METHANOL: PROPERTIES AND USES

Issued: December 23, 2019; revised January 31, 2020
Author: SGS INSPIRE team

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[7] *Methanol as a fuel for spark ignition engines: a review and analysis* → *Learn more*

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1 EXECUTIVE SUMMARY

SGS INSPIRE has prepared this report for The Methanol Institute. The core of this report is the explanation of the main physical and chemical properties of methanol, as well as how these properties affect the different types of existing engines in the market.

SGS has performed an analysis of physical properties on nineteen samples of gasoline, methanol, ethanol, methyl tert-butyl ether (MTBE) and tertbutyl alcohol (TBA) in different blending ratio. Nineteen samples were blended and analyzed by SGS: three base ones (Methanol 100%, Ethanol 100%, and reference Non-oxy BOB), six methanol-gasoline blends (M5, M10, M15, M25, M85 with 56% v/v methanol and M85 with 85% v/v methanol), eight methanol-ethanol-gasoline blends (M3, E2; M1.5, E1.5; M5, E2; M1.5, E5; M15, E5; M25, E5; M15, E10; M10, E10), one methanol-MTBE-gasoline blend (M5, MTBE 6) and one gasoline-methanol-TBA blend (M15, TBA 5).

In total, 203 properties have been analyzed in the laboratory, making a total of 3,857 tests. All significant properties of fuels used in spark-ignition engines have been studied.

With the help of the results obtained, SGS INSPIRE has been able to prove the theory of the behavior of the main fuel properties related to methanol.

The results of these tests showed the following:

- There is no copper corrosion in methanol gasoline blends, just some light tarnish
- Density values of the different blends are within the European standards limits
- Gasoline-methanol blends evaporate faster at a lower temperature when methanol and ethanol are added to gasoline
- RVP increases with the addition of methanol and ethanol in low and middle blends (up to 25 % vol.) but decreases when the methanol content reaches 56 % vol. and higher
- Methanol or ethanol addition in gasoline does not have a significant impact on electrical conductivity despite the fact that both alcohols are electrically conductive
- Methanol does not contain gum, and therefore high methanol blends have barely none existent gum in the fuel, which favors the functioning of induction-systems
- Octane increases when methanol is added to gasoline. RON is approximately 100 when methanol is between 10 % vol. and 25 % vol.

- All low and medium blends (up to 30 % vol. of methanol and ethanol combined) have a similar calorific value to gasoline, which makes them suitable fuels for SI engines. For higher methanol blends, starting at 50 % vol. methanol, calorific value drops significantly, resulting in less efficient fuels for SI engines
- Water content in tested methanol gasoline blends is negligible

Pure alcohols have a very low peroxide and nitrogen content and the addition of methanol and ethanol to gasoline lowers peroxide content, which is desirable for the good functioning of the fuel systems.

This report also includes a review of the existing literature and scientific evidence on the benefits and shortcomings of methanol as a fuel, and the uses of methanol fuel in different energy sectors.

It explains that methanol can be blended with gasoline and other alcohol fuels, and its different blends can be used in flex-fuel vehicles. Low blends can also be used in the existing fleet of vehicles. To be used as a neat fuel, modifications must be made to conventional engines.

High methanol blends, from 85 % vol., have a lower vapor pressure value compared to gasoline. Methanol has a higher octane rate compared to gasoline, but a lower calorific value, which means that more fuel must be used to run the same distance compared to gasoline. However; to increase the engine's efficiency fuel system can be modified and optimized.

Moreover, most literature indicates that methanol has lower nitrogen oxides (NO_X) and particulate matter (PM) emissions than conventional fuels.

There were trials to establish the use of methanol as a road transportation fuel in the past, however; the low oil prices triggered that gasoline and diesel were the preferred fuels at that time. Methanol use could be expanded as a road transportation fuel in low blends in the existing fleet; however, for the use of high blends, the appropiate fuel infrastructure should be put in place, and the fleet of flex-fuel vehicles should increase significantly.

There are other uses for methanol that have been studied and are currently being researched in the aviation sector, the electricity sector, but particularly, in the shipping sector. There have been several successful projects proving that methanol can be an adequate shipping fuel.

2 INTRODUCTION

Methanol has been extensively used in racing since the early 1920s. Blends containing methanol and benzene were often used in Grand Prix cars, especially as supercharging was developed as a tool to extract maximum performance from a given engine swept volume (and charge cooling was not widely used). Among others, Alfa Romeo and Bugatti used such mixtures in their pre-war Grand Prix cars.[1]

Aviation also represented an arena where methanol was used for its benefits in terms of octane number and latent heat, but only on take-off, and to an extent when maximum power was required. Further research suggested that methanol is not a suitable fuel for aviation. It can, however, be a pre-stage product to produce renewable aviation fuels through the Power-to-Liquids (PtL) pathway.

In the 1980s and 1990s, California launched M85 fuel trial, driven primarily by air quality considerations. Methanol caused significantly lower unburned hydrocarbon (UHC) and NO_x emissions than typical gasolines in use at the time. During that time, 15,000 M85- gasoline flex-fuel vehicles, ranging from light-duty to buses and trucks, were sold and operated in California. The trial was successful, and furthermore, the toxicity of methanol was not found to be an issue. However, methanol did not become a substantial fuel in the United States (U.S.) because of its introduction in a period of rapidly falling petroleum prices, which eliminated the economic incentive. Methanol was afterwards displaced by ethanol as the oxygenate of choice in gasoline blends. Nevertheless, these programs have demonstrated that methanol is a viable transportation fuel.[2]

The interest in methanol as a fuel is currently picking up also in other regions, for example in China. The strongest driver currently seems to be in the marine sector. It is also increasingly being used as a blend component, added to gasoline together with ethanol.

This is demonstrated in Israel[3], Australia[4] and in the Junior World Rally Championship which holds races across Europe[5].

In Italy, ENI and FCA have partnered to develop a new fuel called A20, with 15 % vol. methanol and 5 % vol. ethanol. Initial tests performed with the ENI fleet have proven successful[6].

2.1 STANDARDS

The World-Wide Fuel Charter, 6th Edition, published in October 2019, says that the use of methanol is only acceptable if: (i) specified by applicable standards (e.g., maximum 3 % v/v methanol in standard EN 228); (ii) consumed in vehicles compatible with its use; and (iii) stated in the owner's manual. The 5th edition of the World-Wide Fuel Charter from 2013 stated that methanol was not permitted.

In the United States, the Octamix Waiver allows for a methanol content of 5 % vol. In addition to the volume % limitations (5 vol. % max for methanol and 2.5 vol% min for co-solvents) and approved corrosion inhibiter, the overall blending restriction is the oxygen content, which should not exceed 3.7 weight %. The co-solvents may include one or mixture of ethanol, propanols, butanols, pentanols, hexanols, heptanols and/or octanols provided that:

- ethanol/propanols/butanols must compose a minimum of 60 % by weight of the co-solvent mixture;
- pentanols/hexanols/heptanols/octanols have maximum 40 % by weight of the co-solvent mixture;
- heptanols/octanols are limited to 5 weight % of the co-solvent mixture.

This Octamix waiver was issued under the Clean Air Act section 211(f)(4) – substantially similar rule.

According to the U.S. American Society for Testing and Materials (ASTM) D4814 – 19 Standard Specification for Automotive Spark-Ignition Engine Fuel, maximum methanol content in gasoline is set at 0.3 % vol. In the U.S. there is a specific standard for methanol blends (M51–M85) for methanol-capable automotive SI engines, ASTM D5797-18.

In the European Union, according to the standard EN 228:2012 + A1:2017, Automotive fuels – Unleaded petrol – Requirements and test methods, published in June 2017, the methanol limit is allowed up to 3 % vol. in both gasoline grades – E5 (gasoline blended with maximum 5 % vol. of ethanol) and E10 (gasoline blended with maximum 10 % vol. of ethanol)

In China, high methanol blends, mainly used in public transportation, such as city buses and taxis, have been given legal status with the establishment of national standards for M85 (GB/T 23799-2009) and fuel methanol, M100 (GB/T 23510-2009) in 2009. In 2012 China's Ministry of Industry and Information Technology (MIIT) initiated a methanol vehicle program where over 1,000 methanol-fueled vehicles of 32 different models were tested in 10 cities (5 provinces), and accumulating 200 million kilometers of total mileage. Methanol Vehicle Pilot Project covered M100 and M85 blends authorized by the government. Similarly, the vehicles included in

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[1] *Ludvigsen K. Classic Racing Engines. Sparkford, Somerset, UK: Haynes Publishing; 2001*

[2] *afdc.energy.gov/files/pdfs/mit_methanol_white_paper.pdf* ⟶ *Learn more*

[3] *www.methanol.org/wp-content/uploads/2017/06/Dor-Methanol-Economy-June-2017.pdf* ⟶ *Learn more*

[4] *methanolfuels.org/wp-content/uploads/2013/05/Grant-Lukey-Coogee-Energy-Australia.pdf* ⟶ *Learn more*

[5] *methanolfuels.org/on-the-road/demonstration-projects/* ⟶ *Learn more*

[6] *Eni and FCA have developed A20, a new fuel that pairs emissions reduction with energy efficiency* ⟶ *Learn more*

the program were those listed in Announcement Vehicle Producers and Products by MIIT: M100 taxis, M100 buses, dual fuel methanol-diesel trucks, and M100 multi-functional automobiles. In the course of the project some cities expanded the vehicle fleet which, in consequence, led to a number of 7000 vehicles covered by the project in 2019, at the time of its completion. According to the Methanol Institute, today, the cities of Guiyang and Xi'an each have over 10,000 M100 taxies in operation and 20-25 M100 fueling stations each with 16 dispensers.

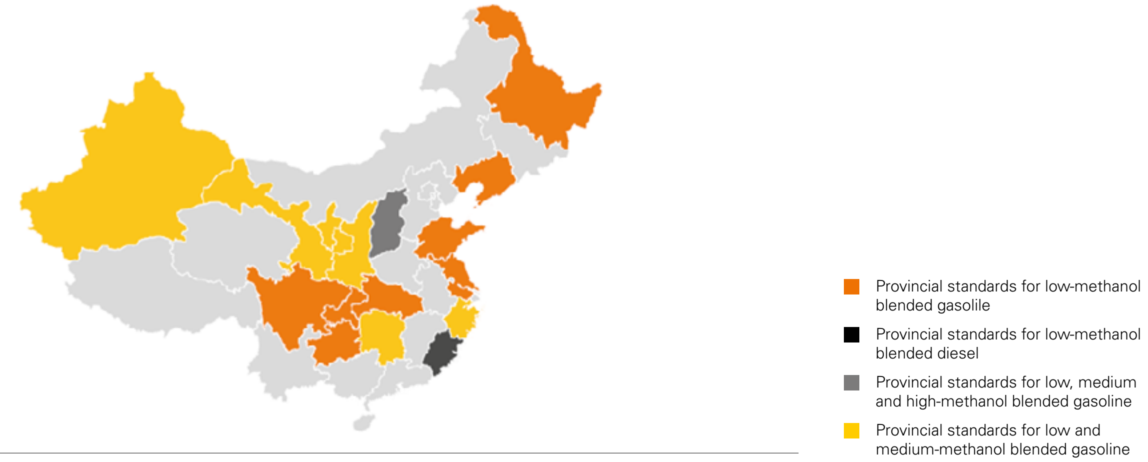
Based on the results of this extensive pilot program, in March 2019 eight ministries of China's central government led by the powerful Ministry of Industry and Information Technology (MIIT), along with the National Development and Reform Commission (NDRC), Ministry of Science and Technology (MOST), Ministry of Public Security (MOPS), Ministry of Ecology and Environment (MEE, former Ministry of Environmental Protection), Ministry of Transportation (MOT), National Health Commission (NHC) and State Administration for Market Regulation (SAMR) issued a promotional policy paper (Paper 61) – "Guidance of Developing Methanol Vehicles Applications in Some Parts of China" – to deploy methanol fueled vehicles across China.

As MIIT noted in explaining the policy, "Based on the characteristics of China's resource endowment and the development status of methanol vehicles, promoting the development of methanol vehicles is in line with China's national conditions, which is not only conducive to giving full play to China's coal resources advantages, promoting the transformation and upgrading of traditional industries, but also promoting the development of green recycling and diversifying energy source and to ensure national energy security."

M15 is present in the commercial fleet in some provinces in China. However, China is still lacking the national standard for M15 despite years in review.

Currently, 16 out of 23 provincial governments have put forward 23 local standards for methanol blended gasoline and one for methanol blended diesel. Most of them are for low-methanol blends. Nonetheless, methanol fuel specifications between different provinces, provincial and national standards are not aligned. They vary in the limits, test methods and blend level. The Figure on the next page shows provinces that have methanol standards. However, most provincial specifications are not aligned with the current China VIA specifications, especially in sulfur content. Therefore, those specifications are no longer valid.

PROVINCES WITH SPECIFICATIONS ON METHANOL BLENDS



Source: SGS INSPIRE Compilation

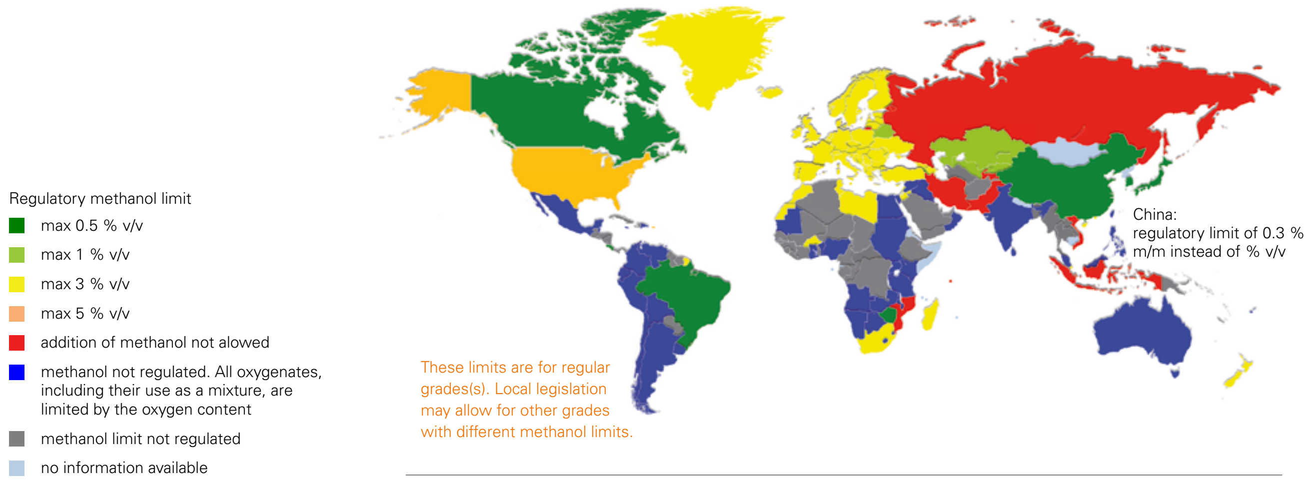
In December 2017, India released the draft specifications of reference fuels for M15, M100 and MD95 (95 vol.% methanol and 5 vol. % of diesel additives), which were further updated in 2019 (IS 17076:2019). In 2019, India published a standard for anhydrous methanol used as a blending component, IS 17075:2019.

