Annex Report Number 56

**A Report from the Advanced Motor Fuels Technology Collaboration**




# Methanol as Motor Fuel Appendix

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ADVANCED MOTOR FUELS
IEA-AMF
Technology Collaboration Programme on
Advanced Motor Fuels

August 2020

Technology Collaboration Programme
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## Executive Summary

Global warming is a major threat for continuation of humankind as we know it today, and concerted actions are needed in all economic sectors to reduce GHG emissions. Improving energy efficiency of engines is not enough, and thus fossil-free fuels are required to alleviate climate burden especially of the transport sector. The most effective fuels are those with minimum GHG emissions and minimum pollutants along the well-to-wheel (WTW) chain, while compatible with common internal combustion engines and fuel infrastructure. There are many alternative fuel options (e.g. methane, methanol and other hydrocarbons as well as hydrogen) using different resources – mainly renewables – and conversion technologies. Providing renewable fuels for combustion engines does not renounce the need for adaptation of advanced technologies, such as electric powertrains.

In this Annex 56 various aspects of methanol as fuel for the transport sector are reviewed and evaluated: from its production to its application in engines, including advantages and disadvantages. Barriers and an outlook on the potential and possibilities of methanol as motor fuel are given.

Renewable transport fuels such as methanol could become an important solution to combat global warming and air pollution for sectors and regions where the electrification of the powertrain is challenging, e. g. in the shipping sector. The greenhouse gas saving potential of renewable methanol are quite high and the physical properties of methanol support a clean and efficient combustion. Therefore, the operational production capacities have to be strengthened massively to get a perceptible impact of substituting fossil energy carrier in the future. A wide range of resources could be utilized to produce renewable methanol, from bio- and waste-based streams to renewable hydrogen and circular $CO_2$. Methanol as motor fuel was demonstrated in large vehicle fleet during the 1980/90s. Despite technical success methanol was not a commercial success. Recently, there is again an increasing interest on methanol as fuel. Prominent examples are China as largest user of methanol as automotive fuel and Europe where methanol is being considered as marine fuel or to be used in fuel cell electric vehicles.

Internal combustion engines using methanol as a fuel could be further developed for high efficiency to gain maximum energy and pollutant savings. However, if methanol will be applied as automotive fuel with higher blending rates or as pure fuel technical adjustments of the fuel

existing infrastructure are required (e.g. modifications of some fuel-carrying materials, safety measures).

Key findings from the report are summarized as follows:

- **Methanol is a multipurpose fuel** as it could be used straight or as blending component in fuels, for the production of fuel additives (e.g. MTBE, FAME and MTG) or for fuel cell application.
- **Several concepts for internal combustion engines are available for using methanol** in passenger cars, light-duty and heavy-duty engines as well as in ships.
- **Straight methanol burns with very low particle and $NO_X$ emissions** in refitted engines. A further reduction of pollutants could be expected for future high efficiency combustion engines.
- **Methanol could significantly increase the engine efficiency in dedicated engines.** Therefore additional research and development is needed to realize this potential – also from an OEM perspective.
- The existing fuel infrastructure requires no adjustments for low level methanol blends. **For higher methanol blends and straight methanol, the adjustments of the existing fuel infrastructure are well known.** There are consideration needed regarding material compatibility and safety handling.
- **In order to support GHG mitigation in transport, production capacity of sustainable renewable methanol has to increase** from the current level of less than 1 million tonnes per year to cover a part of the transport sector. Today methanol is mainly produced from fossil resources at the global production capacity of about 125 million tonnes.
- **Production costs and GHG reduction potentials of renewable methanol** produced on an industrial scale **can be competitive** to established renewable fuels, if using suitable resources like waste wood and cultivated wood.
- **Supporting elements on strategic, regulatory, technical and communicative level** are of overarching importance like for any alternative fuel in transport.

## Authors

The studies and reports submitted under Annex 56 were carried out and authored by numerous researchers as indicated below.

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## Content

## Context and participants

This summary report is based on five technical reports completed in five countries participating in Annex 56: Methanol as motor fuel, under the Technology Collaboration Programme (TCP) of Advanced Motor Fuels (AMF) of the International Energy Agency (IEA).

Technion (Israel Institute of Technology), VTT and FNR acted as operating agent for the Annex 56 project.

The technical reports and corresponding organizations in charge of the participating countries are as follows:

| | |
|---|---|
| Appendix I: | General issues on methanol as motor fuel (Fachagentur Nachwachsende Rohstoffe e.V. (FNR) and DBFZ Deutsches Biomasseforschungszentrum gemeinnützige GmbH, Germany) [1] |
| Appendix II: | Heavy duty methanol engines (Fachagentur Nachwachsende Rohstoffe e.V. (FNR) and DBFZ Deutsches Biomasseforschungszentrum gemeinnützige GmbH, Germany) [2] |
| Appendix III: | Marine methanol (VTT Technical Research Centre of Finland LTD, Finland) [3] |
| Appendix IV: | High efficiency methanol engines – HEME (Lund University, Sweden) [4] |
| Appendix V: | Methanol as motor fuel – Barriers of commercialization (Danish Technological Institute, Denmark) [5] |

The authors would like to acknowledge the Executive Committee of the IEA-AMF for supporting this Annex and the Methanol Institute for co-funding related to the technical report preparation and dissemination.

# Appendix I: General issues on methanol as motor fuel

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Annex 56

A Report from the Advanced Motor Fuels Technology Collaboration Programme

# Methanol as motor fuel
# Appendix I: General issues on methanol as motor fuel

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(DBFZ Deutsches Biomasseforschungszentrum gemeinnützige GmbH)

June 2020

## Executive summary

Renewable transport fuels such as methanol could become an important solution to combat global warming and air pollution for sectors and regions where the electrification of the powertrain is challenging, e. g. in the shipping sector. The greenhouse gas saving potential of renewable methanol could be quite high. To achieve this goal, the operational production capacities have to be increased massively to get a perceptible impact of substituting fossil energy carrier in the future. A wide range of resources could be utilized to produce renewable methanol, from bio- and waste-based streams to renewable hydrogen and circular $CO_2$. Methanol as motor fuel was demonstrated in large vehicle fleet during the 1980/90s. Despite technical success methanol was not a commercial success. Recently, there is again an increasing interest on methanol as fuel. Prominent examples are China as largest user of methanol as automotive fuel and Europe where methanol is being considered as marine fuel or to be used in fuel cell electric vehicles. Table 1 summarized the reviewed aspects on technology aspects and characteristics of methanol.

Table 1 Tabular summary of general issues on methanol as motor fuel

| Aspects | Description [1–3] |
|---|---|
| Conversion technologies | Fossil: Pretreatment, synthesis gas production (usually steam reforming of natural gas or coal gasification), synthesis gas conditioning, methanol synthesis, product treatment (distillation)<br>Renewable: Biomass pretreatment, synthesis gas production (steam reforming of biogas/biomethane, gasification of solid biomass or intermediates such as pyrolysis slurry, biochar, water electrolysis, carbon dioxide capture), synthesis gas conditioning, methanol synthesis, product treatment (distillation) |
| R&D needs<br>(conversion technologies) | Improve synthesis efficiency esp. for biomass and power as resources (catalyst improvement, operational modes, efficiency increase), methanol as base for different other product synthesis, carbon dioxide capture and storage (CCS), carbon capture and utilization (CCU), methanol-to-gasoline synthesis |
| Raw materials / resources | Fossil: Natural gas, coal, lignite, heavy petroleum fractions, peat<br>Renewable: wood (industrial lumber, waste wood, short rotation forestry), black liquor, stalk biomass (straw, triticale, miscanthus), biogas, sewage sludge, municipal solid waste, water, (renewable) carbon dioxide, renewable power |
| Production capacity | Fossil: 125 million tons in 2016<br>Renewable: < 1 million tons in 2019 (e.g. Enerkem-plant in Canada, CRI-plant in Island) |
| Production demand | Global demand of 85 million tons in 2016 |
| Area of application | Chemical intermediate for formaldehyde, acetic acid, methanol-to-olefins and other chemical intermediates<br>Energy carrier for pure methanol (fuel blending and pure), methyl tert-butyl ether (MTBE), dimethyl ether (DME), methanol-to-gasoline (MTG) and biodiesel (FAME) |
| Technology Readiness Level (TRL) and Fuel Readiness Level (FRL) | Fossil: TRL 9 / FRL 9<br>Renewable: TRL 3 to 9 / FRL 8 |
| GHG emissions | Fossil : 91 to 262 g $CO_2$-eq/MJ (fossil fuel comparator according RED II: 94 g $CO_2$-eq $MJ^{-1}$)<br>Renewable: 3 to 69 g $CO_2$-eq $MJ^{-1}$ |
| Fuel production costs<br>(normalized to 2018) | Fossil: 17.3 to 19.4 EUR $GJ^{-1}$* (* market price 2018/2019)<br>Renewable: 20 to 87.3 EUR $GJ^{-1}$ |
| Fuel standards | ASTM D4814 (M2.75)<br>EN 228 (M3)<br>SI 90 (M15)<br>IS 17076:2019 (M15)<br>ASTM D5797 (M85)<br>GB/T 23510-2009 (M100)<br>GB/T 23799-2009 (M85) |
| Compatibility of engines | M56 or GEM fuels in flex fuel vehicles/engines; |

| Aspects | Description [1–3] |
|---|---|
| | M3 to M15 compatible with conventional spark ignition engines;<br>M85, M100, MD95, MED95 adopted engines necessary |
| Compatibility of infrastructure | Distribution infrastructure existing, further expansion depending on area of application (ship versus road vehicle) necessary |
| Safety information (GHS) | <br>Signal word: Danger<br>Hazards: H225, H301+H311+H331, H370<br>Precautionary: P210, P270, P280, P303+P361+P353, P304+P340, P308+P311 |
| R&D needs<br>(fuel application) | Improvements in combustion technology, fuel standardization (esp. with high methanol content), development in local infrastructure (sea port, road) |

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## Acknowledgement

The project was carried out on behalf of the Fachagentur Nachwachsende Rohstoffe e.V. (FNR). It was supported by the Federal Ministry of Food and Agriculture (BMEL) on the basis of a resolution of the German Bundestag (funding no. 19NR005).

With support from

Federal Ministry of Food and Agriculture

by decision of the German Bundestag

# Contents

## Abbreviations

| | |
|---|---|
| CCS | Carbon Capture and Storage |
| CCU | Carbon capture and utilization |
| CLP | European regulation on classification, labelling and packaging of chemicals (Regulation (EC) 1272/2008) |
| DC | Direct current |
| DME | Dimethyl ether |
| EC | European council |
| FAME | Fatty acid methyl ester |
| FFV | Flex fuel vehicle |
| FRL | Fuel readiness level |
| GHG | Greenhouse gas |
| GHS | Globally harmonized system |
| M100 | SI-fuel with 100 vol% methanol |
| M15 | SI-fuel with 15 vol% methanol |
| M3 | SI-fuel with 3 vol% methanol |
| M56 | SI-fuel with 56 vol% methanol |
| M85 | SI-fuel with 85 vol% methanol |
| MD95 | CI-fuel with 95 vol% methanol |
| MED95 | CI-fuel with 95 vol% methanol-ethanol-mixture |
| MMA | Methyl methacrylate |
| MSW | Municipal solid waste |
| MTA | Methanol-to-aromatics |
| MTBE | Methyl tert-butyl ether |
| MTG | Methanol-to-gasoline |
| MTO | Methanol-to-olefins |
| PET | Polyethylene terephthalate |
| R&D | Research and development |
| REACH | European regulation on registration, evaluation, authorization and restriction of chemicals (Regulation (EC) 1907/2006) |
| RED II | European renewable energy directive (Directive (EU) 2018/2001) |
| SynBioPtX | Synergies of biomass-based and electricity-based fuels and product processes |
| TRL | Technical readiness level |

# 1. Historical aspects

## 1.1. Production

Historically, methanol was produced by pyrolysis of wood. The first industrial scale methanol plant started production in 1923 and was developed by BASF in Leuna (Germany). The developed high-pressure methanol synthesis converted a coal based synthesis gas of hydrogen and carbon monoxide at a zinc chromate catalyst, at pressures above 300 bar and temperatures of about 300 to 400 °C. The first modern low-pressure methanol synthesis was developed by Imperial Chemical Industries (ICI) in the 1960s. This synthesis used natural gas as resources and a copper, zinc and chromium catalyst at a pressure of 30 to 120 bar and a temperature of 200 to 300 °C. Nowadays, the main syntheses are comparable to the developments in the 1960s and 1970s with further optimization in the synthesis process as well as in the used catalysts. Modern methanol plants have a capacity of 5,000 tones methanol per day (5,000 MTPD). For example, China, as one of the main producers and end user of methanol as motor fuel, uses typically its low-cost coal as resources for methanol production in order to become more independent of crude oil imports in terms of energy supply [3,4].

## 1.2. Use as motor fuel

After use of methanol as motor fuel during the World Wars due to gasoline shortages in Germany and France, methanol as motor fuel received attention again during the oil crises of the 1970s [5]. Small vehicle fleet trials of methanol-blended gasoline were done in Germany in mid-1970's [3]. Larger fleet trials were conducted in Germany, Sweden, New Zealand and China in the late 1970s and early 1980s. The interest on methanol as alternative fuel and also octane booster when lead was banned in gasoline resulted in several programs during 1980 to 1990, mainly in the California (USA). In the late 1980s Volkswagen developed FFV and in the 1990s participated in the test program in California as well with about 100 vehicles. A consortia with Volkswagen (Germany), FEV (Germany) and EPA (USA) presented a M100 (pure methanol) engine concept. [6] By the mid-1990s, over 21,000 methanol M85 flexible fuel vehicles (FFV) capable of operating on methanol or gasoline were used in the U.S. with approximately 15,000 of these in California, which had over 100 refueling stations [7]. While the methanol FFV program was a technical success, rising methanol pricing in the mid- to late-1990s during a period of slumping gasoline pump prices diminished interest in methanol fuels. Moreover, ethanol as fuel received more relevance on the market. The methanol program in California ended in 2005. Automobile industry (e.g. Ford, Chrysler and GM, Volkswagen) stopped building methanol FFVs by the late-1990s, switching their attention to ethanol-fueled vehicles. High performance experiences with methanol as automotive fuel has been obtained in racing (e.g. in the U.S. USAC Indy car competition starting in 1965 and CART circuit from 1979 to 2007 as well as in Europe [7]).

Low levels of methanol (M3) were blended in gasoline fuels and were sold in Europe mainly during the 1980s and early-1990s.

Nowadays, methanol is used as fuel mainly in Chinese road transport (M15, M30, M85 and M100) and in the shipping sector (e.g. Stena Line, Methanex vessels). [8,9]

# 2. Conversion technologies

The production of methanol can be subdivided into the steps of (i) synthesis gas production, (ii) crude methanol synthesis and (iii) product purification (**Fehler! Verweisquelle konnte nicht gefunden werden.**).

The synthesis gas is obtained from a variety of fossil and renewable resources such as natural gas, coal and lignite, municipal solid waste, lignocellulose, biogas or or using electricity for hydrogen electrolysis. Currently, methanol is mainly produced of natural gas and coal. Conventional processes for synthesis gas production are autothermal reforming and gasification. Other conversion technologies like anaerobic fermentation and electrolysis can be brought into focus, if using renewable raw materials [3].

A distinction is made between three different catalytic processes in the industrial methanol synthesis. The initially developed high-pressure process worked due to the low catalyst activity and the volume contraction of the reaction at pressures of 250 to 350 bar and temperatures of 360 to 380 °C. The medium-pressure process operates at 100 to 250 bar and 220 to 300 °C, the low-pressure process at 50 to 100 bar and 200 to 300 °C. Each method works with specific catalysts and mass ratios of carbon monoxide and carbon dioxide to hydrogen. Decisive criteria for the selection of the method are investment costs, efficiency, energy requirement and the supply of carbon monoxide and carbon dioxide. [3,10]

At the end of the methanol production, the distillation of crude methanol removes byproducts such as water, ethanol and dimethyl ether [3,10]. Further information on raw materials and conversion technologies for methanol production as described below can be found e.g. in Bertau et al. [3].

