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Application of synthetic renewable methanol to power the future propulsion

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Abstract

As CO₂ emissions from traffic must be reduced and fossil-based traffic fuels need to phase out, bio-based traffic fuels alone cannot meet the future demand due to their restricted availability. Another way to support fossil phase-out is to include synthetic fuels that are produced from circular carbon sources with renewable energy. Several different fuel types have been proposed, while, methanol only requires little processing from raw materials and could be used directly or as a drop-in fuel for some of the current engine fleet. CO₂ emissions arising from fuel production are significantly reduced for synthetic renewable methanol compared to the production of fossil gasoline. Methanol has numerous advantages over the currently used fossil fuels with high RON and flame speed in spark-ignition engines as well as high efficiency and low emissions in combustion ignition engines. Feasible options for engine development or upgrading for methanol have been presented separately in the past work but not considering the whole value chain. The results indicate that high concentration methanol blends will increase significantly tank-to-wheel efficiency, lower energy consumption and CO₂ emissions, while their volumetric fuel consumption will increase compared to gasoline, due to the low calorific content of methanol. The work visualizes the impact on CO₂ emissions for methanol-fueled transport applications and overall suitability for propulsion. For marine sector, successful demonstrations reveal high maturity of engine technology using methanol fuel. This work also highlights further development needs of synthetic renewable methanol to become a sustainable future transport fuel.

Introduction

The world is facing climate change due to the extensive use of fossil energy and CO₂ emissions from which 25% originates from the traffic sector [1]. We need solutions that can provide significant CO₂ emission reductions with a fast timetable. While the electric vehicle fleet is emerging, the replacement of the entire current passenger vehicle fleet is not possible with the current mineral mining rate required for lithium-ion battery production [2]. Moreover, every day thousands of passenger vehicles running on liquid fuels are sold all over the world will still require liquid fuels for decades [3]. Fast actions also affecting the current fleet must be accomplished to significantly reduce greenhouse gas (GHG) emissions. For this, we could utilize synthetic renewable fuels that are produced from captured CO₂ and hydrogen gas produced by renewable electricity also referred to as the power-to-fuel process as visualized in Fig. 1. These liquid fuels are carbon neutral and can work as the second step after raw material limited biofuels towards more sustainable traffic as the CO₂ emitted in the combustion process can be recovered and reused.

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As a first step in the fossil-fuel phase out, new biomass-based liquid fuels enter the market, as they are already commercially more mature, and their transformation to liquid fuels is already in the scale-up and pre-commercial stage. In these fuels, CO₂ has been captured from the air by plants and already processed to long chain hydrocarbons with solar energy. As part of the upgrade has been done by nature, their implementation will be more cost-effective. Nevertheless, when a larger share of fossil-based fuels is replaced by renewable fuels, the quantity of bio-based raw materials would increase significantly. As this raw material cannot compete with food production, it should be mainly from waste sources and these small waste streams have a different chemical composition that further challenges their processing. With the use of CO₂ as the carbon source, the process can be fully optimized for only one raw material stream that is not limited to quantity.

Figure 1. The circularity of carbon dioxide in the production of synthetic renewable methanol.

The future traffic solutions require chemical energy carriers that have higher energy density than what can be obtained with Li-ion batteries. Several energy-carrier molecules are proposed varying from gaseous hydrogen, ammonia to carbon-based energy carriers starting from

methanol, and up to long hydrocarbons that can be utilized fully as the currently liquid fuels [4]. In all power-to-X processes hydrogen has an important role and it can be produced with several methods [5]. Currently, it is produced from natural gas or biogas that will not allow us the detachment from the fossil or bio-based sources. Therefore, the most appealing option would be water electrolysis where a water molecule is split to hydrogen and oxygen gases [6]. Thus, the natural question is why we would not use hydrogen directly as an energy carrier in traffic. Hydrogen can be converted back to electricity by fuel cells with high efficiency and this can run an electrical engine for propulsion. Nevertheless, utilization of fuel cell vehicles would require full replacement of current passenger vehicle fleet and in addition, new infrastructure for hydrogen distribution and fueling with 700 bar pressure. This is not environmentally or economically sustainable now, even though few fuel cell vehicle models are available for commercial use and will have a role at niche markets. The same challenge to replace the whole fleet is faced if we want to utilize ammonia as an energy carrier. Whereas carbon-based energy carriers are suitable also for the current fleet and therefore they can be taken into use with a shorter timetable [7].

When hydrogen is further processed to more energy-dense carbon-based energy carriers, the efficiency of the full process will reduce due to the further processing. As methanol synthesis from CO_2 and H_2 only involves one process step, it has good potential to become the most efficient carbon-based energy carrier. Despite its high potential, there is a lack of further investments, for example in the shipping industry [8]. The current production of methanol is mostly relying on natural gas resources that will not have strong enough effect to significantly reduce GHG emissions [8]. In this process, the natural gas is first processed to synthesis gas ($\text{CO} + \text{H}_2$) and then further processed to methanol. For the synthetic route, we change the process input directly to $\text{CO}_2 + \text{H}_2$ mixture, and, therefore, the requirement for the catalyst materials alters due to the additional water component produced as a side product of methanol that is not existing at high quantities if synthetic gas is used as a raw material. Therefore, synthetic methanol production requires further optimized process conditions. There have been some models of industrial-scale methanol plants using CO_2 and hydrogen as feedstock [9,10]. However, even at an industrial scale, the plant fails to reach break-even under the current market conditions. Here, we provide techno-economic analysis of a CO_2 -based methanol plant to investigate the significant cost parameters to achieve economic feasibility.

In this work, we also address the possibility of methanol utilization in engines. The end-use of methanol is associated with certain challenges mainly related to the mixture formation and ignitability. The very high latent heat combined with a very low cetane number implies that some additional techniques will be required for standard combustion technologies to comply with methanol. Nevertheless, this could be possible in a relatively fast manner with the current fleet together with a significant emission reduction [11]. For fuel use there has been doubts for safety and toxicity of new fuels entering to market. Fossil fuels are mixtures of different hydrocarbons which most are organic solvents. Additionally, fossil fuels contain benzene and other aromatic hydrocarbons that are known to be carcinogenic whereas methanol is a single organic solvent. Methanol has a higher toxicity level 1187-2769 mg/kg compared to gasoline > 5000 mg/kg [12], but it is good to keep in mind that methanol is water soluble and will dilute in nature fast to non-toxic levels unlike gasoline. Overall, proper handling of all transport fuels is need that can be achieved with careful planning particularly the storage and delivery.