Israel also counts with a methanol blend standard, SI 90 part 4, from 2016. This standard is for gasoline 95 containing 15 % vol. methanol. Regular and premium gasoline standard, SI 90 part 2 from 2014, allows 3 % vol. methanol in gasoline.

Recently, Italy released standard NC 627-02 for Alternative Alcohol-Based High Octane Fuel (A20).

The next figure shows the regulatory limits for methanol in gasoline worldwide.

REGULATORY LIMITS OF METHANOL IN GASOLINE



Source: SGS INSPIRE Compilation

3 PROPERTIES WHICH ARE IMPORTANT TO METHANOL[7]

According to the literature reviewed in preparation of this report, methanol has several physical and chemical characteristics that make it a good fuel but also some shortcomings. They are briefly summarized in the list below; and their fuller description, including the reasons for and methods of overcoming the shortcomings, is provided further in the text.

3.1 BENEFITS

- High resistance to knocking combustion (high octane number), due to which higher compression ratios may be applied, resulting in very high efficiency of the engine
- Cleaner (soot-free) combustion
- Lower lean flammability limit, resulting in the possibility of lean mixture application and, consequently, better economy and lower emissions of NO_X, hydrocarbon (HC) and carbon monoxide (CO)
- Higher heat of evaporation, resulting in a higher temperature drop in the Venturi nozzle of the carburetor and therefore higher volumetric efficiency
- Lower combustion temperature, resulting in lower NO_X, emission
- Higher volatility, resulting in better distribution among cylinders of air-fuel ratios and mass of fuel per cycle of multi-cylinder carburetor engines

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[7] *Methanol as a fuel for spark ignition engines: a review and analysis* ⟶ Learn more

3.2 SHORTCOMINGS

- Poor self-ignition properties (long ignition delay)
- Poor miscibility with mineral fuels (especially with diesel oil) in the presence of water
- Difficulty in starting a cold engine
- Corrosion and chemical degradation of materials
- Evaporation in fuel lines (vapor locks)
- Poor lubrication properties resulting from low viscosity
- Degradation of oil lubrication properties

3.3 PROPERTIES OF METHANOL AS A FUEL FOR SPARK-IGNITION (SI) ENGINES

Fewer modifications to the engine are expected when methanol is used in SI engines as compared to compression ignition (CI) engines. Low methanol blends do not require modifications.

From a technical point of view, neat methanol may be a very good fuel for SI engines, especially in areas with a warm climate. The engine fuel system needs to be modified due to the lower calorific value and smaller stoichiometric air-fuel ratio of methanol for its combustion in comparison with gasoline. With this optimization a better engine efficiency may be expected, mainly due to:

- Application of a higher compression ratio (CR)
- Possibility of operation on a leaner mixture
- Recovery of the latent heat of evaporation in the heat balance of the engine[8].

FROM A TECHNICAL POINT OF VIEW, NEAT METHANOL MAY BE A VERY GOOD FUEL FOR SI ENGINES, ESPECIALLY IN AREAS WITH A WARM CLIMATE

The efficiency of an optimized methanol-fueled engine may reach 40 %;[9] for direct injection methanol engines, more than achieved by turbo-charged diesel engines or gasoline hybrids. More on this topic is provided in the section of the report covering RON. However; in cold climate countries it is necessary to improve cold start by providing:

- A heating inlet duct and/or
- An ignition improver, that is an additive added to liquid methanol.

The advantages of the application of neat methanol to SI engines are lower emissions of CO, HC and NO_X[10]. However, emissions of aldehydes are higher, but they can be neutralized by a catalytic process.

It is important to mention that miscibility of methanol and conventional fuels is poor and may result in fuel separation. Because of that, neat methanol and mixtures of gasoline-methanol require fuel additives.[11]

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[8] *Bergmann, H. K. A high efficient alcohol vapour aspirating spark ignition engine with heat recovery. SAE paper 821190, 1982*

[9] *Pischinger, F. Alcohol fuels for automotive engines. Development of transport fuels. Report RTD 6/3, 1990 (FEV-Motorentechnik, Achen, Germany)*

[10] *Lee, W., Konig, A. and Bernhardt, W. Versuche mit Methanol und Methanol-Benzin-Mischkraftsteffen. Report MTZ 5,1976*

[11] *Methanol as a fuel for spark ignition engines: a review and analysis* ⟶ Learn more

3.4 PROPERTIES OF METHANOL AS A FUEL FOR COMPRESSION-IGNITION (CI) ENGINES

Methanol has lower heating value than diesel due to its partially oxidized state, therefore more fuel is needed to obtain the same performance as that of a diesel-fueled engine. Its high stoichiometric fuel/air ratio, high oxygen content and high hydrogen/carbon (H/C) ratio may be beneficial for improving the combustion and reducing the soot and smoke[12].

However, engines operating on methanol and other oxygenated fuels emit more aldehyde emissions such as formaldehyde[13, 14, 15]. Formaldehyde can cause eye irritation and the formation of smog[16]. The use of an exhaust catalyst is helpful to reduce these emissions.

Methanol has higher latent heat of vaporization than diesel so that it extracts more heat as it vaporizes compared to diesel, therefore it can lead to a cooling effect on the cylinder charge[17]. Because of the cooling effect on the charge, the cylinder temperature may decrease and therefore emissions of NO_x would be reduced. Because of the fact that methanol has poor ignition behavior due to its low cetane number, high latent heat of vaporization and high ignition temperature, it results in ignition delay. This is why it should be used with another fuel that is easier ignitable or with ignition improver[18]

Methanol has very low viscosity compared to diesel fuel therefore it can be easily injected, atomized and mixed with air. In this case, a lubricant additive should be added to the fuel to improve the lubrication.

3.4.1. SGS SAMPLES AND TESTS PERFORMED ON METHANOL BLENDS

SGS laboratory prepared nineteen samples blending different amounts of methanol, ethanol, methyl tert-butyl ether (MTBE) and tert-butyl alcohol (TBA) in gasoline and conducted a thorough analysis of physical properties to understand the behavior of the fuel depending on addition of methanol.

The table below depicts the fuels used and the content of the blending compounds.

TABLE: SGS FUEL SAMPLES AND THEIR DIFFERENT BLEND RATIO

SAMPLES	METHANOL CONTENT	ETHANOL CONTENT	MTBE CONTENT	TBA CONTENT	ACRONYM
Sample 1	3 %	2 %			Gasoline M3, E2
Sample 2	1.5 %	1.5 %			Gasoline M1.5, E1.5
Sample 3	5 %	2 %			Gasoline M5, E2
Sample 4	5 %				Gasoline M5
Sample 5	1.5 %	5 %			Gasoline M1.5, E5
Sample 6	5 %		6 %		Gasoline M5, MTBE 6
Sample 7	15 %				Gasoline M15
Sample 8	15 %			5 %	Gasoline M15, TBA 5
Sample 9	15 %	5 %			Gasoline M15, E5
Sample 10	25 %				Gasoline M25
Sample 11	25 %	5 %			Gasoline M25, E5
Sample 12	15 %	10 %			Gasoline M15, E10
Sample 13	10 %	10 %			Gasoline M10, E10
Sample 14	10 %				Gasoline M10
Sample 15	56 %				M85 (56 % vol. MeOH)
Sample 16	85 %				M85 (85 % vol. MeOH)
Sample 17		100 %			E100
Sample 18	100 %				M100
Sample 19	Non-oxy BOB				Ref. Non-oxy BOB

Source: SGS

203 properties have been analyzed for the nineteen samples made in the laboratory, making a total of 3,857 tests. All significant properties of fuels used in spark-ignition engines have been studied, i.e. octane, octane enhancers, RVP, density, volatility, oxygenates, hydrocarbons, oxidation stability, gum content, water content, heat of combustion, metals and paraffins amongst others.

3.5 METAL CORROSION

Gasoline and gasoline-methanol blends are shipped, stored, and delivered in metallic pipes and tanks. The fuel handling system in vehicles is mostly made of metals. Thus, the ability of fuel to be noncorrosive to metals is an important and desired property. Many pipelines and fuel producer internal specifications also contain limits on corrosion of iron (steel). There are ASTM specifications for the corrosion propensity of gasoline to silver and copper. Methanol is not corrosive to most metals, but still most methanol gasoline blends will employ corrosion inhibitors, as it is done in ethanol gasoline blends like E10. SGS test results show, as explained later, that coper corrosion is not an issue for methanol gasoline blends.

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[12] *An experimental study on the performance parameters of an experimental CI engine fueled with diesel–methanol–dodecanol blends*
→ *Learn more*

[13] *Heywood JB. Internal combustion engine fundamentals. Singapore: McGraw-Hill; 1988*

[14] *Thring RH. Alternative fuels for spark-ignition engines. SAE 1983. Paper No. 831685. p. 4715–25*

[15] *Kowalewicz A. Methanol as a fuel for spark ignition engines: a review and analysis. Proc Inst Mech Eng 1993; 207:43–52*

[16] *Thring RH. Alternative fuels for spark-ignition engines. SAE 1983. Paper No. 831685. p. 4715–25*

[17] *Wagner TO, Gray DS, Zarah BY, Kozinski AA. Practicality of alcohols as motor fuel. SAE 1979. Paper No. 790429. p. 1591–607*

[18] *S. Verhels et al., Progress in Energy and Combustion Science 70 (2019) pages 43-88*

3.5.1 ELECTRICAL CONDUCTIVITY

Methanol, like ethanol, contains soluble and insoluble contaminants like halide ions.[19] These ions increase the conductivity of the fuel.

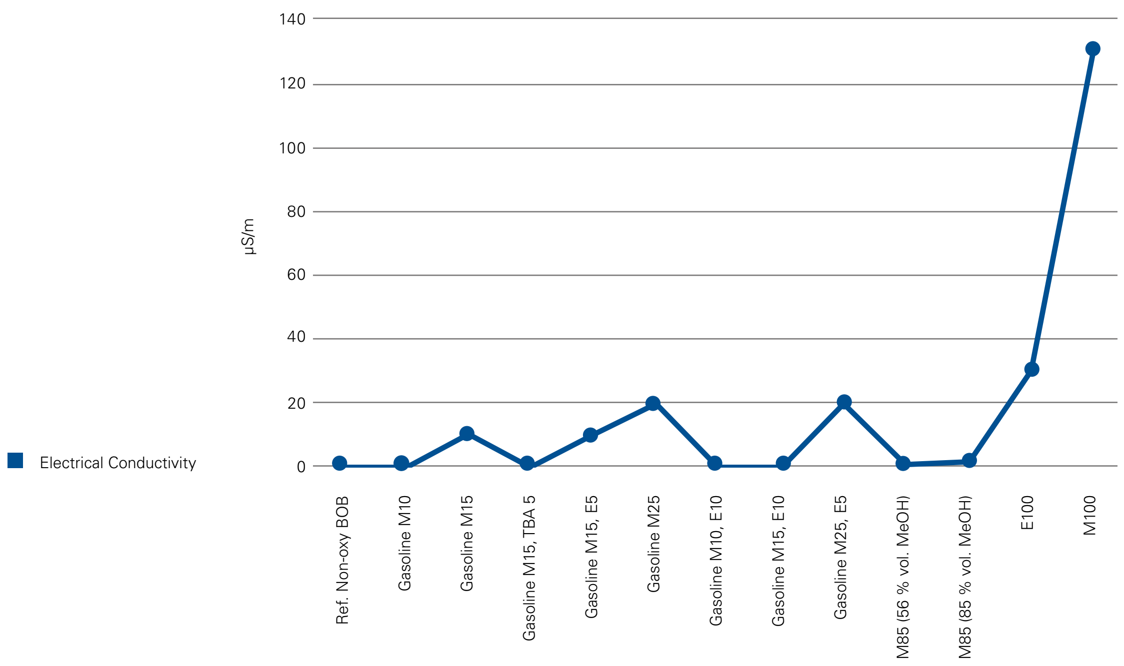
Methanol is therefore electrically conductive. Corrosion behaviors that are dependent on conductive fluid behavior, such as electrochemical and galvanic corrosion, can be enhanced by an increase in the alcohol fuel’s electrical conductivity due to absorbed water and contaminants.

3.5.1.1 SGS LABORATORY RESULTS

Gasoline + EtOH + MeOH

Electrical conductivity for gasoline-methanol-ethanol blends has an average value of 10 µS/m. Pure alcohols have a much higher electrical conductivity, as can be seen in the figure below. It can be observed that methanol or ethanol addition in gasoline does not have a significant impact on electrical conductivity despite the fact that ethanol, but particularly methanol, are electrically conductive.

ELECTRICAL CONDUCTIVITY VALUES GASOLINE + ETOH + MEOH



Source: SGS

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[19] Brinkman, N., Halsall, R., Jorgensen, S.W., & Kirwan, J.E., "The Development of Improved Fuel Specifications for Methanol (M85) and Ethanol (Ed85), SAE Technical Paper 940764

3.5.2 OXIDATION STABILITY

The oxidation stability may be used as an indication of the tendency for motor gasoline to form gum in storage. However, its correlation with the formation of gum in storage may vary under different storage conditions and with different gasolines.

3.5.3 EXISTENT GUM

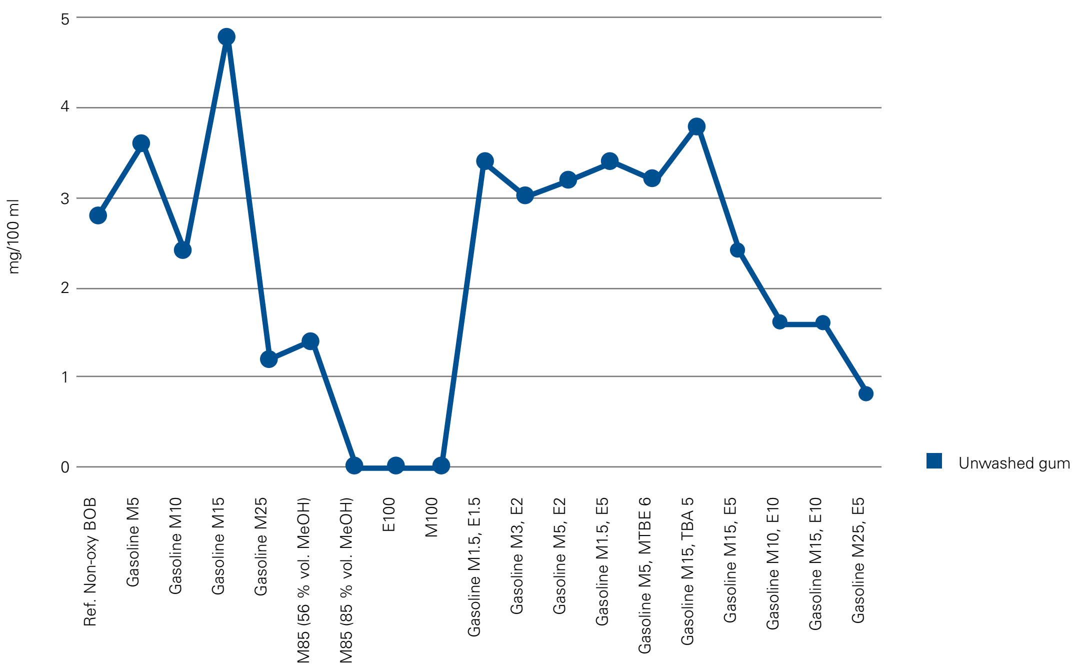
High gum can cause induction system deposits and sticking of intake valves, and in most instances, it can be assumed that low gum will ensure the absence of induction-system difficulties.