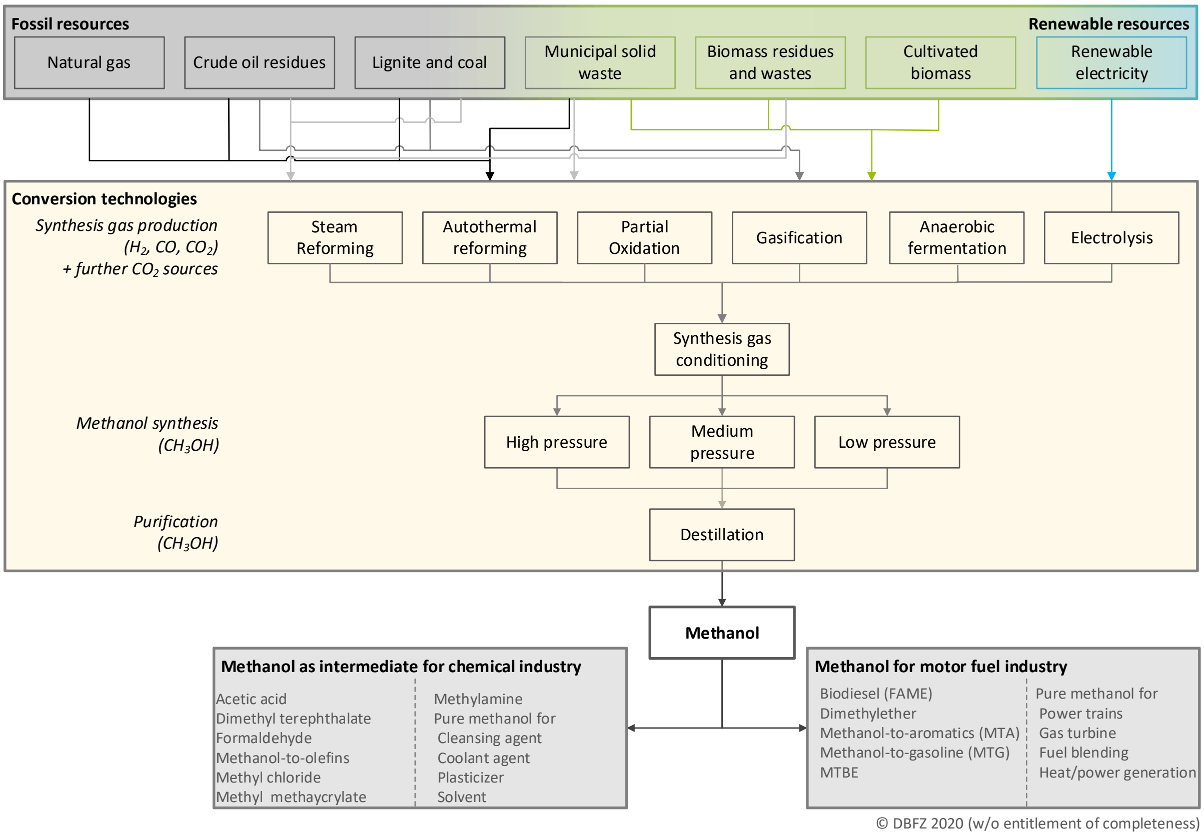


Figure 1 Resources, conversion technology and application of methanol [1,3]

## 2.1. Raw materials and resources

Economic methanol synthesis requires cheap synthesis gas. The costs of synthesis gas are mainly driven by the quality, quantity, mining, preparation and transport of the used resources (global parameters) as well as taxation and government regulations of renewable resources (local parameters). While today methanol is produced mainly from natural gas and coal, especially the range of renewable raw materials will increase in the future in order to enable decarbonization.

*Natural gas*. Natural gas production is increasing due to new drilling and hydrofracking technologies to open up previously unrecorded reserves. This leads to a cost reduction for natural gas and increasing displacement of coal as a raw material in non-renewable methanol production [2]. In addition to conventional natural gas, shale gas, tight gas (e.g. oil sand) and coal-bed methane are also used [3].

*Coal and lignite.* Largest fossil reserves are available on coal. Due to the available reserves, even global distribution and geopolitical crises, coal will continue to be a low-budget energy and carbon source in the future [11]. However, for methanol production, coal is increasingly becoming too expensive as a raw material due to the more complex preparation for gasification. Methanol as a by-product of a complex coal-to-power or coal-to-chemical plant could be more reasonable economically [3]. At the same time, high ecological risks are increasingly being counteracted [11].

*Crude oil residues and heavy oil.* Crude oil residues such as vacuum residues and petroleum coke are generated in oil refineries, characterized by a high sulphur content and are available in liquid as well as solid form. They are commonly used as fuel for industrial heat generation. If sulphur content gets critically, an alternative use as resource for chemicals is possible [3].

*Lignocellulosic biomass.* Wood, woody residues, stalk material and other lignocellulosic biomass appears to be attractive resources for renewable methanol production [12]. Wood is one of the most available renewable resources in world and typically used as firewood, but it gets more and more in focus to other applications. As dried biomass, it can be gasified and conditioned to synthesis gas for methanol synthesis, heat and power generation [3,12].

*Biogas.* Wet biomass such as energy crops, silage, manure, sludge and waste/residuals can be fermented in a biogas plant to synthesis gas with water, methane, carbon monoxide, carbon dioxide and hydrogen content. Usually this gas mixture is used for heat and power generation or for pure methane production. However, there also exist concepts, where a part of the $CH_4/CO_2$ gas mixture is channeled off and synthesized in combination with water vapor to methanol [3,13].

*Municipal solid waste and sewage sludge.* The daily available volume of waste and sludge in industrial countries is very high. With treatment technologies adapted to the specific raw material, these energy sources can also be converted via gasification into a synthesis gas. Comparable to lignocellulosic biomass and biogas, the treatment and the supply/transportation of the biomass is a bottle neck of economic application [3].

*Renewable electricity and (renewable carbon).* Renewable electricity (solar, wind and geothermal) and recycled (renewable) carbon dioxide (industry or environment) can be used as resources for a renewable methanol production. The renewable electricity is converted into hydrogen via electrolysis [14,15].

## 2.2. Synthesis gas production

Synthesis gas conversion for methanol production is mainly conducted by steam reforming or partial oxidation of natural gas and autothermal gasification of coal today. Considering the use of renewable resources, a combination of different raw materials and conversion technologies is possible, if using a wide range of resources. For example, a combination of biomass and renewable power as well as electrolysis and gasification or fermentation leads to a SynBioPtX product [16]. The focus of all technologies is to provide hydrogen, carbon dioxide and carbon monoxide as starting substances for downstream methanol synthesis [1,3]. The description of the different processes comes from Bertau et al. [3].

*Steam reforming.* Steam reforming is established large-scale processes for the production of synthesis gas from carbonaceous energy sources and water. Natural gas is mainly used as raw material. Other suitable raw materials are crude oil residues, biogas or biomass. The steam reforming process is characterized by preheated methane (hydrocarbon) to initiate the endothermic steam reforming reaction. The following water-gas shift reaction and the carbon formation allow an optimization of the synthesis gas composition.

Steam reforming reaction: $C_mH_n + m\,H_2O \leftrightarrow m\,CO + (m + n/2)\,H_2$

Water gas shift reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$

Carbon formation: $2\,CO \leftrightarrow CO_2 + C$

*Partial oxidation.* A sub-stoichometric fuel-air mixture is partially (exothermic) combusted to produce a hydrogen-rich synthesis gas. The process can be carried out purely thermally at high temperatures (1,200 °C and more) and pressures (30 bar and more) or catalytically at comparatively lower temperatures (800 to 900 °C) and atmospheric pressure. The choice of technique depends on the sulfur content of the fuel used. Low sulfur content allow the use of catalysts and avoid catalyst poisoning. The disadvantage of this technology is the production of hydrogen exclusively from the used fuel and not water.

Partial oxidation reaction: $2\,C_mH_n + m\,O_2 \leftrightarrow 2m\,CO + n\,H_2$

*Autothermal reforming (oxidative steam reforming).* Autothermal reforming is a combination of steam reforming and partial oxidation to optimize the efficiency of the synthesis gas conversion. The two processes are combined in such way that the advantage of oxidation (provision of thermal energy) with the advantage of steam reforming (higher hydrogen yield) optimally complements. Example of large-scale process: Lurgi-combined reforming process.

Autothermal reforming reaction: $4\,C_mH_n + 2m\,H_2O + m\,O_2 \leftrightarrow 4m\,CO + (2m + 2n)\,H_2$

*Gasification.* Gasification is carried out as an autothermal process with water vapor and air as if using a sulfur rich resource such as coal/lignite. Energy for the endothermic water gas reaction is supplied by the combustion of coal or biomass. The desired carbon monoxide to hydrogen ratio is adjusted by the water gas shift reaction. Depending on the type of resource to be processed, various gasification techniques are established. Commonly known process techniques are e.g. fluidized bed gasification for lignite, peat and biomass, fixed-bed gasification for coal, lignite and biomass and entrained flow gasification for coal, petroleum coke and biomass [3]. Biomethanol production is based on a process path similar to the production of methanol from fossil fuels. Due to partly inhomogeneous properties of biomass, synthesis gas production is more complex. It usually consists of two process steps - biomass pretreatment and gasification. Biomass pretreatment is mainly focused on the adaptation of biomass to requirements of entry system of the gasification process and on biomass drying. In addition to market-ready mechanical processes for adjusting the biomass (e.g. hackers) and thermal processes for fuel drying (e.g. belt dryers), thermochemical processes (pyrolysis and torrefaction) for fuel homogenization are currently also under development. The Enerkem plant in Canada is working with this technology [3,17].

Gasification of carbon: $C + H_2O \leftrightarrow CO + H_2$

$$C + O_2 \leftrightarrow CO_2$$

$$2\,C + O_2 \leftrightarrow 2\,CO$$

$$C + CO_2 \leftrightarrow 2\,CO$$

*Anaerobic fermentation.* Anaerobic fermentation of biomass generates biogas, a product consisting of methane, carbon dioxide and diverse by-products such as hydrogen, hydrogen sulfide, ammonia, nitrogen and oxygen. Biogas results through the natural process of microbial degradation of organic substances under anoxic conditions (absence of oxygen). Biogas process consists of several stages, each of which is carried out by microorganisms of different metabolic types. Polymeric components of the biomass (e.g. cellulose, lignin or proteins) are first converted into monomeric (low molecular weight) substances by microbial exoenzymes. Low-molecular substances are broken down by fermenting microorganisms to alcohols, organic acids, carbon dioxide and hydrogen. Alcohols and organic acids are converted into acetic acid and hydrogen by acetogenic bacteria. In the final stage, the end products methane and water are formed from carbon dioxide, hydrogen and acetic acid with the help of methanogenic archaea. If using biogas for methanol production, the separated biomethane or the pure biogas are processed via reformer to synthesis gas. The concept of BioMCN plant in The Netherlands is designed with this technology, but still working with natural gas and $CO_2$ certificates [17–19].

*Electrolysis.* Water electrolysis is the decomposition of water into hydrogen and oxygen gas due to the passage of an (renewable) electric current. A DC electrical power source is connected to two electrodes, or two plates which are placed in the water. Hydrogen will appear at the cathode (where electrons enter the water), and oxygen will appear at the anode. If using electrolysis for hydrogen generation, the carbon dioxides of the synthesis gas have to be provided by carbon dioxide capture of $CO_2$ emitting industry, atmosphere or biogas plants [3,20]. The CRI plant in Iceland is working with this power based technology (geothermal energy for power supply) [17].

Water electrolysis reaction: $2\,H_2O \rightarrow 2\,H_2 + O_2$

## 2.3. Crude methanol production

The processes for producing methanol from synthesis gas are classified according to the reaction pressure of the methanol synthesis. There are three different pressure ranges: A high-pressure process operates at pressures of 250 to 350 bar and temperature of 360 to 380 °C. This process was historically the first industrial scale process, but it is not used anymore, because of high operating costs. A medium pressure method uses a pressure of 100 to 250 bar at a temperature range from 220 to 300 °C, whilst a low pressure method is carried out at a pressure of 50 to 100 bar and temperatures between 200 and 300 °C. Each process works with specific catalysts and carbon monoxide/dioxide to hydrogen ratios. Commonly, methanol is produced industrially from synthesis gas in the low or medium pressure process, nowadays. The resulting crude methanol is partly contaminated with by-products such as DME and higher alcohols [3]. Reactions that are involved in a methanol synthesis are:

Methanol synthesis: $CO + 2\,H_2 \leftrightarrow CH_3OH$

$$CO_2 + 3\,H_2 \leftrightarrow CH_3OH + H_2O$$

Both reactions are under pressure exothermic and are accompanied by a decrease in volume. If necessary, the $CO/CO_2$ ratio can be optimized by the water gas shift reaction.

There have been established several process designs in the last six decades. Commercial designs are fox example Johnson Matthey/Davy process, three Lurgi process design (conventional, MegaMethanol and GigaMethanol), Holder Topsøe process and the Mitsubishi Heavy Industry process.

### 2.4. Product treatment

Depending on catalysts and operating conditions, a methanol synthesis produces different by-products such as DME and higher alcohols. In addition, the product contains also water vapor and unreacted synthesis gas. The purity of raw methanol my sufficient for combustion in internal combustion engines. [3,21] For further processing in the chemical industry, methanol must be treated by distillation. Low boiling components such as dimethyl ether are separated in a low boiler column. Higher-boiling fractions are separated as bottoms in a further distillation stage in a high boiler column, with methanol being withdrawn overhead. The by-products are being recycled as far as possible into the process or will continue to be used in other applications of the chemical industry [3,22]. At the end of this process, the product can be used as pure methanol or as chemical intermediate.

## 3. Area of applications

As shown in Figure 1, there is a wide range of application for methanol as chemical intermediate as well as energy carrier.

Primary chemical derivatives of methanol including:

*Formaldehyde.* Due to its reactivity, it is an important molecule for global industry (textiles, construction, chemical, wood processing and carpeting) and used as disinfectant, preservative and chemical. It is itself an intermediate for other products such as resins, lubricants, thermoplastics or sealants. Formaldehyde is produced industrially by oxidative dehydrogenation of methanol or methanol oxidation.

*Acetic acid.* Acetic acid is used in the food industry, pharmaceutical industry and as an intermediate for products such as polymers. Industrial production of acetic acid is via methanol carbonylation.

*Methylamine.* Methylamine is an important intermediate in the chemical and processing industries. It is used for the synthesis of pharmaceuticals, solvents, herbicides and pesticides. It is produced from methanol and ammonia.

*Methyl chloride (Chloromethane).* Large scale use is for production of organosilicon compounds. It is produced from methanol, sulfuric acid and sodium chloride.

*Dimethyl terephthalate.* DMT is used in the production of polyesters such as polyethylene terephthalate (PET). It is synthesized according to series of different liquid-phase oxidation and esterification processes.

*Methyl methacrylate.* MMA is the intermediate for polymethyl methacrylate (acrylic glass). There are several processes industrialized for MMA production (e.g. direct oxidation process, direct oxidation esterification process).

*Methanol-to-olefins.* In the MTO process, the methanol is converted to olefins such as ethylene and propylene. These olefins can be reacted to produce polyolefins, which are used to make many plastic materials.

Methanol and methanol-based energy carriers in fuel industry are:

Pure *methanol* for fuel blending. It is used in passenger, light duty, heavy duty and marine vehicles as substitute for gasoline and diesel fuel. Common blending rates are M15 (15 vol.-% methanol in gasoline), M56, M85, M100, MD95 (95 vol.-% methanol in diesel) and MED95 (95 vol.-% methanol and ethanol in diesel).

Pure *methanol* is also used as energy carrier for heat and power generators, gas turbines and direct methanol fuel cells.

*Methyl tert-butyl ether.* MTBE is used as anti-knocking agent in gasoline fuel (and solvent in chemical industry). It is produced by the reaction of methanol and isobutene.

*Dimethyl ether.* DME can be used as fuel substitute for diesel and LPG application (liquefied petroleum gas). DME is also used for propellant, refrigerant and as intermediate for alkene production via MTO-process. DME is a byproduct of the methanol synthesis.

*Methanol-to-gasoline.* MTG is a process to produce a high-octane gasoline from methanol or dimethyl ether by catalytic reaction on a zeolite catalyst.

*Biodiesel (FAME).* Methanol is used for transesterification of oil and fat containing biomass in biodiesel production.

## 4. Overview on methanol market

The production capacity (125 million tons or 2.4 EJ in 2016) as well as the demand (85 million tons or 1.7 EJ in 2016) of methanol have risen rapidly in the past years (Figure 2). Sixty percent of global methanol demand are used as intermediate in chemical industry. The other forty percent are used as energy carrier in fuel industry. A further increase is to be expected in the coming years. The expected increases of 10% to 20% per year are such asly to be driven by Chinese demand (China plans to reduce dependency from crude oil) and the continuously increasing energy demand in transport and power supply. In 2016, products from the MTO process as well as pure methanol and MTBE for fuel blending were already the second, third and fourth largest quantity sector for methanol. Global top producer are BASF, Methanex, Methanol Holding (Trinidad) Limited (MHTL/SCC), Saudi Basic Industries Corporation (SABIC), Mitsui, Mitsubishi Gas Chemical (MGC) and Zagros Petrochemical. [2,3,23,24] The German production volume is about 1.1 million tones methanol per year [25].

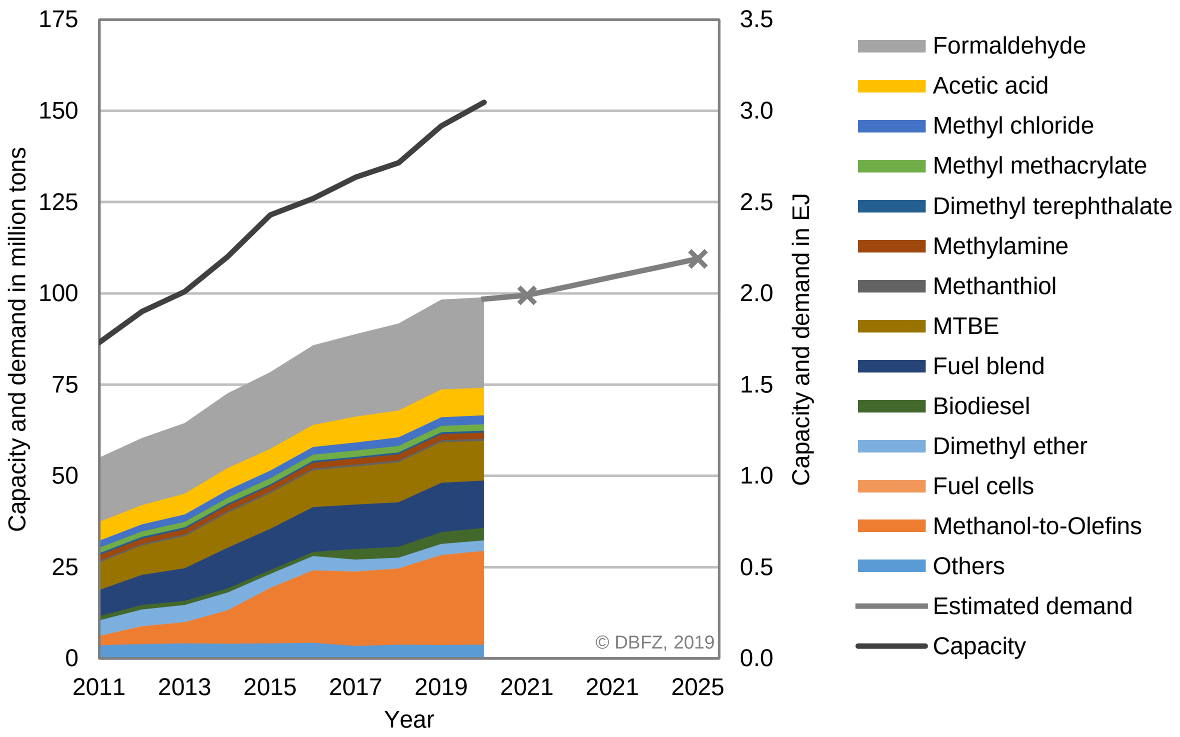


Figure 2 Capacity and demand of methanol (DBFZ based on [2,3,23,26])

Regardless, the methanol quantities annual available could only substitute a small proportion of the world's final energy consumption in the transport sector (120 EJ in 2020) and this methanol is mainly produced from fossil resources. [27] Assuming for instance that M3 in gasoline will be implemented across the European Union (approximately 80 million tons gasoline in 2018), about 2.5 million tons of methanol would be required [28].

