alcohol and ether as alternative fuels in spark ignition engine: a review. Renew. Sustain. Energy Rev. **82**, 2586–2605 (2018). https://doi.org/10.1016/j.rser.2017.09.074
6. Salvi, B.L.; Subramanian, K.A.; Panwar, N.L.: Alternative fuels for transportation vehicles: a technical review. Renew. Sustain. Energy Rev. **25**, 404–419 (2013). https://doi.org/10.1016/j.rser.2013.04.017
7. Sangeeta, S.; Moka, M.; Pande, M.; Rani, R.; Gakhar, M.; Sharma, J.; Rani, A.N.: Bhaskarwar, alternative fuels: an overview of current trends and scope for future. Renew. Sustain. Energy Rev. **32**, 697–712 (2014). https://doi.org/10.1016/j.rser.2014.01.023
8. Bharath, B.K.: Effect of ternary blends on the noise, vibration, and emission characteristics of an automotive spark ignition engine. Energy Sources Part A Recover. Util. Environ. Effects (2020). https://doi.org/10.1080/15567036.2020.1788673
9. Malaquias, A.C.T.; Netto, N.A.D.; Filho, F.A.R.; da Costa, R.B.R.; Langeani, M.; Baêta, J.G.C.: The misleading total replacement of internal combustion engines by electric motors and a study of the Brazilian ethanol importance for the sustainable future of mobility: a review. J. Braz. Soc. Mech. Sci. Eng. **41**, 1–23 (2019). https://doi.org/10.1007/s40430-019-2076-1
10. Schifter, I.; González, U.; Díaz, L.; Sánchez-Reyna, G.; Mejía-Centeno, I.; González-Macías, C.: Comparison of performance and emissions for gasoline-oxygenated blends up to 20 percent oxygen and implications for combustion on a spark-ignited engine. Fuel **208**, 673–681 (2017). https://doi.org/10.1016/j.fuel.2017.07.065
11. Tian, Z.; Zhen, X.; Wang, Y.; Liu, D.; Li, X.: Combustion and emission characteristics of n-butanol-gasoline blends in SI direct injection gasoline engine. Renew. Energy **146**, 267–279 (2020). https://doi.org/10.1016/j.renene.2019.06.041
12. He, J.; Chen, H.; Geng, L.; Xie, B.; Zhao, X.; Zhang, P.: Investigation on combustion and emission characteristics of diesel and gasoline blends with exhaust gas recirculation. Energy Sources Part A Recover. Util. Environ. Effects (2019). https://doi.org/10.1080/15567036.2019.1651796
13. Rathour, R.K.; Ahuja, V.; Bhatia, R.K.; Bhatt, A.K.: Biobutanol: new era of biofuels. Int. J. Energy Res. **42**, 4532–4545 (2018). https://doi.org/10.1002/er.4180
14. Demirel, Y.: 1.22. Biofuels **1**, 875–908 (2018). https://doi.org/10.1016/B978-0-12-809597-3.00125-5
15. Smith, J.L.; Workman, P.C.: Alcohol for Motor Fuels (2014). www.ext.colostate.edu. Accessed 12 Feb 2019
16. Qian, Y.; Li, Z.; Yu, L.; Wang, X.; Lu, X.: Review of the state-of-the-art of particulate matter emissions from modern gasoline fueled engines. Appl. Energy **238**, 1269–1298 (2019). https://doi.org/10.1016/j.apenergy.2019.01.179
17. Awad, O.I.; Mamat, R.; Ibrahim, T.K.; Hammid, A.T.; Yusri, I.M.; Hamidi, M.A.; Humada, A.M.; Yusop, A.F.: Overview of the oxygenated fuels in spark ignition engine: environmental and performance. Renew. Sustain. Energy Rev. **91**, 394–408 (2018). https://doi.org/10.1016/j.rser.2018.03.107
18. Zaharin, M.S.M.; Abdullah, N.R.; Masjuki, H.H.; Ali, O.M.; Najafi, G.; Yusaf, T.: Evaluation on physicochemical properties of iso-butanol additives in ethanol-gasoline blend on performance and emission characteristics of a spark-ignition engine. Appl. Therm. Eng. (2018). https://doi.org/10.1016/j.applthermaleng.2018.08.057
19. El-Seesy, A.I.; Nour, M.; Attia, A.M.A.; He, Z.; Hassan, H.: Investigation the effect of adding graphene oxide into diesel/higher alcohols blends on a diesel engine performance. Int. J. Green Energy **17**, 233–253 (2020). https://doi.org/10.1080/15435075.2020.1722132
20. Torres, E.A.; da Silva, J.A.M.; Silva, L.F.: Evaluation of ethanol as additive for NOx and PM reduction in CI engines fueled with diesel–biodiesel blends using a pump assembly. J. Braz. Soc.

