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Review

Methanol Combustion Characteristics in Compression Ignition Engines: A Critical Review

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Abstract: Methanol has been identified as a transition fuel for the decarbonisation of combustion-based industries, including automotive and maritime. This study aims to conduct a critical review of methanol combustion in compression ignition engines and analyse the reviewed studies' results to quantify methanol use's impact on engine performance and emissions characteristics. The diesel and diesel–methanol operation of these engines are comparatively assessed, demonstrating the trade-offs between the methanol fraction, the key engine performance parameters, including brake thermal efficiency, peak in-cylinder pressure, heat release rate, and temperature, as well as the carbon dioxide, carbon monoxide, nitrogen oxides, and particulate matter emissions. The types of the reviewed engines considering the main two combustion methods, namely premixed and diffusion combustion, are discussed. Research gaps are identified, and recommendations for future research directions to address existing challenges for the wider use of methanol as a marine fuel are provided. This comprehensive review provides insights supporting methanol engine operation, and it is expected to lead to further studies towards more efficient use of methanol-fueled marine engines.

Keywords: comprehensive review; methanol combustion; internal combustion engines; compression ignition; research directions; marine engines

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1. Introduction

The production and consumption of fossil fuels are expected to consume the available CO_2 budget much earlier than 2050, resulting in significant climate implications [1]. The shipping sector, though important for worldwide trade, is responsible for a significant fraction of the worldwide emissions [2]. To curtail the shipping sector's environmental footprint, the International Maritime Organisation (IMO) set the following targets for carbon dioxide (CO_2) emissions per transport work reduction: 40% by 2030 and at least 50% by 2050. The adoption of alternative fuels with a reduced carbon-to-hydrogen ratio has been identified as a pathway to decarbonise the shipping sector [3]. Limitations on non-greenhouse gas emissions, including nitrogen oxides (NOx) and sulphur oxides (SOx), which are stricter for exhaust control areas (ECAs), impose further challenges for the use of alternative fuels [4]. Methanol has attracted significant interest from the power generation industry [5] as well as the transportation sectors [6]. Among the potential alternative (low carbon) fuels, methanol is considered a short- to medium-term solution for decarbonising shipping operations [7]. Methanol has several characteristics different from conventional diesel fuels, including its high molar expansion ratio (denoting the products to reactants moles ratio), contributing to the increase in in-cylinder pressure [8]. In addition, methanol is a high octane and low cetane fuel, and its high laminar flame velocity and the employed compression ratio range render it unsuitable for compression ignition combustion [9]. For the maritime sector, methanol presents several benefits compared to other alternative and conventional fuels. Compared to carbon-free fuels (hydrogen and ammonia), it requires lower storage volumes and simpler storage systems [10]; hydrogen requires cryogenic conditions, whereas ammonia requires increased safety measures due to its toxic nature. Furthermore, methanol exhibits significant cost benefits due to the existing production technologies [11]. Methanol sea transportation can be treated similarly to other liquid hydrocarbon fuels via product carriers. Methanol is considered a highly flammable, high-toxicity fuel according to international guidelines. Examples of operational safety for methanol are provided in safe handling manuals [12].

Methanol's lower carbon-to-hydrogen ratio results in reduced carbon emissions, whereas methanol production from renewable energy reduces the lifecycle carbon footprint [13]. However, there are several barriers to methanol's wide adoption as a marine fuel. The methanol auto-ignition temperature is more than double that of diesel fuels, requiring very high compression ratios when used as a single fuel in compression ignition engines. Hence, methanol use in dual-fuel engines, which employ pilot diesel fuel to initiate combustion, is typically expected. Its lower energy density, compared to diesel, increases the required shipboard storage space. The lubricity of methanol is a common issue among alcohol fuels that can be compensated using lubricating additives [14]. Other challenges associated with methanol-fueled engines and shipboard methanol use include its water miscibility and toxicity.

Tian et al. [15] focused on the emissions from compression ignition engines using methanol and considered a lifecycle perspective from production to consumption, as well as several fuel combinations, including hydrogen/methanol, along with diesel. Verhelst et al. [16] considered the effects of methanol fuel in several automotive engines, as well as methanol production methods and lifecycle emissions perspective. Zhen and Wang [17] reviewed the methanol fuel studies for both spark and compression ignition engines with a focus on its use along with other alternative fuels, such as biodiesel and hydrogen, among others, while the supply, demand, and economic benefits were also examined. However, a comprehensive review of engines fueled by methanol at different energy fractions is not reported in the pertinent literature.

For marine applications, which is the focus of the study, different combustion strategies can be applied in dual-fuel engines. Typically, high cetane fuel (diesel) is directly injected within the engine cylinders to initiate combustion, whereas the methanol can be injected either in the intake ports or directly in-cylinder. The methanol port injection results in a premixed combustion method, as methanol forms a homogenous mixture with in-cylinder air prior to ignition [13]. Guo et al. [18] reported that direct methanol injection in marine engines resulted in similar performance parameters and noise while being associated with the reduction of NOx and soot emissions. On the contrary, the partially premixed methanol combustion improved the engine efficiency and provided an important reduction of NOx and soot emissions.

Shipboard storage and the use of methanol fuel are expected to have similar safety implications with other low flashpoint fuels (e.g., liquified natural gas or liquefied petroleum gas) [10]. Methanol shipboard storage requires minor modifications of the existing diesel fuel storage and feeding systems, although a higher amount of methanol is required to provide the same ship range as diesel fuels [10].

The aim of this study is to conduct a comprehensive literature review to identify the impact of using methanol in compression ignition engines, comparatively assessing the engine's performance and emissions characteristics. This study focuses on compression ignition engines, as this engine type is widely used in the maritime sector. This review included a total of 88 studies, 77 of which examined, either experimentally or numerically, the impact of methanol fraction on engine performance and emissions parameters. This study reviewed different experimental setups, combustion methods, engine designs, and injection types (port or direct). The studies are categorised based on the methanol combustion method, particularly premixed or diffusion combustion. For each of these methods, the impact of methanol use on the engine performance and emissions parameters is discussed. The remainder of this study is structured as follows. Section 2 describes the steps of the study's methodology. Section 3 discusses the study's results and the identified research gaps, concluding on the key remarks. Section 4 summarises the main findings and discusses recommendations for future research directions.

2. Methodology

This study follows the methodological steps presented in the flowchart of Figure 1. Step 1 defines this study's scope along with the boundaries. Step 2 identifies the sources and databases that are employed to retrieve publications and information pertinent to methanol combustion, its and use in internal combustion engines, and these engine specifications. Step 3 focuses on the identification of parameters of interest, which include methanol properties, the engine settings and injection characteristics (injection timing and injection delay), the engine performance parameters (combustion efficiency, thermal efficiency, in-cylinder temperature and pressure, ignition delay, heat release rate, and specific fuel consumption), as well as emissions parameters (NOx, CO_2, CO, and PM).

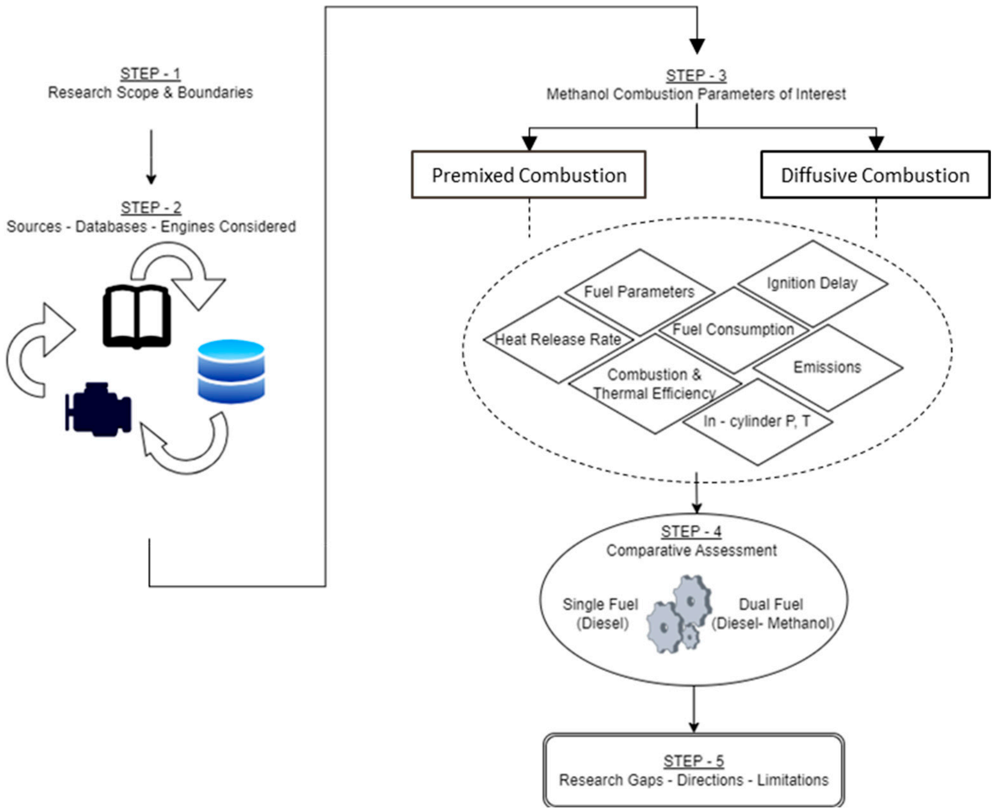


Figure 1. Methodology flowchart.

Step 4 deals with the comparative assessment of the selected parameters considering the diesel and diesel–methanol operation. Lastly, Step 5 focuses on the identification of the key research gaps and the recommendations for future research directions to enable the wide use of methanol as fuel in marine engines.