Methanol producers are usually located in regions where natural gas or coal is increasingly being mined or an excellent infrastructure of natural gas or coal supply is available. As renewable methanol production capacities increase, other regions will be able to establish themselves - regardless of the available coal and natural gas reserves. A list of plants producing renewable methanol (commercial scale, R&D concepts) is shown in Table 2. [3,24,29,30]

Table 2 Methanol plants with renewable production capacities [29]

| Company | Country | Scale | Comments |
|---|---|---|---|
| Enerkem | Canada | Demo | Capacity: 220 kton based on MSW-gasification |
| CRI | Iceland | Demo | Capacity: 4 kton based on Power-to-Methanol |

| Company | Country | Scale | Comments |
|---|---|---|---|
| Oberon | USA | Demo | Capacity: 12.5 kton based autothermal reforming of biogas and natural gas |
| BioMCN | The Netherlands | Demo | Capacity: 450 kton; only $CO_2$ certificates trade |
| Varmlandsmetanol | Sweden | Demo concept | Capacity: 100 kton, domestic forest residues |
| W2C | The Netherlands | Demo concept | Capacity: 220 kton, waste to chemicals |
| Silva Green Fuel | Norway | Demo concept | Wood to methanol |
| Blue Fuel Energy | Canada | Demo concept | Power to methanol/fuel |
| Liquid Wind | Sweden | Demo concept | Capacity: 8 kton, Power to methanol |
| Port of Antwerp | Belgium | Demo concept | Power to methanol |
| Swiss Liquid Future | Switzerland | Commercial concept | Capacity: 5,000 kton, Power to methanol |
| $MefCO_2$ | Germany | Pilot concept | Capacity: 0.4 kton, Power to methanol |
| FReSMe | | Pilot concept | Power to methanol |
| Biogo | Germany | R&D | Mini-scale MTO/MTG plant |
| LowLands Methanol | The Netherlands | R&D | Waste to methanol |
| Bioliq | Germany | R&D | Biomass to methanol/fuel |
| Kopernikus (P2X) | Germany | R&D | Power to methanol |
| Carbon2Chem | Germany | R&D | Power to methanol |
| KEROSyN100 | Germany | R&D | Power to methanol, MTG |

# 5. Fuel properties of methanol

Methanol is the simplest representative of the group of alcohols. Under ambient conditions, methanol is a clear, colorless, flammable and volatile liquid with an alcoholic odor. It mixes with many organic solvents and in any ratio with water [3,31]. Further properties of methanol compared to other fuels are shown in Table 3.

Methanol has positive properties regarding its use as fuel in internal combustion engines [32]:

- High octane number and high knocking resistance;
- No carbon-to-carbon bonds (soot-free combustion);
- High oxygen content (avoidance of fuel rich combustion zones);
- High heat of evaporation and high volumetric efficiency;
- Low lean flammability limit;
- High volatility

Nonetheless, there are also adverse properties according to fuel and material:

- Low volumetric energy content;
- Low vapor pressure and low cold starting performance of engines;
- Tendency to evaporate in fuel lines;
- Corrosive and chemical degradation of materials;
- Low cetane number and adverse self-ignition properties;
- Poor miscibility with diesel;
- Poor lubrication properties and degradation of oil lubrication properties.

*Combustion properties.* The high knocking resistance and high heat of vaporization of methanol allow higher compression ratios and thus also a higher thermodynamic efficiency compared to gasoline-fueled engines. Due to the molecular structure (bounded oxygen and no carbon-carbon bonds), the use of methanol as fuel can additionally reduce soot emissions (depending on methanol content). On the other hand, properties such as low energy content, viscosity, corrosive behavior and seal-swelling properties requires significant adjustments in the fuel system (fuel tank, seals, pumps and injectors). In order to counteract the low ignition quality and the high evaporation enthalpy, considerable adjustments are necessary in combustion process (homogenization and ignition delay). Moreover, incomplete combustion of methanol gives rise to formaldehyde and formic acid as pollutants. [3,31,33]

*Transport properties.* Properties such as flash point, flammability limits, corrosive behavior and toxicity cause higher attention when handling with methanol. [3,31]

Table 3 Typical properties of methanol and other fuels [3,31,33]

| Property | Unit | Methanol | Ethanol | MTBE | Propane | Methane | Hydrogen | Gasoline | Diesel |
|---|---|---|---|---|---|---|---|---|---|
| Chemical Formula | - | $CH_3OH$ | $C_2H_5OH$ | $(CH_3)_3COCH_3$ | $C_3H_8$ | $CH_4$ | $H_2$ | C4 to C12 | C3 to C25 |
| Molecular Weight | g mol$^{-1}$ | 32.04 | 46.07 | 88.15 | 44.1 | 16.04 | 2.02 | 100-105 | 200 |
| Carbon content | wt.-% | 37.5 | 52.2 | 66.1 | 82 | 75 | 0 | 85 to 88 | 84 to 87 |
| Hydrogen content | wt.-% | 12.6 | 13.1 | 13.7 | 18 | 25 | 100 | 12 to 15 | 33 to 16 |
| Oxygen content | wt.-% | 49.9 | 34.7 | 18.2 | 0 | 0 | 0 | 0 | 0 |
| Density at 15 °C | kg m$^{-3}$ | 796 | 794 | 744 | 508 | 168 (at 200 bar) | 40 at (700 bar) | 720 to 780 | 810 to 890 |
| Boiling temperature | °C | 65 | 78 | 55 | -42 | -162 | -253 | 30 to 225 | 190 to 350 |
| Reid vapor pressure | kPa | 32 | 16 | 54 | 1,430 | 16,500 | - | 55 to 100 | 1 |
| Research octane number | - | 109 | 108 | 117 | 112 | - | 130+ | 80 to 100 | - |
| Motor octane number | - | 92 | 92 | 101 | 97 | - | - | 81 to 90 | - |
| Cetane number | - | 3 | 5 | - | - | - | - | 5 to 20 | 40 to 55 |
| Water solubility at 20 °C<br>Fuel in water<br>Water in fuel | <br>vol.-%<br>vol.-% | <br>100<br>100 | <br>100<br>100 | <br>4.3<br>1.4 | <br>-<br>- | <br>-<br>- | <br>-<br>- | <br>Negligible<br>Negligible | <br>Negligible<br>Negligible |
| Freezing point | °C | -98 | -114 | -109 | -188 | -182 | -259 | -40 | -40 to 0 |
| Viscosity at 15 °C | cP | 0.59 | 1.19 | 0.35 | - | - | - | 0.37 to 0.44 | 2.6 to 4.1 |
| Flash point | °C | 9 | 12 | -28 | -104 | -188 | - | -40 to -30 | > 55 |
| Autoignition temperature | °C | 470 | 425 | 460 | 470 | 595 | 560 | 250 to 460 | 220 to 300 |
| Flammability limits<br>Lower<br>Higher | <br>vol.-%<br>vol.-% | <br>7.3<br>36 | <br>4.3<br>19 | <br>1.6<br>8.4 | <br>2.2<br>9.5 | <br>5.3<br>15 | <br>4.1<br>74 | <br>1.4<br>7.6 | <br>1<br>6 |
| Latent heat of vaporization<br>at 15 °C | <br>kJ kg$^{-1}$<br>kJ mol$^{-1}$ | <br>1,177<br>38 | <br>921<br>42 | <br>321<br>28 | <br>449<br>20 | <br>509<br>8 | <br>447<br>1 | <br>349<br>35 | <br>233<br>47 |
| Lower heating value | MJ kg$^{-1}$ | 19.9 | 26.8 | 35.1 | 46.4 | 50.0 | 120.0 | 40.0 to 42.0 | 41.0 to 43.0 |
| Upper Heating value | MJ kg$^{-1}$ | 22.7 | 29.7 | 42.5 | 50.3 | 55.5 | 141.8 | 42.0 to 44.5 | 43.0 to 45.5 |
| Stoichiometric air-fuel ratio | - | 6.5 | 9 | 11.7 | 15.7 | 17.2 | 34.3 | 14.7 | 14.7 |

*Fuel standards*. Fuel standards define specifications of fuels and allow refineries, fuel traders, automotive and engine companies to appropriately examine and process these fuel ensure their quality towards safe and efficient use. They binding for a market role out. For methanol, there are several fuel standards of major interest; most of them related to the automotive sector. Global methanol fuel standards are shown in Figure 3. Further information according global methanol fuel standardization are shown in [32].

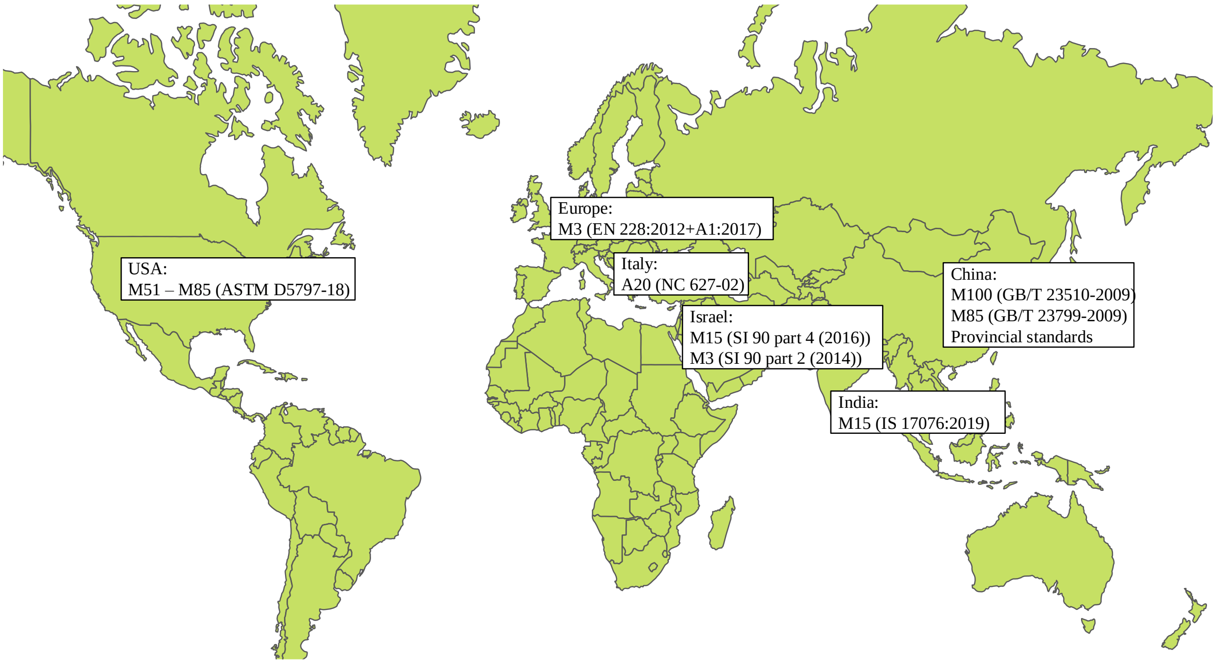


Figure 3 Global fuel standards [32]

Regardless of this, there is still a need to catch up with the standardization of methanol as a fuel in many regions worldwide.

*Material compatibility*. Most materials used for gasoline are also suitable for use with methanol blends. In order to resist phase separation, maintain stability and safety for methanol-gasoline blends corrosion inhibitors, co-solvents, and alcohol compatible materials are needed. [32,34] In contrast to other hydrocarbons, methanol is a polar molecule and thus corrosive to individual metals and alloys as well as elastomers and polymers that are widely used in engine fuel systems. This is also true for distribution, filling and tank equipment in the mineral oil industry. Elastomers and polymers that are not recommended include fluorosilicone (FVMQ), fluororubber (FPM, FKM), hydrogenated nitrile butadiene rubber (HNBR), neoprene (CR), nitrile butadiene rubber (NBR), polyurethane (PUR) and polyvinyl chloride (PVC). Metals that are not compatible with methanol are aluminium, copper, titanium, zinc and some of their alloys. [34–36]

Table 4 Conditionally resistant material with methanol [34]

| Material | Conditionally resistant |
|---|---|
| Metals and alloys | Aluminium<br>Copper<br>Titanium<br>Zinc |
| Elastomers | Fluorosilicone (FVMQ)<br>Fluororubber (FPM, FKM)<br>Hydrogenated nitrile butadiene rubber (HNBR)<br>Neoprene (CR)*<br>Nitrile butadiene rubber (NBR)*<br>Polyurethane (PUR) |
| Polymers | Styrene acrylonitrile resin (SAN) |

| Material | Conditionally resistant |
|---|---|
| | Poylamide 12 (PA 12, Nylon) |
| | Polysulfone (PSU) |
| | Polystyrene (PS) |
| | Polyvinyl chloride (PVC) |

** Recommended for hoses and gaskets, but not for seals*

## 6. GHG emissions of methanol

In this chapter, the greenhouse gas (GHG) emissions of methanol from various resources are presented.

*Methodology*. The GHG emissions of methanol are compiled from ten different studies and databases. These studies and databases were analyzed regarding used resources, defined system boundaries, applied assessment methods, level of transparency and GHG emissions results (Table 6).

The resources investigated include waste wood, cultivated wood, biogas from manure and energy crops, black liquor, hard coal, lignite, natural gas, hydrogen from renewable electricity and biogenic $CO_2$. They are grouped into renewable and fossil methanol (Table 6 and Figure 4).

In this study review, the system boundary covers raw material extraction, methanol production, transport and distribution processes and fuel in use. According to the Renewable Energy Directive (RED II), Annex V [37] the GHG emissions from renewable fuel in use is considered to be zero due to the short-term closed carbon cycle In contrast, the GHG emissions from the use of fossil-based methanol is accounted due to emission of fossil carbon dioxide. In order to ensure the comparability of results deriving from different studies, the system boundaries have to be the same for all. Since in some studies the GHG balancing ends at methanol production gate (cradle to gate), the default transport and distribution value of the final fuel from RED II [37] are added. In addition, the GHG emissions from the combustion of fossil-based methanol are added to the results in the studies with cradle to gate approaches.