Mech. Sci. Eng. **42**, 1–12 (2020). https://doi.org/10.1007/s40430-020-02494-0

21. Pearson, J.W.G.; Turner, R.J.; Holland, B.; Peck, R.: Alcohol-based fuels in high performance engines. Fuels Emiss. Conf. (2007). https://doi.org/10.4271/2007-01-0056
22. Aghahossein Shirazi, S.; Abdollahipoor, B.; Martinson, J.; Windom, B.; Foust, T.D.; Reardon, K.F.: Effects of dual-alcohol gasoline blends on physiochemical properties and volatility behavior. Fuel **252**, 542–552 (2019). https://doi.org/10.1016/j.fuel.2019.04.105
23. Melikoglu, M.; Singh, V.; Webb, C.; States, U.; Kong, H.; Kingdom, U.: Biochemical production of bioalcohols. In: Luque, R.; Clarka, J. (Eds.) Handbook of Biofuels Production, 2nd edn. Elsevier Ltd, Amsterdam (2016). https://doi.org/10.1016/B978-0-08-100455-5.00009-6
24. Sakthivel, P.; Subramanian, K.A.; Mathai, R.: Indian scenario of ethanol fuel and its utilization in automotive transportation sector. Resour. Conserv. Recycl. **132**, 102–120 (2018). https://doi.org/10.1016/j.resconrec.2018.01.012
25. Mourad, M.; Mahmoud, K.R.M.: Performance investigation of passenger vehicle fueled by propanol/gasoline blend according to a city driving cycle. Energy **149**, 741–749 (2018). https://doi.org/10.1016/j.energy.2018.02.099
26. Thangavel, V.; Momula, S.Y.; Gosala, D.B.; Asvathanarayanan, R.: Experimental studies on simultaneous injection of ethanol-gasoline and n-butanol-gasoline in the intake port of a four stroke SI engine. Renew. Energy **91**, 347–360 (2016). https://doi.org/10.1016/j.renene.2016.01.074
27. Surisetty, V.R.; Dalai, A.K.; Kozinski, J.: Alcohols as alternative fuels: an overview. Appl. Catal. A Gen. **404**, 1–11 (2011). https://doi.org/10.1016/j.apcata.2011.07.021
28. Szwaja, S.; Naber, J.D.: Combustion of n -butanol in a spark-ignition IC engine. Fuel **89**, 1573–1582 (2010). https://doi.org/10.1016/j.fuel.2009.08.043
29. Saraswat, R.B.V.K.: India's Leapfrog to Methanol Economy (2017). http://niti.gov.in/writereaddata/files/document_publication/ArticleonMethanolEconomy_Website.pdf. Accessed 12 Feb 2019
30. Hongsong, L.; Yanju, W.; Rui, Y.; Ying, W.; Shenghua, L.; Jie, L.: Effects of methanol/gasoline blends on a spark ignition engine performance and emissions. Energy Fuels **22**, 1254–1259 (2008)
31. Manoj, U.; Mishra, P.C.; Sahoo, A.K.; Subhashree, P.: Advances in Interdisciplinary Engineering. Springer, Berlin (2019) https://doi.org/10.1007/978-981-13-6577-5
32. Bechtold, R.L.; Goodman, M.B.: Use of Methanol as a Transportation Fuel (2007). http://www.methanol.org/wp-content/uploads/2016/06/Methanol-Use-in-Transportation.pdf. Accessed 12 Feb 2019
33. Yao, Y.; Chang, Y.; Huang, R.; Zhang, L.; Masanet, E.: Environmental implications of the methanol economy in China: well-to-wheel comparison of energy and environmental emissions for different methanol fuel production pathways. J. Clean. Prod. **172**, 1381–1390 (2018). https://doi.org/10.1016/j.jclepro.2017.10.232
34. Yusri, I.M.; Mamat, R.; Azmi, W.H.; Najafi, G.; Sidik, N.A.C.; Awad, O.I.: Experimental investigation of combustion, emissions and thermal balance of secondary butyl alcohol-gasoline blends in a spark ignition engine. Energy Convers. Manag. **123**, 1–14 (2016). https://doi.org/10.1016/j.enconman.2016.05.082
35. Simikic, M.; Tomic, M.; Savin, L.; Micic, R.; Ivanisevic, I.; Ivanisevic, M.: Influence of biodiesel on the performances of farm tractors: experimental testing in stationary and non-stationary conditions. Renew. Energy **121**, 677–687 (2018). https://doi.org/10.1016/j.renene.2018.01.069
36. Garcia, I.L.: Feedstocks and challenges to biofuel development 5. In: Luque, R.; Clark, J. (Eds.) Handbook of Biofuels Production, 2nd edn. Elsevier Ltd, Amsterdam (2016). https://doi.org/10.1016/B978-0-08-100455-5.00005-9
37. Raslavičius, L.; Keršys, A.; Starevičius, M.; Sapragonas, J.; Bazaras, Ž: Biofuels, sustainability and the transport sector in Lithuania. Renew. Sustain. Energy Rev. **32**, 328–346 (2014). https://doi.org/10.1016/j.rser.2014.01.019
38. IEA, Global Energy & CO2 Status Report, IEA, Paris (2019). https://www.iea.org/reports/global-energy-CO2-status-report-2019. Accessed 12 Feb 2019
39. Li, Q.; Liu, H.; Zhang, Y.; Yan, Z.; Deng, F.; Huang, Z.: Experimental and kinetic modeling study of laminar flame characteristics of higher mixed alcohols. Fuel Process. Technol. **188**, 30–42 (2019). https://doi.org/10.1016/j.fuproc.2019.01.010
40. Elfasakhany, A.: Exhaust emissions and performance of ternary iso-butanol–bio-methanol–gasoline and n-butanol–bio-ethanol–gasoline fuel blends in spark-ignition engines: assessment and comparison. Energy **158**, 830–844 (2018). https://doi.org/10.1016/j.energy.2018.05.120
41. Qi, D.H.; Lee, C.F.: Combustion and emissions behaviour for ethanol–gasoline-blended fuels in a multipoint electronic fuel injection engine. Int. J. Sustain. Energy. **35**, 323–338 (2016). https://doi.org/10.1080/14786451.2014.895004
42. Balki, M.K.; Sayin, C.: The effect of compression ratio on the performance, emissions and combustion of an SI (spark ignition) engine fueled with pure ethanol, methanol and unleaded gasoline. Energy **71**, 194–201 (2014). https://doi.org/10.1016/j.energy.2014.04.074
43. Wallner, T.; Frazee, R.: Study of regulated and non-regulated emissions from combustion of gasoline, alcohol fuels and their blends in a DI-SI engine. Security (2010). https://doi.org/10.4271/2010-01-1571
44. Qi, D.H.; Jia, C.C.; Feng, Y.M.: Combustion and emissions behaviour for methanol-gasoline blended fuels in a multipoint electronic fuel injection engine. Int. J. Sustain. Energy **33**, 985–999 (2014). https://doi.org/10.1080/14786451.2013.774004
45. Elfasakhany, A.: Investigations on performance and pollutant emissions of spark-ignition engines fueled with n-butanol-, isobutanol-, ethanol-, methanol-, and acetone-gasoline blends: a comparative study. Renew. Sustain. Energy Rev. **71**, 404–413 (2017). https://doi.org/10.1016/j.rser.2016.12.070
46. Sebastian Verhelst, J.W.; Sileghem, L.; Vancoillie, J.: Methanol as a fuel for internal combustion engines. Prog. Energy Combust. Sci. **70**, 43–88 (2019). https://doi.org/10.1016/j.pecs.2018.10.001
47. Zhen, X.; Wang, Y.: An overview of methanol as an internal combustion engine fuel. Renew. Sustain. Energy Rev. **52**, 477–493 (2015). https://doi.org/10.1016/j.rser.2015.07.083
48. Kowalewicz, A.: Methanol as a fuel for spark ignition engines: a review and analysis. Proc. Inst. Mech. Eng. Part D J. Automob. Eng. **207**, 43 (1993). https://doi.org/10.1243/PIME_PROC_1993_207_158_02
49. Pettersson, L.; Sjostrom, K.: Decomposed methanol as a fuel—a review. Combust. Sci. Technol. **80**, 265–303 (1991). https://doi.org/10.1080/00102209108951788
50. Çelebi, Y.; Aydın, H.: An overview on the light alcohol fuels in diesel engines. Fuel **236**, 890–911 (2019). https://doi.org/10.1016/j.fuel.2018.08.138
51. Keshavarz, A.; Mirvakili, A.; Chahibakhsh, S.; Shariati, A.; Rahimpour, M.R.: Simultaneous methanol production and separation in the methanol synthesis reactor to increase methanol production. Chem. Eng. Process. Process Intensif. **158**, 108176 (2020). https://doi.org/10.1016/j.cep.2020.108176