2.1. Scope and Boundaries

The scope of this study is to conduct a critical review of methanol combustion in compression ignition engines by analysing and quantifying the impact of different fractions and combustion methods. This review focuses on internal combustion engines of the compression ignition type, which are widely employed in the maritime sector, with diesel fuel substitution by methanol aiming to comparatively assess these engines performance and emissions parameters, as well as identify trade-offs (as a function of the methanol energy fraction). Subsequently, the research gaps for scaling up the derived findings for marine engines are identified, and recommendations for research directions are proposed.

This study does not consider spark ignition engines fueled by methanol and combinations of methanol with other fuels. Though scarce, in-cylinder injection at the early phase of the compression stroke can also be employed, which resulted in adequate mixing of methanol and air (and hence methanol premixed combustion); however, the current study doesn't include any of such cases.

2.2. Employed Sources

The searched databases included the published literature available online as well as material published from industrial sources. The following keywords were employed: methanol combustion; marine engines; methanol engines; premixed methanol combustion; direct methanol injection; methanol kinetics; and methanol review. In total, 88 publications were identified, focusing on the partial diesel substitution with methanol in compression ignition internal combustion engines. A total of 77 publications dealt with either experimental or numerical investigations of several engine configurations, cylinder numbers, combustion methods and two injection types (port injection and in-cylinder direct injection). The identified studies also included methanol combustion fundamental research and reaction mechanisms.

2.3. Engines Particulars

The reviewed publications investigated engines with nominal power in the range 5.2–2000 kW. For most cases, limited diesel fuel substitution rates in the range of 10–15% (energy basis) were studied for technical reasons. However, several studies investigated higher methanol fractions up to 80%. The compression ratio of these engines was in the range 17.0:1–22.4:1. Most studies involved four-cylinder engines, with a smaller number of studies focusing on single-cylinder engines. The taxonomy of the identified studies is illustrated in Figure 2, whereas more information about the investigated engines and their particulars is provided in Table A1 (Appendix A).

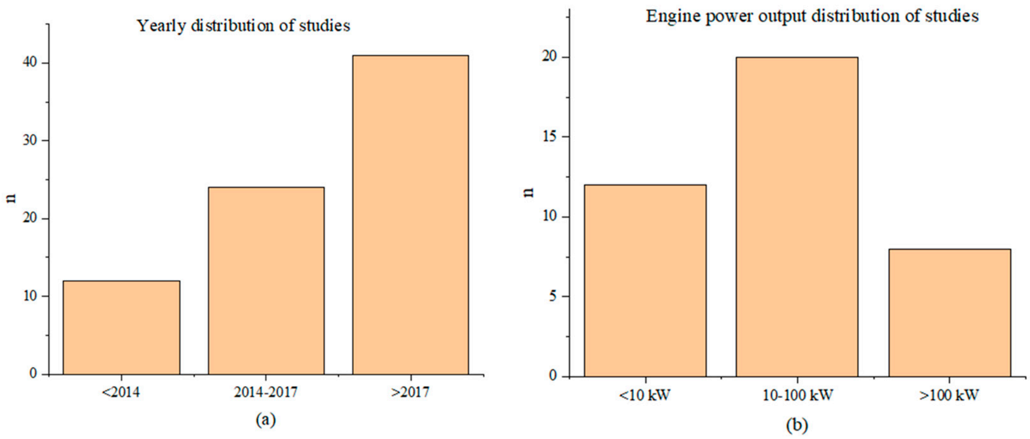


Figure 2. The studies' taxonomy and engine categorisation. (**a**) Yearly distribution of studies, and (**b**) engine power output categorisation (studies with engines investigation).

Figure 2a denotes that methanol combustion in compression ignition engines has attracted growing interest, as most studies were published after 2017. Figure 2b provides the taxonomy of the studied engines based on their nominal power ranges. The engines' power output in the range of 10–100 kW refers to smaller engines requiring limited test facilities. Power output less than 10 kW corresponds to single-cylinder engines, whereas a few studies focused on power output up to 2 MW.

2.4. Methanol Injection Types

The engines investigated in the reviewed publications employed the following two methanol injection types (and the corresponding injection systems): port injection and in-cylinder direct injection. Port injection of liquid methanol takes place at the intake port when the intake valve is open (and with the exhaust valve closed), whereas in some rare cases, methanol is injected downstream of the turbocharger compressor. The methanol in-cylinder direct injection usually takes place close to the top dead centre. In both cases, the high-reactivity fuel (most frequently diesel) was directly injected in-cylinder. The methanol direct and port injection types are almost evenly studied, as shown in Figure 3. A total of 16 publications investigated premixed combustion, with 10 focusing on the high-temperature combustion method.

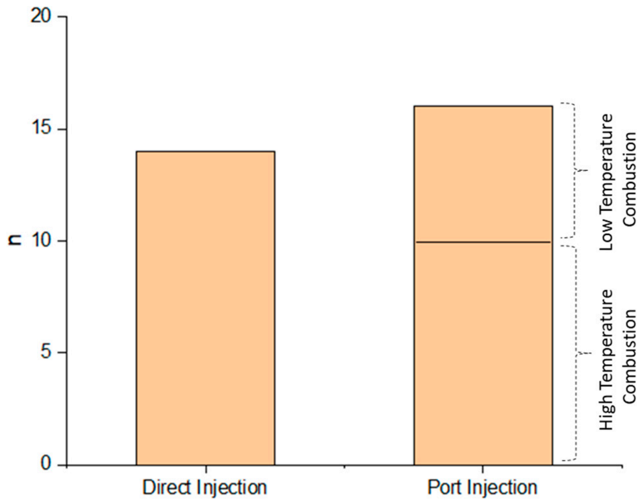


Figure 3. Methanol injection types were reported in the reviewed studies.

Premixed injection provides adequate time for methanol evaporation and its effective mixing with air, forming an almost homogeneous mixture and resulting in premixed methanol combustion (as delineated in the following section). However, three studies focused on methanol fumigation, which implies methanol injection or vaporisation (by using a carburettor) into the engine intake manifold [19–21].

The methanol direct injection took place either via a unified methanol–diesel single injector or different injectors (for methanol and diesel). In most cases, different injection pressures were employed. This injection type leads to a methanol spray formation, subsequent evaporation, and mixing, resulting in a diffusion combustion method (described in the following section).

2.5. Methanol Combustion Methods

Methanol premixed combustion includes several methods mainly classified in the categories of low-temperature combustion (LTC) and high-temperature combustion (HTC). The combustion temperature (and hence its classification) mainly depends on the injection timing and start of combustion of the high-reactivity fuel (most frequently diesel). The methanol premixed combustion (both HTC and LTC) is characterised by a faster burning rate (compared to the methanol diffusion combustion). However, the high-reactivity fuel (typically diesel) is directly injected into the engine cylinder; the heat release rate consists of two parts, one reflecting methanol premixed combustion and one representing the high-reactivity fuel diffusion combustion.

The LTC typically improves efficiency and reduces emissions, whereas it pertains to the following methods: Homogenous Charge Compression Ignition (HCCI), Premixed Charge Compression Ignition (PCCI), and Reactivity-Controlled Compression Ignition (RCCI) [22]. Table 1 summarises the key advantages and challenges of the LTC methods.

Figure 4 illustrates the local equivalence ratio–temperature (Φ–T) map for the LTC methods and the diesel diffusion combustion; the latter is classified as high temperature.

RCCI typically accommodated the low-reactivity fuel injection at the intake port, whereas the high-reactivity fuel is directly injected (−15 °CA to 0 °CA TDC). The low-reactivity fuel reaches premixed conditions (homogeneous mixture) prior to the start of combustion, whereas close to the TDC, the in-cylinder mixture consists of areas with high and low reactivity [23]. RCCI engines achieve higher efficiency [24] and lower emissions compared to engines operating with other LTC methods [25–28]. On the contrary, PCCI includes the high-reactivity fuel injection close to TDC (–30 °CA to 0 °CA) to allow for more effective combustion control. HCCI considers the port injection of both high-reactivity fuel and methanol, resulting in homogenous charge and fully premixed combustion.

Partially Premixed Compression Ignition (PPCI) exhibits similar characteristics to PCCI; however, only a portion of the low-reactivity fuel is premixed with air, while the rest is introduced later in the compression stroke, allowing partially premixed charge [29]. PPCI requires lean mixtures and high compression ratios, as demonstrated in the review study of Kumar et al. [30]. Other low-temperature combustion methods include premixed lean diesel combustion, charge intelligent multiple injection combustion and uniform bulky combustion. However, as these combustion types remain understudied, further research is needed to determine potential benefits as well as the performance and emissions parameters trade-offs [31].

The methanol direct injection, which is classified as HTC, results in methanol diffusion combustion, which takes place after methanol spray formation, droplets break up, evaporation and mixing with the surrounding air. In this case, methanol combustion starts after the diesel combustion starts, and diffusion flames are formed at the boundaries of the prepared methanol–air mixture. Premixed methanol combustion is of a very limited extent or does not occur at all.

Considering the different combustion methods, the results section separately discusses the premixed and diffusion combustion engines associated with the port and direct methanol injection types, respectively.

Table 1. LTC methods' advantages and challenges adapted from [29,32,33].