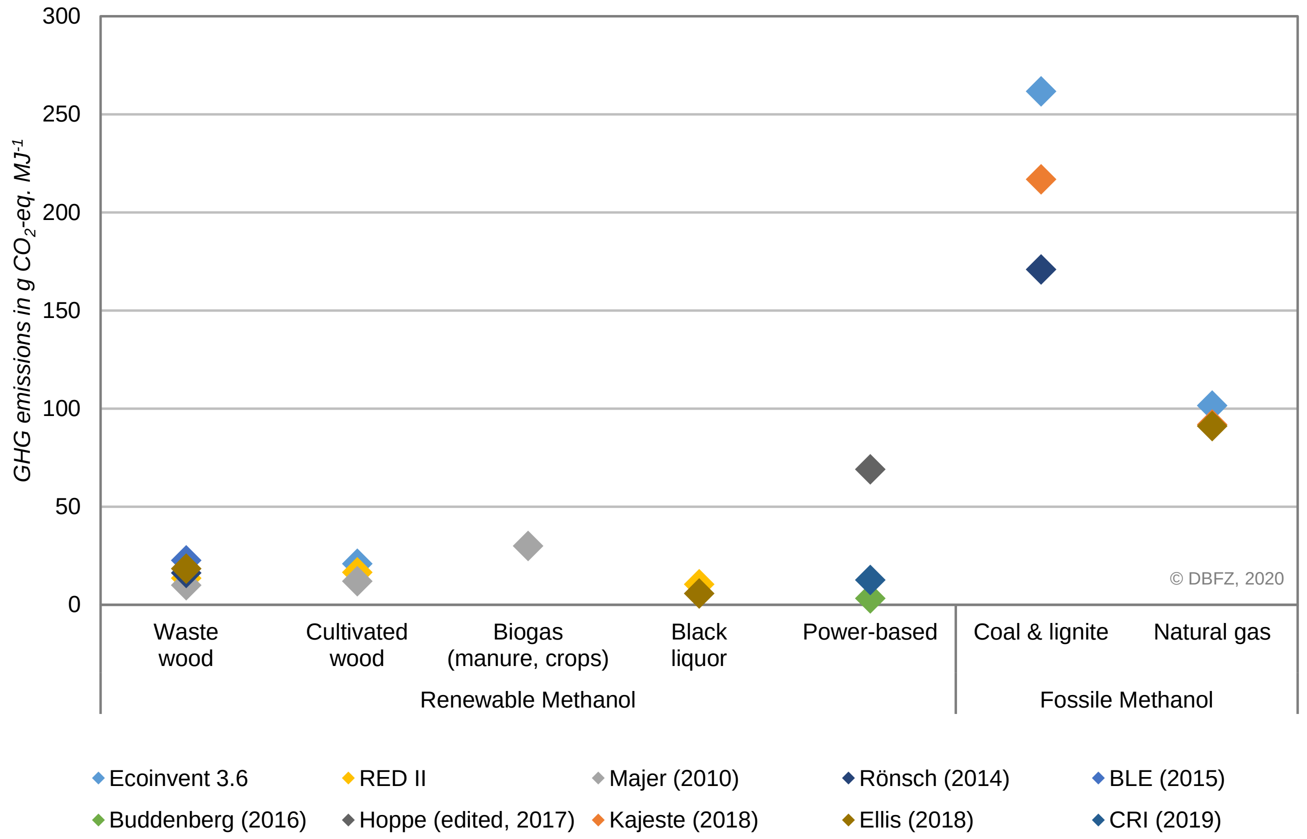


Figure 4 Emission factor of methanol from different resources [21,37–46]

Basically, two different GHG emissions balancing methods were applied in the studies, firstly, the approach according to the ISO guidelines 14040 and 14044 [47], [48] and secondly, the GHG emissions calculation method according to the EU RED (2009/28/EC) , whereas the RED method is a simplified method of the ISO guidelines. [49] In most studies, the calculation of the GHG emissions is described transparently and comprehensibly according to the two guidelines, except for Matzen et al. 2016 [43] and Hoppe et al. 2017 [44]. There is no transparent explanation for the accounting of negative emissions from $CO_2$ capturing in the power-based methanol production. Matzen et al. 2016 published cradle to gate emissions from Methanol production of -56 g $CO_2$-eq. $MJ^{-1}$. [43] This figure contains negative $CO_2$-emissions from $CO_2$ capturing. It could be assumed that the $CO_2$-emissions would be released in the combustion process of methanol. Since there is no transparent breakdown of the GHG emission calculation, values cannot be recalculated without the negative $CO_2$-emissionen. Thus, the figure is not presented in Figure 4. Calculations of Hoppe et al. in 2017 [44] resulted in – 1.5 g $CO_2$-eq. $MJ^{-1}$ methanol. Here, again the negative $CO_2$ emissions originates from biogenic $CO_2$ uptake. Assuming these emissions are released during the use-phase and considering the additional GHG emissions of distribution the recalculated value is 69 g $CO_2$-eq. $MJ^{-1}$ (see Table 6).

*Results.* Production and use of biomass-based methanol causes GHG emissions between 3.2-69 g $CO_2$-eq. $MJ^{-1}$. Lowest GHG emissions result from the methanol production using renewable electricity from wind and biomass power and biogenic $CO_2$ from the biomass CHP plant (3.2 g $C_2$-eq $MJ^{-1}$, [42]) and from methanol production using black liquor (5.7 g $CO_2$-eq. $MJ^{-1}$, [21] integrated with pulp mill), see Figure 4 and Table 6. The highest GHG emissions are potentially caused by the recalculated methanol production based on power-based methanol assessed in Hoppe et al. 2017. Here, the input stream of $CO_2$ from biogas production is associated with negative GHG emissions within the cradle to gate-approach. Assuming that these $CO_2$ emissions are released during the use phase, the $CO_2$ credit is compensated. The recalculated result is 69.0 g $C_2$-eq $MJ^{-1}$, see Figure 4 and Table 6.The studies investigating renewable methanol show a wide range of GHG emissions. The reasons are i) various resources used (waste biomaterial such as waste wood, cultivated crops, electricity and $CO_2$ from different sources) and ii) different frame conditions and assumptions defined.

Fossil methanol production results in highest GHG emissions whereas the GHG emissions of hard coal-based methanol (217 and 262 g $CO_2$-eq. $MJ^{-1}$ [45], [38] ) are approximately twice as high as of natural gas-based Methanol (92 and 102 g $CO_2$-eq. $MJ^{-1}$ [45], [38]). GHG emissions of methanol from lignite are higher than GHG emissions of natural gas, but lower than of hard coal (see Figure 4, Table 6). In contrast to the combustion of biomass-based methanol, GHG emissions from combusting fossil-based methanol (69 g $CO_2$-eq. $MJ^{-1}$) are taken into account for GHG balancing.

In comparing the default values of the European Renewable Energy Directive binding from 2021 onwards (RED II) [37] for methanol to other renewable fuels it becomes clear that methanol potentially causes relatively low GHG emissions (see Table 5). If biogas/biomethane from wet manure alone would to be used to produce methanol, negative GHG emissions could even be achieved.

Table 5 Default values of methanol and other renewable fuels according to RED II [37]

| Renewable fuel | Default value according to RED II g $CO_2$ eq. $MJ^{-1}$ |
|---|---|
| Methanol | 10.4 -16.2 |
| Biodiesel/FAME | 14.9 – 75.7 |
| HVO | 16.0 – 73.3 |
| Bioethanol | 15.7 – 71.7 |
| FT-Diesel | 10.2 -16.7 |
| DME | 10.2 -16.2 |
| Biomethane | -100.0 – 73.0 |

Table 6 Summary and characteristics of the studies investigated

| Study | Classification | Resources | System boundaries | Assessment methods | Level of transparency | GHGs in g $CO_2$-eq $MJ^{-1}$ |
|---|---|---|---|---|---|---|
| Ecoinvent vs. 3.6, 2019 [38] | Biomass-based | Wood chips | From raw material extraction until methanol production gate; DBFZ add the RED II default value of 2.0 g $CO_2$-eq $MJ^{-1}$ for transport and distribution of MeOH | ISO 14040/44, GWP 100, IPCC 2013 | transparent | 20.91 |
| | Fossil-based | Natural gas | From raw material extraction until methanol production gate; DBFZ add the RED II default value of 2.0 g $CO_2$-eq. $MJ^{-1}$ for transport and distribution and the combustion emission of MeOH of 69 g $CO_2$-eq. $MJ^{-1}$ | ISO 14040/44, GWP 100, IPCC 2013 | transparent | 101.57 |
| | | Hard coal | From raw material extraction until methanol production gate; DBFZ add the RED II default value of 2.0 g $CO_2$-eq. $MJ^{-1}$ for transport and distribution and the combustion emission of MeOH of 69 g $CO_2$-eq. $MJ^{-1}$ | ISO 14040/44, GWP 100, IPCC 2013 | transparent | 261.77 |
| RED II, Annex V, 2018 [37] | Biomass-based | Waste wood | From raw material extraction until use phase | RED II, Annex 5, GWP 100, IPCC 2007 | transparent | 13.50 |
| | | Cultivated wood | From raw material extraction until use phase | RED II, Annex 5, GWP 100, IPCC 2007 | transparent | 16.50 |
| | | Black liquor | From raw material extraction until use phase | RED II, Annex 5, GWP 100, IPCC 2007 | transparent | 10.40 |
| Majer et al., 2010 [39] | Biomass-based | Waste wood | From raw material extraction until use phase | RED, Annex V, GWP 100, IPCC 2001 | transparent | 10.00 |
| | | Cultivated wood | From raw material extraction until use phase | RED, Annex V, GWP 100, IPCC 2001 | transparent | 12.00 |
| | | Biogas (manure, crops) | From raw material extraction until use phase | RED, Annex V, GWP 100, IPCC 2001 | transparent | 30.00 |
| Rönsch et al., 2014 | Biomass-based | Waste wood | From raw material extraction until use phase | ISO 14040/44, | transparent | 16.11 |

| | | | | | | |
|---|---|---|---|---|---|---|
| [40] | | | | GWP 100 | | |
| | Fossil-based | Lignite | From raw material extraction until use phase | ISO 14040/44, GWP 100 | transparent | 170.83 |
| BLE 2016 (within GHG quote 2015) [41] | Biomass-based | Waste wood | From raw material extraction until use phase | RED II, Annex 5, GWP 100, IPCC 2007 | Not fully transpar-ent due to statis-tical aggregation | 22.60 |
| Buddenberg et al., 2016 [42] | Power-based | Renewable electricity, flue gas from biomass plant | From raw material extraction until methanol production gate; DBFZ add the RED II default value of 2.0 g $CO_2$-eq. $MJ^{-1}$ for transport and distribution of MeOH | No information | Not fully transparent | 3.23 |
| Matzen et al., 2016 [43] | Power-based | Renewable electricity, $CO_2$ from ethanol plant | From raw material extraction until use phase, includes the ethanol production | ISO 14040/44, GWP 100 | No explanation for the accounting of negative emissions from $CO_2$ capturing | -56.43 |
| Hoppe et al., 2017 [44] | Power – based | Renewable electricity, $CO_2$ from biogas process | From raw material extraction until methanol production gate; the supply of $CO_2$ input stream is excluded; DBFZ add the RED II default value of 2.0 g $CO_2$-eq. $MJ^{-1}$ for transport and distribution of MeOH | ISO 14040/44, GWP 100 | No explanation for the accounting of negative emissions from $CO_2$ input | 0.50 |
| Hoppe et al., 2017, edited by DBFZ | Power – based | Renewable electricity, $CO_2$ from biogas process | From raw material extraction until methanol production gate; the supply of $CO_2$ input stream is excluded; DBFZ add the RED II default value of 2.0 g $CO_2$-eq. $MJ^{-1}$ for transport and distribution of MeOH; DBFZ doesn't account for negative $CO_2$-input emissions under assumption that these are released during use phase | ISO 14040/44, GWP 100 | No explanation for the accounting of negative emissions from $CO_2$ input. Here, DBFZ doesn't account for nega-tive CO2-input emission | 69.00 |
| Kajeste et al., 2018 [45] | Fossil-based | Natural gas | From raw material extraction until methanol production gate; DBFZ add the RED II default value of 2.0 g $CO_2$-eq. $MJ^{-1}$ for transport and distribution and the combustion emission of MeOH of 69 g $CO_2$-eq. $MJ^{-1}$ | ISO 14040/44, GWP 100, IPCC 2007 | transparent | 91.78 |
| | | Hard coal | From raw material extraction until methanol production gate; DBFZ add the RED II default value of 2.0 g $CO_2$-eq. $MJ^{-1}$ for transport and distribution and the combustion emission of MeOH of 69 g $CO_2$-eq. $MJ^{-1}$ | ISO 14040/44, GWP 100, IPCC 2007 | transparent | 216.93 |
| Ellis et al., 2018 | | Waste wood | From raw material extraction until use phase | ISO 14040/44, | transparent | 18.30 |

| | | | | | | |
|---|---|---|---|---|---|---|
| [21] | Biomass-based | | | GWP 100, IPCC 2013 | | |
| | | Black liquor | From raw material extraction until use phase | ISO 14040/44, GWP 100, IPCC 2013 | transparent | 5.70 |
| | Fossil-based | Natural gas | From raw material extraction until use phase (including fossil $CO_2$ emission from combustion) | ISO 14040/44, GWP 100, IPCC 2013 | transparent | 91.00 |
| CRI (Carbon Recycling International) 2019 [46] | Power-based | Renewable electricity, flue gas (geothermal energy plant) | From raw material extraction until use phase | ISCC-PLUS | no balancing date, but a ISCC PLUS certificate | 12.06 |

# 7. Cost evaluation of methanol

In the following paragraph, costs (EUR $GJ^{-}$) of fossil-based and biomass-based methanol are presented comparatively. A first overview considering fossil-based methanol prices during the last 35 years are provided in Figure 5 [50–54]. For comparison, prices of methanol in the USA and Europe are shown. As diagramed, the two methanol spot market prices are over the whole period of time comparable and have the same peaks, as it is to be expected with a globally traded product. An analysis of the trend pointed out the influence of the oil price related to the methanol price. To show this analogy, the Europe Brent Crude Oil Spot price is added for comparison in Figure 5. Especially in the last 10 years after the commercial crisis from 2008/09, there has been a similar trend between the methanol and the oil price. In contrast, supposed correlation between the methanol and the natural gas price cannot be seen. Since 2010, the price range of fossil methanol (Europe and US) is with the exception of singular peaks between 10 and 20 EUR $GJ^{-1}$, the price of Brent Oil ranged between 5 and 17 EUR $GJ^{-1}$ and the price of natural gas between 3 and 5 EUR $GJ^{-1}$. Compared to established renewable fuels such as biodiesel (FAME) from rapeseed (Europe: 20 – 30 EUR $GJ^{-1}$) and bioethanol (Europe: 20 – 35 EUR $GJ^{-1}$; US: 15 – 25 EUR $GJ^{-1}$) fossil methanol would be more competitive [1].

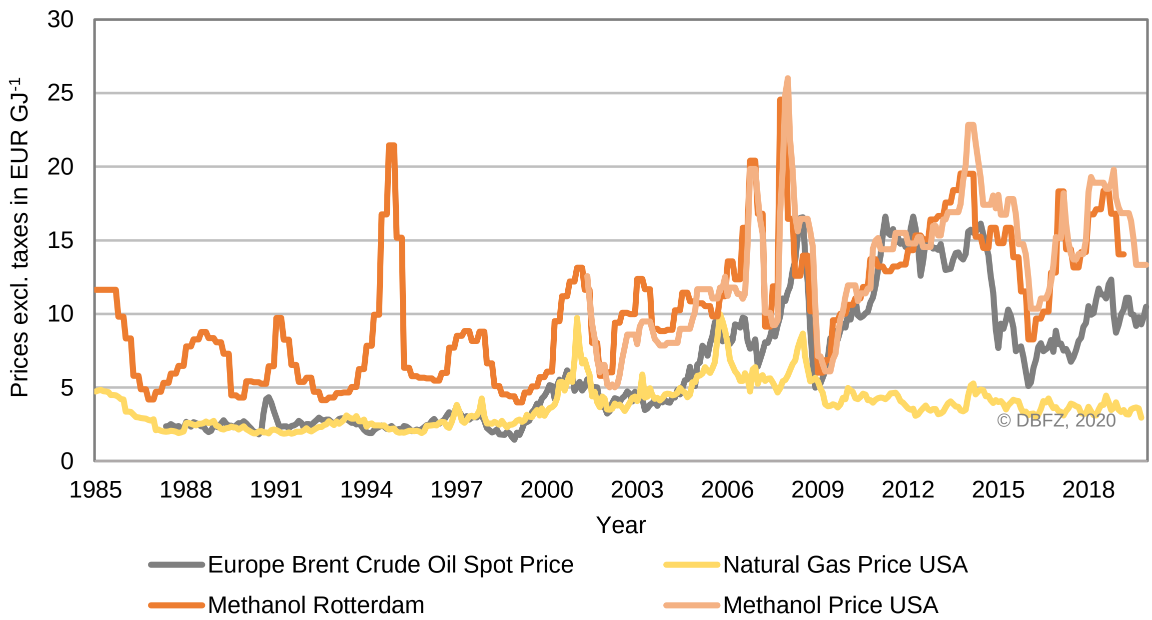


Figure 5 Price development Methanol in relation to oil and gas [50–54]

To analyse the price structure of the fossil-based methanol price, Boulamanti et al. have made an assembly over different producer countries and the production prices in 2017 [55]. Parts of the results are shown in Figure 6. According to this, the most important factor is the price difference between various producer countries. Main factor for this difference is the resources price difference of the producer countries. Resources of fossil-based methanol is natural gas or coal and thereafter the local natural gas price affects the methanol price, although a general dependency of the world market prices cannot be reported, as shown above. In the natural gas, producing countries such as Saudi Arabia, Russia and the USA the producing price for methanol is lower than in the other considered countries. The second relevant component with influence on the methanol price are the labour costs, with a share of 11-60%.

The analysis shows a strong variations of methanol prices, which can be analysed as a dependency from the world oil price. This can be expected to be continued in the next years. To isolate the price development from the fossil world market prices a fossil free methanol production is necessary. Therefore, different options are discussed, the prices of this options will be elaborated in the next paragraph.

Costs of different bases of methanol production are compiled from eight different studies and databases. The resources investigated in Figure 7 include waste wood, cultivated wood, biogas from manure and energy crops, natural gas, hydrogen from renewable electricity and biogenic $CO_2$. They are grouped into renewable and fossil-based methanol. For production route from cultivated wood five studies [39,40,56–58], for power-based methanol three studies [59–61] are referred. For the production from waste wood [39] and biogas [39] only one study can be cited. The natural gas route is calculated from the same sources [50–54] as the diagram above with the average price of the figured period of time. The results show, that fossil-free produced methanol cannot compete against fossil-based methanol. Costs of producing renewable methanol are already higher than the market price of fossil methanol. Based on a review of different studies, **Fehler! Verweisquelle konnte nicht gefunden werden.** shows that renewable methanol cannot compete against fossil methanol, even cost aspects are depending on the development stage of the respective technology but also the calculated settings and boundary conditions..