3.5.3.1 SGS LABORATORY RESULTS

The conclusion we can draw from the laboratory results is that methanol does not contain gum, and therefore high methanol blends have barely none existent gum in the fuel. No other correlation can be drawn from the other samples; however, it does not have a significant meaning because below 5 mg/100 ml the gum content can be considered negligible

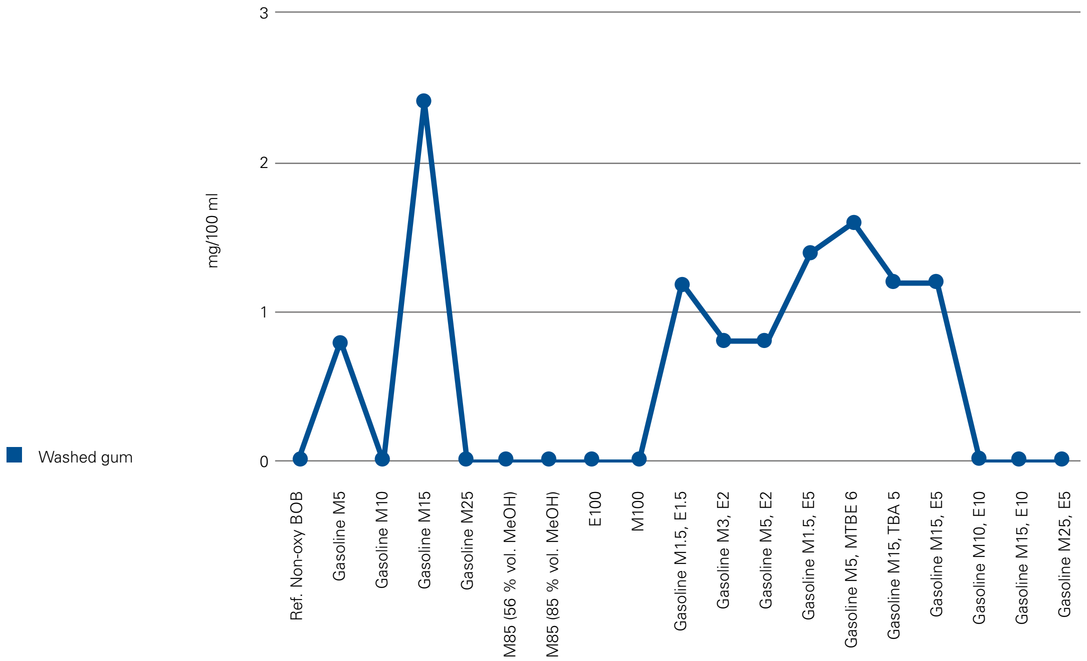
Gasoline + EtOH + MeOH

EXISTENT GUM UNWASHED VALUES GASOLINE + ETOH + MEOH



Source: SGS

EXISTENT GUM WASHED VALUES GASOLINE + ETOH + MEOH



Source: SGS

3.5.4 TOTAL ACID NUMBER (ACIDITY)

Methanol is an acid, albeit weak. It attacks the oxide coating that normally protects the aluminum from corrosion.

The resulting methoxide salts are soluble in methanol, resulting in a clean aluminum surface, which is readily oxidized by dissolved oxygen. Also, the methanol can act as an oxidizer.

This reciprocal process effectively fuels corrosion until either the metal is eaten away, or the concentration of methanol is negligible. Methanol's corrosivity has been addressed with methanol-compatible materials and fuel additives that serve as corrosion inhibitors.

Generally, light alcohols are more corrosive to both ferrous and non-ferrous metals than gasoline. The polarity of methanol and ethanol causes dry corrosion, but often this corrosion is reinforced by ionic impurities such as chloride ions in the fuel. As alcohols are hygroscopic, dissolved or separated water molecules can trigger wet corrosion phenomena. When using hydrous methanol as a fuel, special attention should thus be paid to this. (However; according to the Methanol Institute, all methanol sold in the market is anhydrous.) It has also been documented[20] that a combination of three contaminants (chloride ion, acetic acid, and ethyl acetate) produces a synergistic effect in hydrous ethanol, and any resulting corrosion is many times greater than that by any single contaminant.

3.6 COPPER CORROSION

In the project Test of metal corrosion by methanol and methanol-gasoline, Shuping et.al., many kinds of metal samples were dipped in methanol and methanol-gasoline. No obvious corrosion happened with the samples in pure methanol and M85, but the copper sample in M15 was obviously corroded. On the M100 electro-chemical test, where copper samples separately act as anode and cathode, surface appearance shows that the copper connected with anode shows pitting corrosion and the sample connected with cathode has no more corrosion. So, copper corrosion in M15 is both chemical corrosion and electro-chemical corrosion. Anode protection is necessary when the engine is fueled with methanol.[21]

Test of metal corrosion by methanol and methanol-gasoline ⟶ *Learn more*

The effect of copper additions of 1, 3 and 5 atomic percentage (at-%) on the corrosion behavior of aluminum in a solution of 0.5 molar[22] sulfuric acid (H_2SO_4) + 2 parts per million (ppm) hydrofluoric acid + methanol at 50 °C temperature found in a direct methanol fuel cell, has been evaluated using electrochemical techniques. Electrochemical techniques included potentiodynamic polarization curves, electrochemical impedance spectroscopy and electrochemical noise measurements. Methanol concentrations included 1, 5, 10 and 20 molar. Results have shown that corrosion resistance increases with an increase in methanol concentration. The addition of copper (Cu) to aluminum (Al) increases the corrosion rate of the former by the formation of micro galvanic cells, inducing localized typo of corrosion also.[23]

3.6.1 SGS LABORATORY RESULTS

All samples tested in the laboratory had a result in the copper corrosion test of 1a, which means that there is no corrosion in the samples, just some light tarnish. In gasoline European standard EN 228:2012 + A1:2017, copper corrosion grade should be 1.

3.7 SILVER CORROSION

Copper is also sensitive to corrosive sulfur compounds, but silver is even more sensitive. Silver corrosion issues are known since 1962 in aviation turbine fuel (ATF) as there were some cases where the copper corrosion test was not adequate to test the non-corrosivity of the fuel on silver

Silver Strip Corrosion Test for Gasoline

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[20] *M. Walker, R. Chance, Corrosion of metals and the effectiveness of inhibitors in ethanol fuels, SAE paper no. 831828 (1983)*

[21] *Anodic Protection* ⟶ *Learn more*

[22] *Molar refers to the unit of concentration molarity, which is equal to the number of moles per liter of a solution. In chemistry, the term most often refers to molar concentration of a solute in a solution. Molar concentration has the units mol/L or M*

[23] *Effect of methanol on the corrosion behaviour of Al-Cu Alloys in sulphuric acid, Vergara-Juarez et al.* ⟶ *Learn more*

surfaces. Since that time, the silver corrosion test was integrated in the ATF specification.

Silver corrosion is important for gasoline because some fuel tank level sensing components are made from silver alloys. Sulfur compounds in fuel – especially hydrogen sulfide, light mercaptans, and dissolved elemental sulfur – separately and in combination can corrode and tarnish these silver alloy sensing elements and result in erroneous fuel level readings. Likewise, these sulfur compounds can also tarnish and corrode copper-containing alloys such as brass. Both the silver (ASTM D7667 or ASTM D7671) and copper (ASTM D130) tests are performed using test procedures that expose metallic strips to fuel for a specified time under controlled conditions. No literature has been found stating that methanol corrodes silver.

3.8 STEEL CORROSION

According to methanol safety data sheet, methanol is corrosive to type 12L14 carbon steel at room temperature and type 3003 aluminum, copper (10–100 % methanol solution) and admiralty brass, at 93° C.

Parts of the engine fuel-intake systems are made from aluminum. This is why compatible material for fuel tanks, gasket and engine intake must be used.

A variety of metallic parts have been identified as potentially sensitive to degradation by methanol/gasoline blends in the range of 10–15 % vol. methanol. The most frequently referred to metals are:

- Terne steel or terne plate, which are used in fuel tanks
- Magnesium and
- Aluminum, which are used in carburetors and fuel pump bodies[24]. Both materials have exhibited extensive corrosion potential in bench scale tests[25, 26, 27]

Terne steel, which is sheet steel that is hot dipped in a tin-lead solution to retard corrosion, is almost exclusively used in current automotive fuel tanks. Bench scale tests by Leng[28] on pure methanol have shown severe degradation or dissolution of the lead/tin coating of terne plated steel. A report by Poteat[29] showed accelerated corrosion of terne plate when a 10 % vol. methanol blend was compared to indolene as a base. But both indolene and the methanol blend corroded terne steel at a small fraction of the rate of pure methanol.

Uniform corrosion leads eventually to a removal of the protective terne lining of the fuel tank, which in turn leads to accelerated corrosion of the fuel tank steel.[30] Keller[31] presented data indicating that little corrosion of terne plate occurred in methanol blends, however, it did not occur in dry pure methanol.

Fleet test results using terne metal in the gas tanks have not shown any catastrophic failure of the tanks due to corrosion by gasoline/methanol blends under 15 % methanol[32, 33, 34, 35, 36].

To expand on the issue of galvanic corrosion in methanol/gasoline blends, gasoline is known to be a relatively good electrically insulating liquid due to the general non-polar nature of the constituent hydrocarbons. Methanol on the other hand is very polar and conducts electricity much better[37]. Therefore, the presence of methanol in a fuel blend would be expected to increase the tendency and extent of galvanic corrosion[38, 39].

According to the Methanol Institute's publications (e.g. Use of Methanol as a Transportation Fuel prepared by Alliance Technical Services Inc. in November 2007), additives have been found to be effective in reducing the corrosive effects on methanol in gasoline (blends of up to 10%) on copper, cast iron, steel and aluminum.

3.9 NON-METALS

Literature from the 80´s and early 90´s indicate that the non-metals used in fuel systems consisting of many polymers, elastomers, rubbers, etc. have been responsible for the most reported failures of vehicles fueled with methanol/gasoline blends[40, 41]. Methanol attacks some forms of plastic, rubber and coatings.[42]

However, some other investigators have shown no problems in operation of methanol/gasoline blends[43]. Bench scale testing of non-metals has uncovered many sensitive non-metals which are used in automotive fuel systems. Some materials have shown consistent adverse reactions to methanol/gasoline blends. The materials which are particularly sensitive have been identified as natural rubber (not used in current motor vehicles), polyurethane (used as fuel lines in some vehicles), cork gasket material, leather, polyester bonded fiberglass laminate, polyvinyl chloride (PVC), and certain other plastics (polyamides and methylmethacrylate)[44, 45]. A very large class of non-metals appear to be affected inconsistently in various literature references. Nitrile was found to be resistant to methanol/gasoline blends by Leng[46] but to be highly sensitive in bench scale tests by Abu-Isa[47] and Cheng[48]. The following table shows methanol blends compatibility with non-metals.

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[24] *D.J. Bologna, Corrosion Considerations in Design of Automotive Fuel Systems, SAE Paper 789020*

[25] *J. Keller, Methanol Fuel Modification for Highway Vehicle Use; DOE Report HCP/W3683-18*

[26] *I.J. Leng, Fuel Systems for Alcohol-Corrosion and Allied Problems; 4th International Symposium on Alcohol Fuels Technology*

[27] *L.E. Poteat, Compatibility of Automotive Fuel Systems Materials with Methanol Gasoline Fuels*

[28] *I.J. Leng, Fuel Systems for Alcohol-Corrosion and Allied Problems; 4th International Symposium on Alcohol Fuels Technology*

[29] *L.E. Poteat, Compatibility of Automotive Fuel Systems Materials with Methanol Gasoline Fuels*

[30] *Technical Report: a Review of the Compatibility of Methanol/Gasoline Blends With Motor Vehicle Fuel Systems, EPA.* ⟶ *Learn more*

[31] *J. Keller, Methanol Fuel Modifications for Highway Vehicle Use; DOE Report HCP/W3683-18*

[32] *Methanol-Gasoline Blended Fuels in West Germany. Specification and Early Field Experience; B. Niwerhauve 4th International Symposium on Alcohol Fuels Technology*

[33] *G.R. Cassels, Third International Symposium on Alcohol Fuels Technology, B P New Zealand, Experience with Methanol/Gasoline Blends*

[34] *J.C. Ingamells, et al., Methanol as a Motor Fuel or a Gasoline Blending Component. SAE Paper 7501123*

[35] *J. Duncan, et al., The MK15 Blend Test Programme of the New Zealand Liquid Fuels Trust Board; 4th International Symposium on Alchohol Fuels Technology*

[36] *K. Stamper, Fleet Trials Using Methanol/Gasoline Blends; 4th International Symposium on Alcohol Fuels Technology*

[37] *L.E. Poteat, Compatibility of Automotive Fuel Systems Materials with Methanol Gasoline Fuels*

[38] *J. Keller, Methanol Fuel Modification for Highway Vehicle Use; DOE Report HCP/W3683-18*

[39] *L.E. Poteat, Compatibility of Automotive Fuel Systems Materials with Methanol Gasoline Fuels*

[40] *Methanol-Gasoline Blended Fuels in West Germany. Specification and Early Field Experience; B. Niwerhauve 4th International Symposium on Alcohol Fuels Technology*

[41] *J. Duncan, et al., The MK15 Blend Test Programme of the New Zealand Liquid Fuels Trust Board; 4th International Symposium on Alcohol Fuels Technology*

[42] *Methanol Material Safety Data Sheet, Methanex Corporation* ⟶ *Learn more*

[43] *I.J. Leng, Fuel Systems for Alcohol-Corrosion and Allied Problems; 4th International Symposium on Alcohol Fuels Technology*

[44] *J. Keller, Methanol Fuel Modification for Highway Vehicle Use; DOE Report HCP/W3683-18*