Despite the concerns, the use of methanol has been already demonstrated in road transport on the Chinese market [13]. The important fact is that methanol is not a drop-in fuel, hence, its utilization in higher concentrations than 3% with gasoline requires a series of optimizations. Therefore, only vehicles dedicated to methanol can utilize higher concentration blends while ensuring the durability of the engine. In this study, the end-use performance of various methanol blends from M3 to M100 was investigated. The objective was to reveal the fuel consumption and emissions of various blends and discover optimal compositions that achieve higher performance than fossil gasoline in terms of energy use per distance, carbon dioxide emissions, and tank-to-wheel (TTW) efficiency. Even higher potential can be attributed to the marine sector where few demonstration vessels have been already in operation [14]. Different types of combustion concepts can be applied to utilize methanol to tackle the above-mentioned challenges.

Methanol production from CO_2 and hydrogen with renewable electricity as well as combustion properties of methanol itself have been reported earlier.

The novelty of this paper is to provide the reader with the value chain analysis of methanol production and utilization in the transport sector, where the specific focus is paid on:

- An efficient production of methanol from CO_2 streams and hydrogen from renewable electricity.
- The implications of methanol utilization as fuel in various internal combustion engines.
- Modeling the end-use performance of methanol-gasoline blends in the entire concentration spectrum (0% to 100%) from the perspective of the current fleet of light-duty spark-ignition engines.
- Identification of advances and challenges for synthetic renewable methanol production and utilization in the transportation with comparison to counterpart fossil fuels.

Methanol production from carbon dioxide and hydrogen

Methodology

For our process concept on synthetic renewable methanol production, only pure feedstock of CO_2 and H_2 are considered. Their availability is not limited, and their chemical properties are constant regardless of their origin that is an advantage over biomass-based renewable methanol production. In this study, the hydrogen is produced with water electrolysis by an alkaline electrolyzer powered by renewable electricity. As the CO_2 source, we use purified CO_2 stream from industry (industry type not specified in this work) with no additional gaseous components (removal of nitrogen). We do not consider CO as a raw material for this process as we utilize the fully circular CO_2 from industrial tailpipe emissions according to Fig. 1.

Methanol production from CO_2 and H_2 occurs under similar process conditions and follows the same conversion pathways (Eqs. 1-3) as the traditional natural gas-based synthesis [15]. Eqs. 1 and 3 show the main difference between the CO - and CO_2 -based methanol. In syngas-based methanol, where CO is the main carbon source, less water is produced, as compared to CO_2 -based methanol synthesis, where for each mole of methanol also one mole of water is produced. This also means that this pathway consumes more hydrogen and that the

equipment and catalyst must tackle the additionally generated water. Therefore, optimization of catalyst and reaction conditions are necessary when shifting from one feedstock to another [16].

In this paper, the production of methanol was considered by process simulation developed in Aspen Plus V11. A simplified process flowsheet of the developed synthesis process from pure CO₂ and H₂ is presented in Fig. 2. The detailed description of the developed process model for an industrial-scale methanol plant is presented in Nyári et al. [17]. The stoichiometric mixture of pressurized pure CO₂ and H₂ gases are mixed with the pressurized recycled gases, and heated to 230 °C. The gases are fed to an isothermal plug-flow reactor at 50 bar, where the reactions (Eqs. 1-3) are considered with kinetic modeling with the additional formation of dimethyl ether (DME) according to Ng et al. [18]. After the reactor, products are cooled and separated into liquid and gaseous streams. The latter are recycled after a purge, while the liquid raw methanol is sent to a two-column distillation, where the first column removes water, and the second one removes the remainder of non-reacted gases. Finally, the purged and non-reacted gases are combusted, as they contain methanol and hydrogen, to produce heat for the process.

Figure 2. Simplified process flowsheet of the developed.

The plant produces 50 kilotonnes per annum (kta) chemical-grade methanol that can be used as a transport fuel or also as a raw material for the chemical industry. The scope of the developed methanol synthesis plant is considered starting from the injection of the raw materials until the distillation and separation of the final chemical-grade methanol product. The alkaline electrolyzer and the carbon capture plant are not part of the developed process model and these feedstocks are imported as raw materials.

The plant is investigated from a techno-economic point of view with the technical evaluation of the developed methanol plant including energy efficiency, mass and energy balance, and feedstock conversion efficiencies as listed in Nyári et al. [17]. The economic analysis examines the viability of methanol production from CO₂ and H₂. The net present value method is used to calculate the levelized cost of methanol (LCoMeOH) which is then compared to the 10-year posted

average European contract price provided by Methanex [19]. The most important economic parameters used are presented in Table 1, while a detailed list of economic parameters and considerations can be found elsewhere [17].

The generation cost of raw materials is taken at an entry-level to the synthesis plant and they are not further divided into their cost components. However, the alkaline water electrolyzer part is assumed to be co-owned by the methanol plant owners, which enables in the sensitivity analysis the option of co-selling the produced oxygen by-product. Moreover, the produced H₂ is only transported by a pipe, therefore, its transportation costs are not considered here. For the cost of CO₂, the emission allowance on the EU market was used which represents the market value of emitted CO₂. As this value is independent on the source and technology, it is a good measure for the market value of CO₂. Ideally, this value for emission allowance should be higher than for actual capture, which would propagate the use of carbon capture and utilization technologies. However, currently, the actual price of CO₂ is linked to oil and natural gas price due to its utilization in enhanced oil recovery and urea production ranging between 15-30 USD/t CO₂ [20].

Table 1. Parameters of the economic analysis of methanol production from CO₂ and H₂.