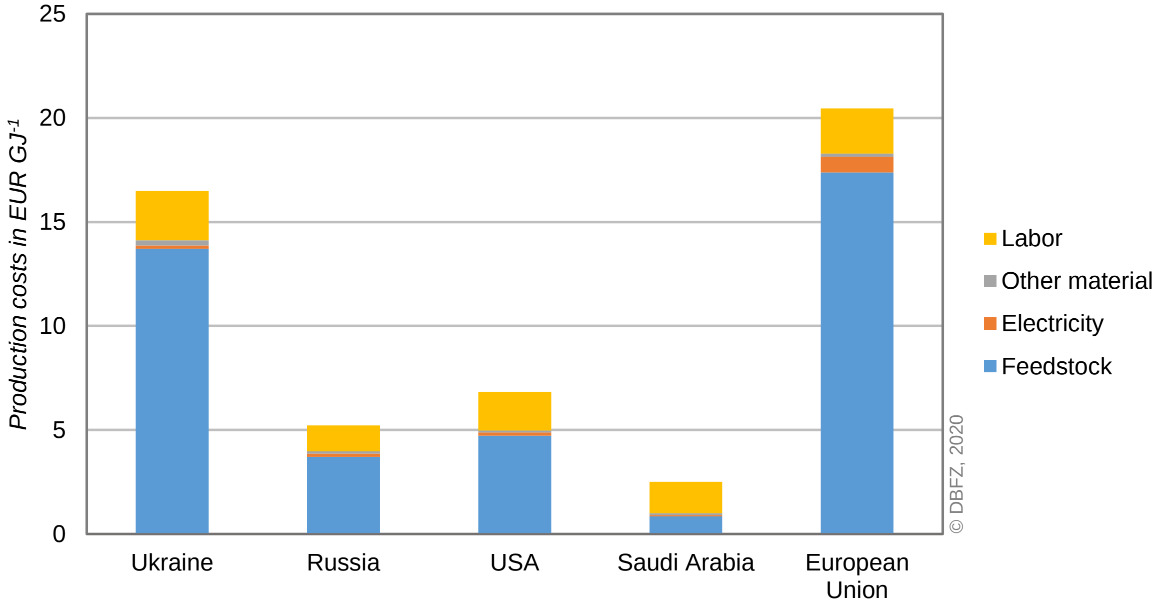


Figure 6 Price breakdown for methanol based on natural gas in different countries [55]

In summary renewable methanol is more expensive on the market than fossil methanol. One possibility to reduce costs of methanol is to use a lower purity than 99.85% required for the chemical industry [21]. Combustion engines operate even though purity of methanol is 90% (ref. in [21]).

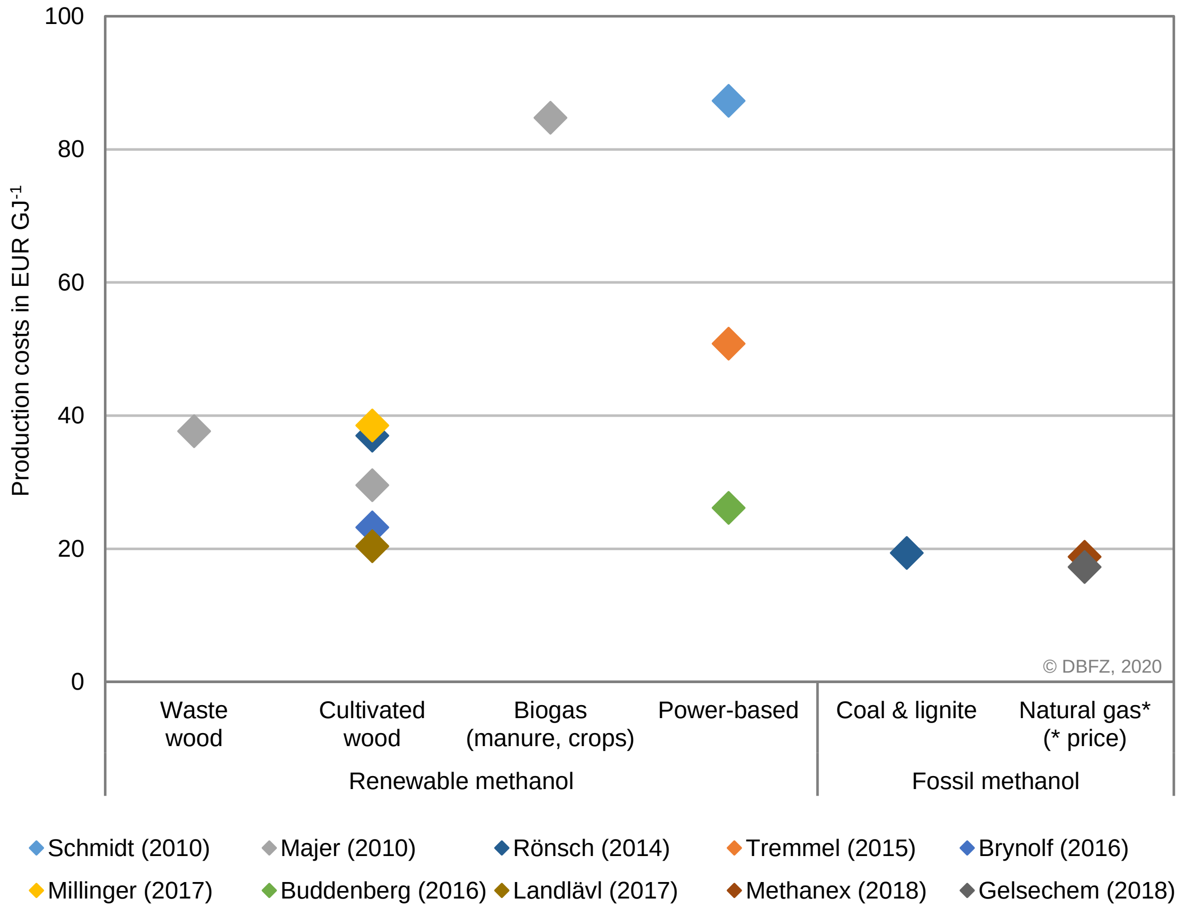


Figure 7 Cost of methanol from different resources (normalized 2018) [39,40,50,56–63]

# 8. Transport, storage and handling

The infrastructure for the transport of methanol is mainly characterized by freight traffic (ship, road and rail) which is well established. Transport via pipeline has only become established within chemical parks or ports. Various vehicle-specific regulations (e.g. ADR [64], RID [65], ADN [66], IMDG-Code [67], ERG [68]) specify the requirements for transportation.

*Shipping.* Similar to other liquid fuels, transport to water takes place in double-hulled tanker ships with methanol compatible firefighting equipment and material as well as an appropriate methanol leak detection.

*Rail transport.* The requirements are comparable to the transport of other highly flammable liquid fuels such as gasoline and ethanol. The tank wagon should be able to allow pressure relief in order to accommodate thermal expansion and needs a grounding against static charge.

*Road transport.* The requirements to transport methanol on road are comparable to rail transport.

Storage. Similar to transportation requirements, the requirements of storage methanol are similar to gasoline storage. Methanol is typically stored in floating roof tanks at marine terminals and docks, tank farms at chemical parks and portable container for final use. The Methanol institute has created a Technical bulletin for methanol drums.

Further information are presented in the Methanol Safe Handling Manual of the Methanol Institute [2].

Various measures are required when handling, storing and transporting methanol. The following subsections correspond to European requirements and are part of the safety data sheet of methanol [3,69].

## 8.1. Handling and storage

*Precautions for safe handling.* Provision of sufficient ventilation. Use extractor hood (laboratory). Handle and open container with care. Clear contaminated areas thoroughly. Keep away from sources of ignition - No smoking. Take precautionary measures against static discharge. Due to danger of explosion, prevent leakage of vapors into cellars, flues and ditches. When using do not eat or drink. Thorough skin-cleansing after handling the product. When using do not smoke.

*Conditions for safe storage.* Keep container tightly closed. Store locked up. Ground/bond container and receiving equipment. Use local and general ventilation. Recommended storage temperature: 15 – 25 °C.

## 8.2. Personal protective equipment

*Eye/face protection.* Use safety goggle with side protection.

*Skin protection.* Flame-retardant protective clothing.

*Hand protection.* Wear suitable gloves, which are tested according to EN 374. Type of material: Butyl caoutchouc (butyl rubber). Take recovery periods for skin regeneration. Preventive skin protection (barrier creams/ointments) is recommended.

*Respiratory protection.* Respiratory protection necessary at: Aerosol or mist formation. Type: A (against organic gases and vapors with a boiling point of > 65 °C, color code: Brown).

## 8.3. Accidental release measures

*Personal precautions.* Wearing of suitable protective equipment. Do not breathe vapor/spray. Avoidance of ignition sources.

*Environmental precautions.* Keep away from drains, surface and ground water. Explosive properties.

*Advices on how to contain and clean up a spill.* Covering of drains. Absorb with liquid-binding material (e.g. sand, diatomaceous earth, acid- or universal binding agents). Place in appropriate containers for disposal. Ventilate affected area.

## 8.4. Disposal considerations

*Waste treatment methods.* This material and its container must be disposed of as hazardous waste. Dispose of contents/container in accordance with local/regional/national/international regulations.

Sewage disposal-relevant information. Do not empty into drains.

*Waste treatment of container/packaging.* It is a dangerous waste; only packaging which are approved (e.g. acc. to ADR) may be used.

## 8.5. Transport Information

| | |
|---|---|
| UN Number: | 1230 |
| Transport hazard class: | 3 (flammable liquids) |
| Subsidiary risk: | 6.1 (poison) |
| Danger labels: |  |
| Packing group: | II (substance presenting medium danger) |
| Environmental hazards: | none (non-environmentally hazardous acc. to the dangerous goods regulations) |



Special precautions for transport sectors are listed in ADR for European road transport [64], RID for European rail transport [65], ADN for European inland waterway transport [66], IMDG-Code for international sea shipping [70], ICAO-TI or IATA DGR for international civil aviation [71] and ERG for American requirements [68].

# 9. Health and safety information

Various health and safety regulations have been established based on the physical and toxicological properties of pure methanol. The safety information regarding the pure components cannot be applied to mixtures, i.e. methanol blends.

*Human toxicology.* Typical routes of methanol exposure in human body are inhalation, absorption through the skin because of contact, eye contact, and ingestion (eating or drinking). The human body absorbs and distributes methanol easily and rapidly (60% to 85% by inhalation exposure). [2] Metabolism and toxicity of methanol are similar to those found with ethylene glycol. Non-metabolized methanol is only of low toxicity. Toxic are essentially its degradation products such as formaldehyde and formic acid. In particular, formic acid leads after a latency period of 6 to 30 hours without symptoms to the formation of the typical poisoning symptoms of methanol. [22,72] The poisoning symptoms of methanol poisoning proceed in three phases. Directly after intake of methanol shows a narcotic stage as with ethanol, but the intoxicating effect is lower than with ethanol. After the latency period, headache, weakness, nausea, vomiting, dizziness, and accelerated breathing are associated with metabolic acidosis. Temporary vision disorders arise first by edema at the retina. In the further course, complete degeneration of the optic nerve can lead to complete irreversible blindness. Deadly poisoning occurs because of respiratory paralysis. Doses from 0.1 g of methanol per kg of body weight are dangerous, over 1.0 g per kg of body weight life threatening. [22,73] Single symptoms can lead to chronic symptoms as well as disorders of the visual and central nervous system and other organ toxicity. [2]

*Environmental toxicology.* According to the screening information data set (SIDS) of the OECD, methanol is a low-proritiy chemical whose properties are not considered harmful to the environment under normal circumstances. [2] Methanol is completely miscible with water in all proportions. The methanol-water mixture is very stable. Therefore, it is very difficult to remediate methanol contaminations. In contrast to crude oil (derivatives), methanol quickly dissolves in case of accidents on the high sea, due to its good miscibility and fast diffusion in water. Otherwise, if toxic quantities of methanol are present in water or mineral surfaces, it biodegrades rapidly. [2,3]

Further health and safety information are described and explained in the Methanol Safe Handling Manual of the Methanol Institute [2]. The following aspects according to classification of possible hazards (Table 7), occupational exposure limits (Table 8), human health and environmental threshold levels (Table 9), labelling of methanol, symptoms and effects of incubation of methanol as well as description of first aid and firefighting measures correspond to European requirements (e.g. CLP and REACH) and are part of the safety data sheet of methanol [69].

Table 7 Classification of possible hazards according to regulation (EC) No 1272/2008 (CLP)

| Section | Hazard class | Hazard class and category | Hazard statement |
|---|---|---|---|
| 2.6 | flammable liquid | (Flam. Liq. 2) | H225 |
| 3.1O | acute toxicity (oral) | (Acute Tox. 3) | H301 |
| 3.1D | acute toxicity (dermal) | (Acute Tox. 3) | H311 |
| 3.1I | acute toxicity (inhal.) | (Acute Tox. 3) | H331 |
| 3.8 | specific target organ toxicity - single exposure | (STOT SE 1) H | H370 |

Table 8 Occupational exposure limit values (Workplace Exposure Limits)

| Country | Long-term limit in ppm | Long-term limit in mg $m^{-3}$ | Short-term limit in ppm | Short-term limit in mg $m^{-3}$ | Source |
|---|---|---|---|---|---|
| EU | 200 | 260 | - | - | 2006/15/EG |
| Germany | 200 | 270 | 800 | 1,080 | TRGS 900 |

Table 9 Human health and environmental threshold levels

| Threshold level for | Threshold level | Route of exposure, environmental compartment | Exposure time |
|---|---|---|---|
| Human (employee industry) | 260 mg $m^{-3}$ | inhalatory | acute and chronic local effects |
| Human (employee industry) | 40 mg $m^{-3}$ | dermal | acute and chronic local effects |
| Human (employee industry) | 260 mg $m^{-3}$ | inhalatory | acute and chronic local effects |
| Environment | 20.8 mg $l^{-1}$ | freshwater | short-term (single instance) |
| Environment | 2.08 mg $l^{-1}$ | marine water | short-term (single instance) |
| Environment | 100 mg $l^{-1}$ | sewage treatment plant (STP) | short-term (single instance) |
| Environment | 77 mg $kg^{-1}$ | freshwater sediment | short-term (single instance) |
| Environment | 7.7 mg $kg^{-1}$ | marine sediment | short-term (single instance) |
| Environment | 100 mg $kg^{-1}$ | soil | short-term (single instance) |

Labelling of methanol according to regulation (EC) No 1272/2008 (CLP)

*Signal word:* **Danger**

*Pictograms:* GHS02: 

GHS06: 

GHS08: 

*Hazards:* H225: Highly flammable liquid and vapor

H301+H311+H331: Toxic if swallowed, in contact with skin or if inhaled

H370: Causes damage to organs

*Precautionary:* P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

P270: Do not eat, drink or smoke when using this product.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

P303+P361+P353: IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water [or shower].

P304+P340: IF INHALED: Remove person to fresh air and keep comfortable for breathing.

P308+P311: IF exposed or concerned: Call a POISON CENTER/doctor.

<u>Symptoms and effects (acute and delayed)</u>

*After eye contact.* Conjunctival redness of the eyes, Conjunctivitis (pink eye).

*Following skin contact.* Has degreasing effect on the skin.

*After ingestion.* Abdominal pain, Malaise, Vomiting, Loss of righting reflex, and ataxia, Serious physical decay of vision, Risk of blindness, Poisoning effect on central nervous system can cause convulsions, laboured breathing and loss of consciousness, Headaches and dizziness may occur, proceeding to fainting or unconsciousness, Large doses may result in coma and death, Following inhalation. Cough.

<u>Description of first aid measures</u>

*General notes.* Take off immediately all contaminated clothing. Self-protection of the first aider.

*Following inhalation.* Call a physician immediately. If breathing is irregular or stopped, administer artificial respiration.

*Following skin contact.* After contact with skin, wash immediately with plenty of water.

*Following eye contact.* Rinse cautiously with water for several minutes. In all cases of doubt, or when symptoms persist, seek medical advice.

*Following ingestion.* Rinse mouth immediately and drink plenty of water. Call a physician immediately.

<u>Description of firefighting measures</u>

*Extinguishing media.* Co-ordinate firefighting measures to the fire surroundings, water spray, foam, alcohol resistant foam, dry extinguishing powder and carbon dioxide ($CO_2$).

*Special hazards arising from the substance or mixture.* Combustible. Vapors are heavier than air, spread along floors and form explosive mixtures with air.

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# Appendix II: Heavy Duty methanol engines

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Annex 56

A Report from the Advanced Motor Fuels Technology Collaboration Programme

# Methanol as motor fuel
# Appendix II: Heavy-duty methanol engine

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## Acknowledgement

The project was carried out on behalf of the Fachagentur Nachwachsende Rohstoffe e.V. (FNR). It was supported by the Federal Ministry of Food and Agriculture (BMEL) on the basis of a resolution of the German Bundestag (funding no. 19NR005).

With support from

Federal Ministry of Food and Agriculture

by decision of the German Bundestag

# Contents

# Abbreviation

| | |
|---|---|
| CI | Compression ignition |
| DF | Dual fuel |
| DME | Dimethyl ether |
| ED95 | CI-fuel with 95 vol% ethanol |
| FAME | Fatty acid methyl ester |
| HDV | Heavy-duty vehicle |
| HPDI | High pressure direct injection |
| HVO | Hydrotreated vegetable oils |
| LNG | Liquid natural gas |
| Mxxx | Methanol-gasoline fuel with xxx vol% methanol |
| MD95 | CI-fuel with 95 vol% methanol |
| MED95 | CI-fuel with 95 vol% methanol-ethanol-mixture |
| $NO_X$ | Nitrogen oxides |
| OME | Polyoxymethylene dimethyl ethers |
| PFI | Port fuel injection |
| PHEV | Plug-In hybrid electric vehicle |
| PM | Particulate matter |
| SI | Spark ignition |

# 1. General aspects

In general, heavy-duty vehicles (HDV, e.g. trucks and buses) are operated by diesel engines (CI-engine) due to higher fuel efficiency and lower final torque compared to spark ignition engines (SI-engine), which leads to better operating characteristics and cost-saving application for heavy-duty vehicles. Comparatively higher engine-out emissions of CI-engines – especially $NO_X$ and PM pollutants – due to the heterogeneous combustion are disadvantageous of this engine concept. To comply with the specified emission limits, these pollutants have to be reduced through complex and cost-intensive exhaust gas after-treatment. In mid-term future, with increasing demands on pollutant avoidance and fleet consumption, economical alternative fuels with cleaner combustion properties can play a significant role as an energy carrier for HDV powertrains. Mainly discussed alternatives for HDV application are liquid natural gas (LNG), paraffinic hydrocarbons (HVO, Fischer-Tropsch fuels), fatty acid methyl ester (FAME), alcohols (methanol, ethanol), ethers (DME: dimethyl ether, OME: poly(oxymethylene) dimethyl ether) and hydrogen. All of these alternatives need modification in the engine system and even partially in the infrastructure [1–4].