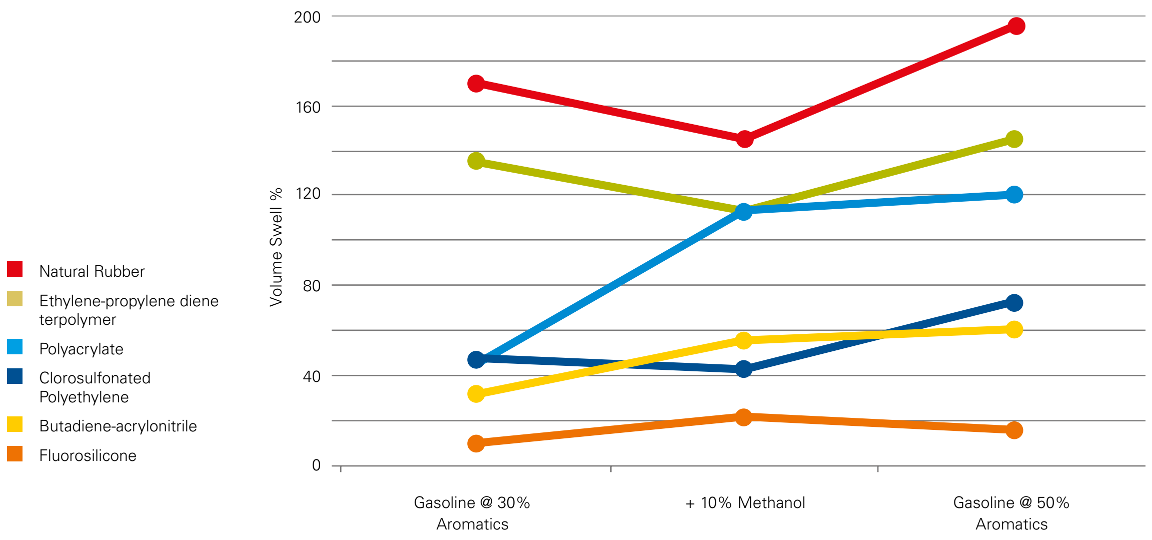
[45] *I.J. Leng, Fuel Systems for Alcohol-Corrosion and Allied Problems; 4th International Symposium on Alcohol Fuels Technology*

[46] *I.J. Leng, Fuel Systems for Alcohol-Corrosion and Allied Problems; 4th International Symposium on Alcohol Fuels Technology*

[47] *Ismat A. Abu-Isa, Effects of Mixture of Gasoline with Methanol and with Ethanol on Automotive Elastomers; GMR Report-3137*

[48] *Technical Report: a Review of the Compatibility of Methanol/Gasoline Blends With Motor Vehicle Fuel Systems*

MATERIAL COMPATIBILITY WITH METHANOL BLENDS



Source: Methanol Institute

It is therefore important to use compatible non-metal materials in any fuel-wetted parts.

3.9.1 PEROXIDE CONTENT

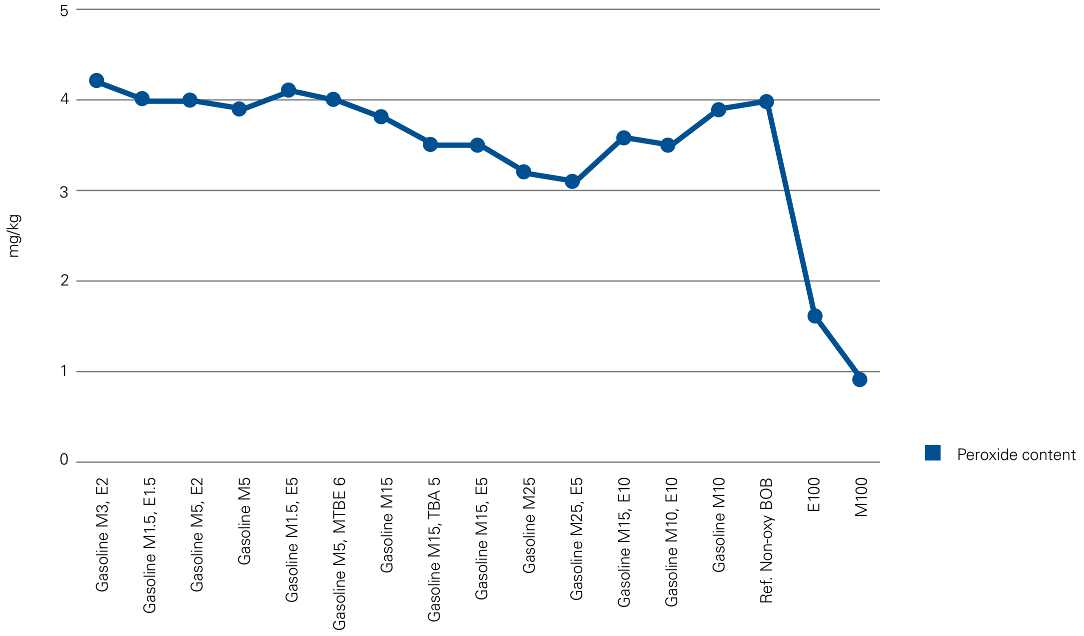
According to standard ASTM D6447 – 09 (2014), Test Method for Hydroperoxide Number of Aviation Turbine Fuels by Voltammetric Analysis, the magnitude of the hydroperoxide number is an indication of the quantity of oxidizing constituents present. The deterioration of the fuel results in the formation of hydroperoxides and other oxygen-carrying compounds. The determination of the hydroperoxide number of fuels is significant because of the adverse effect of hydroperoxides upon certain elastomers in the fuel systems.

3.9.1.1 SGS LABORATORY RESULTS

Gasoline + EtOH + MeOH

Pure alcohols have a very low peroxide content, as shown in the figure below. The addition of methanol and ethanol to gasoline lowers peroxide content, but only in values close to 1 ppm. This is desirable since peroxides can attack fuel system elastomers and copper commutators in fuel pumps.

PEROXIDE CONTENT OF GASOLINE + ETOH + MEOH



Source: SGS

3.10 DENSITY (15 °C)

Variations in fuel density result in variations in engine power and, consequently, in engine emissions and fuel consumption. The European EPEFE-programme found that fuel density also influences injection timing of mechanically-controlled injection equipment, which also affects emissions and fuel consumption. Therefore, in order to optimize engine performance and tailpipe emissions, both minimum and maximum density limits must be defined in a fairly narrow range[49]. Methanol has a similar density compared to gasoline but only half the calorific value, however because of a high octane number the mileage per liter is approximately the same as for gasoline (The Research Octane Number, RON is 109 in methanol).[50]

FUEL	HHV MJ/KG	LHV MJ/KG	DENSITY G/CM³
Methanol	22.9	20.1	0.794
Dimethyl ether (DME)	31.7	28.9	0.665
Ethanol	29.8	27.0	0.789
Gasoline, conventional	44.9	44.9	0.745
Diesel, conventional	46.5	43.4	0.837
Diesel, Fisher-Tropsch	45.5	43.2	0.797

Source: GREET Transportation Fuel Cycle Analysis Model.
HHV = Higher Heating Value. LHV = Lower Heating Value

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[49] *WORLDWIDE FUEL CHARTER, gasoline and diesel fuel ⟶ learn more*

[50] *http://www.starch.dk/methanol/energy/img/tm01-02e.pdf ⟶ Learn more*

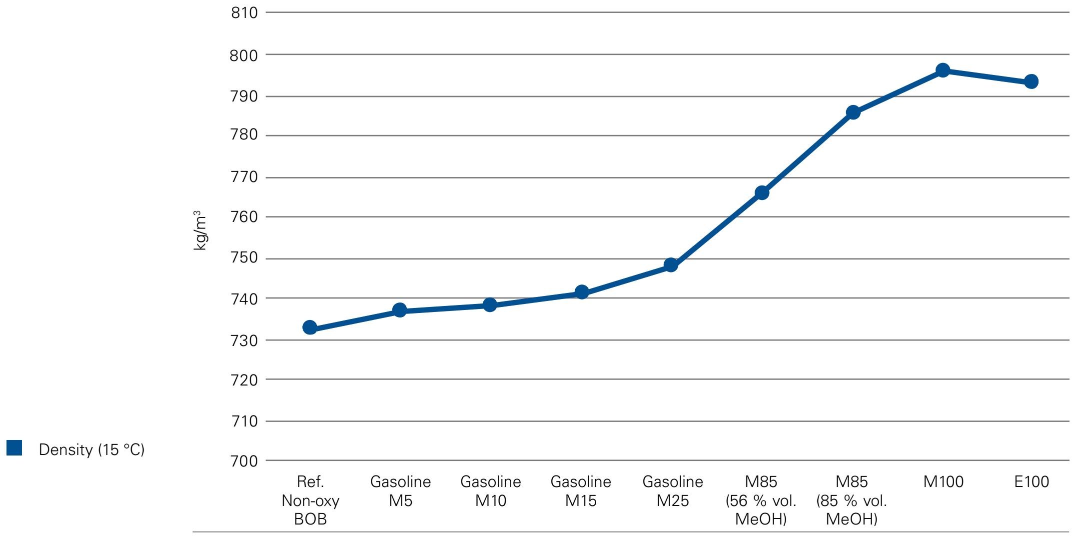
The study Engine performance and exhaust gas emissions of methanol and ethanol–diesel blends, Sayin et al.[51], investigated the effects of methanol and diesel fuel blends on compression ignition engine performance and exhaust emissions of a four-cylinder, four-stroke, direct injection, turbocharged diesel engine. Methanol blended diesel fuels ranged from 0 % vol. to 15 % vol. of methanol content with an increment of 5 %. The tests were performed by varying engine speed between 1000 min-1 to 2700 min-1 by an engine testing dynamometer. Results indicated that brake specific fuel consumption and NO$_X$ emissions increased while brake thermal efficiency, CO and HC decreased relative to single diesel fuel operation with increasing amount of methanol in the fuel mixture.[52]

3.10.1 SGS LABORATORY RESULTS

Gasoline + Methanol

The lab results confirm that gasoline is less dense than ethanol and both are less dense than methanol. They also show how density increases when the methanol content raises. Density starts increasing steeper when methanol content is 25 % vol., and reduces this speed when methanol content is 85 % vol. However, at this methanol blending level density is above the recommended value of 775 kg/m^3. Mid and low blends, including methanol blend at the level of 56 % vol. are in compliance with the standard EN228.

DENSITY VALUES IN GASOLINE + MEOH SAMPLES

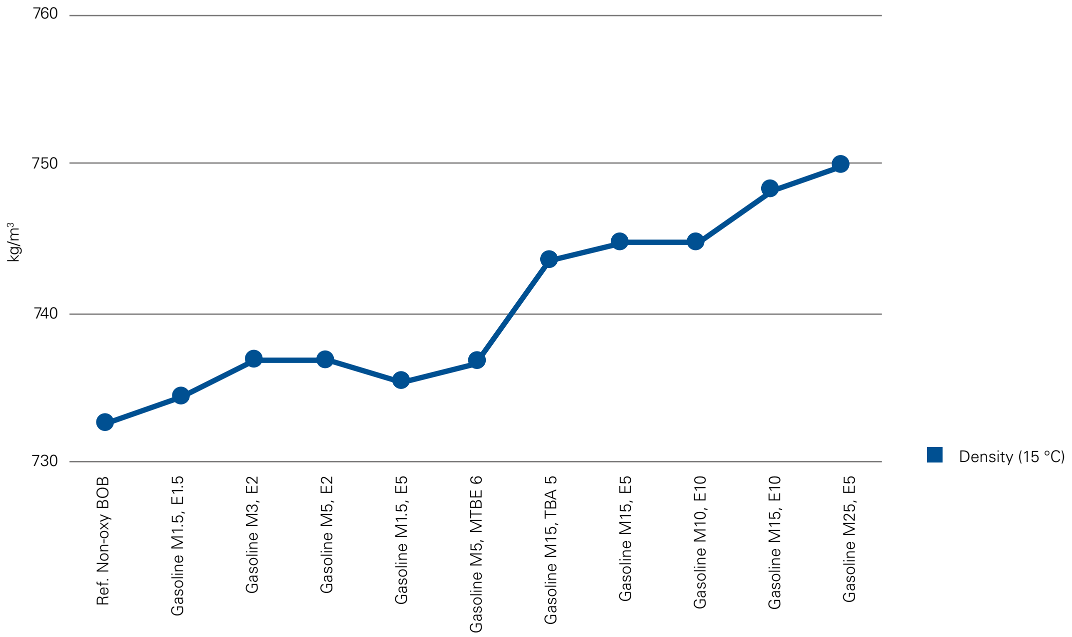


Source: SGS

Gasoline + Ethanol + Methanol

Density has a slow-pace increase when methanol and ethanol are added in small volumes. It increases faster with middle methanol blends, regardless of the volume of ethanol added. However, even though there is an increasing trend, the increase in density in the different blends is not very significant and always remains within the limits established in the European standard on gasoline quality EN228, i.e. between 720–775 kg/m^3.

DENSITY VALUES IN GASOLINE + ETOH + MEOH SAMPLES



Source: SGS

3.11 DISTILLATION

Distillation is defined by the temperature at which a certain volume percentage of a liquid evaporates and is recovered by cooling.

The distillation characteristics of hydrocarbons have an important effect on their safety and performance, especially in the case of fuels and solvents. The boiling range gives information on the composition, the properties, and the behavior of fuels during storage and use. Volatility is the major determinant of the tendency of a hydrocarbon mixture to produce potentially explosive vapors. The distillation characteristics are

THE DISTILLATION CHARACTERISTICS OF HYDROCARBONS HAVE AN IMPORTANT EFFECT ON THEIR SAFETY AND PERFORMANCE, ESPECIALLY IN THE CASE OF FUELS AND SOLVENTS.

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[51] *Engine performance and exhaust gas emissions of methanol and ethanol–diesel blends, Sayin et al.*

[52] *https://www.researchgate.net/publication/266246401_An_experimental_investigation_on_effects_of_methanol_blended_diesel_fuels_to_engine_performance_and_emissions_of_a_diesel_engine* ⟶ *Learn more*

critically important for both aviation and automotive gasolines, affecting starting, warm-up, and tendency to vaporlock at high operating temperatures or at high altitude, or both. The presence of high boiling components in these and other fuels can significantly affect the degree of formation of solid combustion deposits.

Distillation limits are often included in petroleum product specifications, in commercial contract agreements, process refinery/control applications, and in regulatory requirements.