Combustion Method	Advantages	Challenges
PCCI [1]	NOx and PM reduction due to homogenous fuel–air mixture formation	Low combustion efficiency High CO and HC emissions
HCCI [2]	Low in-cylinder temperature and equivalence ratio Low emissions	To achieve in-cylinder homogenous charge conditions Increased knocking and noise effects To control the combustion start (depending on the charge mixture temperature) Operation at highly diluted mixtures causes instabilities (increasing knocking and ringing intensity) at high loads
RCCI [3]	Fuel flexibility (accommodating low-reactivity fuels, such as methanol, ethanol, natural gas) Possible single fuel operation with cetane number improver Possible single fuel operation with cetane number improver Low NOx and soot emissions	High-load operation requires the EGR
	Low injection pressures are required	High in-cylinder pressure rise

[1] PCCI—Premixed Charge Compression Ignition; [2] HCCI—Homogeneous Charge Compression Ignition; [3] RCCI—Reactivity-controlled Compression Ignition.

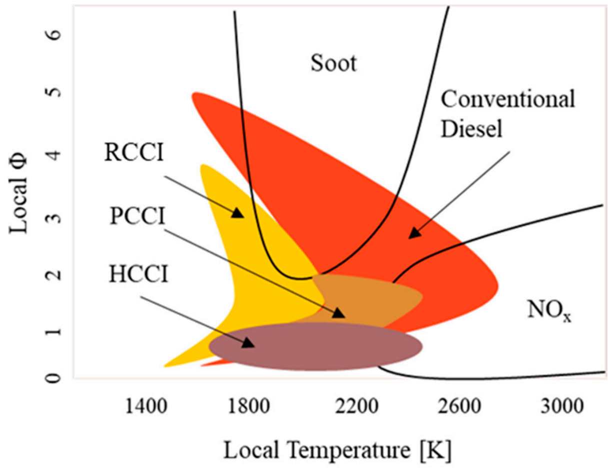


Figure 4. Local equivalence ratio–temperature (Φ–T) map illustrating areas of the diesel combustion (that is characterised as HTC) and low-temperature combustion (LTC) adapted from [34].

2.6. Fuels Characteristics

This section discusses methanol fuel characteristics compared to other fuels with established production technologies and use in dual-fuel engines, which were also considered in the reviewed studies. From the data presented in Table 2, methanol has a similar volumetric density to ethanol and diesel, while its lower heating value (LHV) is almost half compared to diesel fuel (and less than half compared to methane), implying challenges for the storage system. Methanol exhibits higher laminar burning velocity compared to diesel fuel (at the testing conditions: T = 340 K, P = 1 atm, Φ = 1) and, hence, is expected to undergo a slower combustion. Methanol's latent heat of vaporisation is much higher compared to other fuels (ammonia or hydrogen) [11]. Diesel fuel substitution by methanol results in significant benefits pertinent to the engine's environmental footprint, with lower CO_2 emissions (due to its significantly lower carbon content) and almost zero sulphur emissions (due to the insignificant sulphur content), which renders methanol suitable for short- to medium-term compliance with pertinent regulations of the shipping sector.

Table 2. Methanol fuel properties compared to other alternative fuels and diesel; adapted from Refs. [35–40].

Property	Diesel (MGO) [1]	Methanol	Ethanol	Methane [2]
Molecular formula	C_{10}–C_{15}	CH_3OH	C_2H_5OH	CH_4
Lower Heating Value (MJ/kg)	42.5	20.2	27	55.5
Octane number	17	111	103	120
Cetane number	51	3	9	0
Stoichiometric air-fuel ratio	14.3	6.5	9	17.2
Heat of Vaporisation (kJ/kg)	359	1100	900	219
Laminar burning velocity (cm/s) [3]	30	60	40	35
Density at 20 °C (kg/m^3)	847	795	790	431
Carbon content (%) w/w	85	37.5	52	74.8
Hydrogen content (%) w/w	13.5	50	35	25.1
Flashpoint (°C)	68	12	13	85
Viscosity (mm^2/s) at 40 °C	2.72	0.58	1.08	1.87
Auto-ignition Temperature (°C)	210–250	463	420	810
Sulphur content (ppm)	10	<0.5	<330	<8

[1] MGO—marine gas oil. [2] Methane is used in marine engines in gas form. [3] at 340 K, 1 bar, Φ = 1.

The methanol energy fraction (MEF) is estimated by the following equation:

$$MEF = \frac{m_{CH_3OH}\ LHV_{CH_3OH}}{(m_D\ LHV_D) + (m_{CH_3OH}\ LHV_{CH_3OH})} \tag{1}$$

In cases where the methanol mass fraction (*MMF*) was provided, the following equation was employed to derive the corresponding *MEF*:

$$MEF = \frac{LHV_{CH_3OH}}{\left(\frac{1}{MMF} - 1\right)LHV_D + LHV_{CH_3OH}} \tag{2}$$

3. Results

The results of this study are presented and discussed by considering the two main combustion methods of premixed and diffusion combustion engines. Important engine parameters, such as the brake thermal efficiency, the in-cylinder pressure and temperature, emissions and fundamental methanol combustion research, are discussed.

3.1. Methanol Premixed Combustion Engines

This section provides the results of the studies focusing on premixed methanol combustion for different energy fractions.

3.1.1. Combustion Parameters

Heat release rate

Ning et al. [41] reported that the MEF up to 30% resulted in a threefold increase in the peak heat release rate, whereas further MEF increase provided opposite trade-offs. Datta et al. [42] reported that an 8% MEF fraction resulted in the peak heat release rate increase, which was attributed to the longer ignition delay and resultant increase of the fuel burned during the premixed combustion phase.

Maximum in-cylinder temperature and Exhaust gas temperature

Li et al. [13] showed by simulation that the in-cylinder high-temperature area extends as the MEF increases. Zincir et al. [43] measured the exhaust temperature at 600 K for up to full diesel substitution for a premixed combustion engine at low loads. Yasin et al. [44] reported that the exhaust gas temperature slightly increases with the increase in MEF. Zhang et al. [45] studied methanol and other alcohol fuels' energy fractions up to 20%, concluding that the in-cylinder temperature increases by around 2% compared to the diesel mode. Datta et al. [42] studied experimentally the diesel–methanol dual-fuel operation, reporting that the exhaust gas temperature was measured in the ranges 417–558 K and 420–560 K at the diesel mode and 15% MEF, respectively.

Ignition delay and knocking effects

Increased MEF resulted in longer ignition delay [13], which, in turn, led to a higher amount of fuel burned at the premixed combustion phase, increasing the peak HRR and improving the engine thermal efficiency. Ning et al. [41] compared diesel and other alcohol fuels, concluding that methanol use results in longer ignition delay due to higher heat of vaporisation, in combination with its low heating value resulting in lower in-cylinder temperature. Wei et al. [46] reported that the MEF 52% resulted in retarding the start of combustion 5.5 °CA BTDC to 3 °CA ATDC (compared to the diesel mode).

Ning et al. [41] estimated the knock intensity (or ringing intensity—RI) as a function of the methanol fraction. The higher knocking intensity was found to be 3.02 MW/m^2 for 30% MEF (lower than the critical value of 5 MW/m^2), concluding that knocking did not occur at these operating conditions. RI increases from 0% to 40%, with its maximum values appearing at 20% MEF. Datta et al. [42] reported that the increase in alcohol fraction resulted in a longer ignition delay, reaching 25 °CA at the full load for 15% MEF (instead of 15.7 °CA for the diesel mode). Li et al. [13] argued that methanol premixed combustion (compared to diesel diffusion combustion) significantly shortens the combustion duration for increased methanol fractions.

3.1.2. Performance Parameters

Brake thermal efficiency

Cheng et al. [47] reported higher engine efficiency for the diesel mode, ranging 15–35% from low to high loads, compared to 13% to 34% with 17% MEF. At low loads, the brake thermal efficiency decreased up to 13% with the MEF increase; however, at high loads, the MEF increase resulted in a slight efficiency increase. Zincir et al. [43] reported that at low engine loads, the engine operating with methanol retained high efficiency (45% instead of 34% for the diesel mode). Saxena et al. [48] argued that even a small methanol fraction resulted in improved thermal efficiency at higher loads due to the higher oxygen content, lower cetane number (causing longer ignition delay, hence more pronounced premixed combustion phase resulting in higher combustion temperatures), higher heat of vaporisation (resulting in lower compression work), and lower flame temperature.

The decrease in engine brake thermal efficiency at fixed engine load is attributed to methanol combustion characteristics. As methanol has significantly lower LHV (compared to diesel fuel), to maintain the same energy input, a greater amount of methanol/diesel fuel is required [49]. For constant injection pressure, the injection duration will be longer in the case of methanol–diesel engine operation. Ning et al. [41] discussed that 40% MEF in a diesel engine resulted in the engine brake thermal efficiency reduction from 36.7% to 34.5% due to the ignition delay increase affecting the combustion duration, hence leading to a decrease of the engine indicated efficiency; this finding is also supported by [50]. Zhang et al. [45] reported an engine thermal efficiency decrease of around 5% for 20% MEF. Wang et al. [51] argued that dual-fuel methanol engines with high MEF greater than 10% can achieve higher thermal efficiency, as the cylinder pressure during the compression is much lower than the diesel mode, the higher methanol heat of vaporisation reduces the compression work, whereas the reduced exhaust gas temperature reduces the heat loss irreversibility. Some studies reported that brake thermal efficiency increased with methanol fuel, especially at medium and high loads. This was attributed to an improved combustion rate that leads to almost constant volume combustion [35].

Figure 5a presents the effect of methanol energy fraction on BTE change (compared to the diesel mode) for both the premixed and diffusion combustion engines. Different symbols denote different clusters of engines, whereas whenever available, high and low loads are indicated.