Current research activities in the HDV sector are focused in reducing costs of operation (higher engine efficiency, lower pollution and waste energy level) as well as in electrification/hybridization of vehicles. In combination with alternative motor fuels, a number of new low temperature SI and CI combustion systems have been developed during the last years. In this context, many ways of using methanol in diesel engines have been researched including usage in blends, emulsions, fumigation, with addition of ignition improvers, in dual injection engines and in engines modified to achieve direct compression ignition of methanol. Further information about advanced engine systems in operation with methanol are described in Appendix IV (High efficiency methanol engines). [1,5–7]

Alternatively, using conventional SI-engines operated by methanol (M85) offer an alternative especially for light and medium duty vehicles. However, this change from compression ignition to spark ignition will induce a lower thermal efficiency [8]. Furthermore, modern direct injection, spark ignition combustion concepts with high compression ratio and a highly turbocharged, downsized engine can achieve low $NO_X$ and PM emissions as well as a high efficiency, if using pure methanol (M100). This positive effect is caused by the high octane number of methanol [9–11].

In the 1980 and 1990s, a number of heavy-duty (fleet) tests with methanol engines (M85-SI engines) have been performed. A selection of corresponding technical reports is shown below:

- Sypher-Mueller International. Alternative fuels for heavy duty engines status of fleet trials, 1991. [12]
- Motta R, Norton P, Kelly K, Chandler K, Schumacher BL, Clark N. Alternative Fuel Transit Buses: Final Results from the National Renewable Energy Laboratory (NREL) Vehicle Evaluation Program, 1996. [13]
- Huff SP, Hodgson JW. Demonstration of the fuel economy potential of a vehicle fueled with M85, 1993. [14]
- Wagner JR. Alternative fuels for vehicles fleet demonstration program, 1997 [15]

# 2. Infrastructure

General infrastructure impacts are explained in Appendix I (General issues on methanol as motor fuel).

To introduce methanol (blends) in road transport, a sufficient methanol infrastructure have to be set up. At service stations, the methanol (blend) has to be stored in double-walled, grounded tanks made (material: stainless steel, carbon steel, or methanol resistant fiberglass) with safety precautions against the ingress of moisture and flammable methanol vapor (floating roof, conservation vent with a flame arrestor or nitrogen blanketing). Storage as underground tank is preferred to avoid high temperature impacts, but needs further safety precautions such as a concrete vault and a lining of the area surrounding the tank to avoid methanol penetration. Existing petroleum tanks have to be completely cleaned (petroleum, sediments and water) before storing methanol. The liner may need to be replaced with a methanol resistant liner and seals have to be replaced with methanol resistant seals [5,16]. Comparable requirements also apply to fuel pumps and dispensing hoses at the service station. Fuel transporting pipes have to be double-walled; all used materials have to be methanol resistant, including e.g. dispensers equipped with ultra-fine filters (3 µm pores diameter). Due to high affinity of fine filters to build-up static electricity and low conductivity of methanol, shorter maintenances are necessary to avoid erosion at fuel pumps [5]. In addition, innovative fuel pumps were developed in Denmark in the last decade that can flexibly adjust the mixing ratios between gasoline and methanol [17].

# 3. Material compatibility

Gasoline and methanol are stored and transported in metallic pipes and tanks, also the fuel handling in vehicles based mostly on metallic product. Methanol is not corrosive for most metals. It is conditionally resistant against galvanized metals. For this reason methanol fuel blends will employ corrosion inhibitors to mitigate any risk [18–20]. Methanol attacks some forms of elastomers and polymers (Table 1), which caused most of reported failures of vehicles fueled with methanol-gasoline blends. There are a high number of methanol resistant materials available. Flexible fuel vehicles show the possibility of the use resistant material for both methanol and gasoline as well.

Table 1 Conditionally resistant material with methanol [19]

| Material | Conditionally resistant |
|---|---|
| Metals and alloys | Aluminum<br>Copper<br>Zinc |
| Elastomers | Fluorosilicone (FVMQ)<br>Fluororubber (FPM, FKM)<br>Hydrogenated nitrile butadiene rubber (HNBR)<br>Neoprene (CR)*<br>Nitrile butadiene rubber (NBR)*<br>Polyurethane (PUR) |
| Polymers | Styrene acrylonitrile resin (SAN)<br>Poylamide 12 (PA 12, Nylon)<br>Polysulfone (PSU)<br>Polystyrene (PS)<br>Polyvinyl chloride (PVC) |

** Recommended for hoses and gaskets, but not for seals*

# 4. Engine developments in heavy-duty vehicles

Many ways of using methanol in combustion engines for heavy-duty application have been investigated since 1980s, including use as blend, emulsion, fumigation, and with the addition of ignition improvers [5,8,10,21–24]. There are differences in engine performance and emissions depending on the used combustion method. These will be introduced and described in the following sections. Complementarily, a comparison of various methanol engine concepts according to engine performance and exhaust emissions is provided in Appendix III (Marine technical report) [25] and in the SUMMETH project [20].

## 4.1. Compression ignition engine with ignition improved Methanol (MD95)

The use of ignition improvers to push the cetane number of methanol enables the use of high amounts of methanol in conventional compression ignition engines; in that case an adoption of the injection system is necessary for compensating the low heating value of methanol. This approach is suitable for retrofitting diesel engines. and is defined as MD95: methanol as diesel fuel with 95 vol% methanol and 5 vol% ignition improver). A comparable approach is implemented for ED95 fuel, which is used in Sweden for instance: 95 vol% ethanol with 5 vol% ignition improver. Benefits in performance and exhaust emissions are potentially possible compared to conventional diesel engine and it is comparable to ED95 application. In Aakko-Saksa et al. [25], the used heavy-duty engine emitted lower CO and $NO_X$, comparable total organic gases and engine performance as well as higher PM compared to ED95 fuel. Overall, the results show that the MD95 concept can be a potential solution to introduce methanol to the road transport sector, but further investigations are necessary [5,20,25,26]. This method is mainly used in northern European countries.

## 4.2. Direct injected spark ignition engine with Methanol (DISI)

Modern methanol (M100) driven, direct injection, spark ignition combustion concepts with high compression ratio and a highly turbocharged, downsized engine can achieve low $NO_X$ and PM emissions as well as a high efficiency. This positive effect is due to the high octane number of methanol. Diesel engines can be readily modified to spark ignition engines by placing spark plugs where diesel fuel injectors are located. The methanol gets port-injected at the intake manifold. This modification method is temporarily being used to convert CI-engines to natural gas operated SI-engines and allow the combustion of methanol with very low $NO_X$ and PM emissions as well as high efficiency [9,10]. In 2019, Chinese car manufacturer Geely launched a M100 methanol fuel heavy truck with this engine type [27].

## 4.3. Dual fuel compression ignition engine with port-injected Methanol (DF-PFI-CI)

Fumigation is an alternative concept to introduce methanol into a diesel engine by carburetion in the intake manifold. The ignition occurs by diesel fuel injection. This approach requires a secondary fuel system and a complex controlling for the maximum possible methanol amount, which depends on the engine load. Misfiring or engine knock can occur, if the substituting methanol content to high. Using methanol fumigation in turbocharged engines, the introducing of methanol is much more complex, due to the necessary installation of injection system downstream to the compressor. The advantages of this method are the possibility of switching to straight diesel fuel operation, the substitution of high amounts of diesel fuel and a well-suited retrofit application. This concept is mainly investigated in China, Finland and Sweden [5,23]. Cheung et al. [28] investigated the engine performance of a CI with port-injected (fumigated) methanol (10%, 20% and 30% methanol substitute rate), and observed that brake thermal efficiency decrease at low engine loads and is without changes or slightly increase at medium and high loads. Mentioned reasons in loos efficiency are cooler air/fuel mixture due to the higher latent heat of evaporation of methanol and unburned methanol emission due to valve overlapping. The improved efficiency at high load is explained by homogenous methanol/air mixture and the methanol provided oxygen during diffusion combustion. Other studies confirm these results [22,24]. This combustion mode has the potential for reducing $NO_X$ (especially NO) and particulates emissions in the whole range of engine operation, but it could lead to a significant increase in HC, CO emissions and $NO_2$ emission. Especially, the increase of unburned methanol and formaldehyde emissions gain in importance with increase in fumigation level [22,24,28–30]. Peng et al. [year] observed a slight increase for particulate matter at high loads, but also a decrease at low and medium loads, where both the number and the mass concentration of particulate matter decreased equally [31].

## 4.4. Others

In addition to the variants mentioned above, other combustion methods have been considered for heavy-duty application as well.

The dual fuel CI engine with directly injected methanol uses two separate direct injection systems in the combustion chamber, one for methanol as energy carrier (M100) and one for diesel fuel as ignition improver of the fuel-air-mixture. This approach allows the substitution of high amounts of diesel fuel [5]. Direct injection of methanol can be done in two ways: In the first variant, injection takes place during the intake stroke; in the second variant during the compression stroke [32]. Emission quantity of the direct injection during the intake stroke is comparable to the engine behavior with port-injected methanol, but the combustion is slightly less efficient. In contrast, the DI during the combustion stroke caused lower combustion efficiency and high emissions than the port-injection [32].

The port injected spark ignition engine with methanol-gasoline-blends is similar to light duty application (cf. Part B of the Summary Report). Fleet tests in the 1990s used this engine type. Typical blends are M15, M56 and M85. Because of low reduced thermal efficiency, the conventional SI engines are not used as heavy-duty engine [8].

The compression ignition engine with Methanol-Diesel-Blends/Emulsions. The limited solubility of methanol in diesel complicates comparable blending such as methanol-gasoline-blends. Several research was done to find ways of using methanol through emulsions. The maximum amount of methanol in emulsion is between 10 and 30 vol%. The disadvantages, i.e. high amount of expensive emulsifier, change in cetane number, viscous flow behavior at low temperatures, separation in presence of water, material compatibility, of these emulsions prevent a commercial use [5,33,34].

## 4.5. Examples of Methanol heavy-duty application

Methanol heavy-duty applications were mainly tested in China in the last decade. There was launched a methanol vehicle project in 2012. Table 2 shows the vehicles, engine concept and the manufacture of the Chinese methanol heavy-duty vehicles. Other test trails are unknown to the authors.

Table 2 Methanol heavy-duty application [35,36]

| Application | Engine | Manufacture | Mode | Year |
|---|---|---|---|---|
| Yuan Cheng methanol heavy-truck | DISI | Geely | commercial | 2019 |
| 96 Buses in Changzhi (Shanxi, China) | Dual fuel | Zhengzhou Yutong Bus | Fleet test | 2019 |
| 5 Self-dumping trucks in Yulin (Shannxi, China) | Dual fuel | Shaanxi Heavy Auto Enterprise | Fleet test | 2019 |
| 15 Multi purpose vehicles in Baoji (Shannxi, China) | Dual fuel | Shaanxi Tongjia Automobile Co. | Fleet test | 2019 |
| Test truck by Tianjin University | Dual fuel | Tianjin University | Demonstration vehicle | |
| Trucks in coal mines | Dual fuel | FAW | Fleet test | |

## 4.6. Potential future development (R&D&I)

Methanol as fuel for heavy-duty application is a promising option to reduce the need for fossil diesel. It enables energy-efficient operation of the engine and reducing pollutants such as particulate matter and nitrogen oxides. Therefore additional research and development is needed to realize this potential – also from an OEM perspective. Table 3 shows an overview of further R&D&I. [1,5,9]

Table 3 Research and development for Methanol HDV application [1,5,9]

| Engine type | Challenges (-) & opportunities (+) | R & I needs |
|---|---|---|
| DISI,<br><br>SI lean | (–) Drivability and emissions control<br><br>(–) Potential for non-regulated aldehyde emissions<br><br>(+) Engine thermal efficiency matching or exceeding that of CI diesel engines throughout the operating area<br><br>(+) Reduction of tail pipe $NO_X$ and PM emissions | Significant potential was demonstrated during early testing. Furthermore detailed testing is required to fully understand the detailed R&I needs.<br><br>Dedicated and optimized methanol combustion, fuel, control and after-treatment systems with the aim to improve consumption and pollutant emissions. |

| | | |
|---|---|---|
| | (+) Dedicated fuel injection technology and control might allow further thermal efficiency improvements and pollutant emission reduction<br>(+) Potentially well suited to being combined with increased electric propulsion (PHEV, Range Extender) | Lean SI system development with specific advanced ignition systems, after-treatment and control systems.<br>Develop high efficiency, low pollutant and low cost engines for use in PHEV/Range Extender application. |
| MD95 | (+) Potential to demonstrate an optimized alcohol based fuel with appropriate additives in CI engine technology<br>(+) Reduction of tail pipe pollutant emissions<br>(+) A single liquid fuel diesel alternative that makes the infrastructure issue much easier | Suitability of methanol with an ignition improver (MD95)<br>Suitability of methanol-ethanol-mixture with an ignition improver (MED95)<br>Dedicated and optimized alcohol (with an ignition enhancer) combustion, fuel, control and after-treatment systems with the aim to improve consumption and pollutant emissions |
| DF-PFI-CI | (+) Currently very immature technology in HDV, but principle demonstrated in shipping and similar to Natural Gas Dual Fuel<br>(–) Potential corrosion issues<br>(–) Potential for non-regulated aldehyde emissions<br>(+) Dedicated fuel injection technology (HPDI) and control might allow further thermal efficiency improvements<br>(+) Multifuel capabilities to bridge fuel transition<br>(+) Engine thermal efficiency matching or exceeding that of CI diesel engines throughout the operating area<br>(+) Further reduction of tail pipe pollutant emissions due to lower engine out emissions.<br>(+) Lack of engine out PM allows further $NO_X$ reduction and / or improved fuel economy | Significant potential was demonstrated during early testing. Furthermore detailed testing is required to fully understand the detailed R&I needs<br>Assess corrosion issue and develop new materials / additives<br>Assess the scale of aldehyde emissions and reduction options<br>Optimized injection equipment for methanol/alcohol dual fuel applications<br>Optimized combustion, after-treatment and control systems |

# 5. Costs of operation

As can be seen from the previous chapter (especially 4.5), there were various activities concerning heavy-duty vehicles powered by methanol. However, in each case with only a small amount of vehicles. Unfortunately there is only sparse and isolated data comes from this projects to the cost of operation for methanol heavy-duty vehicles.

Most of available data for cost of operation is related to the China heavy-duty vehicle market, due to the long experience with methanol as motor fuel. For more than 40 years methanol has been supported in China and has reached now a tiny market share, but it has not penetrated the market yet. Nowadays, around 50 service station are operating with methanol naibly for PC/LDV application [37]. Since 2006 the Zhejiang Geely Holding Group (Geely) has been developing a methanol vehicle [38]. Geely is the first self-researched enterprise in China to develop a methanol heavy-duty vehicle. After 14 years of research and development they have been presented 2019 the first methanol powered heavy-duty truck (M100) [27]. Geely’s heavy-duty vehicle powered by methanol is promoted for less than 50,000 EUR [39,40].

Before reaching the whole market with the M100 methanol heavy-duty truck, it is also possible to convert a diesel truck into a heavy-duty vehicle that can run with methanol and diesel. This conversion would cost around 3,000 EUR [37,40]. The China Internal Combustion Engine Industry Association suggest that this investment charge off after around 100,000 kilometers [37].

The amortization is possible through the lower methanol fuel cost per kilometer, compared to diesel. The saving is specified with over 50% comparing with vehicles with the same displacement [41,42]. The fuel cost saving results from two different reasons: On the one hand methanol has a higher efficiency, on the other hand, in China, methanol is 25% cheaper compared with diesel on energy basis [10]. There is also a comparable difference concerning methanol and natural gas powered vehicles. For the bus test (6105-M-methanol bus) a difference of 23% per kilometer is stated. [41]

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# Appendix III: Marine methanol

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A Report from the Advanced Motor Fuels Technology Collaboration Programme

# Annex 56
# Marine methanol

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November 2019

## *Motivation*

The shipping sector is facing challenges along with tightening emission regulations. In the sulphur emission control areas (SECA), fuel with sulphur content below 0.1% or scrubbers are needed. Furthermore, sulphur content of marine fuels will be limited to max. 0.5% globally in 2020 (IMO MEPC, 2016). Tier III regulations are challenging in the NOx emissions control areas (NECA) for new vessels. Additionally, need to control black carbon emissions from shipping is evaluated by the IMO, and HFO-ban in the Arctic region is considered. At the same time, GHG strategy of the IMO is ambitious: cutting $CO_2$ emissions from shipping by 50% by 2050 (strategy 2018, rev. in 2023). In addition to larger ships, regulations for smaller vessels are also tightening.

Consequently, clean, sustainable and climate-neutral fuels and engine technologies are needed. There are many characteristics that are desired for the advanced fuel of choice:

- Commercial engines available on market.
- Low emissions even without exhaust aftertreatment devices (cost savings) to meet requirements of emission control areas.
- Compatible with existing infrastructure, or only minor modifications needed.
- Affordable relative to other advanced fuel options.
- Available in sufficient volumes.
- Sufficient quality (stability, impurities, corrosiveness)
- Safe

Methanol is one of the advanced fuel options considered for marine engines. However, technical feasibility and economy aspects need careful consideration before decisions on technologies are taken by industry and politicians. Special feature of shipping industry is that due to large size and high fuel consumption of ships, even ship-specific technology choices can be taken.