Parameters	Value	Notes
Design and construction time	3 years	CAPEX is equally divided
Operational time	25 years	Only annual OPEX occurs
Yearly operating time	8760 hours	
Discount rate	7%	
Reference year	2019	All equipment price was calculated to this year
O ₂ production	7.95 kg/kg H ₂	Typical alkaline electrolyzer
Selling price of O ₂	100 €/t	[21]
Cost of CO ₂	25 €/t	[22]
Cost of H ₂	2740 €/t	Provided by Vattenfall AB for production with a typical alkaline electrolyzer [23]
Cost of electricity	30 €/MWh	Provided by Vattenfall AB for the Nordic electricity mix [23]

CO₂ emissions and energy efficiencies of methanol blend production

CO₂ emissions arising from the production of different methanol and gasoline blends are compared to pure gasoline [24] and pure methanol. The calculation only considers emissions from the production: for gasoline the emissions from the refinery process, while for methanol the emissions from the synthesis plant operation. Emissions from the production and exploitation of raw materials, such as the production of hydrogen and CO₂ for methanol, and obtaining the crude oil is not considered, neither the emissions associated with transportation and distribution. For methanol production, two options are considered with regards the electricity consumption. In one scenario the current electricity mix of the Nordic EU countries is considered for the emissions, as it is highly non-fossil-based [25], while for a second scenario fossil-free electricity is taken, which means that there are no

CO₂ emissions at all from the electricity production. The energy efficiency of producing pure gasoline and methanol are also compared through a range of blends. Energy efficiency here means how much primary energy is needed to produce 1 MJ of the required fuel. For the case of methanol primary energies are hydrogen, electricity, and steam. The energy efficiency of pure gasoline is taken from Specht et al. [26].

Results

Technical results of methanol production

The developed plant successfully generates 50 kt methanol annually with purity level at 99.88 w-% which is above chemical-grade. The impurity in methanol is mostly, 0.12 w-%, the non-reacted CO₂. During the distillation step, the by-product DME was removed, although, the reactor only produces a minor fraction of DME compared to methanol, 0.04 w-% versus 5.8 w-%. The process also generates a significant amount of water, as expected from the equilibrium reactions (Eqs. 1-3.), which is removed in the first distillation column.

The raw material consumption is close to stoichiometric, only exceeding it by 2.9 w-% and 3.7 w-% for CO₂ and H₂ respectively. As feedstock conversions were considered for the whole process including the combustion of gases, 100% conversion was expected for hydrogen. Regarding the conversion of CO₂, the CO₂ generated from the off-gas stream combustion is also included. The values presented in Table 2 are consistent with earlier publications [27–29]. The combustion of the gases that were removed during the purge or purification steps produced enough heat, and after the heat integration, the plant does not require hot utility to be sourced from outside of the plant which can be seen in Table 2. CO₂ emission of the plant means here the amount of CO₂ leaving the plant in the end streams. As fossil-free electricity was assumed for the whole process, the electricity consumption does not emit CO₂ or other GHG.

Table 2. Technical results of the developed methanol plant.

Parameters	This paper	[29]	Units
CO ₂ usage	1.41	1.41	kg/kg methanol
H ₂ usage	0.194	0.194	kg/kg methanol
Overall CO ₂ conversion	97.09	97.25	%
Overall H ₂ conversion	100	100	%
Hot utility	0	0	kWh/kg methanol
Cooling utility	1.51	2.83	kWh/kg methanol
Electricity usage	0.16	-0.06	kWh/kg methanol
CO ₂ emission	0.041	0.04	kg/kg methanol
Energy efficiency	83.51	84.37*	%

*Calculation based in lower heating value of hydrogen

Fig. 3 compares the CO₂ emission of different methanol and gasoline blends ranging from pure gasoline to pure methanol. CO₂ emission of pure methanol is significantly lower compared to pure gasoline. Emissions of CO₂ for methanol production originate from the combustion of the off-gas streams. When comparing the production of methanol with different electricity mixes, Nordic mix versus fossil-free, there is a negligible difference only, due to the Nordic electricity mix being 90% fossil-free already [25].

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Fig. 4 shows the change (in %) compared to the reference pure gasoline for CO₂ emission and energy efficiency of the production of different blends and pure methanol. The results indicate that the production of pure methanol is 10% less efficient, meaning that to produce the same amount of MJ of methanol than gasoline it needs 10% more primary energy input. However, while from the energy efficiency point of view gasoline and blends that have low methanol content are advantageous when examining the CO₂ emissions, it is evident from Fig. 4 that more a blend contains methanol the lower are the emissions. Furthermore, if the CO₂-based methanol is produced with fossil-free electricity, the CO₂ emission saving is over 70%.

Figure 3. CO₂ emissions from productions of gasoline and methanol blends with different electricity mixes.

Figure 4. Changes in CO₂ emission and energy efficiency of production of methanol blends compared to pure gasoline.

Economic results of methanol production

For the investment decision, it is vital to estimate the levelized cost for the synthetic renewable methanol commodity and in this study, it was found to be at 690 €/t. Fig. 5 presents how the different cost components affect the final LCoMeOH. As can be seen, this cost is more than double the 10-year average of Methanex, which is at 336 €/t

[19] and also, above the 10-year maximum which is 450 €/t. Fig. 5 also identifies the main reason behind this excessive cost as the high cost of hydrogen. Compared to it, all the other cost components have a significantly smaller contribution to LCoMeOH. If the hydrogen cost could be reduced significantly, the LCoMeOH could become compatible with fossil methanol.

Figure 5. Cost component distribution of the levelized cost of methanol. (H₂ is taken as raw material, the electricity cost is only for the synthesis plant and not for H₂ production.)

Sensitivity analysis of the main economic parameters influencing the LCoMeOH was also investigated with selected parameters of cost of electricity, cost of CO₂, and the scale of annual output, and the results are presented in Fig. 6. It is good to keep in mind that the cost of electricity and the output scale has also influenced the cost of hydrogen, their effect is presented in Table 3.

Table 3. Levelized cost of H₂ (LCoH₂) depending on electricity cost and the annual output of the methanol plant [23].

Annual output of MeOH plant [kta]	Cost of electricity [€/MWh]	LCoH ₂ [€/t]
50	20	2190
50	30	2740
50	40	3290
10	30	3120
250	30	2650

In the present study, the most significant effect on the LCoMeOH was found to be from the co-selling of the O₂ by-product from the electrolyzer, as can be seen in Fig. 6. This option creates an additional 7.7 million € annual income for the plant and brings down the LCoMeOH from the original 690 €/t to 535 €/t. Electricity cost plays an important role in the LCoMeOH as it heavily influences the cost of hydrogen. A 10 €/MWh change in the electricity cost has an approximate ±15% effect on the LCoMeOH. As it is anticipated from Fig. 5, the variation in the CO₂ price has a negligible influence on the final methanol cost, which is more visible in Fig. 6. Meanwhile, the scale of annual output substantially alters the LCoMeOH. While a

fivefold annual output results in a 3.3% decrease in the final methanol cost, having only one-fifth production of the original scale LCoMeOH rises by more than 50%.