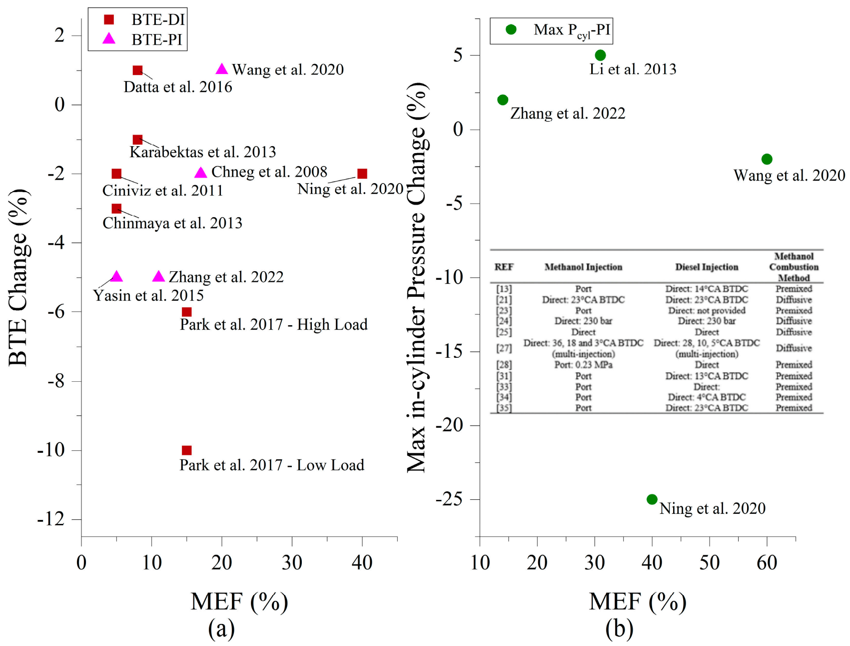


Figure 5. Influence of methanol energy fraction on engine brake thermal efficiency (**a**) and maximum in-cylinder pressure (**b**) change compared to the diesel mode. The methanol and diesel injection parameters are superimposed. DI—direct injection; PI—port injection.

In-cylinder pressure

Ning et al. [41] quantified the combustion effects on the maximum in-cylinder pressure for up to 40% MEF in diesel engines. Compared to diesel mode, the use of alcohol fuels significantly reduced the peak in-cylinder pressure. Zhang et al. [45] reported that the 20% MEF in a diesel engine resulted in a 2% increase in the maximum in-cylinder pressure, which was attributed to the low methanol cetane number, faster evaporation, and more uniform atomisation. Figure 5b presents the influence of MEF on the in-cylinder maximum pressure for the premixed combustion engines studied in the preceding publications.

3.1.3. Emissions Parameters

CO_2 emissions

The methanol carbon-to-energy ratio is slightly lower compared to diesel $\left(\frac{C_d}{LHV_d} = 2\,\frac{C_{\%w/w}}{MJ}, \frac{C_M}{LHV_M} = 1.85\,\frac{C_{\%w/w}}{MJ}\right)$, implying that only slight CO_2 emissions reduction is expected for methanol-fueled engines. However, green methanol production is expected to reduce the lifecycle CO_2 emissions. Although the CO_2 emissions also depend on the engine efficiency, similar trade-offs for CO_2 emissions are expected for premixed and diffusion combustion engines. Hence, only the CO_2 emissions are reported in this section.

Cheng et al. [47] reported that 17% MEF on a diesel–methanol dual-fuel engine resulted in a 7% carbon emissions reduction at the same operating conditions compared to the diesel mode. However, for low loads, the exhibited carbon reduction is not so pronounced, as the engine's thermal efficiency reduces, increasing fuel consumption and resulting in higher CO_2 emissions. Datta et al. [42] reported that the 15% MEF resulted in lower CO_2 emissions, especially at low loads. Kumar et al. [52] studied the 90% MEF in a locomotive engine, reporting around a 15% CO_2 emissions reduction compared to the diesel mode.

NOx and PM emissions

NOx emissions are generated due to the fuel nitrogen content as well as the nitrogen oxidation. Cheng et al. [47] reported that 17% MEF led to 11% NOx emissions reduction, reaching 20% at low loads, compared to the diesel mode operation. Methanol, due to its higher latent heat of vaporisation (compared to diesel), absorbs more heat and, thus, reduces the combustion temperature, leading to lower NOx emissions. Compared to hydrogen fuel, engines with premixed methanol combustion at 50% MEF exhibited higher thermal efficiency and lower NOx emissions at both low and high loads, whereas their total hydrocarbon emissions were increased [53].

Li et al. [13] numerically verified the NOx emissions reduction for 50% MEF. Zincir et al. [43] reported the NOx emissions increase with the engine load increase; however, the NOx emissions reduction of around 93% was achieved compared to the diesel mode. Yasin et al. [44] reported that at 5% MEF, higher NO emissions were achieved at medium loads due to higher in-cylinder temperature and increased methanol oxygen content compared to the diesel mode. Liu et al. [54] reported that the MEF increase positively impacts NOx emissions, especially at low loads. Zhang et al. [45] reported that 20% MEF resulted in an increase in NOx emissions due to local oxygen enrichment. Wang et al. [51] studied dual-fuel engines with high methanol fractions, concluding that the NOx emissions significantly reduced for 10% MEF, as the in-cylinder temperature does not reach the range for NO formation (2200–3000 K). Rakopoulos et al. [55] studied the effect of 17% MEF of n-butanol (alcohol fuel with similar characteristics to methanol) on a heavy-duty diesel engine, concluding that the turbocharger lag exhibits the most significant contributor to NO emissions increase. Zhu et al. [56] reported a 20% increase in NO_x emissions with an increase of 41% in MEF.

Cheng et al. [47] reported that particulate matter (PM) decreases by up to 50%, with MEF by up to 17%. Yusop et al. [57] experimentally verified the PM emissions reduction of up to 40% with 20% MEF.

CO emissions

Li et al. [13] reported a 70% CO emissions reduction for 50% MEF compared to the diesel mode. Zincir et al. [43] reported that methanol combustion exhibited lower CO emissions at high loads, whereas at very low loads (around 10%), CO emissions are tripled, attributed to the formation of wider fuel-rich zones, within which the fuel oxidation is slower. Yasin et al. [44] argue that a small MEF (5%) resulted in significant CO emissions reduction. Ning et al. [41] reported that MEF in the range 30–40% increased the CO emissions, whereas Liu et al. [54] found that CO emissions increase with the methanol fraction increase at low loads.

3.2. Methanol Diffusion Combustion Engines

This section reviews the findings of studies focused on diffusion combustion, where methanol is directly injected into the engine cylinder(s).

3.2.1. Combustion Parameters

Heat release rate

The methanol use in diesel dual-fuel engines significantly impacts the heat release rate. This finding was also supported by Emiroglu and Sen [58], reporting a 15% increase in peak HRR for 10% MEF, attributed to the methanol's lower cetane number, causing longer ignition delay, hence retarding the combustion start.

Maximum in-cylinder and Exhaust gas Temperature

This section discusses the effects of methanol combustion on the in-cylinder temperature (considering its maximum values) and the exhaust gas temperature downstream of the exhaust valve (TEG). Though insignificant, the small rise in exhaust gas temperature is attributed to methanol's faster combustion due to its oxygen content. The same study reported the reduction of the maximum in-cylinder temperature (ranging 1130–1580 K) for 15% MEF, compared to the diesel mode (ranging 1180–1700 K). This is attributed to the higher methanol heat of vaporisation, leading to higher heat absorption, which, in turn, results in lower flame temperature and, therefore, lower in-cylinder temperature. Karabektas et al. [59] reported that 15% MEF reduced the exhaust gas temperature by around 30 K. Liu et al. [54] reported the decrease of in-cylinder temperature with the increase of methanol fraction in dual-fuel engines.

Ignition delay and knocking effects

Rakopoulos et al. [60] reported an increase in ignition delay under 8% MEF due to the low cetane number of the low-reactivity fuel. Chinmaya et al. [61] reported an ignition delay of around 17 °CA for 5% MEF (compared to 9.8 °CA for the diesel mode). Huang et al. [62] and Pucilowski [63] argued that methanol combustion leads to the formation of inactive H_2O_2 at low-temperature diesel oxidation, resulting in poor diesel atomisation and hence increasing the ignition delay. Yin et al. [64] examined the introduction of 20% and 50% MEF directly in-cylinder and determined that ringing intensity increased with the MEF increase; however, the in-cylinder pressure did not exceed the limit of 8 bar/°CA.

3.2.2. Performance Parameters

Brake thermal efficiency

Chinmaya et al. [61] reported that the engine brake thermal efficiency (BTE) increased by a similar percentage for both the diesel and diesel–methanol modes. For methanol MEF up to 8%, the BTE increased from 32.9% to 33.8%.

According to [65], 8% MEF resulted in a 2% BTE reduction at high loads, whereas similar BTE was reported at low and medium loads. Karabektas et al. [59] performed experiments, reporting BTE reduction in the range 24.6–21.8% for 5% MEF and above [61]. Park et al. [66] numerically investigated different methanol fractions, concluding that the BTE decreases around 10% for 6% MEF at low loads (compared to the diesel mode).

In-cylinder pressure

Chinmaya et al. [61] discussed that a 5% MEF in a high-speed diesel engine at medium loads leads to a similar pressure profile compared to the diesel mode. For 24% MEF, the maximum in-cylinder pressure (Pmax) reduced from 65.2 bar to 46 bar (30% reduction) for a single-cylinder high-speed engine at high loads, attributed to methanol higher latent heat of vaporisation, which leads to much lower in-cylinder temperature and pressure [67]. Yin et al. [68] demonstrated that the in-cylinder pressure increases with increasing MEF; a slight Pmax increase for 20% MEF and a significant Pmax increase for 55% MEF were reported.