## *Infrastructure*

Methanol is a major commodity produced from natural gas and transported by tankers to different countries where methanol is further distributed routinely by road and rail. Therefore infrastructure for methanol is widely available for shipping purposes, and only minor changes are needed.

Distribution of methanol from renewable production plants to smaller vessels can be done by bunkering by tanker truck for conventional fuels. Methanol is routinely transported by tanker truck to customers. As a liquid fuel, methanol could serve even overseas marine transport.

## *Methanol engines for ships*

Diesel engines are known for their high efficiency and low fuel consumption. However, methanol engines could be even more efficient than diesel engines (Tuner, 2016; Björnestrand, 2017; Shamun et al., 2017), using e.g. direct-injection lean operation. Lowest efficiency is expected for concepts running at stoichiometric air-to-fuel ratio, which, however, show ultra-low emissions as three-way catalyst can be used (Tuner, 2016; Björnestrand, 2017).

*Methanol is corrosive and material compatibility needs to be verified* for each engine concept. In-cylinder corrosion is to be considered particularly if the engines are used at low loads or frequent start-stop operation without proper warming up of an engine, which is relevant concern for smaller vessels (Ellis *et al.*, 2018).

*For shipping, there are dual-fuel marine methanol engines on market.* Dual-fuel diesel engines for methanol use in large marine engines have been developed by Wärtsilä and MAN. Wärtsilä has developed a methanol-diesel retrofit concept for four-stroke medium-speed marine engines, called GD methanol-diesel, which has the advantage of using diesel as a back-up fuel (used in the Stena Germanica ferry). In this technology, changes in the cylinder heads, fuel injectors and fuel pumps are needed, as well as a special common rail system and ECU (Haraldson, 2014; Stojcevski, Jay and Vicenzi, 2016). Retrofitting reduces costs, although if the engine is too old it might be more cost effective to replace the complete engine. However, retrofitting has also challenges depending on the generation of the engine to be modified. (Ellis *et al.*, 2018).

Another dual-fuel engine concept for methanol developed by MAN for newbuilds is used in several tankers by Waterfront Shipping (Lampert, 2017; Co, 2018).

*Additised alcohol for diesel cycle, MD95 concept, has been tested* based on already commercially available engine, namely Scania's engine designed for ethanol with ignition improver and lubricity additive (ED95). This concept has been used since 1985 in over 600 buses supplied by Scania to several countries. The modifications to the diesel engines include increased compression ratio (28:1), a special fuel injection system and a catalyst to control aldehyde emissions.(Hedberg, 2007) This monofuel alcohol engine concept was studied with ethanol ED95 fuels, and preliminarily also with methanol using the commercial additives of ED95, by Nylund et al. (Nylund *et al.*, 2015; Schramm, 2016). New research on MD95 concept was conducted in the SUMMETH project (Aakko-Saksa *et al.*, 2020).

*Spark-ignited engines,* such as PFI-SI or DI-SI could be used in vessels, with pistons and cylinder heads adapted for spark plugs. These engines are on market for cars, and some smaller size classes for smaller vessels. Some promising advanced combustion systems are under development as described in report by (Verhelst and Tuner, 2019) and in Appendix 1 (contribution from Aalto University, Finland).

*The power output* from methanol engines are expected to be similar to those of diesel engines (Table 1), but compression ratio is high for MD95 and PFI-SI engine is vulnerable to knock.

***Table 1**. Comparison of various methanol engine concepts in comparison with HFO/diesel use in marine diesel engines.*

| Engine type | Status | Robust | Power, efficiency | SOx | HC, CO | NOx | PM |
|---|---|---|---|---|---|---|---|
| HFO/diesel | Reference | 0 | 0 | 0 | 0 | - | - |
| Dual-fuel | Large ships, on market | - | 0 | + | 0 | + | + |
| MD95 with ox.cat. | ED95 engine on market | - | - | + | 0 | + | + |

0 = similar performance with methanol as with HFO/diesel
– = worse performance with methanol than with HFO/diesel
+ = better performance with methanol than with HFO/diesel

## *Pollutants and climate emissions*

Methanol has low emissions in many respects. Its high oxygen content means low carbon based soot emissions in engine combustion. In dual-fuel engines, diesel pilot results in some soot emissions, but still lower than from conventional diesel engines. For MD95, there are no soot emissions, but some unburned additives are seen on particulate filters.

Dual-Fuel and MD95 concepts can reduce $NO_x$ emission down to approximately 2 g/kWh without SCR system, and even lower $NO_x$ can be achieved by the use of lean operation or EGR. For current SECA low SOx emissions with methanol alleviates costs as exhaust aftertreatment with scrubbers are not needed. HC, CO and aldehyde emissions measured from methanol engines have been low and to secure low emissions of organic gases, low-cost oxidizing catalysts can be used. Methanol engines are less noisy than diesel. (Corbett and Winebrake, 2018; Ellis *et al.*, 2018).

*Notable is that impacts of accidental spills of methanol would be less than those of a HFO/diesel spill as methanol is biodegradable.* (Ellis et al., 2018). Thus there are clear environmental benefits for vessels and ships switching to operation on methanol fuels.

In the SUMMETH project, use of methanol as a fuel in smaller vessels showed lower environmental impacts as compared to marine diesel fuels of today. A fuel life cycle comparison showed that methanol produced from renewable feedstock (e.g. wood residuals and pulp mill black liquor) can result in GHG emissions reductions of 75 to 90% (Fig. 1). Methanol produced from fossil feedstock results in a slightly higher GHG emission than conventional petroleum fuels. (Ellis *et al.*, 2018). Results from another evaluation are shown in Fig. 2. *(Corbett and Winebrake, 2018).*

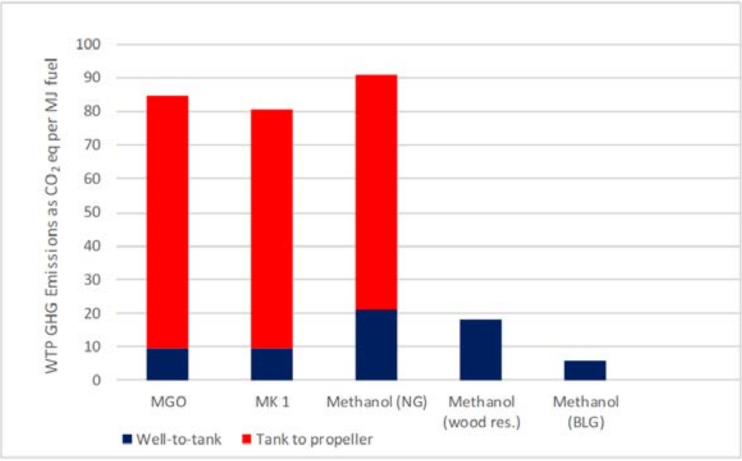


***Figure 1****. GHG emissions per MJ fuel for methanol from natural, wood residues, and black liquor gasification (BLG) as compared to marine gasoil and MK 1 diesel. (Ellis et al., 2018).*

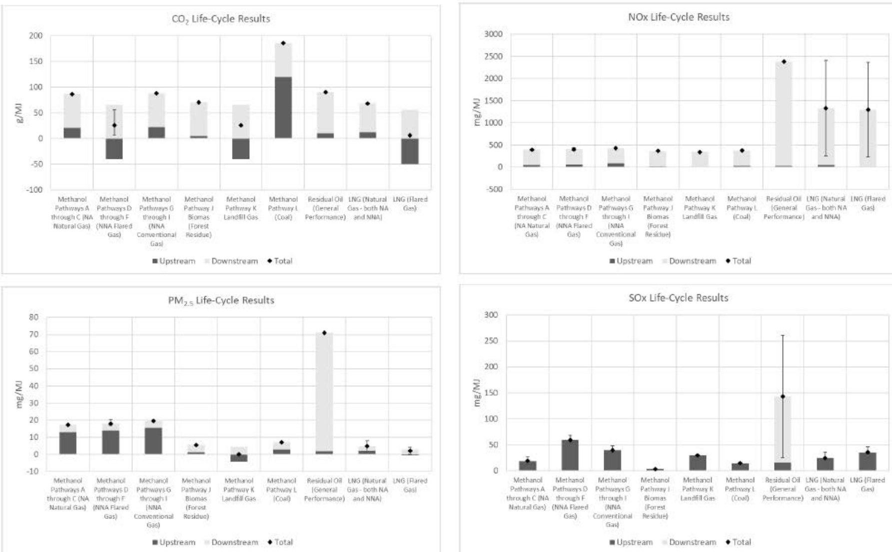


***Figure 2**. Summary of Life-Cycle Results for Methanol Compared with Residual Oil and LNG, for $CO_2$, $NO_x$, PM2.5, and $SO_x$. (Corbett and Winebrake, 2018).*

## *Safety*

The large ships using methanol in dual-fuel engines, the Stena Germanica and the Waterfront shipping chemical tankers, have undergone safety assessments prior to approval and to date have been operating safely. International regulations for use of methanol as a ship fuel are under development at the IMO, and classification societies have developed tentative or provisions rules. These international regulations provide guidance for good practice for handling methanol as a marine fuel also in smaller vessels. (Ellis *et al.*, 2018).

For small vessels some requirements applicable for large ships are not suitable, e.g. some automation requirements. However, less special arrangements are necessary for methanol use in smaller vessels than in larger ships. Practically, requirements would be very similar to those for gasoline. (Ellis *et al.*, 2018).

## *Costs of operation*

Cost of operation depends mainly on the fuel consumption of the engine. Therefore methanol engines have potential for low operating costs when compared to fuels at similar market price (fossil or renewable counterparts). However, for the MD95 concept additives increase fuel price to some extent, although additive use might be minimized with the intake manifold injection system. (Ellis *et al.*, 2018).

## *Costs of production*

**Biomass based methanol**

In Finland, several techno-economic studies of low-carbon fuels produced from cellulosic feedstocks have been conducted. Hannula and Kurkela (Hannula and Kurkela, 2013) studied 20 individual BTL plant designs to convert biomass into methanol, dimethyl ether (DME), Fischer-Tropsch liquids (FT) or synthetic gasoline (MTG) based on pressurised fluidised-bed oxygen gasification. The results showed that BTL fuels could be produced at reasonable costs (Fig. 3). FT liquids and synthetic gasoline were more expensive than methanol and DME, whereas FT and MTG are drop-in fuels meaning low system costs. The district heat (or cooling) output for these plants varied from 34 to 83 MW (lowest for methanol, highest for LTFT). Low heat output is desired to fit better to the existing networks.

All of the BTL plant designs examined demonstrated low cost of captured $CO_2$ (compression, transport and storage) with total costs in a BTL plant of 36–92 €/ton$CO_2$. BTL plants studied were attracting at crude oil price of 110-150 $/bbl. The lower end of the production cost estimates would not require substantial incentives to break even. However, cost of first-of-a-kind BTL plants is high, and thus regulatory actions and significant public support are necessary. (Hannula and Kurkela, 2013).

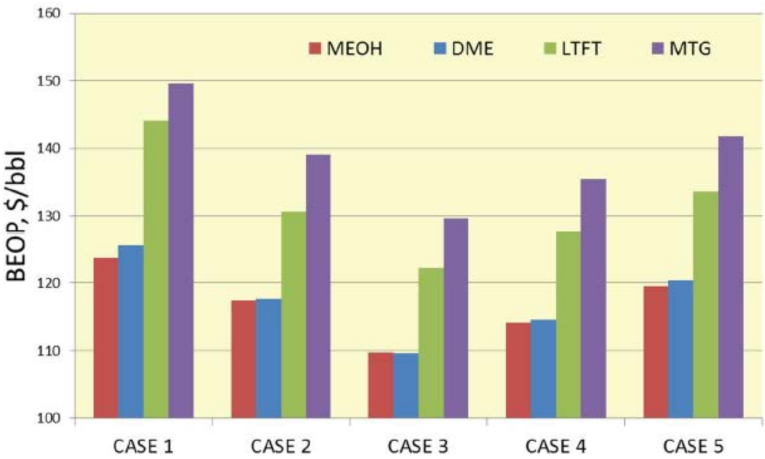


*Fig. 3. Levelised production cost estimates of fuel (LCOF) for the examined plant designs. The horizontal red lines show the comparable price of gasoline (before tax, refining margin 0.3 $/gal, exchange rate: 1 € = 1.326 $) with crude oil prices 100 $/bbl and 150 $/bbl. The cost estimates have been calculated for mature technology at 300 MWth (of biomass) scale, without investment support, $CO_2$ credits or tax assumptions.* (Hannula and Kurkela, 2013).

In Sweden, production of methanol from wood biomass, including gasification of wood residual and gasification of pulp mill black liquor, was tested. In a pilot plant, methanol was produced from pulp mill black liquor in Piteå successfully, but an industrial scale facility was not built up due to uncertainties regarding regulations and taxes. Also a plant using forest residues as feedstock, Värmlandsmetanol, was planned and designed. A small plant producing methanol from pulp production by-products at Södra's pulp mill in Mönsterås was running showing that technology is mature for production of methanol from biomass. In Sweden, biomass potential is sufficient to produce enough methanol for the smaller vessel segment. (Ellis *et al.*, 2018).

**Electro-fuel e-methanol**

Costs of producing electro-fuels have been studied by e.g. Hannula and

Reiner and Brynolf et al. (Hannula and Reiner, 2017; Brynolf *et al.*, 2018). The cost of electrolytic renewable hydrogen is dominated by the renewable electricity price. Hannula has estimated that the production costs of e-methane could be 1.5-2.5 times higher than those of hydrogen, while e-methanol would be slightly more costly than e-methane, and e-diesel (Fischer-Tropsch) is the most expensive (appr. 1.4 x e-methane costs). *When considering additional storage and distribution costs, differences in costs between liquid and gaseous fuels narrows*. Whether to use e-hydrogen directly or after conversion to e-fuels is governed by the type of end-use. (Hannula and Reiner, 2017).

Production of e-methanol from $CO_2$ is being tested in Sweden. A pilot project producing methanol from steel mill flue gases started in 2017. A feasibility study was completed for a small-medium scale plant to produce methanol from wind energy and $CO_2$ of primarily biogen origin (Liquid Wind ref. in (Ellis *et al.*, 2018)).

**Fossil methanol costs**

The cost of methanol produced from fossil feedstock has been mostly higher than MGO (Fig. 4) *(Corbett and Winebrake, 2018).* Production costs of renewable methanol are on average higher than prices of MGO and methanol from fossil feedstock, but the low range of the estimates show production costs that are almost competitive. Due to the higher cost of methanol as compared to other fuels, incentives, targets, or other measures are needed to drive its uptake as a marine fuel. Measures such as stricter emissions regulations favour the uptake of methanol, as other measures to meet these goals would be even more costly.

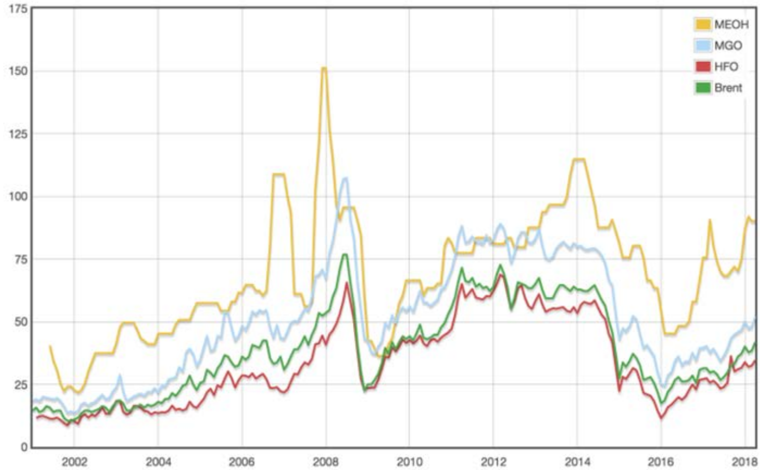

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***Figure 4****. Historical price of crude oil (Brent), conventional marine fuels (HFO, MGO) and fossil methanol from 2001 to 2018 ([http://marinemethanol.com/meohprice](http://marinemethanol.com/meohprice) in (Corbett and Winebrake, 2018)).*

**Possibilites to reduce methanol production costs**

One possibility to reduce costs of methanol is to use a lower purity than the 99.85% specified for the chemical industry (Ellis *et al.*, 2018). Combustion engines have been shown to operate even when purity of methanol is 90% (ref. in (Ellis *et al.*, 2018)). So far using a lower purity "fuel grade" methanol has been impractical, however, it could be an opportunity for smaller plants producing local renewable methanol for marine sector.

## *Competing technologies*

Summary of some aspects on competing technologies to reduce emission from shipping is presented in Table 2.