Figure 6. Sensitivity analysis of cost parameters.

The use of methanol in internal combustion engines

Next, we will focus on the properties of methanol and link them to the expected consequences of in-engine use. As already pointed out, methanol can be produced efficiently, and it is also one of the most widely used chemicals [11]. Furthermore, when thinking about the feasibility of utilization, methanol is liquid in normal atmospheric conditions making it easy to store and transport compared to gaseous fuels. For the same reason, its energy density is also high. This will increase the possibilities for its end-use. When combustion characteristics are considered, methanol has a single carbon atom similarly to methane and thus it is difficult for a methanol molecule to form carbonaceous particulate matter (PM) during combustion. Also advantageous is that methanol is not a mixture of compounds of which the properties can change depending on the source as is the case e.g. diesel or gasoline.

Effect of methanol properties on engine combustion

In the following, we turn to investigate more detailed properties of methanol that will affect the combustible methanol-air mixture. The physical properties that are generally of importance for any liquid fuel are 1) density, 2) heat of vaporization, 3) viscosity, 4) vapor pressure, 5) surface tension, 6) specific heat, and 7) heat conductivity. Of these, we will consider the properties 1) - 5). Although methanol is a lightweight molecule (molar weight is 32 g/mol) it has a relatively high liquid density (see Table 4). The high density of methanol is close to that of diesel implying that the injection velocity and near-nozzle fuel-air mixing characteristics are observed to be rather similar between diesel and methanol [30]. Perhaps one of the most influential physical quantities of methanol is its very high heat of evaporation, almost five times higher compared to e.g. diesel, see Table 4. This implies that during methanol evaporation, it strongly cools the surrounding mixture. This has some important consequences: a) the combustion temperature will be lower, b) the engine volumetric efficiency will increase, c) NO_x emissions will be lower, and d) ignition delay time will be longer. The first three are typically beneficial for the engine combustion process while the last one is somewhat problematic especially for the diesel combustion process. During the direct methanol injection event, strong local cooling may take place due to the very high latent heat [30]. This effectively increases the liquid

length (liquid spray distance from the nozzle before it has been fully evaporated) for methanol sprays.

Next, we consider the effect of viscosity, surface tension, and vapor pressure. The viscosity of methanol is much lower compared to diesel fuel but on a similar level with gasoline. Thus, for SI engines, the viscosity is typically not an issue. However, diesel engine injectors require lubrication, but typical lubrication additives are not likely to provide enough lubrication with methanol [31]. Special injectors may be needed in diesel engines in order to cope with the low viscosity of methanol. When considering evaporation, vapor pressure has a governing role. The vapor pressure of methanol is higher than that of diesel but lower compared to gasoline. For SI engines, this may bring cold-start problems while in diesel engines somewhat faster evaporation could be observed. However, this is partly negated by the cooler charge due to the very high heat of evaporation. The droplet sizes produced by the injection event will be most affected by liquid viscosity and surface tension. The surface tension of methanol is close to that of gasoline meaning that it is lower than the surface tension of diesel. In the SI engine, having typically plenty of time to evaporate after injection, this does not have a significant impact. However, in diesel engines methanol will atomize faster yielding smaller droplets [32].

When considering the ignition characteristics of methanol, it has a very low cetane number (~3). Consequently, methanol will not auto-ignite in the normal diesel engine environment. Also, the very low cetane number of methanol may be further impacted by the lower charge temperature. Thus, some measures need to be taken to ignite methanol in diesel engines. Typical measures to overcome this problem are to either increase the engine compression ratio (CR) (and so increase the top dead center temperature), or to increase the engine intake temperature. The use of ignition improvers is also typical but their effect on the ignition delay is only moderate. For the operation of a SI engine, the effect of ignition delay time is not relevant as low cetane number implies high octane number (Research Octane Number, RON=109). Indeed, methanol is an excellent fuel for SI engines having a very high octane number (resisting knock), providing high volumetric efficiency (due to the cooling effect), and low NO_x.

Next, we consider the combustion characteristic of methanol. When considering the CO₂ emissions of methanol, it is observed that methanol has a lower carbon to hydrogen ratio compared to diesel or gasoline. Thus, when calculating the CO₂ emissions on an energy basis (g CO₂/MJ), a 7% reduction is observed in CO₂ emissions compared to gasoline. Previously it was observed that combustion temperatures were lower for methanol due to high latent heat but additionally the adiabatic temperature is lower for methanol compared to gasoline or diesel. This will lower the maximum combustion temperatures contributing to lower NO_x (in addition to high latent heat). The lower heating value of methanol is about half of that compared to diesel or gasoline. Thus, one needs about two times more methanol compared to gasoline/diesel if the same energy input is required. Finally, methanol has oxygen in the molecule (50% of the molecular weight). This also explains the much lower heating value. On the other hand, due to the oxygen, the additional oxygen requirement for methanol is much lower compared to diesel or gasoline (stoichiometric air-fuel ratio for methanol is 6.5 while it is about 14.7 for gasoline or diesel). For diesel combustion, this implies a much leaner combustion process that can be connected to lower soot and combustion temperatures. In addition, due to the available oxygen, methanol hardly produces any PM during combustion.

Using methanol in compression ignition engines

In the previous section, we provided a discussion on the effect of methanol properties on combustion. It was noted that methanol is a very good SI engine fuel mainly due to its very high octane number and higher flame speed. However, legislation is limiting the use of methanol in gasoline to low amounts at the moment. The markets for SI engines are primarily automotive, motorcycles, and leisure, i.e. smaller engines. Most commercial applications use compression ignition (CI) engines. Thereby, there is a strong interest to find proper ways to use methanol in CI engines.

There are two main ways of using methanol in CI engines: 1) fumigation where methanol is injected into the intake manifold with low injection pressure, 2) direct injection (DI) of methanol into the engine cylinder. Option 1) is close to the SI engine concept where ignition is provided either by a spark plug or by a high-reactivity pilot fuel ignition (typically diesel). The concept is rather easily achievable while the associated challenges are similar to SI engines: possible issues with knocking although methanol has a high RON value, potential problems with CO and hydrocarbon (HC) emissions, and probable engine efficiency issues (due to low CR). Option 2) requires the use of a special nozzle that can accommodate two fuels or a special cylinder head where two separate injectors can be installed. Both options are not easily achievable. Typically, the 'ignition fuel' is diesel demanding some optimization for its timing and dosing. In principle, it is possible to operate a DI methanol engine without a diesel pilot-fuel, but this will require very high CR or very high intake air temperature, both of which incorporate some challenges in normal engine use. From the mentioned options, the DI concept with a diesel pilot spray has several benefits over the other choices including the possibility for low emissions, high efficiency, and reliable and robust operation [11,31].