According to the Handbook of MTBE and other Gasoline Oxygenates, methanol changes the shape of the gasoline distillation curve drastically. Research compiled in this Handbook has observed that the presence of methanol leads to a much greater fraction distilled up to 70°C. It causes the blend to distill much faster at temperatures below methanol´s boiling point, that is 65°C.[53]

The addition of alcohols led to changes in the distillation curves; a plateau area shows up close to the "steam point" of the alcohol. In the case of addition of 20 % methanol to the mixture (M20), the plateau area in the distillation curve is below the M100 pure methanol distillation point (64.5° C). Lower values are obtained for the distillation temperature starting from more than 10 °C below the methanol distillation temperature. The size of this range extends over a longer, almost double range from the 20 % vol. added methanol, which is higher than the volumetric proportion of methanol in the blend. This is due to the interaction of methanol molecules with mild HC, leading to the formation of azeotropes, with synergistic effects of increasing volatility.[54]

The M20 mixture showed a higher volatility of the light fractions, the value of the E70 parameter (the percentage of the gasoline sample that evaporates at 70°C) exceeded the upper limit mentioned in the EN 228 standard. In the case of triple blends with two alcohols, the distillation curves deviated less from those of pure gasoline. According to another study, based on distillation trend in a region of T20-T70 results, it is shown that a gasoline blend with two different alcohols provides better influence towards engine operability than a gasoline blend containing higher concentration of one alcohol[55]. In all cases the characteristic values of the volatility of the triple blends were within the ranges specified in the EN228 standard.[56]

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[53] *Handbook of MTBE and Other Gasoline Oxygenates* ⟶ Learn more

[54] *Hadler A Ott L Bruno T 2009 Study of azeotropic mixtures with the advanced distillation curve approach Fluid Phase Equilibria Volume 28 pp 49-59*

[55] *Experimental determination of distillation curves of alcohols/gasoline blends as bio-fuel for si enginess* ⟶ Learn more

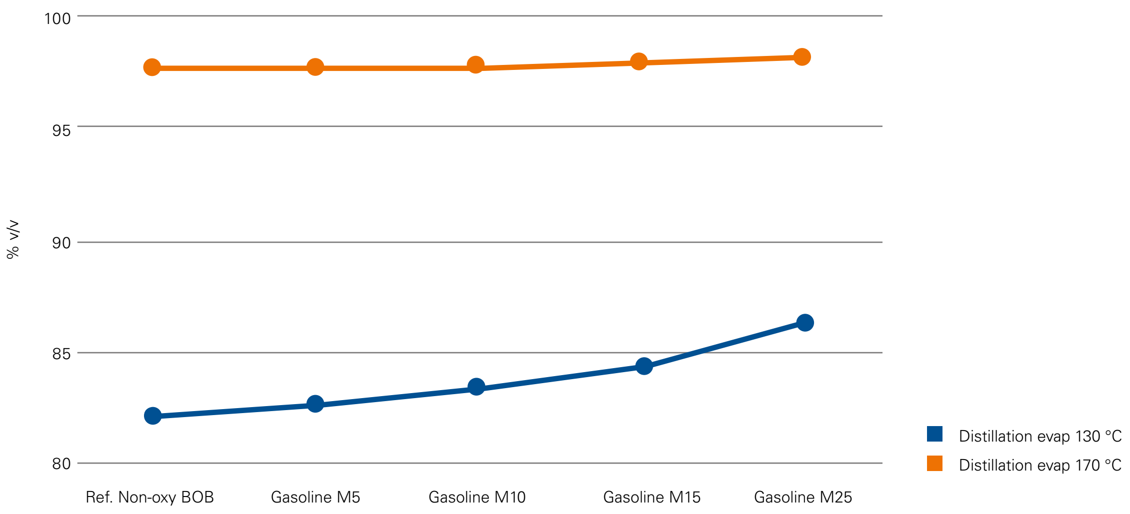
[56] *Experimental Study on the Distillation Capacity of Alcohol-Gasoline Blends*

3.11.1 SGS LABORATORY RESULTS

Gasoline + Methanol

The gasoline-methanol blend evaporated faster at a lower temperature when methanol is added to gasoline. The evaporation occurs also faster when the methanol content is above 15 % vol.

DISTILLATION EVAPORATION VALUES (% VOL.) IN GASOLINE + MEOH SAMPLES

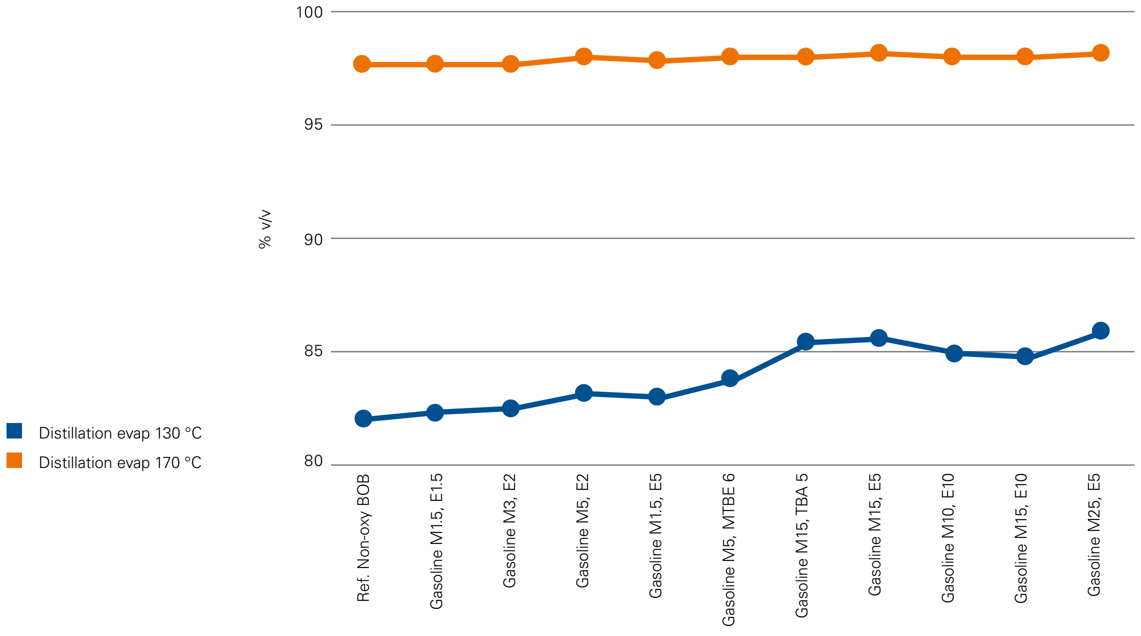


Source: SGS

Gasoline + Ethanol + Methanol

The same thing happens when ethanol and methanol are added. The gasoline-methanol blend evaporated faster at a lower temperature when methanol and ethanol are added to gasoline. The evaporation occurs faster when the methanol content is above 15 % vol., and even faster when ethanol content is low compared to methanol.

DISTILLATION EVAPORATION VALUES (% VOL.) IN GASOLINE + ETOH + MEOH SAMPLES



Source: SGS

EN 228 does not include these properties but includes Distillation Evaporation 100 °C (between 46 % vol. and 72 % vol. depending on RON and oxygenates content) and Distillation Evaporation 150 °C (> 75 % vol.), which shows that the results for gasoline and methanol samples are in line with EN specifications.

3.12 VAPOR LOCK INDEX

Vapor lock is a condition where gasoline vaporizes in a fuel tank or fuel line before being injected into the cylinder, preventing an engine from starting.

In the methanol studies consulted for the purposes of this paper, it is proven that the vapor pressure of mixtures increases with the increase in alcohol volume compared with base gasoline. Alcohol concentration in gasoline has a non-linear effect on reid vapor pressure (RVP).[57]

The ASTM D-86 distillation curves of reformulated gasolines by addition of alcohols show a decrease of boiling temperatures in the first part of the curve due to the formation of azeotropes with low boiling temperature between some components of base gasoline and alcohols. The decreasing boiling temperature in the front end of the distillation curve exhibits the decreasing Drivability Index and increasing of Vapor Lock Index. The higher alcohols (alcohols with a higher number of carbons than ethanol) seem to be more favorable than methanol and ethanol in reformulated gasolines composition because they do not modify volatility values as much.[58, 59]

Today’s fuel injected engines encounter hot-fuel handling drivability problems (hot starting, stumble, surge, backfire, and stalling) rather than true vapor lock. Vapor lock protection is a specification limit on the minimum temperature for a gasoline vapor-liquid ratio of 20:1.

VAPOR LOCK PROTECTION CLASS AND ITS REQUIREMENTS

ASTM D 5188	1	2	3	4	5	6
Temperature, °C (°F) for a Vapor-Liquid Ratio of 20, min	54 (129)	50 (122)	47 (116)	42 (107)	39 (102)	35 (95)
Special Requirements for Area V (high elevations) of D4814 Temperature, °C (°F) fora Vapor-Liquid Ratio of 20, min	54 (129)	50 (122)	47 (116)	47 (116)	41 (105)	35 (95)

Source: ASTM D 4814-19

3.13 VAPOR PRESSURE

A minimum vapor pressure is required to ensure good cold starting and drivability. A maximum vapor pressure is required to control the evaporative emissions from the vehicle. Therefore, requirements contain both a high and a low threshold.

Pure methanol has a very low vapor pressure, so, theoretically, the vapor in the tank can possibly ignite[60]. Literature does not provide any evidence that this has happened in real conditions. However, the alcohol-gasoline mixtures have a significant impact on the volatility properties. The RVP increases with the addition of methanol, and decreases with the addition of isopropanol, tertbutanol and isobutanol compared to base gasoline. When ethanol is added to gasoline up to 8 % vol., the vapor pressure of the mixture increases compared to the vapor pressure of base gasoline. Above E8 blend it decreases.[61]

Methanol lowers the vapor pressure when added in percentages above 82 % vol. This means that M85 will have a lower vapor pressure than the base gasoline. At 82 % methanol the vapor pressure is equal to the base gasoline. A blend between 70 %–82 % methanol will result in a higher vapor pressure.

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[57] *Vapor Pressure of Mixtures of Gasolines and Gasoline-Alcohol Blends* ⟶ *Learn more*

[58] *The Volatility of Reformulated Gasolines with Alcohols* ⟶ *Learn more*

[59] *Properties of gasoline-ethanol-methanol ternary fuel blend compared with ethanol-gasoline and methanol-gasoline fuel blends* ⟶ *Learn more*

[60] *http://www.energyresourcefulness.org/Fuels/methanol_fuels/methanol_fuels_general.html* ⟶ *Learn more*

[61] *The Volatility of Reformulated Gasolines with Alcohols* ⟶ *Learn more*

M100 has a vapor pressure of only 32 kPa. This is too low for use in winter and in summer. This fuel is therefore not desirable for vehicles with indirect injection (port injection).[62] It could, however, be used in vehicles with direct injection, which are on the market.

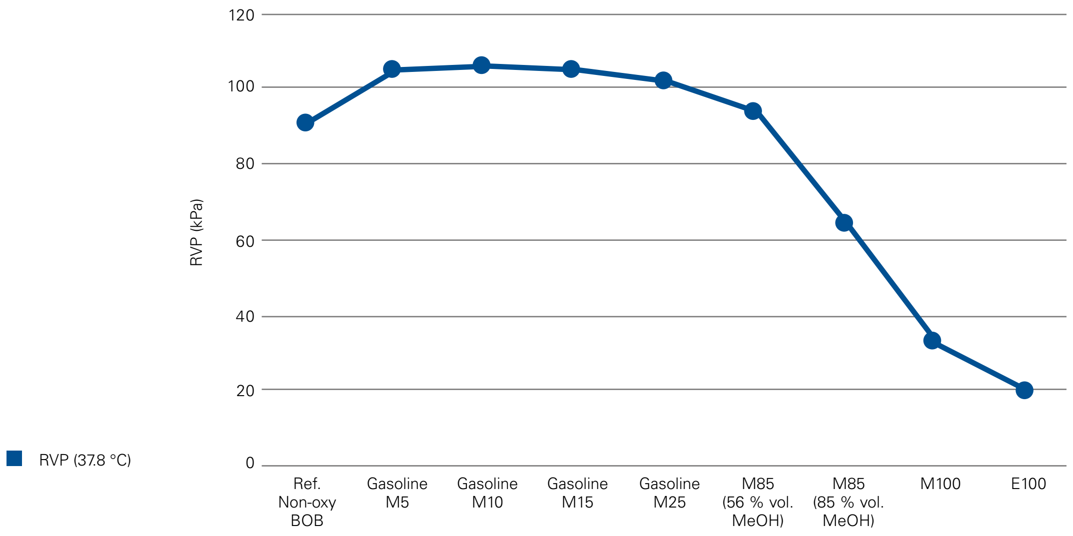
In conclusion, vapor pressure is not a problem for high blends of methanol; for low blends it can easily be handled by adjusting the before oxygenate blending (BOB) at the refinery. A blend of 82 % methanol (M82) will result in a neutral vapor pressure, i.e. compliant with the EN 228 gasoline standard.[63]

3.13.1 SGS LABORATORY RESULTS

Gasoline + Methanol

The vapor pressure of gasoline starts increasing with the addition of methanol in small quantities, it remains more or less stable until the methanol reaches 25 % vol., when RVP starts decreasing. With methanol content of 56 % vol., the decrease is more pronounced, and it decreases steeper, until achieving a very low RVP value. These results coincide with the literature discussed in this report. M100 and E100 have a very low RVP value, while the non-oxy BOB used for these tests has a very high RVP value.

RVP VALUES GASOLINE + MEOH (37.8 °C)



Source: SGS

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[62] http://danskbiomethanol.dk/Papers/Report%20DK.pdf → Learn more

[63] http://danskbiomethanol.dk/Papers/Report%20DK.pdf → Learn more

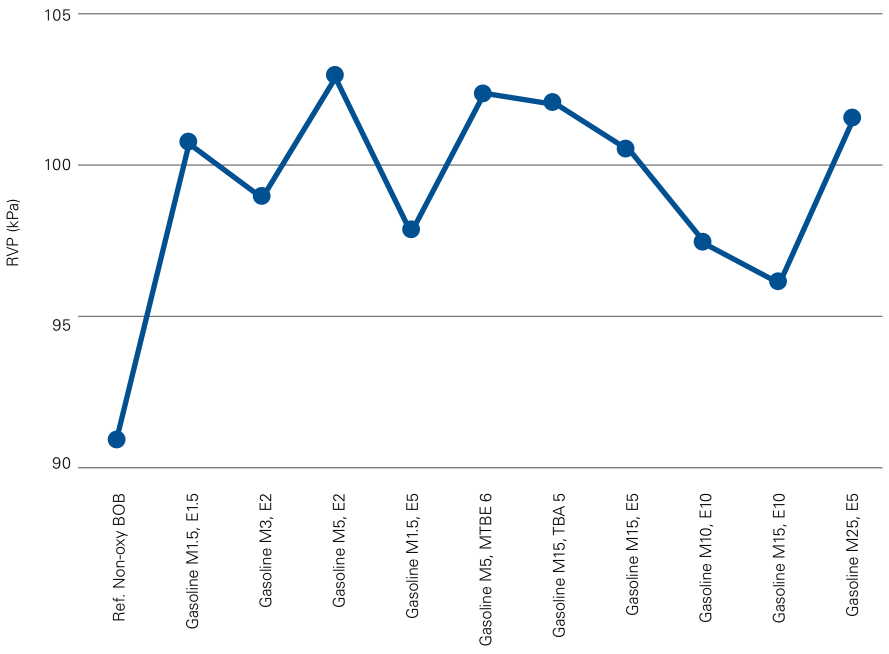
Gasoline + Ethanol + Methanol

As can be seen, RVP dramatically increases with the addition of methanol and ethanol in a content of 1.5 % vol. each to gasoline. The increase is almost 10 kPa, more than 10 %.

RVP decreases a bit when more methanol than ethanol is added (but still both in small quantities), but reaches the highest RVP value when the methanol content is 5 % vol. and the ethanol content is 2 % vol. It decreases again when the blends are the opposite (more ethanol than methanol), but increases when both methanol and MTBE are added in quantities around 5 % vol.