3.2.3. Emissions Parameters

NOx emissions and PM emissions

Karabektas et al. [59] reported NOx emissions decreased by 7% at low loads and 1–2% at high loads for 8% MEF, resulting in a reduction. Guo et al. [18] reported that NOx emissions decreased by up to 8.3% (compared to the diesel mode) at high engine speed for 30%MEF, whereas the NOx emissions increased at low engine speeds due to the thermal NOx formation. Ciniviz et al. [65] reported a 38% increase in thermal NOx emissions for 5% MEF compared to diesel operation. Emiroglu and Sen [58] reported that the MEF increase resulted in a 6% NOx increase, attributed to gas residence time and higher oxygen content leading to higher in-cylinder temperature. Park et al. [66] reported a 47% decrease in the brake-specific NOx emissions for 15% MEF. Lu et al. [67] justified the NO_2 emissions formation for high MEF, concluding that it is dominated by the NO and HO_2 radicals and can be considerably limited by using exhaust gas recirculation (EGR). Guo et al. [18] found that the PM emissions substantially reduced (up to 83% compared to the diesel mode) at low loads; however, the soot emissions considerably increased for MEF above 30%.

CO emissions

Carbon monoxide emissions are indicators of incomplete combustion and are considered harmful to humans. Sayin [68] concluded that the MEF increase led to reduced CO emissions, attributed to lower methanol carbon content, whereas the methanol pressure injection increase (from 200 bar to 220 bar) led to a further 14% reduction in CO emissions. Guo et al. [18] reported a 73% decrease in CO emissions at low loads but not a so pronounced impact at high loads. Ciniviz et al. [65] performed experiments reporting an average 33% CO reduction for 8% MEF, whereas higher boost pressure reduces CO emissions, as it increases the engine volumetric efficiency. Chimmaya et al. [61] reported that a 5% MEF fraction led to a 15% CO emissions reduction at low loads. Huang et al. [69] reported a significant (11%) reduction of CO under 9% MEF. Zhu et al. [56] reported that CO emissions quadrupled for 80% MEF, which was attributed to incomplete combustion.

3.3. Methanol Combustion Kinetics

Yalamanchili et al. [70] proposed a reduced combustion mechanism consisting of the five reactions listed in Table 3, which was experimentally validated and subsequently employed for assessing the effects of different initial conditions (temperature, concentration, and pressure) on methanol ignition delay. Skodje et al. [71] identified the reactions $CH_3OH + HO_2 \leftrightarrow CH_3O + H_2O$ and $CH_3OH + O_2 \leftrightarrow CH_2OH + HO_2$ as the most important for methanol ignition delay while proposing a methodology to update these reactions coefficients. At high-temperature conditions, the chain-branching reaction ($H + O_2 \leftrightarrow OH + O$) mostly affects the start of ignition. Li et al. [72] provided an updated comprehensive kinetic mechanism for methanol combustion. Table A2 (in Appendix B) provides this C_1/O_2 mechanism studied and validated experimentally in Refs. [73–76] to predict the CO_2 and CO emissions with higher accuracy, whereas Table A3 (Appendix B) lists the considered species of this mechanism. Several reactions have a greater impact than others in the dynamics of autoignition, including the reaction with ID (1) (Table A2) and the chain branching reaction with ID (2) (both in Table A2) [76]. Manias et al. [77] proposed a modified reaction mechanism with a considerable reduction of the ignition delay when adding 3% of CH_2O and H_2O_2 to the methane–air mixture.

Table 3. Reduced five-step mechanism adapted from [70].

Reaction
$CH_3OH + 2H \leftrightarrow 2H_2 + CH_2O$
$CH_2O \leftrightarrow CO + H_2$
$CO + H_2O \leftrightarrow CO_2 + H_2$
$H + H + M \leftrightarrow H_2 + M$
$3H_2 + O_2 \leftrightarrow 2H + 2H_2O$

Wang et al. [78] studied methanol oxidation up to 100 atm using supercritical stirred reactors, reporting onset temperatures of 700 K and 800 K for methanol oxidation at 100 atm and 10 atm, respectively; an updated reaction pathway for methanol oxidation was proposed and linked to the following reactions: $CH_2O + HO_2 \leftrightarrow HOCH_2O_2$, $RO_2 + RO_2 \leftrightarrow HOCH_2O$ (RO) + $HOCH_2O$ (RO) + O_2, and $CH_3OH + RO_2 \leftrightarrow CH_2OH + HOCH_2O_2H$.

Li et al. [79] recommended a methanol oxidation mechanism for high-pressure conditions tested in shock tubes, providing an updated rate constant for CH_3OH + HO_2 reactants. Li et al. [80] performed a kinetic study in shock tubes for the high-temperature methanol/n-heptane surrogate, concluding that increasing the methanol fraction for $\Phi = 1$ reduces the ignition delay due to the key radical HO_2 impacted by the methanol concentration. For lean mixtures, n-heptane increases the mixture reactivity due to its sensitivity to the chain-branching reaction. Zhu et al. [81] identified the dependence of the reactions on the temperature for a wide temperature range for the same surrogates in a rapid compression machine.

Table 4 provides a summary of the key methanol kinetics mechanisms reviewed, along with the main characteristics and application ranges. Research challenges are associated with the development of mechanisms that provide adequate accuracy on both high and low-temperature combustion [82], as well as extending the applicability of the existing mechanisms beyond their application ranges.

Table 4. Kinetics mechanisms reviewed with key outcomes.

Reference	Key Remarks	Range
Yalamanchili et al. [70]	Supports spontaneous ignition	Φ: 0.37–3
Li et al. [72]	Updated rate constants and thermochemical data for OH, HO_2, and CH_2OH	P: 1.5–6 atm T: 850–950 K
Manias et al. [77]	Identification of intermediate species/compounds associated with the ignition delay	T: 600–1600 K P: 7–41 atm Φ: 0.3, 0.5, 1.0
Wang et al. [78]	Ignition delay decreases as the temperature increases at 100 atm and methanol-rich conditions Onset temperature for CH_3OH oxidation at 100 atm is around 700 K	P: 10 and 100 atm T: 550 to 950 K Φ: 0.1, 1.0
Zhu et al. [81]	Ignition delay decreases with increasing pressure, equivalence ratio, and diesel fraction For temperatures above 940 K, longer ignition delay for lower methanol ratios	P: 6–20 bar T: 650–1450 K Φ: 0.5, 1.0, 2.0

3.4. Engine Parametric Investigations

Li et al. [83] numerically studied a dual-fuel engine performance with direct injection of both methanol and pilot diesel fuel by varying the following four parameters: methanol nozzle diameter, methanol injection pressure, diesel and methanol injectors angles (deflection and divergence angles). It was inferred that reducing the nozzle diameter (from 0.4 mm to 0.3 mm) increased the in-cylinder pressure and the peak heat release rate due to the faster methanol evaporation. Furthermore, the ignition delay and combustion duration remained unaffected by the methanol nozzle diameter and injection pressure. The diesel and methanol injector angles exhibited only a slight impact on the in-cylinder pressure, HRR, and ignition delay.

Park et al. [66] investigated the effect of methanol injection timing (ranging from 0 to 8 °CA BTDC) on the engine performance and emissions parameters, concluding that 15% MEF and advanced methanol injection timing resulted in a 3% brake thermal efficiency decrease and 20% NOx emissions increase; the latter attributed to the increased in-cylinder temperature. The advanced injection timing improved the BET, as the combustion duration shortened. Wang et al. [84] studied the injection timing and the intake manifold temperature settings optimisation for 17% MEF, concluding that the injection timing of 7.4 °CA BTDC and the intake temperature of 115 °C improved the BTE at high loads (7% increase BTE efficiency improvement. Saxena and Maurya [85] reported that the methanol injection timing retard resulted in the increase of the maximum pressure rise rate, which can be limited by employing a double injection strategy, whereas the methanol accumulation close to the cylinder walls resulted in unburned fuel and pertinent emissions.

Rodriguez-Fernandez et al. [86] conducted a parametric study for a 35% MEF in a heavy-duty diesel engine, evaluating different parameters, including the intake pressure and temperature, the EGR rate, the dwell angle, the diesel injection pressure, and the pilot fuel ratio. The study concluded that low-temperature and highly premixed combustion conditions, along with EGR, can lead to high efficiency and low emissions trade-offs. Sener et al. [87] studied the optimisation of the combustion chamber geometry, spray angle, and injection pressure. Enoki et al. [88] studied the diesel and methanol injection timings optimisation, identifying the optimal methanol injection timing in the range of 2–3 °CA before diesel injection while highlighting the pre-combustion chamber geometry impact on the mixing of the pilot diesel the methanol fuels. Ning et al. [89] experimentally investigated the effect of methanol injection timing and methanol fraction on a single-cylinder DI engine performance and emissions, reporting the trade-offs between these parameters.