Related to previous literature on methanol fumigation, option 1) above, there are multiple studies on the topic. A port fuel injection (PFI) methanol engine study conducted by Pan et al. [33] shows that increasing the charge air temperature can reduce ignition delay and diminish the HC and CO emissions. Moreover, Liu et al. [34] found that high pilot injection pressure enhances fuel atomization and decreases cycle-to-cycle variation. Additionally, advancing pilot injection can reduce ignition delay, increase brake thermal efficiency, and reduce HC emissions, but it may lead to high NO_x emissions and rapid combustion before TDC [35,36]. Overall, the operation of PFI DF engines requires careful optimization of several parameters such as fuel injection strategy [37], air intake temperature, energy fraction from low-reactivity fuel [38], CR, equivalence ratio [39], and exhaust gas recirculation [40].

Considering option 2) above, DI of methanol aiming for non-premixed methanol combustion, not many studies have been published on the topic. Wang et al. [41] studied such a configuration on a constant volume combustion chamber, providing certain theoretical guidance on the interaction between methanol and diesel sprays. In another study [42], DI of methanol was also considered but aiming for reactivity controlled CI combustion, a different concept not aiming for non-premixed methanol combustion. Nevertheless, promising results were observed highlighting various ways of injecting the fuel. A very recent study by Dong et al. [31] investigates DI of methanol with a diesel pilot using a specially designed cylinder head that can incorporate two separate injectors. Methanol substitution rates (MSR) over 90% were tested with maximum indicated engine efficiency reaching 44%. It was observed that especially at high MSR and high load conditions, good efficiency was achieved with low HC and CO

emissions, and with only moderate NOx emissions. The engine operation was observed to be robust with no challenges in ignition characteristics. Some issues were noted with the low lubricating properties of methanol used in diesel-type injectors, however, the concept was found to be very promising.

Methanol end-use as a transport fuel

Methodology

The end-use part aims to indicate the potential application of methanol in various powertrains of the current and future fleet of light-duty vehicles. The application of methanol in marine engines is also considered. In the road transport, the scope includes drop-in application of methanol with specific blending wall according to EN228 standard in spark-ignition (SI) engines of light-duty vehicles and possible operation with higher concentrations. Based on a literature study and modeling the end-use performance of methanol, potential fuel economy and GHG emissions related benefits are estimated for blends beyond the blending wall. Modeling the end-use performance in the current fleet of unmodified light-duty vehicles is done based on the methodology and model published by Kroyan, Y., et al. [43,44]:

$$\alpha = -0.47 \times A + 2.75 \times B - 2.39 \times C - 1.0 \times D \quad (4)$$

Where, α – relative change of volumetric fuel consumption (FC), A – relative change of RON, B – relative change of density, C – relative change of NCV volume-based (NCVvol), D – oxygen content (O₂).

The results of this model give the change in fuel consumption over the New European Driving Cycle (NEDC). The velocity profile of the NEDC is presented in Fig. 7.

Figure 7. Typical velocity profiles of NEDC.

The CO₂ emissions are calculated based on fuel consumption, density, and carbon content in the fuel, according to the following equation:

$$C[\frac{g}{km}] = FC[\frac{l}{km}] \times \rho[\frac{g}{l}] \times z \times \frac{44}{12} \quad (5)$$

Where, C – CO₂ emissions, FC – absolute fuel consumption, ρ – density of the fuel, z – mass-based carbon content in the fuel. The 44/12 ratio is a molar mass-based ratio between carbon dioxide and carbon.

TTW efficiency calculations are performed based on the energy required to transport a vehicle of a given mass, fuel consumption and energy content of the fuel, according to the following equation:

$$TTW_{Efficiency} = \frac{VEDs[\frac{MJ}{100 km}] \times 100\%}{FC[\frac{l}{100 km}] \times NCV[\frac{MJ}{l}]} \quad (6)$$

Where, VEDs – Vehicle Energy Demand, FC – absolute fuel consumption, NCV – Net Calorific Value.

Assumptions: VEDs (NEDC) = 10.9 ± 1.9 kWh/100 km for a gasoline vehicle of average mass 1354 ± 278 kg and respective fuel consumption while operating with regular EN228 gasoline is 6.6 l/100 km [45]. Additionally, the estimation of the end-use performance of methanol blends in the dedicated engines is based on the literature study.

Methanol is also considered as a promising marine fuel option. It owns many advantageous properties when compared to other alternatives, such as the liquefied natural gas (LNG) or hydrogen. Comparison of those key fuel properties is shown in Table 4. However, even in methanol case, new solutions are needed to switch from fossil-based heavy fuel oil (HFO) or diesel oil (MGO) to methanol. Therefore, the focus is on dedicated internal combustion engines (ICE). The demonstrations of feasible concepts are presented based on the recent developments documented in the literature. Here, the dual-fuel (DF) solutions based on diesel engines are in place with various injection strategies. Finally, the emissions, fuel consumption and efficiency are discussed based on experimental results from different projects.

Table 4. Comparison of methanol properties with other marine fuel alternatives and fossil-based diesel.