In general, RVP is higher when there is more methanol than ethanol in the mix, while RVP values decrease when the difference between methanol and ethanol content is small.

RVP VALUES GASOLINE + ETOH + MEOH (37.8 °C)



Source: SGS

METHANOL CAN ACT AS AN EFFECTIVE KNOCK SUPPRESSANT IN GASOLINE BLENDS WITH OCTANE NUMBERS AS LOW AS 52

3.14 RESEARCH OCTANE NUMBER

For pure methanol, RON and motor octane number (MON) have been reported in the ranges of 106–115 and 82–92, respectively.[64]

Due to its high octane rating, methanol can be used directly as a fuel in flex-fuel cars (including hybrid and plug-in hybrid vehicles) using existing internal combustion engines (ICE).

Methanol can act as an effective knock suppressant in gasoline blends with octane numbers as low as 52.[65]

The octane number represents the resistance of a spark ignition engine to knock (unwanted detonation which can damage the engine). The high intrinsic octane numbers of ethanol and methanol are well known. However, a greater effectiveness of octane number can be achieved through the knock resistance provided by the high level of vaporization cooling that occurs when methanol or ethanol is directly injected into the engine cylinders. A computational model is used to determine the knock resistance and effective octane number of these alcohol fuels when they are directly injected.[66] The model indicates that the effective octane numbers are around 160 for ethanol and 180 for methanol. The high compression ratio, high degree of turbocharging and aggressive engine downsizing enabled by the high effective octane number of methanol could provide an efficiency gain of 30 %–35 % (for combined city-highway driving) relative to conventional gasoline engines. An additional gain of around 10 % can be obtained by using reforming of methanol to enable ultra-lean operation at low loads. The combination of these gains could thus potentially provide an efficiency gain of 40–45 % for direct injection methanol engines. This efficiency gain is significantly greater than the typical 25–30 % gain of turbocharged diesel engines and similar to that of a gasoline-electric hybrid or turbodiesel, at a much more affordable cost.[67]

3.14.1 SGS LABORATORY RESULTS

Gasoline + MeOH + EtOH

The non-oxy BOB sample has a very high octane, and this is why we are only able to see small variations of octane in the methanol/ethanol blends tested by SGS.

RON is approximately 100 when methanol is between 10 % vol. and 25 % vol. With lower methanol concentrations in gasoline, RON decreases up to around 98.5.

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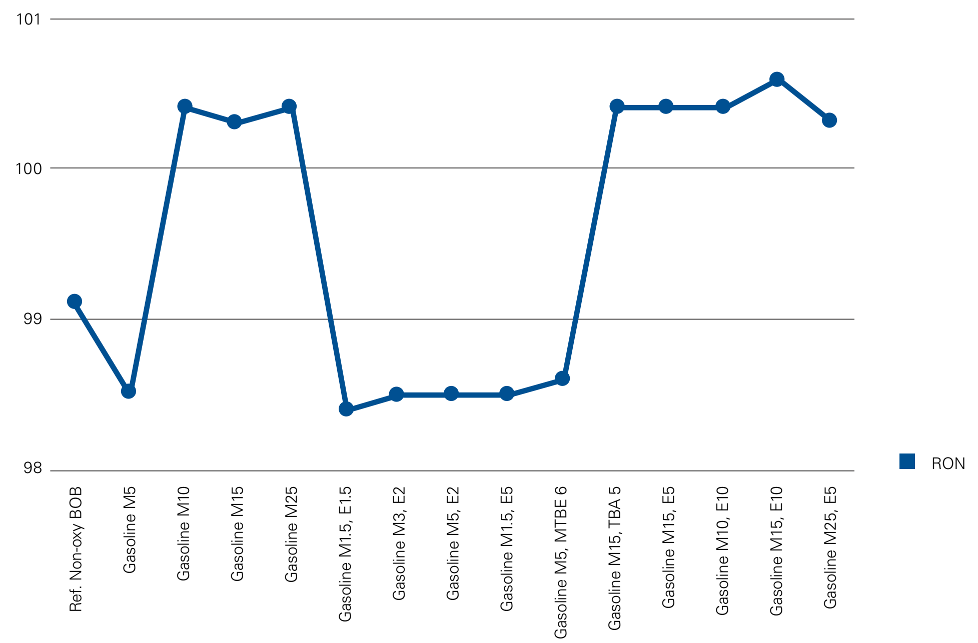
[64] *Handbook of MTBE and Other Gasoline Oxygenates* ⟶ Learn more

[65] *Handbook of MTBE and Other Gasoline Oxygenates* ⟶ Learn more

[66] *Effective Octane and Efficiency Advantages of Direct Injection Alcohol Engines* ⟶ Learn more

[67] *Effective Octane and Efficiency Advantages of Direct Injection Alcohol Engines* ⟶ Learn more

RON GASOLINE + ETOH + MEOH



Source: SGS

3.15 COMBUSTION INCLUDING OXYGENATES

In another study evaluated for this paper[68], engine performance and pollutant emissions from different blended fuels in types (ethanol, methanol and gasoline) and rates (3 % to 10 vol. % methanol and/or ethanol in gasoline) were investigated experimentally. The test results indicated that ethanol-methanol-gasoline blends (EM) burn cleaner than both ethanol-gasoline blends (E) and the neat gasoline fuel (G).

Methanol-gasoline blends (M) show the lowest emissions of CO and unburned hydrocarbons (UHC) among all tested fuels. In numbers:

- The M fuels show lower CO and UHC emissions than the EM fuels by about 5.5 % and 6 %, respectively
- The EM provide lower CO and UHC emissions by about 5 % and 2 %, respectively, compared to E fuels
- The E fuels give a relative decrease in CO and UHC emissions by about 31 % and 14 %, respectively, compared to gasoline

It was also noticed that by adding more ethanol and/or methanol to gasoline the engine produces less emissions:

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[68] *Engine performance and pollutant emission of an SI engine using ethanol–gasoline blended fuels, Hsieh et al.* ⟶ Learn more

- When using EM3 (3 vol. % ethanol and methanol in gasoline), the CO and UHC emissions are decreased by about 17 % and 10 % compared to neat gasoline
- When using EM7, the CO and UHC emissions became lower by about 35 % and 15 % compared to neat gasoline
- When using EM10, the CO and UHC emissions became lower by about 46 % and 23 %, respectively, compared to neat gasoline

It can be also noticed that the addition of ethanol and/or methanol to gasoline at low engine speeds is not as efficient at decreasing emissions as at high engine speeds.

Finally, Hsieh et al. demonstrate that:

- To achieve less emissions of CO and UHC and higher both volumetric efficiency and output torque from SI engines, methanol fuels should be used
- To achieve a higher output power with a low CO and UHC emissions, but higher than methanol fuels, ethanol blends should be used
- To get low moderate emissions of CO and UHC as well as a high moderate volumetric efficiency, torque and power, ethanol methanol fuels should be used[69]

Oxygenated chemical compounds contain oxygen as a part of their chemical structure. The term usually refers to oxygenated chemical compounds added to fuels. Oxygenates are usually employed as gasoline additives to reduce CO and soot that is created during the burning of the fuel. Compounds related to soot, such as polyaromatic hydrocarbons (PAHs) and nitrated PAHs, are also reduced.

The presence of oxygen-containing compounds in gasoline can promote more complete combustion which reduces CO emissions.

3.16 CALORIFIC VALUE CALCULATED FROM COMBUSTION

Methanol fuel requires twice as much volume as gasoline due to its low density and low calorific value, if the octane ratio is not considered.

Gasoline has higher caloric value and higher energy density (about 18,400 BTU/pound) than methanol (9,500 BTU/pound). This is why a large tank for methanol is required to generate equal amount of power as with gasoline fuel.

[69] *Investigations on the effects of ethanol-methanol-gasoline blends in a spark-ignition engine: Performance and emissions analysis*

⟶ *Learn more*

General values of heating or calorific value for fuels for the purposes of this study are:

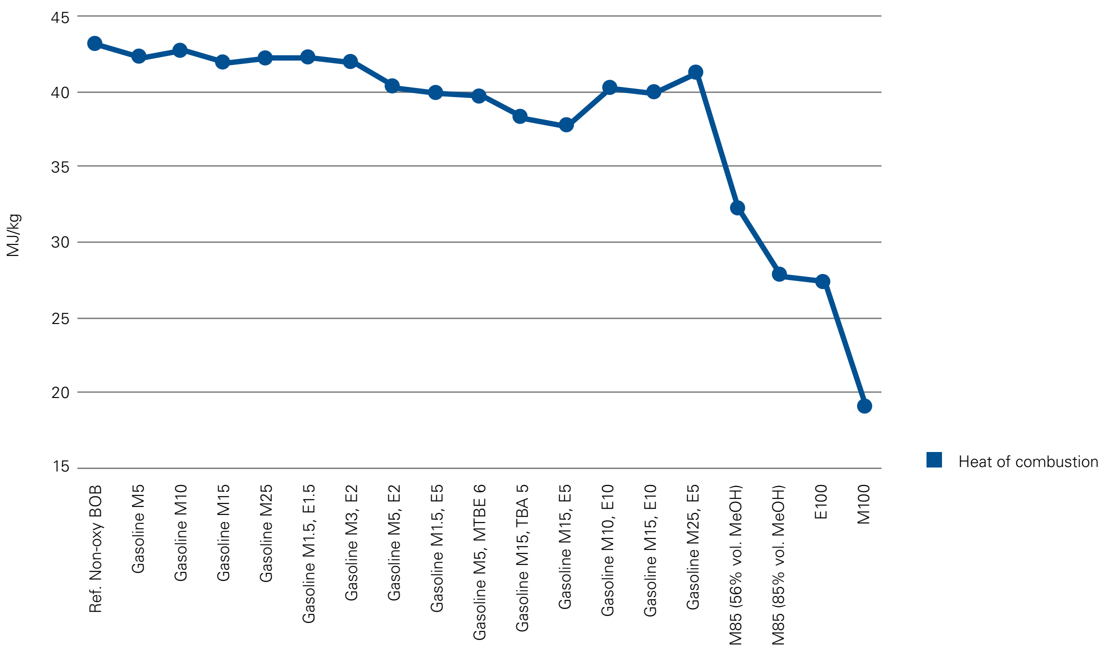
- Gasoline (44–46 MJ/kg)
- Ethanol (29–30 MJ/kg)
- Methanol (22–23 MJ/kg)

3.16.1 SGS LABORATORY RESULTS

Gasoline + MeOH + EtOH

The laboratory results indicate that all low and medium blends (up to 30 % vol. of methanol and ethanol combined) have a similar calorific value to gasoline, which makes them suitable fuels for SI engines. For higher methanol blends, starting at 50 % vol. methanol, calorific value drops significantly, resulting in less efficient fuels for SI engines.

CALORIFIC VALUE OF GASOLINE + ETOH + MEOH



Source: SGS

3.17 AIR FUEL RATIO CALCULATED FROM COMBUSTION

Air-fuel ratio (AFR) is the mass ratio of air to a solid, liquid, or gaseous fuel present in a combustion process. The AFR determines whether a mixture is combustible at all, how much energy is being released, and how much unwanted pollutants are produced in the reaction. If exactly enough air is provided to completely burn all of the fuel, the ratio is known as the stoichiometric mixture, often abbreviated to stoich. Ratios lower than stoichiometric are considered "rich". Rich mixtures are less efficient but may produce more power and burn cooler. Ratios higher than stoichiometric are considered "lean". Lean mixtures are more efficient but may cause higher temperatures, which can lead to the formation of NO_X. Some engines are designed to allow lean-burn.

The AFR is the most critical item to regulate regarding exhaust emissions and fuel economy. The technically correct AFR may be calculated by knowing the molecular formula and weight of the fuel and writing an equation which presumes that all the carbon is oxidized to carbon dioxide (CO_2) and all the hydrogen to water (H_20).

The chemically correct AFR is 14.96 for gasoline, 6.47 for methanol and 9.01 for ethanol. If the engine will aspirate a fixed amount of air at any particular throttle opening, then the carburetor must measure a specific amount of fuel to provide the correct AFR. Thus, compared to gasoline, the carburetor must deliver 2.31 times more methanol. This ratio is slightly greater than the ratio (2.2) based on energy values.[70]

The other issue is the flammability limits of M100. At normal ambient temperatures, the air-fuel mixture ratio of the gasoline vapor above the liquid in the tank is too rich to ignite. This is not true for the alcohols because of their low vapor pressures. The addition of 15 % gasoline moves the flammability limit temperatures to a more acceptable range of risk, close to that of the gasoline vehicle.

3.18 WATER CONTENT

Since methanol is completely miscible in water, before or during methanol droplet burning in air, methanol will absorb water. The effect of water absorption results in a non-d-square combustion behavior and promotes flame extinction. If a Damkohler number[71], becomes too small, then there is insufficient time in the flame surrounding the liquid sphere for the chemical heat release to occur, and the flame is extinguished. This flame extinction occurs when the liquid sphere reaches a critical minimum diameter.[72]

There is literature showing that some cosolvents, mostly isomers with high number of carbon atoms, prevent separation in methanol gasoline blends.[73]

---

[70] *Convert your car to run on alcohol Fuels. Oregon State University* ⟶ *Learn more*

[71] *A Damkohler number is defined as the ratio for determining whether diffusion rates or reaction rates are more 'important' for defining a steady-state chemical distribution over the length and time scales of interest*

[72] *http://web.eng.ucsd.edu/mae/groups/combustion/NASA/water.html* ⟶ *Learn more*

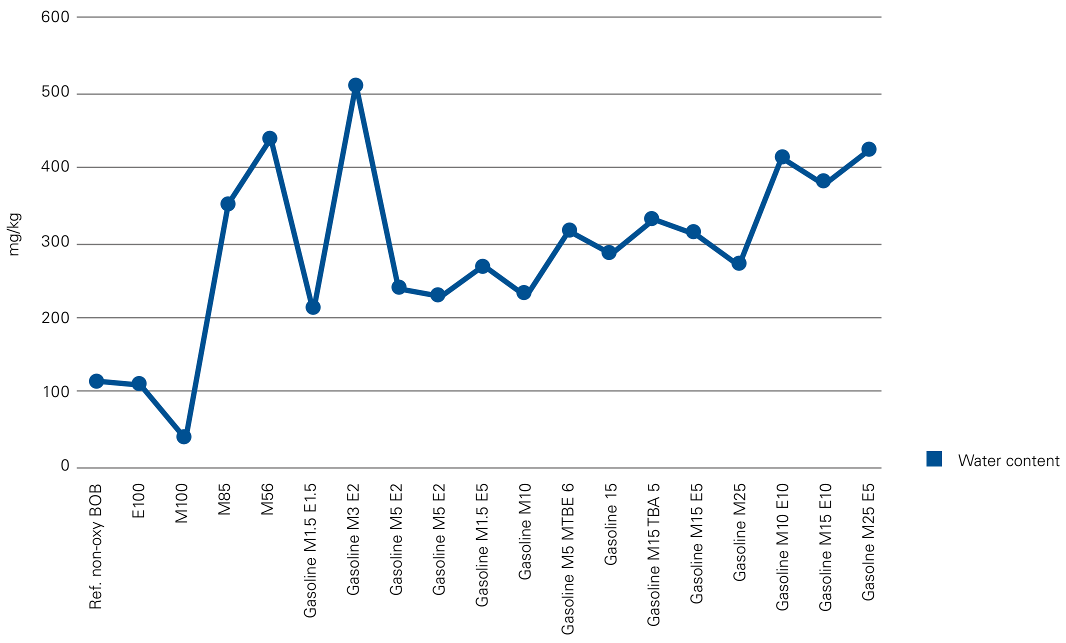
[73] *https://www.rjpbcs.com/pdf/2017_8(2)/[143].pdf* ⟶ *Learn more*

3.18.1 SGS LABORATORY RESULTS

Gasoline + EtOH + MeOH

With these results we cannot prove that water content is directly proportional to methanol content. The samples taken had a high purity and contain almost no water. It is possible that the water absorption showed in the results have taken place in the laboratory during storage of non-oxy gasoline. However, it is important to note that the water content in tested fuels is negligible.