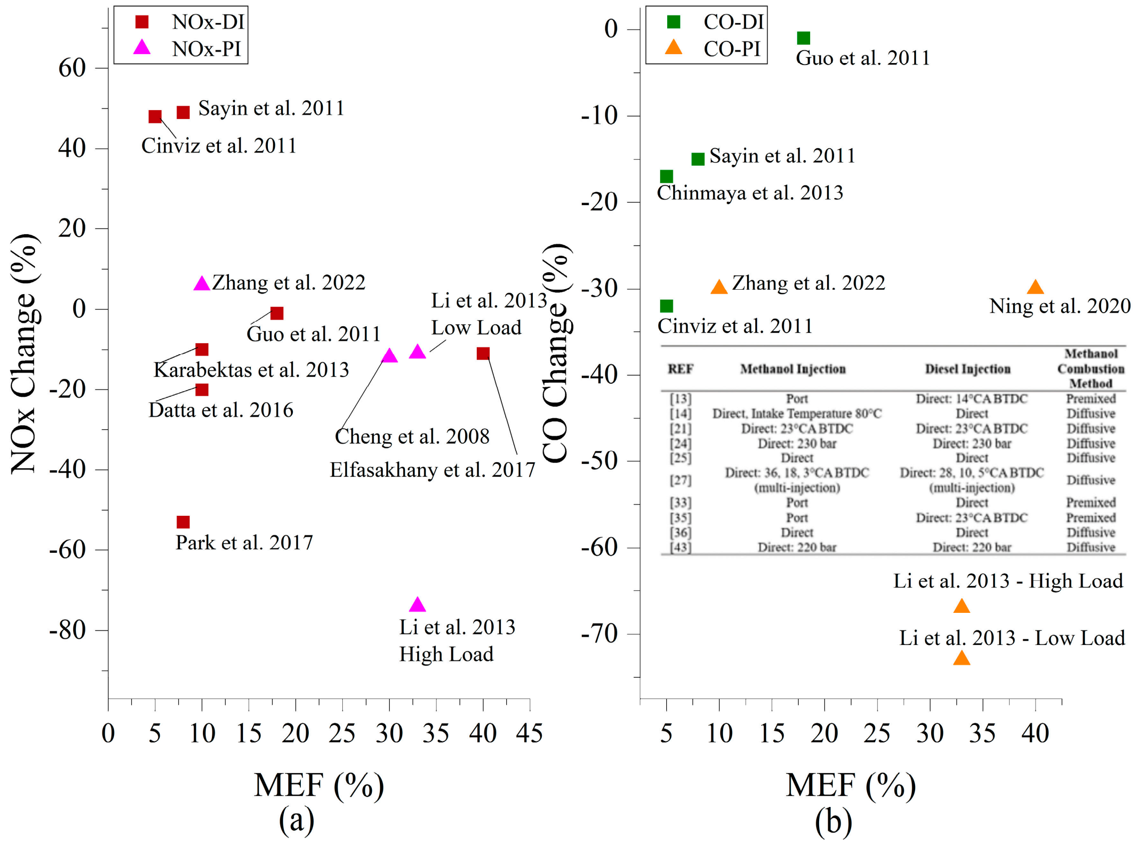
Li et al. [90] studied the multi-objective optimisation in a methanol–diesel dual-fuel direct injection engine considering the methods of reactivity-controlled compression ignition (RCCI) the direct dual-fuel stratification (DDFS), recommending the following: (1) increased injection pressure to promote spray penetration, air-fuel mixing and efficient combustion, (2) increased EGR rate to minimise the NOx emissions and knock intensity, (3) early diesel start of injection, and (4) small diesel and medium methanol spray angles compromising between ignition timing and efficiency.

3.5. Autoignition Enhancement

The greatest challenge for compression ignition engines operating with high MEF pertains to the methanol autoignition. In most engines, this is addressed by using direct injection of a high-reactivity pilot fuel (typically diesel). Methanol autoignition constraints were considered in several studies. Korpuk et al. [91] proposed the use of dimethyl ether (DME) as an ignition enhancer for methanol-diesel engines, reducing the ignition delay by 2–4 °CA. Vanu and Madhavan [92] proposed the diethyl ether (DDE) addition (10% energy fraction), reporting the reduction of the methanol combustion start for dual-fuel engines. Samson et al. [93] concluded that the addition of 1% alkyl nitrate (CEN) in diffusion combustion methanol engines reduced the autoignition dependency on the charge temperature and pressure. Nanthagopal et al. [94] provided valuable insights on the use of oxygenated nanoparticles (aluminium oxide, cerium oxide, zinc oxide, graphene, and others) for methanol dual-fuel engines, reporting improved efficiency and reduced emissions while enhancing methanol ignitability. Low-temperature plasma-assisted combustion [95,96] could address the auto-ignition challenges of low-reactivity fuels, such as methanol, in compression ignition engines.

3.6. Key Findings and Trends of Methanol-Fueled Engines

This section summarises the key findings and trade-offs of the diesel–methanol dual-fuel engines for premixed and diffusion combustion. MEF is employed in the discussions of this section, as this study's scope is to identify the effect of MEF on engine performance and emissions parameters. The engine parameters corresponding to the diesel mode were employed as a baseline. The revealed trade-offs can be affected by the engine settings and injection strategies, as well as the engine subsystems control (e.g., turbocharging system), which impact the engine cylinders' boundary conditions (and hence the engine parameters). Figure 6a,b present the NOx and CO emissions changes versus MEF for the reviewed premixed and diffusion combustion engines.



REF	Methanol Injection	Diesel Injection	Methanol Combustion Method
[13]	Port	Direct: 14°CA BTDC	Premixed
[14]	Direct, Intake Temperature 80°C	Direct	Diffusive
[21]	Direct: 23°CA BTDC	Direct: 23°CA BTDC	Diffusive
[24]	Direct: 230 bar	Direct: 230 bar	Diffusive
[25]	Direct	Direct	Diffusive
[27]	Direct: 36, 18, 3°CA BTDC (multi-injection)	Direct: 28, 10, 5°CA BTDC (multi-injection)	Diffusive
[33]	Port	Direct	Premixed
[35]	Port	Direct: 23°CA BTDC	Premixed
[36]	Direct	Direct	Diffusive
[43]	Direct: 220 bar	Direct: 220 bar	Diffusive

Figure 6. Emission parameters changes compared to the diesel model versus MEF; (**a**) NOx emissions; (**b**) CO emissions. DI—direct injection; PI—port injection.

3.6.1. Methanol Premixed Combustion Engines

The MEF increase led to longer ignition delays and higher heat release rate peaks due to the methanol's lower cetane number [46]. The reviewed studies concur that alcohol fuel oxygen content increases the combustion speed and premixed combustion intensity, leading to higher peak temperatures. The RI increase was attributed to the high oxygen content, which resulted in rapid combustion (associated with high HRR peaks and noise). The RI of premixed combustion engines is high, as the in-cylinder methanol–air mixture is fully premixed and has high reactivity, limiting the maximum MEF to 47–50% to avoid knocking and misfiring [64] (47% was reported for engines with methanol injection upstream of the turbocharger compressor [97]). This limit can be extended to 75% by employing water injection [98] as a knock mitigation strategy.

Methanol premixed combustion engines exhibited lower efficiency compared to diesel, with this trade-off being pronounced with higher MEF. Premixed methanol combustion exhibited quenching effects, leading in most cases to decreased in-cylinder maximum pressure, especially at low loads. However, the reviewed methanol port injection engines exhibited an increase in the in-cylinder maximum pressure due to longer ignition delay and shorter combustion of the premixed methanol mixture.

CO emissions reduced in the range 30–75% for MEFs 10–40%, as a more homogeneous mixture and premixed lean conditions resulted in more effective combustion. MEF in the range 17–20% resulted in decreasing PM emissions in the range 40–50%.

3.6.2. Methanol Diffusion Combustion Engines

MEF of 15% resulted in an 8% reduction of the maximum in-cylinder temperature. For MEF ranging 5–40%, the BTE reduced in the range 2–10%. From the preceding sections, it is inferred that a clear BTE–MEF trade-off cannot be determined. This is attributed to the impact of several parameters, such as the size, injection settings, and geometrical characteristics. However, higher MEF can be realised by employing direct injection, as the mixing of air–methanol is controlled (by the injection rate), resulting in lower RI.

Most of the studies reported the NOx emissions decrease compared to the diesel mode due to the lower in-cylinder temperature. However, for low MEF (5–8%), the NOx emissions increased by 50%, which was attributed to the higher methanol oxygen content, resulting in higher in-cylinder temperature levels at high loads. CO emissions were reduced by 2–30% for MEFs in the range 5–18%.

3.6.3. Comparison of Premixed and Diffusion Combustion Engines

For both methanol premixed and diffusion combustion engines, the CO_2 emissions were reduced in the range 7–15%. Compared to diffusion, the premixed combustion method resulted in higher BTE due to shorter combustion and hence lower heat transfer losses [99]. For MEF ranging 5–55%, the in-cylinder maximum pressure exhibits contradictory trade-offs depending on the prevailing combustion conditions.

The CO emissions of the methanol-diesel diffusion combustion engines are relatively higher compared to the premixed combustion engines due to the non-homogeneity of the fuel–air mixtures in the former. Methanol direct injection results in higher fuel stratification and higher NOx emissions compared to premixed combustion engines. The NOx emissions reduction is more pronounced in premixed combustion engines due to cleaner combustion as well as lower in-cylinder pressure and temperature. Compared to premixed combustion, diffusion combustion engines exhibit shorter ignition delay (for MEF less than 50%) due to higher in-cylinder temperature levels.

Based on the preceding discussions, the flowchart of Figure 7 was developed, which provides a summary of the methanol key properties and their effects on the engine performance and emissions parameters. The conditions that lead to contradicting results presented in the preceding sections are associated with the different MEF, different operating conditions, engine settings and geometrical characteristics, as well as the methanol combustion method. A confidence scale is employed in Figure 7 (for each parameter) to demonstrate confidence in the identified trend.