	Diesel	Methanol	LNG	Liquid H ₂
Cetane number	≥51	3–5	~0	~0
Autoignition temp. (°C)	250	450	~580	~500
NCV (MJ/kg)	43	20.3	~45-50	120
Storage temp. (°C)	20	20	-162	-253
Density at storage temp. (kg/m ³)	830	790	~450	71
Heat of vaporization (kJ/kg)	250	1150	510	460
Viscosity at 20 °C (mPa·s)	2.8	0.59	0.01	0.009

Results

End-use of methanol in light-duty fleet

Methanol is an excellent alternative fuel with great potential for application in on-road and marine transportation. Currently, the use of methanol is very limited. However, due to continuously stricter

emission regulations, in all modes of transportation, methanol is gaining increasing attention. When it comes to road transport, according to the European Standard for Gasoline EN228, methanol can be used directly in unmodified light-duty engines in small concentrations with gasoline, max 3% [46]. The use of methanol in higher concentrations requires dedicated engines. On the Chinese market, there are light- and heavy-duty methanol vehicles, such as Geely [13]. Naturally, there are also methanol fuel standards in China for high concentration methanol blends including even pure methanol M100. Standards are as follow:

- The Additive of Methanol Gasoline for Vehicles, standard number: GB/T 34548-2017, Implemented in 2018
- Determination Method of Methanol Content in Methanol Gasoline for Motor Vehicles, standard number: GB/T31776-2015, implemented in 2015
- Methanol Gasoline (M85) for Motor Vehicles, standard number: GB/T 23799-2009, implemented in 2009
- Fuel Methanol for Motor Vehicles, standard number: GB/T23510-2009, implemented in 2009.

The performance of methanol in regular spark ignition light-duty vehicles

Tested fuels are blends of methanol with EN228 gasoline from 3% to 85%, pure methanol M100, and reference gasoline EN228. Properties of those fuels are summarized in Table 5:

Table 5. Properties of tested fuel blends.

Fuels	RON	Density kg/m ³	NCVvol MJ/l	O ₂ %m/m	C %m/m
Gasoline EN228	95,00	740,00	32,00	0,00	86,60
M10	96,40	745,60	30,39	5,33	81,36
M20	97,80	751,20	28,78	10,58	76,19
M30	99,20	756,80	27,17	15,75	71,11
M40	100,60	762,40	25,56	20,84	66,09
M50	102,00	768,00	23,95	25,86	61,15
M60	103,40	773,60	22,34	30,81	56,29
M70	104,80	779,20	20,73	35,68	51,49
M80	106,20	784,80	19,12	40,49	46,76
M90	107,60	790,40	17,51	45,23	42,10
M100	109,00	796,00	15,90	49,90	37,50

Based on the model (Eq. 6) presented in the Method chapter, the end-use performance of methanol blends is estimated over the NEDC. The end-use performance is presented in Fig. 8 in terms of volumetric fuel consumption [% changes of l/km], energy-based fuel consumption [% changes of MJ/km], and CO₂ emissions [% changes of g/km].

Results indicate that with larger methanol concentrations in the blends, volumetric fuel consumption increases significantly, and reaches 84% higher fuel consumption for M100 compared to reference gasoline. The main reason is coming from low NCVvol of methanol and high oxygen content. However, energy-based fuel consumption increases

slightly until 40% concentration of methanol, reaching nearly 6% higher energy consumption for M40 compared to EN228 gasoline. After that point, the energy consumption of high concentration methanol blends decreases, and for M100 achieves a reduction of 8.6% compared to gasoline.

Figure 8. Fuel and Energy consumption, carbon dioxide emissions, and TTW efficiencies of methanol blends with gasoline.

Therefore, despite higher volumetric fuel consumption, energy consumption remains low for high methanol concentration blends. The non-linear behavior of the energy consumption [MJ/km] is the result of the multiplication of FC [L/km] that increases with growing methanol content, and NCV [MJ/L] which decreases. When it comes to CO₂ emissions, trends are very similar to energy-based fuel consumption, the CO₂ levels grow slightly for methanol blends, achieving maximum for M30 blend, a 4.46% higher CO₂ emission than for regular gasoline. After that point with growing methanol concentration, CO₂ emissions continue to decrease, and for M100, CO₂ emissions are 14.32% lower than for EN228 gasoline. The shape of the CO₂ emission curve comes from the multiplication of mass-based FC [kg/km] that increases with growing methanol content, and carbon content, which decreases. Those opposite trends yield in non-linear behavior of CO₂ emissions. The carbon content of M100 is just 37.5% carbon content, whereas regular gasoline has around 86.6% carbon content. Additionally, the minor impact for the lower CO₂ levels of methanol blends is coming from performance benefits. The opposite curve to CO₂ emissions could be observed for TTW efficiency, where for blends of methanol higher than 75%, TTW efficiency is higher compared to pure gasoline. For M100, the TTW efficiency is 9.41% higher compared to EN228 gasoline, reaching the absolute value of 20.34%. The reason for non-linearity in TTW of methanol blends is the non-linear behavior of the energy consumption, that was taken into account for TTW estimation.

The use of methanol in modified or dedicated light-duty vehicles can bring even further reductions in energy consumption and CO₂ emissions. Therefore, when using it in a specially designed engine that has a higher effective CR (possible due to higher RON), methanol blends can bring a significantly higher thermal efficiency compared to the case when used in the regular unmodified SI engine. Vancoillie et al. [47] reported Brake Thermal Efficiency (BTE) improvement in the

range of 10% for flexible-fuel vehicle-optimized to run on methanol. The authors explained it by lower pumping losses and higher burning velocities. While optimizing the engine even further by increasing the CR, peak BTE could reach up to 42% in extreme cases for CR equal 19:1 [48]. On the other hand, heavier alcohols, such as ethanol or butanol, are significantly more compatible with the present-day ICE technology and could be used in higher concentrations with gasoline compared to methanol. Another very important fact is that methanol, as well as other alcohols, tend to strongly reduce local emissions such as HCs and PM even in low concentrations. It is beneficial, especially for the DI SI engines. However, due to the high heat of vaporization of methanol in the cold engine conditions, this effect can be disadvantageous and increase the local emissions. Therefore, the development of optimized methanol engines for future propulsion is very important.

End-use of methanol in the marine sector

When considering future fuel options in the marine sector, methanol is a very promising candidate with numerous advantages. It is one of the most traded chemicals in the world, meaning that there is already partly available infrastructure in big ports. Additionally, due to its liquid state in normal conditions and similar storage to gasoline, methanol is much easier to handle than gaseous fuels, thus resulting in significantly lower CAPEX than LNG, for instance. However, notably lower calorific content, roughly half of diesel oil (see Table 4), results in a need for bigger fuel tanks. On the other hand, the space required for onboard fuel storage is very similar to the LNG case with cylindrical high-pressure tanks and insulation around. A comparison of the required fuel tank space for the same vessel autonomy in the case of different marine fuels is illustrated in Fig. 9. Additional safety should be considered while planning the placement of these methanol tanks and fuel lines as methanol is a low flashpoint, volatile, and toxic chemical. On the other hand, due to miscibility and fast biodegradability in the water, it is far less toxic for aquatic life than MGO or HFO. Additionally, methanol does not induce methane slip and related Global Warming Potential issues, in contrary to LNG. Questions about its economics remain still open depending on many markets. However, future targets of the International Maritime Organization (IMO) to decrease GHG emissions could foster methanol roll-out in the shipping industry.