WATER CONTENT OF GASOLINE + ETOH + MEOH



Source: SGS

3.19 NITROGEN CONTENT

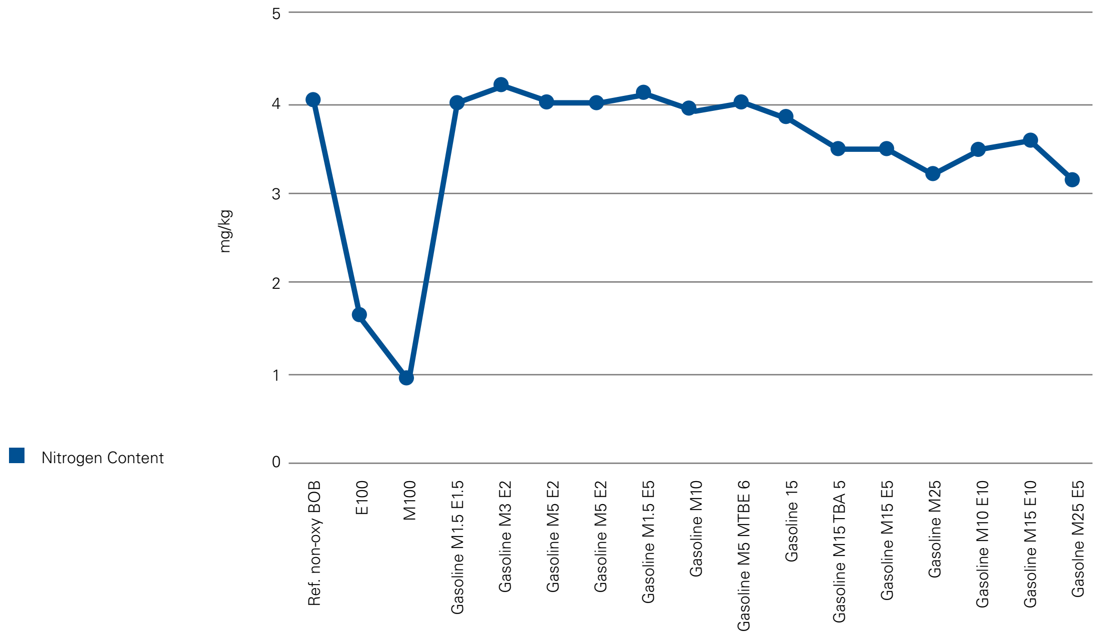
The concentration of nitrogen is a measure of the presence of nitrogen-containing additives. Knowledge of its concentration can be used to predict performance.

3.19.1 SGS LABORATORY RESULTS

Gasoline + EtOH + MeOH

Methanol has a very low nitrogen content, differing from gasoline or methanol and/or ethanol low blends. The addition of methanol and ethanol to gasoline reduces the nitrogen content, but in very low concentrations, close to 1 ppm.

NITROGEN CONTENT OF GASOLINE + ETOH + MEOH



Source: SGS

4 METHANOL USES AS A FUEL

In this section, the different uses of methanol as a fuel, its properties as a fuel in different engines and transportation modes are discussed.

4.1 METHODS OF USING METHANOL AS AN ENGINE FUEL

- In SI engines: principally methanol is considered an SI engine fuel, due to its high autoignition resistance and high heat of vaporization[74]. Methanol can be used as a pure fuel or as a blend component. For high blends, the modifications necessary for SI operation are not too significant. Blending methanol with gasoline will increase the vapor pressure for low methanol concentrations. Thus, it is required to change the formulation of the base gasoline. Cold starting of very high blend alcohols in gasoline has long been challenging; however, recent solutions focus on the engine operation, minimizing the need for additional systems. Dedicated methanol engines would have an increased compression ratio which would at least partly alleviate the cold start issue. There are other modifications required for the ignition system or due to the material compatibility that must be considered. Special catalysts formulations may be necessary[75]
- Many experiments have been carried out on gasoline-methanol blends (especially M 15) used in SI engines. M15 is used in China in the existent fleet; however, literature shows that for most conventional vehicles, the following changes to the engine were performed:
  - Fuel nozzles of the carburetor were enlarged to adjust the AFR to the stoichiometric value of the actual blend
  - The mixture was heated before it entered the engine at cold start
  - The carburetor and fuel line were modified to avoid vapor locks and damage to some of the parts (plastic and rubber, especially) because of corrosion and material degradation. Ignition improvers were necessary in all cases as cold starting aids, especially in cold climates. To avoid phase separation of methanol-gasoline blends, additives were also added
- In CI engines: alcohols have also been used in diesel applications but require more significant modifications than SI engines, again a corollary of their high autoignition resistance. Most changes take place in fuel injection, use of glow plugs, or addition of ignition improvers
- Dual-fueling has also been adopted, recently in large ship engines such as the Stena Germanica, where the methanol is introduced separately to the diesel which is then used as a source of ignition. This obviously requires some significant modification to the fueling system. This is largely common also with liquefied natural gas (LNG) conversions of such engines. Port-fuel injection of the methanol is a possibility in these dual-fuel engines too and is being investigated particularly as a means of providing improved emissions in water craft. For dual fuel engines, the maximum substitution ratio is very important, i.e. the amount of diesel fuel that can be replaced by methanol. This ratio (or the methanol energy fraction) was found to differ significantly between different engines, from as low as 70 %[76] to as high as 85 %[77]. Methanol-Diesel compression ignition of methanol fuel with additive (MD95) can also be used as marine fuel. In most cases the conversion of the base diesel engine to dual fuel operation with methanol is targeted at decreasing the two main pollutants of concern for diesel engines: NO_X and PM. It can lead to a drop in NO_X

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[74] *Methanol as a fuel for internal combustion engines, 2018*

[75] *Methanol as a fuel for internal combustion engines, 2018*

[76] *Song R, Liu J, Wang L, et al. Performance and emissions of a diesel engine fueled with methanol. Energy Fuels 2008; 22 (6):3883–8*

[77] *Liu J, Li Y, Li G, et al. Effect of pilot diesel quantity and fuel delivery advance angle on the performance and emission characteristics of a methanol-fueled diesel engine. Energy Fuels 2010; 24 (3):1611–16*

emissions of up to 50 %[78]. Soot emissions are also suppressed in dual fuel operation

- In SI engines, as a separate fuel stream: as mentioned, it is possible to use an octane-on-demand approach where alcohols are used as an octane booster and introduced separately to gasoline, and only when the knock avoidance afforded by their high-octane numbers and charge cooling effect is required. Thus, increased compression ratio or engine downsizing can be provided, and with them an improvement in vehicle energy consumption

4.1.1 METHANOL ENGINES

Efficiency of Methanol Engines

The efficiency of a methanol-fueled engine is higher than that of gasoline engines. This is for several reasons:

- Combustion losses are lower, that is combustion is more complete and more perfect. This has been investigated by Trzaskowski and Kowalewicz[79]. According to the study Combustion losses of S.I. engine fueled by methanol-gasoline blend, this is also the case for CI engines (with an optimized source of ignition in the case of the methanol engine)
- Heat losses due to cooling are smaller, because the temperature level in the engine cylinder is lower[80, 81]
- The combustion period of methanol fuel (or methanol fraction in the fuel) is shorter due to greater flame speed[82] and takes place closer to top dead center (TDC), which makes the thermodynamic cycle more like the Otto cycle
- The coefficient of molecular conversion of the charge during combustion for alcohol fuels is higher in comparison with petroleum fuels (due to the presence of atomic oxygen and the greater amount of hydrogen in the molecule). Because of this, the work done by the expanding gases in the cylinder is greater

Performance and Emission of the Methanol Engine

Assuming that the energy consumption is the same, torque and power of the engine fueled with methanol are higher than when the engine is fueled with petroleum fuels. This is due to (a) higher thermal efficiency and (b) higher volumetric efficiency of the engine.

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[78] *Effect of Diesel/methanol compound combustion on Diesel engine combustion and emissions.*

[79] *Trzaskowski, A. Combustion losses of S.I. engine fueled by methanol-gasoline blend. Diploma work under the direction of Professor A. Kowalewicz, Radom Technical University, 1991*

[80] *Sobotowski, R. Przyczyny wzrostu mocy silnikbw o Z.I. msilanych metanolem (Reasons of power increase of S.I. methanol engines). Technika Motoryzacyjna 2, 1979*

[81] *Work done on a methanol-fueled engine at Engines Department, Radom Technical University, 1991 (not published)*

[82] *Hirano, M., et al. Burning velocities of methanol-air-water gaseous mixtures. Combust. Flume, 1981,40, 341-343*

If the fuel system is not modified to the greater amount of methanol fuel needed, engine performance as well as vehicle acceleration and maximum speed are lower.

Emissions of NO, from a methanol-fueled engine is generally lower than when petroleum fuel is used because the maximum temperature of the thermodynamic cycle is lower.

These emissions can be lowered even further, by leaning the mixture, made especially feasible by increasing the methanol content in the blend. Emissions of CO and HC are also lower due to more complete and perfect combustion. High emissions of aldehydes are an inherent feature of methanol combustion. Emission of aldehydes from a methanol-fueled engine is much higher than when petroleum fuel is used, therefore adding the oxidation catalyst is necessary. Emission of particulates from a methanol-fueled engine is much lower than when petroleum fuel is used, because methanol is a pure fuel and burns cleaner (due to the chemical structure of the molecule, which contains atomic oxygen).

In general, under the condition of equal fuel energy consumption (energy supplied to the engine with fuel) the higher the fraction of methanol in petroleum fuel, the higher the engine efficiency[83].

4.1.2 BINARY ALCOHOL BLENDS

The M85 and E85 situations in the U.S. are linked because the technology for the former was easily transplanted to the latter, as discussed by Dr. Nichols[84], who also stated that the original Ford M85 development vehicles could operate on any mixture of gasoline, ethanol and methanol in their fuel tanks.

Blending alcohols into gasoline increase fuel octane and tends to improve engine efficiency.[85] However, vapor pressure can increase markedly and under some situations there can be an increase in particulate number (PN) emissions. However, countermeasures for the disadvantages exist and overall, as far as engine performance and efficiency are concerned, there are improvements as alcohol is blended in.

The most important is the problem of phase separation, which can be solved with solubility improvers or higher alcohol cosolvents added to methanol fuel. Many experiments have been performed in the United States and European countries[86, 87] with the following conclusions:

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[83] *Methanol as a fuel for spark ignition engines: a review and analysis* → *Learn more*

[84] *http://www.setamericafree.org/Rnichols.pdf*

[85] *Methanol as a fuel for internal combustion engines, 2018*

[86] *Pischinger, F. Alcohol fuels for automotive engines. Development of transport fuels. Report RTD 6/3, 1990 (FEV-Motorentechnik, Achen, Germany)*

[87] *Lee, W., Konig, A. and Bernhardt, W. Versuche mit Methanol und Methanol-Benzin-Mischkraftsteffen. Report MTZ 5,1976*

- No modifications and no additives are required for mixtures up to 2–3 % by volume of methanol
- When the content of methanol is higher than 5 % it is necessary to change the materials of some parts of the fuel system
- Fueling with gasoline-methanol blends of up to 15 % methanol (M15) requires only minor modification of the fuel system (mainly enlargement of the fuel nozzles to adjust the air-fuel ratio to the stoichiometric value of the actual blend)

The problem of phase separation of blends does not apply when gasoline and methanol are added separately. Two separate fuel systems are then required. In this case, however, CR may be raised, resulting in higher engine efficiency.

4.1.3 TERNARY ALCOHOL BLENDS

Although gasoline-alcohol blends are usually binary, more than one alcohol can be used simultaneously. An example of this approach is so called ternary blends, which can for example comprise of gasoline, ethanol and methanol (so called GEM blends).

Turner et al.[88, 89, 90] presented such a concept in which the stoichiometric AFR is controlled to be the same as that of conventional E85 alcohol-based fuel. In fact, starting from any binary gasoline-ethanol mixture, a ternary blend of gasoline, ethanol and methanol can be devised in which the fraction of each component is chosen to yield the same stoichiometric AFR (for E85, this is ~9.7–9.8:1 depending on the AFR of the gasoline which can vary somewhat).

It was shown by Turner et al. that all the possible iso-stoichiometric ternary blends starting from a binary blend of gasoline and ethanol are practically invisible for the engine control unit (ECU) of flex-fuel vehicles calibrated to run on any ethanol-gasoline blend up to E85.[91] This opens the possibility to use these ternary blends as drop-in fuels for flex-fuel vehicles without the danger of upsetting the on-board diagnostics of the engine management system. Compared to the gasoline tests on the same vehicles, there was an overall efficiency improvement of approximately 5 % when using the alcohol blends. There have not been problems with cold start tests for gasoline-ethanol-methanol mixtures.

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

[89] Turner J.W.G, Pearson R.J, Bell A. et al. Iso-stoichiometric ternary blends of gasoline, ethanol and methanol: Investigations into exhaust emissions, blend properties and octane numbers. SAE paper no. 2012-01-1586; 2012a

[90] Turner JWG, Pearson RJ, Dekker E, et al. Extending the role of alcohols as transport fuels using iso-stoichiometric ternary blends of gasoline, ethanol and methanol. Appl Energy 2013; 102 :72–86

[91] Turner J, Pearson R, Purvis R. et al. GEM ternary blends: Removing the biomass limit by using iso-stoichiometric mixtures of gasoline, ethanol and methanol. SAE paper no. 2011-24-0113; 2011b

4.1.4 M15

M15 is the blending of gasoline with 15 vol. % of methanol. It has been extensively investigated globally with several in-field vehicle fleet trials comprising large numbers of vehicles and significant laboratory research over the past 35 years. M15 fuel blends do not carry a significant loss of performance and require little modification in the fuel system materials used in the vehicle fleets.