52. Methanol Institute, Methanol Production (2020). https://www.methanol.org/methanol-production/. Accessed 10 Dec 2020.
53. Li, Y.; Gong, J.; Deng, Y.; Yuan, W.; Fu, J.; Zhang, B.: Experimental comparative study on combustion, performance and emissions characteristics of methanol, ethanol and butanol in a spark

ignition engine. Appl. Therm. Eng. **115**, 53–63 (2017). https://doi.org/10.1016/j.applthermaleng.2016.12.037
54. Kumari, D.; Singh, R.: Pretreatment of lignocellulosic wastes for biofuel production: a critical review. Renew. Sustain. Energy Rev. **90**, 877–891 (2018). https://doi.org/10.1016/j.rser.2018.03.111
55. Bae, C.; Kim, J.: Alternative fuels for internal combustion engines. Proc. Combust. Inst. **36**, 3389–3413 (2017). https://doi.org/10.1016/j.proci.2016.09.009
56. Pirola, C.; Bozzano, G.; Manenti, F.: Fossil or Renewable Sources for Methanol Production? Elsevier, Amsterdam (2017) https://doi.org/10.1016/B978-0-444-63903-5.00003-0
57. Ali, K.A.; Abdullah, A.Z.; Mohamed, A.R.: Recent development in catalytic technologies for methanol synthesis from renewable sources: a critical review. Renew. Sustain. Energy Rev. **44**, 505–518 (2015). https://doi.org/10.1016/j.rser.2015.01.010
58. Turner, J.W.G.; Pearson, R.J.; Dekker, E.; Iosefa, B.; Johansson, K.; Bergström, K.: Extending the role of alcohols as transport fuels using iso-stoichiometric ternary blends of gasoline, ethanol and methanol. Appl. Energy. **102**, 72–86 (2013). https://doi.org/10.1016/j.apenergy.2012.07.044
59. Methanol Institute, The Methanol Industry. https://www.methanol.org/the-methanol-industry/. Accessed 5 Apr 2020
60. Yadav, P.; Athanassiadis, D.; Yacout, D.M.M.; Tysklind, M.; Upadhyayula, V.K.K.: Environmental impact and environmental cost assessment of methanol production from wood biomass. Environ. Pollut. **265**, 114990 (2020). https://doi.org/10.1016/j.envpol.2020.114990
61. IHS Markit, Chemical Economics Handbook (2017). https://ihsmarkit.com/products/methanol-chemical-economics-handbook.html. Accessed 12 Feb 2019.
62. Dalena, F.; Senatore, A.; Marino, A.; Gordano, A.; Basile, M.; Basile, A.: Methanol Production and Applications: An Overview. Elsevier, Amsterdam (2017) https://doi.org/10.1016/B978-0-444-63903-5.00001-7
63. Lerner, A.; Brear, M.J.; Lacey, J.S.; Gordon, R.L.; Webley, P.A.: Life cycle analysis (LCA) of low emission methanol and di-methyl ether (DME) derived from natural gas. Fuel **220**, 871–878 (2018). https://doi.org/10.1016/j.fuel.2018.02.066
64. Ghasemzadeh, K.; Sadati Tilebon, S.M.; Nasirinezhad, M.; Basile, A.: Economic Assessment of Methanol Production. Elsevier, Amsterdam (2017) https://doi.org/10.1016/B978-0-444-63903-5.00023-6
65. De Klerk, A.: 10—Transport Fuel: Biomass- Coal- Gas- and Waste-to-Liquids Processes. Elsevier, Amsterdam (2020) https://doi.org/10.1016/B978-0-08-102886-5.00010-4
66. Li, C.; Bai, H.; Lu, Y.; Bian, J.; Dong, Y.; Xu, H.: Life-cycle assessment for coal-based methanol production in China. J. Clean. Prod. **188**, 1004–1017 (2018). https://doi.org/10.1016/j.jclepro.2018.04.051
67. Galloni, E.; Fontana, G.; Staccone, S.; Scala, F.: Performance analyses of a spark-ignition engine firing with gasoline-butanol blends at partial load operation. Energy Convers. Manag. **110**, 319–326 (2016). https://doi.org/10.1016/j.enconman.2015.12.038
68. Demirbas, K.; Sahin-Demirbas, A.: Gasoline fuel blends for otto engines and gasoline fuel additives. Energy Sources Part B Econ. Plan. Policy **5**, 243–249 (2010). https://doi.org/10.1080/15567240701759859
69. Ghadikolaei, M.A.: Effect of alcohol blend and fumigation on regulated and unregulated emissions of IC engines—a review. Renew. Sustain. Energy Rev. **57**, 1440–1495 (2016). https://doi.org/10.1016/j.rser.2015.12.128
70. Lappas, A.; Heracleous, E.: Production of Biofuels via Fischer–Tropsch Synthesis: Biomass-to-Liquids. Woodhead Publishing Limited, Singapore (2011) https://doi.org/10.1533/9780857090492.3.493
71. Hobson, C.; Marquez, C.: Renewable Methanol Report, Madrid, Spain (2018). www.methanol.org. Accessed 12 Feb 2019
72. Vita, A.; Italiano, C.; Previtali, D.; Fabiano, C.; Palella, A.; Freni, F.; Bozzano, G.; Pino, L.; Manenti, F.: Methanol synthesis from biogas: a thermodynamic analysis. Renew. Energy **118**, 673–684 (2018). https://doi.org/10.1016/j.renene.2017.11.029
73. Bozzano, G.; Pirola, C.; Italiano, C.; Pelosato, R.; Vita, A.; Manenti, F.: Biogas: A Possible New Pathway to Methanol? Elsevier, Amsterdam (2017) https://doi.org/10.1016/B978-0-444-63965-3.50089-1
74. Sheets, J.P.; Ge, X.; Li, Y.F.; Yu, Z.; Li, Y.: Biological conversion of biogas to methanol using methanotrophs isolated from solid-state anaerobic digestate. Bioresour. Technol. **201**, 50–57 (2016). https://doi.org/10.1016/j.biortech.2015.11.035
75. Brynolf, S.; Taljegard, M.; Grahn, M.; Hansson, J.: Electrofuels for the transport sector: a review of production costs. Renew. Sustain. Energy Rev. **81**, 1887–1905 (2018). https://doi.org/10.1016/j.rser.2017.05.288
76. Hannula, I.: Co-production of synthetic fuels and district heat from biomass residues, carbon dioxide and electricity: performance and cost analysis. Biomass Bioenergy **74**, 26–46 (2015). https://doi.org/10.1016/j.biombioe.2015.01.006
77. Díez-Ramírez, J.; Díaz, J.A.; Dorado, F.; Sánchez, P.: Kinetics of the hydrogenation of CO2 to methanol at atmospheric pressure using a Pd-Cu-Zn/SiC catalyst. Fuel Process. Technol. **173**, 173–181 (2018). https://doi.org/10.1016/j.fuproc.2018.01.024
78. Bozzano, G.; Manenti, F.: Efficient methanol synthesis: perspectives, technologies and optimization strategies. Prog. Energy Combust. Sci. **56**, 71–105 (2016). https://doi.org/10.1016/j.pecs.2016.06.001
79. Ganesh, I.: Conversion of carbon dioxide into methanol—a potential liquid fuel: fundamental challenges and opportunities (a review). Renew. Sustain. Energy Rev. **31**, 221–257 (2014). https://doi.org/10.1016/j.rser.2013.11.045
80. Olah, G.A., Goeppert, A., Prakash, G.K.S.: Beyond Oil and Gas: The Methanol Economy, 2nd edn., pp. 1–334 (2009). https://doi.org/10.1002/9783527627806.