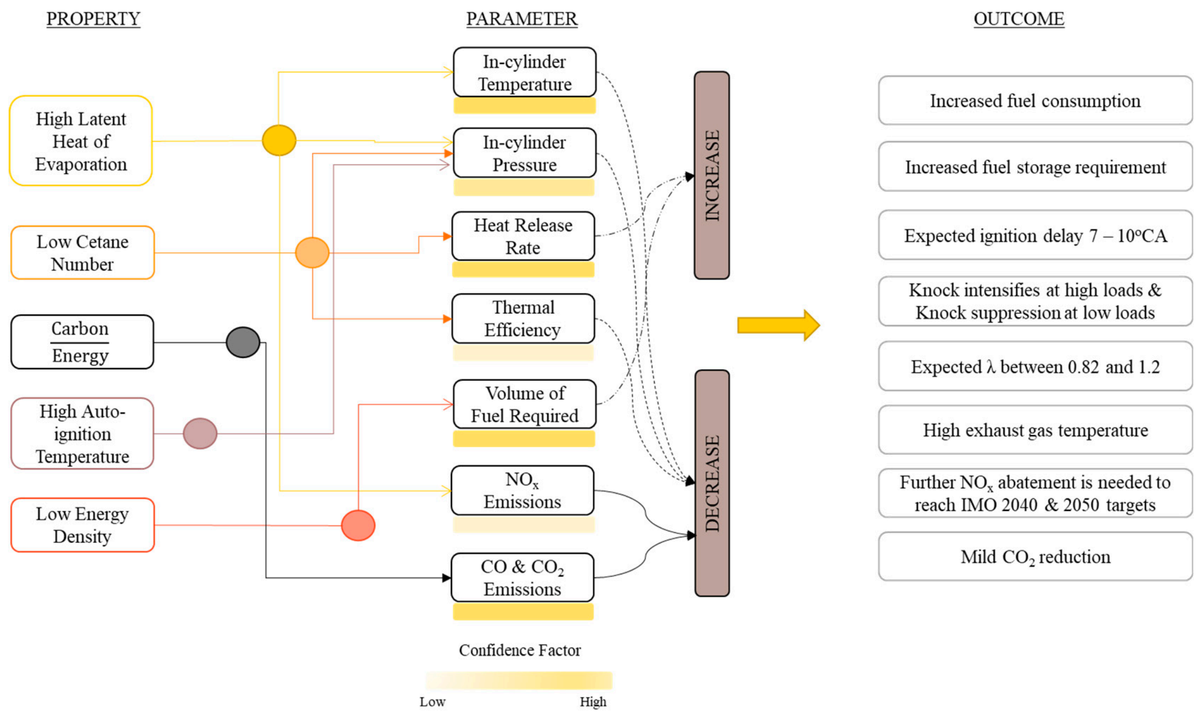


Figure 7. Summary of methanol key properties and their effects on engine performance and emissions parameters.

4. Research Gaps and Directions

Based on the preceding comprehensive literature review for several engine configurations, sizes, injection strategies, and parameter trade-offs, several research challenges are identified, and research directions are proposed. These are listed in Table 5, whereas a brief discussion follows.

Table 5. Research challenges and proposed directions.

Research Challenge	Proposed Directions
Reducing environmental footprint Reducing CO_2 emissions Eliminate NOx, PM, and Methanol Slip	Methanol and low/zero carbon fuel combinations (decarbonisation)
Retrofitting existing engines with methanol	Combustion concepts
Optimal components design	Injection concepts
Address methanol corrosive behaviour	Anti-corrosive Materials
Adverse ignition properties	Ignition enhancers Fuel evaporation
Reliability, availability & maintainability	Simulation-based tools
Marine engine size and power output	Experimental studies
Engine systems (turbocharger, wastegate valve, and controls)	Kinetic models
	Scale-up procedures

Reducing the environmental footprint of marine engines is a challenging undertaking. Methanol-fueled engines exhibit limited CO_2 emissions reduction, even at high MEFs. This challenge can be addressed by considering combinations of methanol and zero-carbon fuels (ammonia and hydrogen), hence paving the way for deeper decarbonisation at the expense of more complicated storage, feeding, and injection systems as well as more complicated combustion processes. Using methanol produced by biomass and renewable energy can contribute to a further decrease in marine engines' environmental footprint, provided that lifecycle-based regulations will be adapted. The considerable reduction or elimination of NOx and PM emissions, as well as methanol slip (due to toxicity), must be addressed, ideally at the engine settings level, without the use of after-treatment units.

Scaling up the findings from small engines to large marine engines is another challenge. Modelling tools and approaches of different complexities (3D, 0D/1D) and levels (component, subsystem, and system) combined with optimisation tools are expected to help address this challenge. In addition, lab-scale and full-scale experimental studies are required to provide evidence for validating models and methods representing the operation of methanol-fueled marine engines at a wide range of operating conditions.

The use of thermodynamic modelling requires the development of combustion models of adequate accuracy. Hence, it is expected that fundamental combustion studies are required to develop effective kinetics mechanisms, which can subsequently be employed in CFD studies to develop phenomenological combustion models and/or refine existing ones. Further research is required to investigate methanol fuel evaporation under different combustion concepts (diffusion or premixed). To identify the methanol-fueled engines' optimal geometries and settings leading to high efficiency and low emissions, optimisation studies combined with modelling tools and experimental validation are required.

Another challenge for developing methanol-fueled marine engines pertains to the methanol's adverse ignition properties. This can be addressed by undertaking research on identifying high-reactivity fuels (and fuel combinations) to facilitate the combustion start. Research on the ignition enhancers that can negate pilot fuel use is expected to contribute to the use of higher MEF (or only methanol) on marine engines.

Retrofitting existing marine diesel engines to convert them into methanol-fueled engines is expected to significantly contribute to the wide adoption of methanol in ship operations. Port injection and premixed methanol combustion concepts must be developed to address this. As high MEFs are constrained for premixed combustion engines due to the methanol physical properties, research on advanced combustion concepts and injection strategies is required. The design of the injection system and its components must be advanced, whereas injection strategies must be developed to achieve close to homogeneous conditions while avoiding wall impingement and thermal non-uniformities.

Methanol's corrosive properties pose challenges for marine engine components. This can be addressed by pursuing research initiatives on anti-corrosive materials and modern manufacturing techniques. Considering that methanol-fueled engines are under development, their safety, reliability, availability, and maintainability remain understudied. Hence, the use and integration of advanced methods and tools from safety and reliability engineering are expected, along with the use of experimental measurements to quantify the wear and degradation of the methanol-fueled engine components.

The wider adoption of methanol as a marine fuel faces several challenges, the major of which are associated with the inadequacy of methanol production to cover the worldwide demand and the required transportation infrastructure. Moreover, financial constraints (which are beyond this study's scope) considerably influence methanol adoption [95]. Notwithstanding these challenges, research advancements according to the preceding directions will expedite the wider methanol use in marine engines.

5. Conclusions

This study conducted a comprehensive review of the pertinent literature to identify the fundamental characteristics of methanol combustion in compression ignition engines. The reviewed experimental and numerical studies results were discussed considering the methods of premixed and diffusion combustion, several methanol fractions and settings, as well as the reported effects on the engine's performance and emissions parameters. The available methanol kinetics mechanisms were reported, whereas combustion methods and parametric studies are discussed. The main research goals and needs were summarised, whereas recommendations for future research pathways were provided. The main findings of this study are summarised in the paragraphs below.

Most of the reviewed studies concur that increasing the methanol fraction in compression ignition engines leads to lower engine efficiency compared to the diesel mode, the extent of which depends on the engine load for both combustion methods.

Methanol-fueled engine emissions are highly dependent on the methanol fraction, engine load, combustion method, and fuel injection strategies. Diesel fuel substitution by methanol leads to lower CO_2 and CO emissions; however, the reviewed literature reported contradictory trends for NOx emissions depending on the operating conditions. Premixed combustion engines exhibit lower NOx and CO emissions compared to diffusion combustion engines.

Contradictory trends were also reported for the in-cylinder maximum pressure, with the affecting parameters being the methanol vaporisation heat, cetane number, and oxygen content, as well as the engine settings (injection timings) and operating conditions (load, speed). A slight increase in the exhaust gas temperature (downstream of the exhaust valve) was reported, whereas contradictory trends were found for the in-cylinder temperature.

Methanol port injection exhibits a limitation of the methanol energy fraction to around 50%, beyond which knocking occurs; however, the methanol diffusion combustion allows for using higher methanol fractions at the expense of higher NOx emissions. The premixed methanol combustion is more challenging in terms of knocking avoidance compared to the methanol diffusion combustion.

The identified research needs for marine engines include the development of fundamental combustion methods, the optimisation of designs, injections and combustion strategies, benchmarking studies, new designs for components/subsystems, combustion models for high methanol fractions, combinations of methanol with zero-carbon fuels, while exploring concepts for fuel agnostic marine engines. These needs can be addressed by promoting a portfolio of diverse activities, including experimental studies, simulation studies considering advanced tools of varying complexities, developing and optimising new designs exploring injection and combustion methods, engine systems optimal control, new materials, coating and lubricants compatible with the methanol use, intelligent health management to promote the engines safety, reliability, and maintainability.

The proposed research directions provide stimuli to researchers and industry for future studies targeting the wide use of methanol in the shipping sector, hence supporting the societal need for decarbonising shipping operations. Similar studies on zero-carbon fuels, including ammonia and hydrogen, are also recommended for future work.