Figure 9. Required fuel tank space for the same autonomy of the vessel in case of fossil diesel oil, methanol, LNG, and liquid hydrogen. Example of a cubic shape tank, where 'a' is an arbitrary unit of the cube's dimension, and for LNG and H₂ cylindrical tanks required plus additional insulation.

Looking from the engine technology perspective, methanol is a very attractive marine fuel. While comparing developments in the market, the most mature and advanced approach is to use methanol in ICE. It should be highlighted that vessels expected to run on methanol need dedicated engines such as in road transport. In this case, however, the CI engine is an appropriate choice, see section Using methanol in

compression ignition engines. As a result, retrofitted diesel engines can run either on MGO/HFO or methanol with pilot MGO. These DF solutions provide flexibility, which is particularly important for ship operators. The dedicated solutions for methanol use in vessels attracted the attention of the shipping industry due to successful tests in various research and industrial projects. Three main variants of CI engines with different combustion concepts, which were demonstrated in the market, are described below and graphically represented in Fig. 10.

Figure 10. Three methanol dual-fuel engine concepts successfully demonstrated in the marine market.

1) Wärtsilä has chosen a methanol CI engine based on pilot assisted diesel (mixing controlled) combustion concept. The medium-speed marine engine's manufacturer designed a novel injector capable of high-pressure methanol injection together with pilot diesel. The company tested this solution on a bench-scale and afterward, retrofitted Stena Germanica, a ferry with four diesel engines of a total of 24 MW maximum power. Stojcevski et al. [14] reported good performance of retrofitted engine characterized by lower specific fuel oil consumption (SFOC), low PM, and no SOx in comparison to operation on MGO only. In that case, NOx emissions were over 50% lower than for MGO. The authors claimed that optimizing the start of injection (SOI) and blending water with methanol could even further lower NOx and enable meeting Tier III NOx limits. Due to lower thermic loads and emissions, the life-span of engine components were expected to be prolonged. Stojcevski also mentioned other practicalities such as similar intervals between oil exchange and comparable airflow (combined effect of lower air-to-fuel ratio and lower NCV in methanol case). For safety measures, Wärtsilä used double walls for all high-pressure methanol fuel lines. In the end, methanol conversion was concluded to be a cost-effective way towards more sustainable fuels.

2) MAN B&W together with Mitsui developed engine technology with high-pressure DI of methanol with separate injectors for methanol and pilot diesel [49]. The dedicated engine is based on diesel engine platform and pilot assisted mixing controlled combustion concept – typical two-stroke low-speed engine with a power output over 1 MW per each cylinder. Methanol was tested as the main fuel with a unit injector. As a consequence of significantly lower calorific content, boosted injection pressure was needed to enable the injection of higher methanol volumes to provide the same power output. At the same time, the diesel fuel system remained unchanged and capable of running only on MGO or HFO in safety mode. MAN applied also a double barrier concept for methanol – double walls were designed for the methanol fuel system. During tests, no wear, corrosion, or failure were reported. The engine operation on methanol (only 5% of pilot diesel) was stable with slightly higher indicated efficiency, and in turn lower SFOC. The even better potential was identified when applying further

engine optimization methods, such as advanced exhaust valve closing. Additionally, NOx emissions were on average 30% lower than in diesel operation. Mayer et al. [49] concluded that targets regarding SFOC and NOx limits were reached during the laboratory tests. The successfully demonstrated engines were installed on 11 methanol carriers so far, while the latest new-builds are complying even with stringent Tier III NOx limits [50].

3) In the Leanship project, PFI was selected as an alternative to DI. This DF combustion concept enables retrofitting of old diesel engines without any extensive modification of the engine components. Coulter et al. [51] reported, however, that the diesel substitution ratio is limited due to misfiring at lower loads and knocking tendency at higher loads – the latter is characteristic for combustion according to premixed flame propagation. Further experimental study on Volvo Penta high-speed marine engine by Dierickx et al. [52] revealed that in this technology methanol energy fraction can be in the range of 25-75% depending on engine load. As a result, a simultaneous decrease in PM and NOx emissions were measured meaning that traditional PM-NOx trade-off valid for diesel-only mode is not any longer observed in DF mode.

Apart from methanol combustion, there are also some other concepts worth mentioning. An innovative approach was proposed by the HyMethShip European project, in which methanol is treated as an intermediate energy carrier [53]. It means that methanol comes from renewable hydrogen and CO₂ stream, as presented in the Production section. However, the membrane technology converts methanol back to hydrogen and CO₂. The combustion of hydrogen does not emit to the atmosphere any GHG, while CO₂ is stored on board and then discharged in the port to be fed back to methanol production. This kind of process is in an early stage of development but aims at zero-emission shipping. Another interesting approach, focusing on direct methanol fuel cells, is rather far from the market uptake. At the moment, the technology enables small-scale demonstrations, while fuel cell stack could serve as a component in the auxiliary power unit of the vessel already having methanol as fuel onboard [54].

Discussion

When considering the end-use of methanol in the future propulsion, it is important to compare the potential of synthetic renewable methanol to the potential from the fossil-based counterparts. In this transition, biofuels will play a significant role, but as they are limited by their raw material, also synthetic fuels are needed for full phase-out of fossil-based fuels. Implementing new alternatives on a well-established field will always require additional inputs for processing and use, and in this context, the value chain must be considered wholly. We have gathered in Table 6 the main advantages and challenges of synthetic methanol and compared that to its fossil-based counterparts at all stages of the value chain.