81. Blumberg, T.; Morosuk, T.; Tsatsaronis, G.: CO2-utilization in the synthesis of methanol: potential analysis and exergetic assessment. Energy **175**, 730–744 (2019). https://doi.org/10.1016/j.energy.2019.03.107
82. Bellotti, D.; Rivarolo, M.; Magistri, L.: Economic feasibility of methanol synthesis as a method for CO2 reduction and energy storage. Energy Procedia **158**, 4721–4728 (2019). https://doi.org/10.1016/j.egypro.2019.01.730
83. Galli, F.; Compagnoni, M.; Vitali, D.; Pirola, C.; Bianchi, C.L.; Villa, A.; Prati, L.; Rossetti, I.: Applied catalysis B: environmental CO2 photoreduction at high pressure to both gas and liquid products over titanium dioxide. Appl. Catal B Environ. **200**, 386–391 (2017). https://doi.org/10.1016/j.apcatb.2016.07.038
84. Gumber, S.; Gurumoorthy, A.V.P.: Methanol Economy Versus Hydrogen Economy. Elsevier, Amsterdam (2018) https://doi.org/10.1016/B978-0-444-63903-5.00025-X
85. Wang, X.; Ge, Y.; Liu, L.; Peng, Z.; Hao, L.; Yin, H.; Ding, Y.; Wang, J.: Evaluation on toxic reduction and fuel economy of a gasoline direct injection- (GDI-) powered passenger car fueled with methanol-gasoline blends with various substitution ratios. Appl. Energy **157**, 134–143 (2015). https://doi.org/10.1016/j.apenergy.2015.08.023
86. Zhang, H.; Wang, L.; Pérez-Fortes, M.; Van Herle, J.; Maréchal, F.; Desideri, U.: Techno-economic optimization of biomass-to-methanol with solid-oxide electrolyzer. Appl. Energy **258**, 114071 (2020). https://doi.org/10.1016/j.apenergy.2019.114071
87. Zhao, H.; Ge, Y.; Hao, C.; Han, X.; Fu, M.; Yu, L.; Shah, A.N.: Carbonyl compound emissions from passenger cars fueled with

methanol/gasoline blends. Sci. Total Environ. **408**, 3607–3613 (2010). https://doi.org/10.1016/j.scitotenv.2010.03.046

88. Wang, Z.; Liu, H.; Long, Y.; Wang, J.; He, X.: Comparative study on alcohols-gasoline and gasoline-alcohols dual-fuel spark ignition (DFSI) combustion for high load extension and high fuel efficiency. Energy **82**, 395–405 (2015). https://doi.org/10.1016/j.energy.2015.01.049
89. Danaiah, P.; Ravi Kumar, P.; Vinay Kumar, D.: The effect of ignition timing and methanol gasoline blends on the performance and emissions of the spark ignition engine. Int. J. Ambient Energy **35**, 132–138 (2014). https://doi.org/10.1080/01430750.2013.789983
90. Methanol Institute, Methanol Use in Gasoline—Blending, Storage and Handling of Gasoline Containing Methanol, Singapore, Washington DC (2016). methanol.org.
91. Babazadeh Shayan, S.; Seyedpour, S.M.; Ommi, F.: Effect of oxygenates blending with gasoline to improve fuel properties. Chin. J. Mech. Eng. **25**, 792–797 (2012). https://doi.org/10.3901/CJME.2012.04.792
92. Liu, S.; Cuty Clemente, E.R.; Hu, T.; Wei, Y.: Study of spark ignition engine fueled with methanol/gasoline fuel blends. Appl. Therm. Eng. **27**, 1904–1910 (2007). https://doi.org/10.1016/j.applthermaleng.2006.12.024
93. Liang, B.; Ge, Y.; Tan, J.; Han, X.; Gao, L.; Hao, L.; Ye, W.; Dai, P.: Comparison of PM emissions from a gasoline direct injected (GDI) vehicle and a port fuel injected (PFI) vehicle measured by electrical low pressure impactor (ELPI) with two fuels: gasoline and M15 methanol gasoline. J. Aerosol Sci. **57**, 22–31 (2013). https://doi.org/10.1016/j.jaerosci.2012.11.008
94. Liu, F.; Hua, Y.; Wu, H.; Fon Lee, C.; Shi, Z.: Experimental and kinetic studies of soot formation in methanol-gasoline coflow diffusion flames. J. Energy Inst. (2017). https://doi.org/10.1016/j.joei.2017.12.002
95. Ministry of New & Renewable Energy, National Policy on Biofuels (2008)
96. Zhen, X.: Methanol As An Internal Combustion on Engine Fuel. Elsevier, Amsterdam (2017) https://doi.org/10.1016/B978-0-444-63903-5.00011-X
97. Vancoillie, J.; Demuynck, J.; Sileghem, L.; Van De Ginste, M.; Verhelst, S.; Brabant, L.; Van Hoorebeke, L.: The potential of methanol as a fuel for flex-fuel and dedicated spark-ignition engines. Appl. Energy **102**, 140–149 (2013). https://doi.org/10.1016/j.apenergy.2012.05.065
98. Liu, H.; Wang, Z.; Long, Y.; Wang, J.: Dual-fuel spark ignition (DFSI) combustion fuelled with different alcohols and gasoline for fuel efficiency. Fuel **157**, 255–260 (2015). https://doi.org/10.1016/j.fuel.2015.04.042
99. Liao, S.Y.; Jiang, D.M.; Cheng, Q.; Huang, Z.H.; Wei, Q.: Investigation of the cold-start combustion characteristics of ethanol-gasoline blends in a constant-volume chamber. Energy Fuels **19**, 813–819 (2005). https://doi.org/10.1021/ef049733l
100. Turner, D.; Xu, H.; Cracknell, R.F.; Natarajan, V.; Chen, X.: Combustion performance of bio-ethanol at various blend ratios in a gasoline direct injection engine. Fuel **90**, 1999–2006 (2011). https://doi.org/10.1016/j.fuel.2010.12.025
101. Abu-Zaid, M.; Badran, O.; Yamin, J.: Effect of methanol addition on the performance of spark ignition engines. Energy Fuels **18**, 312–315 (2004). https://doi.org/10.1021/ef030103d
102. M. Institute, Methanol a Safe and Efficient Automotive Fuel (2020). https://www.einpresswire.com/article/512151498/methanol-a-safe-and-efficient-automotive-fuel-new-reports-find. Accessed 10 Dec 2020.