Although commercial interest in M15 fuel blending declined globally in the mid-1980s, when the price of crude oil collapsed below USD 20 per barrel, the large increase of crude oil prices since 2004 has reestablished commercial interest in M15 fuel use in markets like China, because of very favorable economics. China is the world's largest user of automotive methanol fuel.

In the long term, long distance trials on a modern European gasoline engine ran seamlessly on M15 without any increase in emissions. This was shown on a Fiat 500 MTA FIRE 1.2 8V Euro 6 with a stop-start system. The trials also revealed that the car could run on gasoline with up to 20 % vol. methanol.[92]

4.1.5 M85

Flex-fuel vehicles, which have been widely used in Sweden, Brazil and the U.S., are designed to run on 85 %vol. ethanol (E85). For these vehicles a natural starting point would be M56, M85 or M100. The equivalent methanol blend, which gives the same AFR as E85, is M56. This blend is presently undergoing tests by IEA-Advanced Motor Fuels (AMF)[93] Annex 54 "GDI Engines and Alcohol Fuels". An earlier study from the university of Luleå showed that current E85-cars run just fine on M56. M56 has a bio energy percentage of 38.4 %. Original fuel injectors adapted to E85/M56 are available for certain car models, e.g. Ford F-150, which, however, is not usual on the European market. For M56 the vapor pressure would be a bit higher than neat gasoline, but M85 would have a lower vapor pressure than neat gasoline.[94]

Gasoline cars can also be modified to run on M85. It is quite probable that many car models can be programmed through the on board diagnostic (OBD)-connector, also known as ECU flashing. Swiss company Flashtec SA offers this kind of service.[95]

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[92] http://danskbiomethanol.dk/Papers/Report%20DK.pdf ⟶ Learn more

[93] IEA-AMF is a technology collaboration program on Advanced Motor Fuels of the International Energy Agency

[94] http://danskbiomethanol.dk/Papers/Report%20DK.pdf ⟶ Learn more

[95] http://danskbiomethanol.dk/Papers/Report%20DK.pdf ⟶ Learn more

4.1.6 M100

It is also possible to use neat methanol M100, but this can result in cold-starting issues because the vapor pressure is far too low for cold winters. It may be that cold-starting issues are eliminated on newer vehicles with direct fuel injection but this remains to be verified.[96]

M100 can be used as hydrogen carrier for fuel cells which can be used as electric vehicle range extenders.

THERE IS CURRENTLY A GROWING INTEREST IN METHANOL AS AN ALTERNATIVE FUEL IN THE MARINE SECTOR.

4.2 METHANOL AS A FUEL FOR SHIPPING

There is currently a growing interest in methanol as an alternative fuel in the marine sector. The main reason for this is tightening emissions legislation. For ocean-going vessels, the International Maritime Organization (IMO) has introduced Tier 3 NO_X emission regulations, applicable in the so-called Emission Control Areas (ECAs), e.g. densely populated coastal areas. The allowable sulfur content of marine fuels is also coming down. This has led to several technologies being introduced to meet the more stringent regulations. Next to technologies that allow the continued use of heavy fuel oils (HFO) such as aftertreatment systems, alternative fuels are also gaining traction. Initially, the focus was mostly on liquefied natural gas (LNG). However, making provisions for a liquefied gas storage system has substantial effects on ship design or retrofits. For many applications, methanol is an easier fuel to handle as it is liquid at atmospheric conditions. It can also be made from natural gas. A recent technical report from the EU's Joint Research Centre concluded that LNG and methanol seem to be the most promising alternative fuels for shipping at the moment[97]. This is partly based on methanol's availability in most large ports.

A number of demonstration projects have been looking into methanol use for shipping. The most notable ones are the Stena Germanica 1,500 passenger ferry conversion[98] and the Waterfront Shipping 50,000 deadweight tonnage methanol tanker vessels[99], both demonstrating vessels operating on methanol. In the case of the Stena Germanica, medium-speed, four-stroke marine diesel engines were upgraded by Wärtsilä with injectors allowing the (separate) direct injection of methanol and pilot fuel (marine gasoil, MGO). The Waterfront Shipping tankers run with MAN (Maschinenfabrik Augsburg-Nürnberg) low-speed two-stroke engines, again using separate direct injection of methanol and pilot fuel (MGO or HFO). Measurement data from these engines are limited to the few results presented by the manufacturers showing compliance with emission regulations and reporting efficiencies to be in line with the efficiency on diesel fuel.

TABLE 1: LIST OF PROJECTS INVOLVING THE USE OF METHANOL AS MARINE FUEL

PROJECT NAME	DATES	PROJECT TYPE, COORDINATOR	FUELS TESTED	SHIP TYPES
Methapu Validation of renewable methanol based auxiliary power system for commercial vessels	2006–2009	Prototype EU FP6 Project, coordinated by Wärtsilä, Finland	Methanol in sold oxide fuel cell	Car carrier (PCTC)
Effship Efficient shipping with low emissions	2009–2013	Primarily paper study with some laboratory testing, coordinated by SSPA Sweden AB and ScandiNAOS	Methanol in laboratory trials, other fuels discussed in desk studies	General to most ship types, with case examples of short-sea ro-ro vessel and a Panamax tanker
Spireth Alcohol (spirits) and ethers as marine fuel	2011–2014	Laboratory testing, on-board testing (DME converted from methanol) with an auxiliary diesel engine, coordinated by SSPA Sweden AB and ScandiNAOS	Methanol in a converted main engine (in a lab) DME (converted from methanol on-board) in an auxiliary engine	Passenger Ferry (RoPax)
Methanol: The marine fuel of the future (also referred to as "Pilot Methanol by Zero Vision Tool")	2013–2015	Conversion of main engines and testing on-board, project coordinated by Stena AB	Methanol	RoPax ferry Stena Germanica

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[96] *http://danskbiomethanol.dk/Papers/Report%20DK.pdf* → Learn more

[97] *Moirangthem K, Baxter D. Alternative fuels for marine and inland waterways: An exploratory study. Tech. Rep. Publications Office of the European Union; 2016*

[98] *https://www.stenalinefreight.com/news/Methanol-project* → Learn more

[99] *https://www.wfs- cl.com/news/2017/04/methanol- fueled- vessels- mark- one- year- safe- reliable- and- efficient- operations* → Learn more

PROJECT NAME	DATES	PROJECT TYPE, COORDINATOR	FUELS TESTED	SHIP TYPES
MethaShip	2014–2018	Design study coordinated by Meyer Werft	Methanol and DME	Cruise vessel, RoPax
Waterfront Shipping Tanker newbuilding projects	2013–2016	Commercial ship construction	Methanol (dual fuel engines)	Chemical tankers
LeanShips Low energy and near to zero emissions ships	2015–2019	Horizon 2020 project with 8 demonstrators (1 methanol) coordinated by DAMEN	Methanol, LNG, and conventional	2 cases: Small waterplane area twin hull and trailing suction hopper dredger
proFLASH	2015	Study of the effects of methanol and LNG properties on fire detection and extinguishing systems, coordinated by SP Technical Research Institute of Sweden	Methanol and LNG	All
Summeth Sustainable marine methanol	2015	MARTEC II project coordinated by SSPA, focused on smaller marine engines	Methanol (laboratory engine tests)	Road ferry

Source: Study on the use of ethyl and methyl alcohol as alternative fuels in shipping, European Marine Safety Agency, 2016

In addition to work in public funded projects specifically directed at shipping, there has also been work carried out by engine manufacturers on the use of alcohol fuels in engines. Table 2 lists some examples of engines developed for methanol or ethanol that have been used in "real-world" applications.

TABLE 2: DIESEL CYCLE ENGINE OPERATION INVOLVING METHANOL AND ETHANOL FUELS.

ENGINE MANUFACTURER	FUELS	ENGINE SPEED AND TYPe	ENGINE MODEL	COMMENT
Wärtsilä	Dual fuel methanol and MGO	Medium speed four-stroke marine main engine, pilot ignition	Retrofit kit for Wärtsilä-Sulzer 8 cylinder Z40S	Installed on the ropax ferry Stena Germanica in 2015
MAN Diesel & Turbo	Dual fuel – Conventional fuel together with low flashpoint liquids methanol, ethanol, LPG, gasoline or DME possible	Slow speed two-stroke marine main engine, pilot ignition	ME-LGI series introduced 2013 New production engine	Methanol dual fuel engines installed on chemical tankers to be delivered in 2016
Scania	Ethanol 95 % with additives	High speed 9-liter diesel engine for use in trucks and buses	Scania ED9 Production engine	Scania ethanol engines have been used on public transit buses for many years (first operation in 1985)
Caterpillar	Methanol 100 %	High speed 4-stroke engine, 261 kW, adapted with "glow plug" ignition, used in long-haul trucks	Adapted Caterpillar 3406 DITA Engines (retrofit for test study)	More than 5000 hours operation in a test project in long-haul trucks in 1987-1988

Source: Study on the use of ethyl and methyl alcohol as alternative fuels in shipping, European Marine Safety Agency, 2016

Although results have been good, the limited experience with methanol on ships may be perceived as a barrier. Additional projects and longer term operational experience should help build confidence and acceptance of this fuel.

Regarding ship board installations for fuel storage and transfer, considerations need to be given to material choices due to higher corrosivity of methanol and ethanol as compared to conventional fuels. Both methanol and ethanol have an energy density that is approximately half that of conventional fuels. This requires larger storage volumes or more frequent bunkering and could be a barrier for some ship applications. In the case of the Stena Germanica conversion, existing ballast tanks were converted into methanol fuel storage.[100]

In tests of methanol fuel in marine diesel engines, emissions of nitrogen oxides and particulates have been very low and, being sulfur-free, methanol does not produce sulfur oxide emissions. Nitrogen oxide levels are low, in line with Tier III NO_x emissions (2–4 g/kWh).[101]

To make a fuel attractive for shipping, there must be an adequate infrastructure that covers a large number of ports. Bunkering of ships can be carried out by bunkering vessels, as well as from land, and for both solutions there is a need for terminals that provide fuel. Currently, bunkering of methanol fueled ships is performed by truck[102]. The trucks deliver the methanol to a bunkering facility with pumps built in containers on the quay next to the ferry. This is a solution that is flexible and easy to build. The first of these fueling facilities has been in service since April 2015.

METHANOL IS NOT SUITABLE FOR USE AS A JET FUEL FOR SEVERAL REASONS. ITS ENERGY DENSITY AND SPECIFIC ENERGY DENSITY ARE TOO LOW.

4.3 METHANOL AS A FUEL FOR AVIATION

Methanol is not suitable for use as a jet fuel for several reasons. Its energy density and specific energy density are too low, which means the fuel does not contain sufficient energy for a jet fuel, in either mass or volume terms. The practical implications of these two factors are that the aircraft range would be too short, and even if air-frames were redesigned with significantly larger fuel capacity, their take-off weight would be too high.[103]

Methanol, however, is a pre-stage product to produce renewable aviation fuel with the Power-to-Liquids (PtL) pathway, which produces liquid hydrocarbons based on electric energy, water and CO_2 as resources through methanol synthesis and conversion. The ASTM jet fuel standard for PtL via methanol synthetic fuel is not yet approved.

The production of renewable jet fuel PtL via methanol synthesis and conversion is depicted in the next figure:

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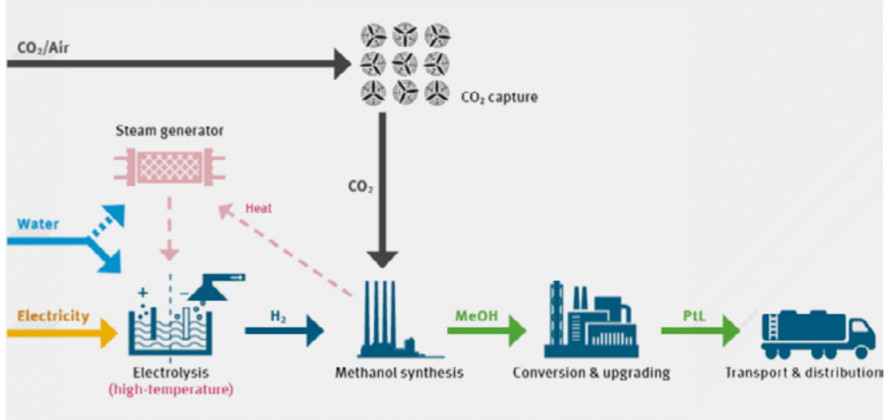
[100] http://www.methanol.org/wp-content/uploads/2016/07/EMSA-Study-on-the-use-of-ethyl-and-methyl-alcohol-as-alternative-fuels-June-2016.pdf → Learn more

[101] http://www.methanol.org/wp-content/uploads/2018/03/FCBI-Methanol-Marine-Fuel-Report-Final-English.pdf → Learn more

[102] Stefenson, 2014

[103] http://www3.imperial.ac.uk/pls/portallive/docs/1/7294712.PDF → Learn more

PTL PRODUCTION VIA METHANOL PATHWAY (HIGH-TEMPERATURE ELECTROLYSIS OPTIONAL)



Source: Power-to-Liquids Potentials and Perspectives for the Future Supply of Renewable Aviation Fuel, German Environment Agency, 2016

Conversion and upgrading of methanol to jet fuel and other hydrocarbons comprises several process steps, notably DME synthesis, olefin synthesis, oligomerization, and hydrotreating.

4.4 FUEL REFORMING USING ENGINE WASTE HEAT

Methanol is a very interesting hydrogen carrier and has therefore also been investigated as an energy vector for powering fuel cell vehicles. The methanol would then be used as fuel, for its convenience (being a liquid), and be reformed on-board to generate hydrogen, or be used directly in a direct-methanol fuel cell (DMFC)[104].

The fact that methanol reforms at a temperature that is low enough to make significant use of low-grade exhaust heat, even at low loads, makes it exceptionally attractive in terms of waste heat recovery on internal combustion engines.

A study by the Massachusetts Institute of Technology (showed that methanol engines in trucks could be 25 % more efficient than diesel engines, with peak efficiencies potentially attaining 55 % to 60 %.[105] These high efficiencies were claimed to be possible using fuel reforming; recovering waste exhaust heat to drive endothermic reactions that convert methanol into syngas with a higher heating value than the methanol. Furthermore, the hydrogen-rich syngas allows much more dilution of the fuel-air charge, lowering peak temperatures and thus heat losses, or mitigating knock and thus enabling even higher CR.

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[104] *Kumar P, Dutta K, Das S, Kundu P. An overview of unsolved deficiencies of direct methanol fuel cell technology: factors and parameters affecting its widespread use. Int J Energy Res 2014; 38 :1367–90*

[105] *Cedrone et al., 2013*

4.5 PRODUCTION OF INDUSTRIAL ELECTRICITY

Methanol can also be used as a substitute for diesel to produce electricity. Most major original equipment manufacturers (OEMs) are capable of supplying and retrofitting equipment with the typical guarantees for power plants to operate on methanol, although they may need adequate lead times. Many OEMs have also demonstrated feasibility and benefits of methanol for power generation through studies and projects.[106]

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[106] *https://adi-analytics.com/2017/09/08/methanol-for-power-generation/ ⟶ Learn more*

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