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Conflicts of Interest: Author Ioannis Vlaskos was employed by the company Winterthur Gas & Diesel. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Abbreviations

ATDC	After Top Dead Centre
bsfc	Brake-Specific Fuel Consumption
BTDC	Before Top Dead Centre
BTE	Brake Thermal Efficiency
CA	Crank Angle
DDFS	Direct Dual Fuel Stratification
ECA	Emission Control Area
EGR	Exhaust Gas Recirculation
HC	Hydrocarbon
HCCI	Homogenous Combustion Compression Ignition
HFO	Heavy Fuel Oil
HRR	Heat Release Rate
ITE	Indicated Thermal Efficiency
LHV	Latent Heating Value
LNG	Liquified Natural Gas
LTC	Low-Temperature Combustion
MEF	Methanol Energy Fraction
MGO	Marine Gas Oil
PM	Particulate Matter
PCCI	Premixed Charge Compression Ignition
PPCI	Partially Premixed Compression Ignition
RCCI	Reactivity Controlled Compression Ignition
RI	Ringing Intensity
SOI	Start of Injection
TDC	Top Dead Centre

Appendix A. Engine Characteristics of Reviewed Publications

Table A1 summarises the particulars and characteristics of the engines investigated in the reviewed literature.

Table A1. The engine particulars of the reviewed studies.

Reference	Provided Engine Characteristics	MEF	Injection Method Diesel (D) Methanol (M)	Injection Characteristics
[13]	Bore: 70 mm Stroke: 50 mm	2.5–65%	D: direct injection M: port injection	D: 14 °CA BTDC M: not provided
[18]	Single cylinder	30%	D: direct injection M: direct injection	Not provided
[61]	Nominal power: 5.2 kW Compression ratio: 17.5 Single cylinder	5%	D: direct injection M: direct injection	D: 23 °CA BTDC M: 23 °CA BTDC
[43]	Nominal power: 49 kW Bore: 130 mm Stroke: 160 mm Marine engine	0–100% mass fraction	D: direct injection M: port injection	M: 40 °CA BTDC
[44]	Nominal power: 32 kW Compression ratio: 22.4	5%	D: direct injection M: port injection	Not provided
[65]	Nominal power: 62.5 kW Compression ratio: 17	5%	D: direct injection M: direct injection	D & M: injection pressure 230 bar
[59]	Nominal power: 14 kW Compression ratio: 17 Single cylinder	8%	D: direct injection M: direct injection	Not provided
[66]	Nominal power: 67 kW Compression ratio: 17 Cylinders: 4	15%	D: direct injection M: direct injection	D: 28 °CA BTDC (1st pilot) 10 °CA BTDC (2nd pilot) 5 °CA ATDC (main) M: 36 °CA BTDC (1st pilot) 18 °CA BTDC (2nd pilot) 3 °CA BTDC (main)

Table A1. *Cont.*

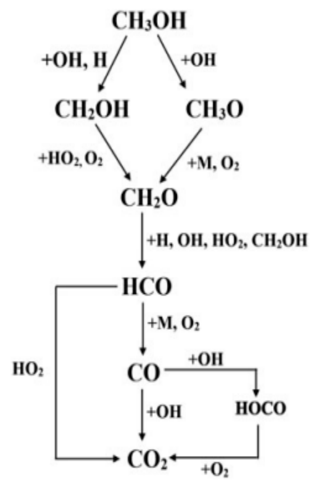
Reference	Provided Engine Characteristics	MEF	Injection Method Diesel (D) Methanol (M)	Injection Characteristics
[47]	Nominal power: 88 kW Cylinders: 4 Compression ratio: 19	5–17%	D: direct injection M: port injection	D: not provided M: injection pressure 30 bar
[41]	Nominal power: 8 kW Compression ratio: 17 Bore: 92 mm Stroke: 75 mm Single cylinder	40%	D: direct injection M: port injection	D: 13 °CA BTDC injection pressure: 1000 bar M: 136 °CA BTDC injection pressure: 4.5 bar
[45]	Nominal power: 220 kW Compression ratio: 14 Cylinders: 4	20%	D: direct injection M: port injection	Not provided
[51]	Nominal power: 103 kW Compression ratio: 17 Cylinders: 4	10–20%	D: direct injection M: port injection	D: 4 °CA BTDC (low load) 0 °CA BTDC (full load) M: not provided
[42]	Nominal power: 3.5 kW Cylinders: 4	8%	D: direct injection M: port injection	D: 23 °CA BTDC
[56]	Bore: 88 mm Stroke: 82 mm Compression Ratio: 15 Single cylinder	5–65%	D: direct injection M: port injection	Variable
[52]	Nominal power: 2312 kW Cylinders: 16 Compression ratio: 11.7 Locomotive engine	90%	D: direct injection M: direct injection	D: 16.4 °CA BTDC M: 14.5 °CA BTDC
[54]	Nominal power: 78 kW Compression ratio: 17.5 Cylinders: 4	50%	D: direct injection M: port injection	D: 7 °CA BTDC M: 10 °CA BTDC to 2 °CA ATDC
[67]	Cylinders: 4 Displacement: 2 L	20%	D: direct injection M: direct injection	Not provided
[55]	Nominal power: 177 kW Compression ratio: 18 Cylinders: 6	17%	D: direct injection M: port injection	D: 5 °CA BTDC M: not provided
[60]	Nominal power: 8 kW Compression ratio: 18	8%	D: direct injection M: direct injection	D & M: injection pressure 200 bar
[46]	Nominal power: 247 kW Compression ratio: 17 Cylinders: 6	52%	D: direct injection M: port injection	D: 5.5 °CA BTDC to 3 °CA ATDC M: compression phase Injection pressure: 4 bar
[83]	Nominal power: 103 kW Compression ratio: 17.1 Cylinders: 4	5–80%	D: direct injection M: direct injection	D: 10 °CA BTDC M: 8, 6, 4 °CA BTDC
[84]	Nominal power: 103 kW Compression ratio: 17 Cylinders: 4	17%	D: direct injection M: port injection	D: 17.4 °CA BTDC M: 130 °CA BTDC
[86]	Compression ratio: 15.8 Bore: 106.5 mm Stroke: 127 mm Single cylinder	35%	D: direct injection M: port injection	D: injection pressure: 600 bar
[89]	Nominal power: 8 kW Compression ratio: 17	24%	D: direct injection M: direct injection	Not provided
[90]	Compression ratio: 17.3 Bore: 82 mm Stroke: 90 mm	Not provided	D: direct injection M: port injection	D: 15 °CA ATDC

D: diesel; M: methanol; m: mass basis; e: energy basis.

Appendix B. Methanol Combustion Mechanism

Table A2 provides the proposed C_1/O_2 mechanism that was studied and validated experimentally in Refs. [71–76] to predict the CO_2 and CO emissions with higher accuracy. Table A3 lists the species considered in this mechanism.

Table A2. C_1/O_2 mechanism for methanol combustion kinetics.

Reaction	ID	Activation Energy (kcal)	Methanol Oxidation Reaction Path
$CH_3O + M \rightarrow CH_2O + H + M$	(1)	15.5	
$CH_3O + H \rightarrow CH_3 + OH$	(2)	0	
$CH_3O + O_2 \rightarrow CH_2O + OH$	(3)	0	
$CH_3O + OH \rightarrow CH_2O + H_2O$	(4)	0	
$CH_3O + O_2 \rightarrow CH_2O + HO_2$	(5)	12.0	
$CH_3O + HO_2 \rightarrow CH_2O + H_2O_2$	(6)	0	
$CH_3O + CO \rightarrow CH_3 + CO_2$	(7)	11.8	
$CH_3O + HCO \rightarrow CH_3OH + CO$	(8)	0	
$2CH_3O \rightarrow CH_3OH + CH_2O$	(9)	0	
$OH + CH_3(+M) \rightarrow CH_3OH(+M)$	(10)	1.33	
$H + CH_2OH(+M) \rightarrow CH_3OH(+M)$	(11)	0.086	
$H + CH_3O\ (+M) \rightarrow CH_3OH(+M)$	(12)	0.05	
$CH_3OH + H \rightarrow CH_2OH + H_2$	(13)	6.1	
$CH_3OH + H \rightarrow CH_3O + H_2$	(14)	6.1	
$CH_3OH + O \rightarrow CH_2OH + OH$	(15)	3.08	
$CH_3OH + OH \rightarrow CH_3O + H_2O$	(16)	0.497	
$CH_3OH + OH \rightarrow CH_2OH + H_2O$	(17)	−0.596	
$CH_3OH + O_2 \rightarrow CH_2OH + HO_2$	(18)	44.9	
$CH_3OH + HCO \rightarrow CH_2OH + CH_2O$	(19)	13.1	
$CH_3OH + HO_2 \rightarrow CH_2OH + H_2O_2$	(20)	19.4	
$CH_3OH + CH_3 \rightarrow CH_2OH + CH_4$	(21)	7.17	
$CH_3O + CH_3OH \rightarrow CH_3OH + CH_2OH$	(22)	4.06	

CH_2OH reacts with H, O, OH, O_2, HO_2 and CH_3 forming CH_2O, H_2, OH, H_2O, HO_2, and H_2O_2. Other reactions with H produce CH_3, with HCO producing CH_3OH and CH_2O. CH_2O reacts with the same species, forming HCO, H_2, OH, H_2O, HO_2, H_2O_2, and CH_4.

Table A3. Species considered in the methanol combustion mechanism in Table A2.

Species	$\Delta H_{f\ (298\ K)}$ (kcal/mol)
Ar	0
CH_2O	–27.7
CH_2OH	–4.25
CH_3	35.06
CH_3O	3.9
CH_3OH	–48.06
CH_4	–17.9
CO	–26.42
CO_2	–94.06
H	52.1
H_2	0
H_2O	–57.8
H_2O_2	–32.53
HCO	10.4
He	0
HO_2	3
N_2	0
O	59.56
O_2	0
OH	8.9

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