103. Herdem, M.S.; Sinaki, M.Y.; Farhad, S.; Hamdullahpur, F.: An overview of the methanol reforming process: comparison of fuels, catalysts, reformers, and systems. Int. J. Energy Res. **43**, 5076–5105 (2019). https://doi.org/10.1002/er.4440
104. Sall, E.D.; Morgenstern, D.A.; Fornango, J.P.; Taylor, J.W.; Chomic, N.; Wheeler, J.: Reforming of ethanol with exhaust heat at automotive scale. Energy Fuels **27**, 5579–5588 (2013). https://doi.org/10.1021/ef4011274
105. Poran, A.; Thawko, A.; Eyal, A.; Tartakovsky, L.: Direct injection internal combustion engine with high-pressure thermochemical recuperation—experimental study of the first prototype. Int. J. Hydrog. Energy **43**, 11969–11980 (2018). https://doi.org/10.1016/j.ijhydene.2018.04.190
106. Tartakovsky, L.; Sheintuch, M.: Fuel reforming in internal combustion engines. Prog. Energy Combust. Sci. **67**, 88–114 (2018). https://doi.org/10.1016/j.pecs.2018.02.003
107. Hosseini, S.E.; Butler, B.: An overview of development and challenges in hydrogen powered vehicles. Int. J. Green Energy **17**, 13–37 (2020). https://doi.org/10.1080/15435075.2019.1685999
108. Casanovas, A.; Divins, N.J.; Rejas, A.; Bosch, R.; Llorca, J.: Finding a suitable catalyst for on-board ethanol reforming using exhaust heat from an internal combustion engine. Int. J. Hydrog. Energy **42**, 13681–13690 (2017). https://doi.org/10.1016/j.ijhydene.2016.11.197
109. Jamal, Y.; Wyszynski, M.L.: On-board generation of hydrogen-rich gaseous fuels-a review. Int. J. Hydrog. Energy **19**, 557–572 (1994). https://doi.org/10.1016/0360-3199(94)90213-5
110. French, R.; Malone, P.: Phase equilibria of ethanol fuel blends. Fluid Phase Equilib. **228–229**, 27–40 (2005). https://doi.org/10.1016/j.fluid.2004.09.012
111. Amine, M.; Awad, E.N.; Ibrahim, V.; Barakat, Y.: Effect of ethyl acetate addition on phase stability, octane number and volatility criteria of ethanol-gasoline blends. Egypt. J. Pet. (2018). https://doi.org/10.1016/j.ejpe.2017.08.007
112. Green, G.J.; Yan, T.Y.: Water tolerance of gasoline-methanol blends. Ind. Eng. Chem. Res. **29**, 1630–1635 (1990). https://doi.org/10.1021/ie00104a009
113. Karaosmanoglu, F.; Isigigur-, A.: A new blending agent and its effects on methanol-gasoline fuels. Energy Sources **22**, 235–245 (2000). https://doi.org/10.1080/00908310050014027
114. Karaosmanoğlu, F.; Işiğigür, A.; Ayşe Aksoy, H.: Methanol-unleaded gasoline blends containing fusel oil fraction as spark ignition engine fuel. Energy Sources **19**, 567–577 (1997). https://doi.org/10.1080/00908319708908873
115. Awad, O.I.; Bin Mamat, R.; Ali, O.M.; Yusri, I.M.: Effect of fuel oil—gasoline fusel blends on the performance and emission characteristics of spark ignition engine: a review. J. Sci. Res. Dev. **3**, 31–36 (2016). https://doi.org/10.1016/j.ymssp.2009.06.005
116. Awad, O.I.; Ali, O.M.; Mamat, R.; Abdullah, A.A.; Najafi, G.; Kamarulzaman, M.K.; Yusri, I.M.; Noor, M.M.: Using fusel oil as a blend in gasoline to improve SI engine efficiencies: a comprehensive review. Renew. Sustain. Energy Rev. **69**, 1232–1242 (2017). https://doi.org/10.1016/j.rser.2016.11.244
117. Solmaz, H.: Combustion, performance and emission characteristics of fusel oil in a spark ignition engine. Fuel Process. Technol. **133**, 20–28 (2015). https://doi.org/10.1016/j.fuproc.2015.01.010
118. Lojkásek, M.; Růžička, V.; Kohoutová, A.: Solubility of water in blends of gasoline, methanol and a solubilizer. Fluid Phase Equilib. **71**, 113–123 (1992). https://doi.org/10.1016/0378-3812(92)85008-V
119. Zhang, J.; Yang, C.; Tang, Y.; Xu, L.; Wang, X.: Development of lactic ester as bifunctional additive of methanol-gasoline. Asian J. Chem. **26**, 4827–4829 (2014). https://doi.org/10.14233/ajchem.2014.16252
120. Yajing, Y.; Yanju, W.; Wenrui, W.; Xiao, C.; Shenghua, L.: The effects of methanol fraction on the azeotropic behaviors of methanol/gasoline mixtures. Int. J. Green Energy. **12**, 1076–1085 (2015). https://doi.org/10.1080/15435075.2014.890102

121. Sharudin, H.; Abdullah, N.R.; Najafi, G.; Mamat, R.; Masjuki, H.H.: Investigation of the effects of iso-butanol additives on spark ignition engine fuelled with methanol-gasoline blends. Appl. Therm. Eng. **114**, 593–600 (2017). https://doi.org/10.1016/j.applthermaleng.2016.12.017
122. Yüksel, F.; Yüksel, B.: The use of ethanol-gasoline blend as a fuel in an SI engine. Renew. Energy **29**, 1181–1191 (2004). https://doi.org/10.1016/j.renene.2003.11.012
123. Nasrollahi, F.; Roodpeyma, S.; Vakili-Nezhaad, G.R.: Liquid-liquid equilibrium calculations for methanol-gasoline blends using continuous thermodynamics. Fluid Phase Equilib. **284**, 1–9 (2009). https://doi.org/10.1016/j.fluid.2009.05.012