Stage in the value chain	Synthetic renewable methanol	Fossil-based counterpart
Feedstock	CO ₂ is a well-available sustainable feedstock	High GHG emissions from feedstock exploitation
	Low cost of CO ₂ if taken from flue gases	Unpredictable cost due to producers
	Development of CO ₂ capture technologies, high cost of electrolyzers	Well established logistics with known players
Conversion	Modifications to processing required	Well-known and optimized processing
	Very low CO ₂ emission, especially with fossil-free electricity	High CO ₂ emission
	Lower conversion efficiency	Very high production energy efficiency
Engine operability	High RON, high heat of evaporation (lower combustion temp, higher volumetric efficiency), oxygen content (low soot)	Straightforward use because engines are designed for gasoline and diesel
	Low energy content, low lubricating properties, ignitability (CI engines)	NOx, soot, and CO ₂ emissions
End-use in LDV	Methanol already utilized in the dedicated LDVs in the Chinese market	The vast majority of LDVs designed to fossil gasoline, methanol can be blended max 3%
	Future generation of SI engines dedicated to methanol with higher thermal efficiencies and lower CO ₂ emissions	Gasoline-powered SI engines of LDVs with low thermal efficiency, lower than CI LDVs
	Many engine optimizations required for higher methanol blends	The price of fossil gasoline lower than synthetic methanol
Safety	Toxic chemical, but water soluble (dilutes fast in nature)	Mixture of several toxic chemicals (non-water soluble) and carcinogenic compounds

Table 6. Benefits and main bottlenecks of renewable synthetic methanol in comparison to fossil-based counterparts. The color is an indication of a benefit (green) or a disadvantage (red).

End-use in Marine	Significantly lower GHG and local emissions, very good engine performance	HFO/ MGO as CO ₂ -intensive fuels with higher local emissions; methane-slip for LNG
	No strong policies supporting carbon-neutral fuels at the moment in the sector	HFO and MGO prices significantly lower than for synthetic methanol
	Technology lock-in: switch to methanol costly due to infrastructure and engine modifications	Engines optimized to use fossil fuels and long lifetime of engines (up to 50 years)
	Liquid at ambient, biodegradable, miscible with water	HFO/MGO far more toxic for aquatic life

Conclusion

Methanol produced from CO₂ and H₂ is good candidate for the defossilization of the traffic sector. Production of methanol from CO₂ and hydrogen is similar process conditions as the already well-known and widely used natural gas-based process. Compared with gasoline production, methanol production has a 10% lower energy efficiency, however, the CO₂ emission is significantly smaller: methanol produced from fossil-free electricity has 70% lower CO₂ emission. Even though the process is technically feasible, with the current market conditions it is not economically viable. The cost of hydrogen needs a considerable decrease to make investments more advantageous, as hydrogenation-based processes are highly dependent on the availability of cheap and clean hydrogen. Moreover, investments to medium-sized plants are preferred over small-scale ones.

For SI engine use, methanol offers great benefits mainly related to high RON, high heat of evaporation, and high flame speed. Because of that, methanol blends allow operating SI light-duty vehicle engines with excellent performance and very low CO₂ emissions. The growing concentration of methanol in the blends with gasoline increases volumetric fuel consumption. However, energy consumption decreases significantly, and TTW efficiency grows. Pure methanol allows running regular engines with 8.6% lower energy consumption, 14.3% lower CO₂ emissions and 9.41% higher TTW efficiency in current fleet of SI engines. Nevertheless, from the practical side, a vehicle that runs on methanol will have a shorter range compared to gasoline if the size of the tank remains the same. Additionally, the current fleet is not compatible with high concentration blends of methanol. The future fleet of SI vehicles, equipped with corrosion-resistant materials and higher effective CR, will allow to explore the full potential of methanol beyond the blending wall levels and ensure the durability of the engine. Currently, the biggest obstacle for commercialization of the methanol dedicated SI engines in EU State Members is the legislation allowing only a small blending percentage of methanol (3% in EN228 standard).

For CI engines, DI of methanol offers potential for high efficiency and low NO_x, soot, and CO₂ emissions. Challenges include the very low cetane number, possible lubricating properties within injectors, and the low energy content. However, solutions to these challenges are already

existing as shown in the present work. In the marine sector, methanol seems to be one of the most promising future solutions. As its liquid state in ambient conditions and biodegradability, it is a perfect fit for marine applications. Partly available infrastructure and maturity of the engine technology are attracting the attention of the corresponding industry. Feasible and successfully demonstrated flexible-fuel engine concepts (Wärtsilä, MAN, Leanship) should be highlighted. At the same time, the current research focus is on optimized methanol combustion and even better performance of retrofitted engines. However, to induce new investments in methanol technology, involvement from all shipping actors is needed, starting from the IMO.

For synthetic renewable fuels to become cost-efficient, their whole value chain must be considered to evaluate their suitability for current fleets, their properties, their hazards as well as their impact on the carbon footprint. The results in the work confirm that synthetic renewable methanol is an appealing alternative for energy carrier in the future traffic solutions. Thus, there are still bottlenecks and challenges that we need to overcome for the economic viability of methanol as an energy carrier, but now is the time to implement synthetic renewable methanol as the next step for the transport energy strategy.

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Definitions/Abbreviations

BTE	Brake Thermal Efficiency
C cont.	Concentration of carbon
CAPEX	Capital Expenditure
CI	Compression Ignition
CR	Compression ratio
DF	Dual-fuel
DI	Direct Injection
DME	Dimethyl ether
EU	European Union
FC	Fuel Consumption
GHG	Greenhouse Gas
HC	Unburned hydrocarbons
HFO	Heavy Fuel Oil
ICE	Internal Combustion Engine
IMO	International Maritime Organization
kta	kiloton per annum
LCoH₂	Levelized cost of hydrogen
LCoMeOH	Levelized cost of methanol

LDV	Light-duty vehicle
LNG	Liquefied Natural Gas
M10	Fuel blend containing 10% of methanol and 90% of gasoline
M100	Pure methanol fuel
M20	Fuel blend containing 10% of methanol and 90% of gasoline
M3	Fuel blend containing 3% of methanol and 97% of gasoline
M40	Fuel blend containing 40% of methanol and 60% of gasoline
M50	Fuel blend containing 50% of methanol and 50% of gasoline
M85	Fuel blend containing 85% of methanol and 15% of gasoline
MGO	Marine gas oil
MSR	Methanol substitution rate
NCV	Net Calorific Value
NEDC	New European Driving Cycle
NO_x	Nitrogen oxides
O₂ cont.	Concentration of oxygen
OPEX	Operational Expenditure
PFI	Port fuel injection
PM	Particulate matter
RON	Research Octane Number
SFOC	Specific Fuel Oil Consumption
SI	Spark-ignition
SOI	Start of injection
SO_x	Sulfur oxides
TTW	Tank-to-wheel