124. Yue, T.; Yue, X.; Chai, F.; Hu, J.; Lai, Y.; He, L.; Zhu, R.: Characteristics of volatile organic compounds (VOCs) from the evaporative emissions of modern passenger cars. Atmos. Environ. **151**, 62–69 (2017). https://doi.org/10.1016/j.atmosenv.2016.12.008
125. Li, L.; Ge, Y.; Wang, M.; Li, J.; Peng, Z.; Song, Y.; Zhang, L.: Effect of gasoline/methanol blends on motorcycle emissions: exhaust and evaporative emissions. Atmos. Environ. **102**, 79–85 (2015). https://doi.org/10.1016/j.atmosenv.2014.11.044
126. Dai, P.; Ge, Y.; Lin, Y.; Su, S.; Liang, B.: Investigation on characteristics of exhaust and evaporative emissions from passenger cars fueled with gasoline/methanol blends. Fuel **113**, 10–16 (2013). https://doi.org/10.1016/j.fuel.2013.05.038
127. Cao, X.; Yao, Z.; Shen, X.; Ye, Y.; Jiang, X.: On-road emission characteristics of VOCs from light-duty gasoline vehicles in Beijing, China. Atmos. Environ. **124**, 146–155 (2016). https://doi.org/10.1016/j.atmosenv.2015.06.019
128. Methanol FUELS, Methanol Fuel in the Environment. http://methanolfuels.wpengine.com/about-methanol/environment/. Accessed 5 Apr 2020
129. Kamboj, S.K.; Karimi, M.N.: A comparison of the performance analysis of the spark ignition engine fuelled with ethanol–iso-octane and methanol–iso-octane fuel blends. Int. J. Sustain. Energy **6451**, 1–12 (2014). https://doi.org/10.1080/14786451.2014.885026
130. Chansauria, P.; Mandloi, R.K.: Effects of ethanol blends on performance of spark ignition engine—a review. Mater. Today Proc. **5**, 4066–4077 (2018). https://doi.org/10.1016/j.matpr.2017.11.668
131. Peng, D.-X.: Effects of biofuels (methanol, ethanol, and butanol) on internal combustion engine performance and exhaust emissions. Chem. Technol. Fuels Oils **54**, 29–36 (2018). https://doi.org/10.1007/s10553-018-0894-y
132. Yusri, I.M.; Mamat, R.; Najafi, G.; Razman, A.; Awad, O.I.; Azmi, W.H.; Ishak, W.F.W.; Shaiful, A.I.M.: Alcohol based automotive fuels from first four alcohol family in compression and spark ignition engine: a review on engine performance and exhaust emissions. Renew. Sustain. Energy Rev. **77**, 169–181 (2017). https://doi.org/10.1016/j.rser.2017.03.080
133. Thakur, A.K.; Kaviti, A.K.; Mehra, R.; Mer, K.K.S.: Progress in performance analysis of ethanol-gasoline blends on SI engine. Renew. Sustain. Energy Rev. **69**, 324–340 (2017). https://doi.org/10.1016/j.rser.2016.11.056
134. Methanol Institute, Methanol Gasoline Blends—Alternative Fuel For Today's Automobiles and Cleaner Burning Octane For Today's Oil Refinery (2016). http://www.methanol.org/wp-content/uploads/2016/06/Blenders-Product-Bulletin-Final.pdf. Accessed 12 Feb 2019
135. Lan, J.; Jiang, J.; Pan, Y.; Dou, Z.; Wang, Q.: Experimental measurements and numerical calculation of auto-ignition temperatures for binary miscible liquid mixtures. Process Saf. Environ. Prot. **113**, 22–29 (2018). https://doi.org/10.1016/j.psep.2017.09.012
136. Duarte, J.; Amador, G.; Garcia, J.; Fontalvo, A.; Vasquez Padilla, R.; Sanjuan, M.; Gonzalez Quiroga, A.: Auto-ignition control in turbocharged internal combustion engines operating with gaseous fuels. Energy **71**, 137–147 (2014). https://doi.org/10.1016/j.energy.2014.04.040
137. Feng, H.; Zhang, J.; Wang, X.; Lee, T.H.: Analysis of auto-ignition characteristics of low-alcohol/iso-octane blends using combined chemical kinetics mechanisms. Fuel **234**, 836–849 (2018). https://doi.org/10.1016/j.fuel.2018.07.008
138. Thakur, A.K.; Kaviti, A.K.: Progress in regulated emissions of ethanol-gasoline blends from a spark ignition engine. Biofuels **7269**, 1–24 (2018). https://doi.org/10.1080/17597269.2018.1464875
139. Canakci, M.; Ozsezen, A.N.; Alptekin, E.; Eyidogan, M.: Impact of alcohol-gasoline fuel blends on the exhaust emission of an SI engine. Renew. Energy **52**, 111–117 (2013). https://doi.org/10.1016/j.renene.2012.09.062
140. Gonca, G.: Influences of different fuel kinds and engine design parameters on the performance characteristics and NO formation of a spark ignition (SI) engine. Appl. Therm. Eng. **127**, 194–202 (2017). https://doi.org/10.1016/j.applthermaleng.2017.08.002
141. Ministry of Road Transport & Highway, Methanol Economy for India: Energy Security, Make in India and Zero Carbon foot print, Press Inf. Bur. (2017). http://pib.nic.in/newsite/PrintRelease.aspx?relid=174919. Accessed 28 Dec 2017.
142. Methanol Institute, 2020 Milestones, Methanol Inst. (2020). https://www.methanol.org/2020-milestones/. Accessed 10 Dec 2020.
143. Department of Chemicals and Petro-Chemicals. (n.d.). http://chemicals.nic.in/goisearch?search_key=methanol. Accessed 12 Feb 2019.
144. Amine, M.; Barakat, Y.: Properties of gasoline-ethanol-methanol ternary fuel blend compared with ethanol-gasoline and methanol-gasoline fuel blends, Egypt. J. Pet. **28**, 371–376 (2019). https://doi.org/10.1016/j.ejpe.2019.08.006
145. Mourad, M.; Mahmoud, K.: Investigation into SI engine performance characteristics and emissions fuelled with ethanol/butanol-gasoline blends. Renew. Energy **143**, 762–771 (2019). https://doi.org/10.1016/j.renene.2019.05.064
146. Pang, X.; Zhang, X.; Wu, S.; Ma, M.; Xiang, Y.; Ma, J.; Ji, J.; Wang, G.; Liu, H.: Effects of C3–C5 alcohols on solubility of alcohols/diesel blends. Fuel **236**, 65–74 (2019). https://doi.org/10.1016/j.fuel.2018.08.129
147. Shirazi, S.A.; Abdollahipoor, B.; Windom, B.; Reardon, K.F.; Foust, T.D.: Effects of blending C3–C4 alcohols on motor gasoline properties and performance of spark ignition engines: a review. Fuel Process. Technol. **197**, 106194 (2020). https://doi.org/10.1016/j.fuproc.2019.106194
148. Elfasakhany, A.: Performance and emissions of spark-ignition engine using ethanol–methanol–gasoline, n-butanol–iso-butanol–gasoline and iso-butanol–ethanol–gasoline blends: a comparative study. Eng. Sci. Technol. Int. J. **19**, 2053–2059 (2016). https://doi.org/10.1016/j.jestch.2016.09.009
149. Jesu Godwin, D.; Edwin Geo, V.; Thiyagarajan, S.; Leenus Jesu Martin, M.; Maiyalagan, T.; Saravanan, C.G.; Aloui, F.: Effect of hydroxyl (OH) group position in alcohol on performance, emission and combustion characteristics of SI engine. Energy Convers. Manag. **189**, 195–201 (2019). https://doi.org/10.1016/j.enconman.2019.03.063
150. Jesu Godwin, D.; Edwin Geo, V.; Thiyagarajan, S.; Leenus Jesu Martin, M.; Maiyalagan, T.; Saravanan, C.G.; Aloui, F.: Effect of higher and lower order alcohol blending with gasoline on performance, emission and combustion characteristics of SI engine. Fuel (2019). https://doi.org/10.1016/j.fuel.2019.115806
151. Yilmaz, I.; Taştan, M.: Investigation of hydrogen addition to methanol-gasoline blends in an SI engine. Int. J. Hydrog. Energy **1**, 10 (2018). https://doi.org/10.1016/j.ijhydene.2018.07.088

152. Gong, C.; Li, Z.; Chen, Y.; Liu, J.; Liu, F.; Han, Y.: Influence of ignition timing on combustion and emissions of a spark-ignition methanol engine with added hydrogen under lean-burn conditions. Fuel **235**, 227–238 (2019). https://doi.org/10.1016/j.fuel.2018.07.097
153. Vinoth Kanna, I.; Paturu, P.: A study of hydrogen as an alternative fuel. Int. J. Ambient Energy **750**, 1–4 (2018). https://doi.org/10.1080/01430750.2018.1484803
154. Elfasakhany, A.: Experimental study of dual n-butanol and iso-butanol additives on spark-ignition engine performance and emissions. Fuel **163**, 166–174 (2016). https://doi.org/10.1016/j.fuel.2015.09.059
155. Elfasakhany, A.; Mahrous, A.F.: Performance and emissions assessment of n-butanol–methanol–gasoline blends as a fuel in spark-ignition engines. Alexandria Eng. J. **55**, 3015–3024 (2016). https://doi.org/10.1016/j.aej.2016.05.016
156. Yusoff, M.N.A.M.; Zulkifli, N.W.M.; Masjuki, H.H.; Harith, M.H.; Syahir, A.Z.; Kalam, M.A.; Mansor, M.F.; Azham, A.; Khuong, L.S.: Performance and emission characteristics of a spark ignition engine fuelled with butanol isomer-gasoline blends. Transp. Res. Part D Transp. Environ. **57**, 23–38 (2017). https://doi.org/10.1016/j.trd.2017.09.004
157. Singh, S.B.; Dhar, A.; Agarwal, A.K.: Technical feasibility study of butanol-gasoline blends for powering medium-duty transportation spark ignition engine. Renew. Energy **76**, 706–716 (2015). https://doi.org/10.1016/j.renene.2014.11.095
158. Elfasakhany, A.: Accepted exhaust emissions and performance of ternary iso-butanol–bio-methanol–gasoline and n-butanol–bio-ethanol–gasoline fuel blends in spark-ignition engines: assessment and comparison. Energy **158**, 830–844 (2018). https://doi.org/10.1016/j.energy.2018.05.120
159. Bauer, F.; Hulteberg, C.: Isobutanol from glycerine—a techno-economic evaluation of a new biofuel production process. Appl. Energy **122**, 261–268 (2014). https://doi.org/10.1016/j.apenergy.2014.02.037
160. Isomaki, R.K.R.; Pitkaaho, S.; Niemisto, J.: Biobutanol production technologies. In: Abraham, M. (Ed.) Encyclopedia of Sustainable Technologies, pp. 285–291. Elsevier, Amsterdam (2017). https://doi.org/10.1016/B978-0-12-409548-9.10112-5
161. Elfasakhany, A.: Experimental investigation on SI engine using gasoline and a hybrid iso-butanol/gasoline fuel. Energy Convers. Manag. **95**, 398–405 (2015). https://doi.org/10.1016/j.enconman.2015.02.022
162. Li, Y.; Nithyanandan, K.; Lee, T.H.; Donahue, R.M.; Lin, Y.; Lee, C.F.; Liao, S.: Effect of water-containing acetone-butanol-ethanol gasoline blends on combustion, performance, and emissions characteristics of a spark-ignition engine. Energy Convers. Manag. **117**, 21–30 (2016). https://doi.org/10.1016/j.enconman.2016.02.083
163. Zunqing Zheng, M.Y.; Li, C.; Li, H.; Zhang, Y.; Zhong, X.: Experimental study on diesel conventional and low temperature combustion by fueling four isomers of butanol. Fuel **141**, 109–119 (2015). https://doi.org/10.1016/j.fuel.2014.10.053
164. Huzir, N.; Aziz, M.A.; Ismail, S.B.; Abdullah, B.; Azmi, N.; Mahmood, N.; Umor, N.A.; Anuar, S.; Muhammad, S.: Agro-industrial waste to biobutanol production: eco-friendly biofuels for next generation. Renew. Sustain. Energy Rev. **94**, 476–485 (2018). https://doi.org/10.1016/j.rser.2018.06.036
165. Gomez-Flores, R.; Nambi, T.; Nicol, R.; Gilroyed, B.; Morrison, M.; Reid, L.M.; Margaritis, A.: Biomass and bioenergy bioethanol and biobutanol production from sugarcorn juice. Biomass Bioenergy (2017). https://doi.org/10.1016/j.biombioe.2017.10.038
166. Wang, Y.; Ho, S.; Yen, H.; Nagarajan, D.; Ren, N.; Li, S.; Hu, Z.; Lee, D.; Kondo, A.; Chang, J.: Current advances on fermentative biobutanol production using third generation feedstock. Biotechnol. Adv. (2017). https://doi.org/10.1016/j.biotechadv.2017.06.001
167. Aakko-saksa, P., Koponen, P., Kihlman, J., Reinikainen, M., Skyttä, E., Rantanen-kolehmainen, L.: Biogasoline Options for Conventional Spark-Ignition Cars (2011)
168. Nagpure, A.S.; Gurjar, B.R.; Kumar, V.; Kumar, P.: Estimation of exhaust and non-exhaust gaseous, particulate matter and air toxics emissions from on-road vehicles in Delhi. Atmos. Environ. **127**, 118–124 (2016). https://doi.org/10.1016/j.atmosenv.2015.12.026
169. Singh, A.: Translating the Paris Agreement into Action in the Pacific: Advances in Global Change Research, pp. 1–323 (2020).
170. Puli, D.; Kumar, P.R.: Performance and emission characteristics of tertiary butyl alcohol gasoline blends on a spark ignition engine. Biofuels **6**, 71–78 (2015). https://doi.org/10.1080/17597269.2015.1050642
171. Balki, M.K.; Sayin, C.; Sarikaya, M.: Optimization of the operating parameters based on Taguchi method in an SI engine used pure gasoline, ethanol and methanol. Fuel **180**, 630–637 (2016). https://doi.org/10.1016/j.fuel.2016.04.098
172. Eyidogan, M.; Ozsezen, A.N.; Canakci, M.; Turkcan, A.: Impact of alcohol-gasoline fuel blends on the performance and combustion characteristics of an SI engine. Fuel **89**, 2713–2720 (2010). https://doi.org/10.1016/j.fuel.2010.01.032
173. Tian, Z.; Zhen, X.; Wang, Y.; Liu, D.; Li, X.: Comparative study on combustion and emission characteristics of methanol, ethanol and butanol fuel in TISI engine. Fuel **259**, 116199 (2020). https://doi.org/10.1016/j.fuel.2019.116199
174. Agarwal, A.K.; Karare, H.; Dhar, A.: Combustion, performance, emissions and particulate characterization of a methanol-gasoline blend (gasohol) fuelled medium duty spark ignition transportation engine. Fuel Process. Technol. **121**, 16–24 (2014). https://doi.org/10.1016/j.fuproc.2013.12.014
175. Gravalos, I.; Xyradakis, P.; Kateris, D.; Gialamas, T.; Loutridis, S.; Avgousti, A.; Georgiadis, A.; Tsiropoulos, Z.: Comparison and analysis of the emissions of a small non-road spark-ignition engine operating under different alcohol–gasoline blended fuels. Int. J. Sustain. Energy **35**, 258–266 (2016). https://doi.org/10.1080/14786451.2014.905579
176. Ozsezen, A.N.: The investigation of thermodynamics and combustion properties of alcohol-gasoline blends in an SI engine. Int. J. Green Energy **12**, 1107–1112 (2015). https://doi.org/10.1080/15435075.2014.892877
177. Çelik, M.B.; Özdalyan, B.; Alkan, F.: The use of pure methanol as fuel at high compression ratio in a single cylinder gasoline engine. Fuel **90**, 1591–1598 (2011). https://doi.org/10.1016/j.fuel.2010.10.035
178. Zhao, H.; Ge, Y.; Tan, J.; Yin, H.; Guo, J.; Zhao, W.; Dai, P.: Effects of different mixing ratios on emissions from passenger cars fueled with methanol/gasoline blends. J. Environ. Sci. **23**, 1831–1838 (2011). https://doi.org/10.1016/S1001-0742(10)60626-2
179. Maejima, K.; Suzuki, T.; Niwa, K.; Numata, H.; Maekawa, A.; Nagase, S.; Ishinishi, N.; Maejima, K.: Toxicity to rats of methanol-fueled engine exhaust inhaled continuously for 28 days. J. Toxicol. Environ. Health **37**, 293–312 (1992). https://doi.org/10.1080/15287399209531671
180. Siwale, L.; Kristóf, L.; Bereczky, A.; Mbarawa, M.; Kolesnikov, A.: Performance, combustion and emission characteristics of n-butanol additive in methanol-gasoline blend fired in a naturally-aspirated spark ignition engine. Fuel Process. Technol. **118**, 318–326 (2014). https://doi.org/10.1016/j.fuproc.2013.10.007
181. Wu, Q.; Xie, X.; Wang, Y.; Roskilly, T.: Experimental investigations on diesel engine performance and emissions using biodiesel adding with carbon coated aluminum nanoparticles. Energy

Procedia **142**, 3603–3608 (2017). https://doi.org/10.1016/j.egypro.2017.12.251

182. Iliev, S.: A comparison of ethanol and methanol blending with gasoline using a 1-D engine model. Procedia Eng. **100**, 1013–1022 (2015). https://doi.org/10.1016/j.proeng.2015.01.461
183. Varol, Y.; Öner, C.; Öztop, H.F.; Altun, Ş: Comparison of methanol, ethanol, or n -butanol blending with unleaded gasoline on exhaust emissions of an SI engine. Energy Sources Part A Recover. Util. Environ. Eff. **36**, 938–948 (2014). https://doi.org/10.1080/15567036.2011.572141
184. Balki, M.K.; Sayin, C.; Canakci, M.: The effect of different alcohol fuels on the performance, emission and combustion characteristics of a gasoline engine. Fuel **115**, 901–906 (2014). https://doi.org/10.1016/j.fuel.2012.09.020
185. Ni, P.; Wang, Z.; Wang, X.; Hou, L.: Regulated and unregulated emissions from a non-road small gasoline engine fueled with gasoline and methanol-gasoline blends. Energy Sources Part A Recover. Util. Environ. Eff. **36**, 1499–1506 (2014). https://doi.org/10.1080/15567036.2010.549913
186. Elfasakhany, A.: Investigations on the effects of ethanol–methanol–gasoline blends in a spark-ignition engine: performance and emissions analysis. Eng. Sci. Technol. Int. J. **18**, 713–719 (2015). https://doi.org/10.1016/j.jestch.2015.05.003
187. Wu, B.; Wang, L.; Shen, X.; Yan, R.; Dong, P.: Comparison of lean burn characteristics of an SI engine fueled with methanol and gasoline under idle condition. Appl. Therm. Eng. **95**, 264–270 (2016). https://doi.org/10.1016/j.applthermaleng.2015.11.029
188. Zervas, E.; Montagne, X.; Lahaye, J.: Emissions of regulated pollutants from a spark ignition engine. Influence of fuel and air/fuel equivalence ratio. Environ. Sci. Technol. **37**, 3232–3238 (2003). https://doi.org/10.1021/es026321n
189. Zhen, X.; Wang, Y.: Numerical analysis on original emissions for a spark ignition methanol engine based on detailed chemical kinetics. Renew. Energy **81**, 43–51 (2015). https://doi.org/10.1016/j.renene.2015.03.027
190. Rifal, M.; Sinaga, N.: Impact of methanol-gasoline fuel blend on the fuel consumption and exhaust emission of a SI engine. AIP Conf. Proc. (2016). https://doi.org/10.1063/1.4945524