***Table 2****. Comparison of various methanol engine concepts in comparison with HFO/diesel use in marine diesel engines.*

| | Global warming emissions benefit | Other emissions | Comments |
|---|---|---|---|
| **HFO & scrubber; MDO/MGO (&SCR)** | No benefit | Low $SO_x$ and/or $NO_x$. | Scrubber capacity limited for fast introduction (port services). MDO/MGO the main immediate option in the SECA. |
| **LNG/LBG (methane)** | **Yes, if renewable origin.** Methane slip to be controlled. | Extremely low $SO_x$, $NO_x$, PM, PAH, VOCs. | Costly investment. LNG cooling efficiency? Retrofitting, de-bunkering, boil-off, methane slip, infrastructure? |
| **Bio/methanol** | **Yes, if renewable origin.** | Low $SO_x$, $NO_x$, PM, PAH. Oxidation catalyst may be needed for organic gases. | Methanol is a bulk chemical. Infrastructure is largely available. Toxicity concerns? Demonstrations and regulations are needed. |
| **Bio/DME** | **Yes, if renewable origin.** | Low $SO_x$, $NO_x$, PM, PAH. | For diesel cycle. Non-toxic. Special engines and infrastructure needed. |
| **Vegetable oils, animal fats** | **Yes, if renewable origin.** | Low $SO_x$, PM, PAH. | Not sufficiently available for large-scale use.<br>Possible regional solutions. |
| **Fuel savings**<br>**Efficiency**<br>**Sails (add-on)**<br>**Low steaming**<br>**Fuel cells**<br>**Transport system** | **Yes, if** unnecessary use of fuels is avoided. | Benefits for health and environment. | Sulphur free fuels could enable high efficiency and heat recovery. LNG and methanol could be utilized also with fuel cells. Commercial agreements needed for promotion. |

## *Research projects*

Research projects on methanol were presented in the 1st Sustainable Shipping Technologies Forum (26-27 September, Graz, Austria):

- MethaShip – renewable methanol a ‘long-term solution’ for emissions reduction Gerhard UNTIEDT/Daniel SAHNEN; MEYER WERFT GmbH & Co. KG, D.
- LeanShips – Low Energy and Near to Zero Emissions Ships Sebastian VERHELST/Louis SILEGHEM/Jeroen DIERICKX; Ghent University.
- SUMMETH – Sustainable Marine Methanol Päivi AAKKO-SAKSA; VTT Technical Research Centre of Finland Ltd.

Methanol is source of hydrogen to fuel cells and thus also marine hydrogen activities were presented:

- MARANDA – Marine application of a new fuel cell powertrain validated in demanding arctic conditions Laurence GRAND-CLEMENT; PersEE Innovation, F.
- HySeasIII – World-first Renewables-Powered Hydrogen Ferry Kevin HARKINS; Ferguson Marine, UK.
- Hydroville – First certified passenger shuttle with hydrogen power ICE Roy CAMPE; CMB Group, B.
- HyMethShip – On the Way to Zero Emission Shipping Nicole WERMUTH; LEC GmbH, A.

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**High-Pressure Direct Injection of Methanol with Diesel Pilot**

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High-pressure direct injection of methanol is investigated in a non-premixed dual-fuel (DF) setup with a diesel pilot. The present DF engine study is carried out via a specially designed new cylinder head (see Fig. 1) operating with both a diesel pilot injector and a centrally located methanol injector. The experiment was conducted at a constant engine speed of 1500 rpm and 16.5 compression ratio. First, the influence of methanol quantity is controlled by methanol injection duration, leading to the increase of methanol mean effective pressure ($FuelMEP_{Methanol}$). This increased Indicated mean effective pressure (IMEP) from 4.17bar to 13.78bar and methanol substitution ratio (MSR) from 45.3% to 95.3% (see Fig. 2). In the heat release rate, three stages were identified in the simultaneous combustion of diesel pilot and methanol. When methanol quantity (MSR) was increased above 95%, combustion remained stable due to high IMEP. Both CA5 and CA50 were retarded, $COV_{IEMP}$ decreased by 5% and HC emissions dropped from 26 g/kWh to 0.6 g/kWh, which suggests that direct injection of methanol is preferable at high IMEP conditions.
In addition, start of injection of the diesel pilot (DSOI) and of the methanol injection (MSOI) were varied to investigate the effects at a constant 6.23 IMEP and 88% MSR. If advancing the setup of DSOI/MSOI, the main combustion phase was forward, $COV_{IEMP}$ decreased slightly and HC emissions dropped by 9 g/kWh. When only advancing DSOI and keeping MSOI constant, ignition became earlier while CA50 was constant and HC emissions were decreased by 7 g/kWh. It indicates that early fuel injection has advantages in the direct injection methanol DF engine. To summarize, it is promising to operate the direct injection methanol engine at high IMEP (high engine load), high MSR and early fuel injection conditions concerning methanol utilization, combustion stability and emissions.

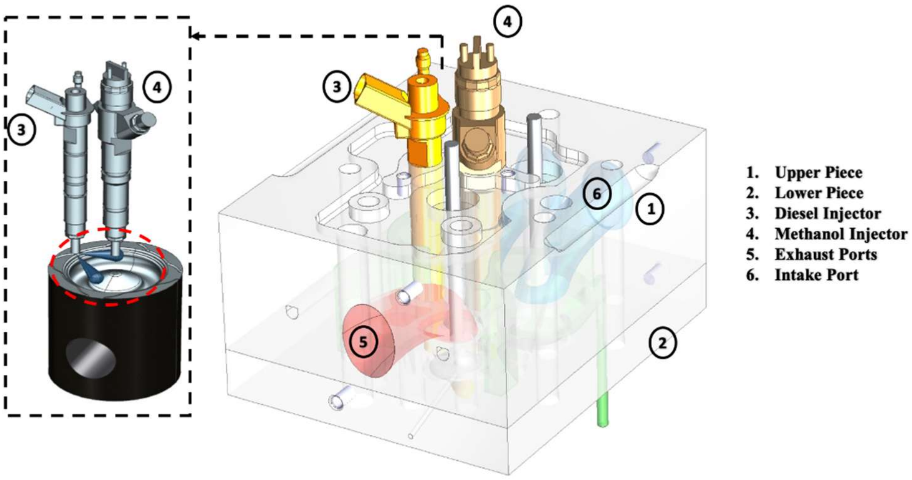
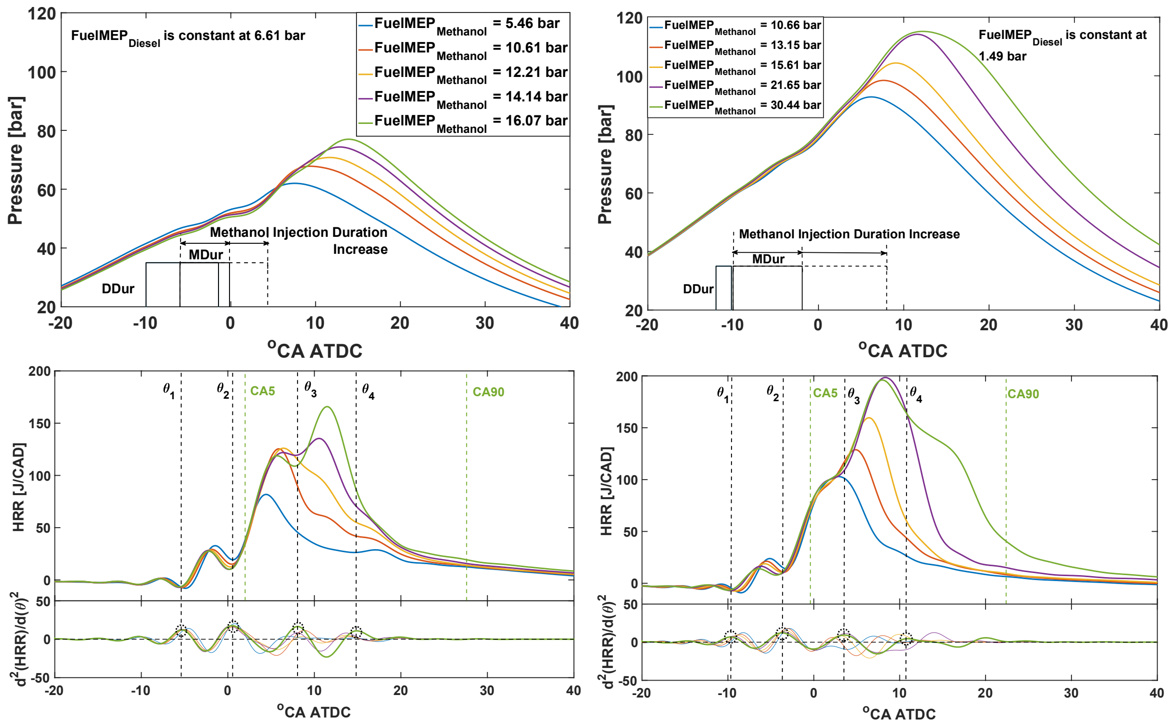



*Fig. 1: Two-injector, Three-valve Cylinder Head Design*




*(a)FuelMEP$_{Diesel}$=6.61bar, FuelMEP$_{Methanol}$=5.46 to 16.07bar (b)FuelMEP$_{Diesel}$=1.49bar, FuelMEP$_{Methanol}$=10.66 to 30.44bar*

*Fig. 2: Cylinder Pressure and HRR Curve of Methanol Quantity Study*

# Appendix IV: High efficiency methanol engines – HEME

Authors: Sebastian Verhelst and Martin Tunér
Lund University, Sweden

# High efficiency methanol engines – HEME

Sebastian Verhelst & Martin Tunér

Lund University

August, 2019

## Executive summary

This report provides insights into the current status and future perspectives of high efficiency methanol engines.

*Current use of high efficiency methanol engines*

Methanol provides several advantageous properties as a fuel, such as high flame speed, high latent heat of vaporization, high hydrogen and oxygen versus carbon ratio as well as a lack of carbon-carbon bonds, that offers higher improved overall engine efficiency and reduced emissions of NOx, soot and $CO_2$, compared to conventional fuels such as gasoline and diesel. The $CO_2$ emissions can be reduced further with high efficiency methanol engines since methanol can be produced cost efficiently from a large variety of renewable feed-stocks in large volumes. The reduced emissions and high efficiency, but also methanol's ability for high power engine operation motivates the current use in as diverse applications as in shipping, motorsports and miniature model airplane engines. However, the beneficial properties have so far not been enough for a large scale market penetration of methanol engines, mainly due to the availability of lower cost fossil gasoline and diesel fuels.

*Potential for even higher efficiency*

The use of methanol instead of gasoline is reported to reach peak efficiency increases in the order of 25% in spark ignited gasoline engines. Another 5 to 10% improvements seem relatively easy to achieve with dedicated methanol engines, primarily through increased compression ratio and increased peak pressure capability. Novell combustion strategies using compression ignition of methanol, such as HCCI, PPC and MD95, show promising results with further gains in efficiency and reduction of emissions, surpassing the efficiencies reached with other fuels. Due to the strong demands on improved fuel efficiency and reductions on emissions and green-house gasses, there is currently a rapid development of combustion engines in general that also benefits the development of high efficiency methanol engines. The beneficial properties of methanol fuel are, however, likely to maintain the benefits in terms of efficiency and emissions over other fuels also in future engines, or alternatively offer similar performance at lower cost.

*Potential future applications for high efficiency methanol engines*

Methanol has been proved to work well in most engine applications, ranging from the smallest, to the biggest, and to the most power dense engines. Partly due to a lack of a dedicated distribution system for methanol fuels for road vehicles, potential initial expansion of methanol engine use is within captive fleets such as within shipping, work machinery, busses and trucks. Such applications are typically consuming large amounts of energy, making efficiency even more important and the impact on environment even greater. The use of methanol would in several of these applications also offer an attractive way to reduce emissions at lower cost than with conventional diesel fuel.

Methanol can also be used to increase the amount of renewable fuels in the car sector, initially as drop-in in gasoline or in E85 compliant vehicles, with so called GEM, gasoline-ethanol-methanol blends. The similarity between methanol and ethanol offers an opportunity to expand the overall use of renewable fuels through the addition of methanol, with no or minor changes to E85 flex-fuel vehicles. Renewable methanol would likely be a relevant combination in hybrid application and a complement to electric vehicles to reduce the needs for fossil fuels in a cost effective way. Low cost efficient methanol engines could be a relevant option for low cost vehicles on emerging markets, fuelled on locally produced methanol. High efficiency methanol engines do not rely on exotic materials or unconventional production methods.

*Obstacles for large scale implementation of high efficiency methanol engines*

The obstacles for large scale implementation of future high efficiency methanol engines are numerous. Appropriate methanol fuel standards and test methods needs to be developed. The corrosiveness of methanol adds a complication to vehicle manufacturers and fuel distributers, that although not a severe issue and well known how to be handled, has to be offset by added performance, reduced costs or improved environmental performance or other fuel candidates will be preferred. The technology readiness level (TRL) requires further work for several applications, especially for the novel compression ignited methanol engine concepts, to comply with all regulations and customer demands. There is demand for research and development on dedicated methanol engines, fuelling systems, emissions aftertreatment devices, cold start performance, etc, for those applications not verified yet, to prove the actual potential.

Apart from the engine technology obstacles there are barriers in terms of legislation, available methanol fuel production and distribution and not the least from competing alternatives, such as vehicle electrification, hydrogen fuel cell technology or the other renewable fuels, where positive developments could reduce the incentives for introducing methanol and high efficiency methanol engines. Currently, however, high efficiency methanol engines seem to offer one of, if not the most cost effective way to reduce climate impact from transportation, and logically offer to be one of a couple of key technologies needed in parallel to replace the enormous amounts of fossil energy currently used. If future legislation will introduce lifecycle assessment, LCA, based regulations (to be investigated by EU 2023) and thus account for all environmental aspects of the use of vehicles in transportation (aka vehicle-, fuel- and electricity-production and use) then a large demand for renewable methanol and high efficiency methanol engines is not unlikely.

## Current status of high efficiency methanol engines

Methanol has a number of fuel properties that enable higher efficiency compared to gasoline or diesel engines [Ver19]. In the following, we will present an overview of recent results obtained on spark ignition (SI) engines and compression ignition (CI) engines, and offer an outlook on further potential gains in efficiency. Finally, we will also touch on the possibility of increasing the efficiency through fuel reforming using waste heat. Much of the material is based on a recent comprehensive review paper [Ver19]; where even more recent data is available those references are additionally cited.

### Spark ignition

Methanol’s high research octane number, high heat of vaporization, and high burning velocity, increase the resistance to autoignition. This opens the possibility for increasing engine efficiency compared to the more knock-limited fuel gasoline. The high burning velocity can also increase efficiency, through shorter combustion duration and thus better combustion phasing; and/or through enabling higher dilution (extended lean burn limit or higher EGR tolerance). Finally, the high heat of vaporization lowers temperatures in the combustion chamber, lowering heat losses (and NOx emissions).

The actual overall efficiency gain depends on the base engine:

- If the base engine is a gasoline engine, which is the case for most published data, and the base engine retains the hardware (i.e. original compression ratio) the gains are limited but can still be substantial.
    - For naturally aspirated engines, efficiency gains depend on the conditions: the effects of lowering heat losses and shorter combustion duration benefit efficiency overall, but the increased knock resistance obviously only benefits those points that are knock limited on gasoline. This also means gains can be expected to be higher for a directly injected (DI) engine than for a port fuel injected (PFI) engine. Published data is however limited to a handful of papers, indicating relative efficiency benefits up to 10% for a PFI engine [Van11] and up to 15% for a DI engine [Sil15]. In the latter case, the increased efficiency and the lower C/H ratio of methanol compared to gasoline, led to a decrease in CO2 emissions of 20.7%.
    - Boosted engines (e.g. downsized engines) are typically more knock limited so are even more suited for exploiting methanol's beneficial fuel properties. Relative efficiency gains of 25% have been reported [Ngu18], on a turbocharged DI engine, where more optimal spark timing can be maintained on methanol instead of knock-limited spark advance on gasoline. The beneficial effect could not be fully exploited as peak pressures are then much higher than on gasoline, possibly reaching higher than the design peak pressure.
    - The data above was all for stoichiometric operation. As mentioned before, methanol also allows higher dilution than gasoline. For the same turbocharged DI engine, lean operation was compared between methanol and gasoline [Ngu19b], leading up to 20% higher efficiency on methanol relative to gasoline, with a peak brake thermal efficiency of 41%. Methanol thus provides further gains than gasoline either with stoichiometric or lean operation.
- If the base engine is a diesel engine, which has then been converted to SI operation, two features are important: first, that the peak pressure limitation is removed, or at least greatly increased over an SI engine block; second, the compression ratio (CR) will typically be higher, making better use of methanol's higher resistance to autoignition. On the other hand, the CR will likely be higher than optimal, possibly imposing a knock limit and leading to higher frictional and heat losses. A higher peak pressure limit can allow a larger improvement of the efficiency since it removes a potential limit for combustion phasing.
  There is very limited data on such engines. A two-valve, turbocharged diesel engine converted to PFI SI operation on methanol but maintaining the original CR of 19.5:1 showed peak brake thermal efficiencies up to 42%, higher than the base engine achieved on diesel [Bru02,Van13]. Equally important is that through the use of EGR, wide open throttle (WOT) operation was possible from full load down to 3.3 bar brake mean effective pressure (BMEP), allowing reductions in pumping losses and thus favouring part load efficiency.
- If the engine could be optimized for dedicated operation on methanol, it would likely have the following features. First, the compression ratio could be higher than for gasoline, leading to an efficiency benefit over the entire load range. Second, with a higher peak pressure capability than for gasoline, peak pressures would not limit combustion phasing. Next, it would be possible to downsize the engine more than what would be possible on gasoline

(Nguyen et al. report 10% additional reduction in displacement would be possible if the peak pressure limit could be increased to 100 bar for their turbocharged DISI engine [Ngu18]). Thanks to optimal combustion phasing and cooler combustion overall, exhaust temperatures would be substantially lower on methanol than on gasoline, so that fuel enrichment would not be necessary to protect the turbine and a variable geometry turbine (VGT) would be more easily implemented. This would benefit efficiency over the load range by reducing pumping losses, and at high loads through stoichiometric operation. Due to the wider dilution tolerance of methanol, the degrees of freedom of a variable valve actuation system would increase, which could be used to benefit part load efficiency (reducing pumping losses for instance through internal EGR).

Summarizing the above, relative peak efficiency increases of the order of 25% over gasoline operation have been reported, for (downsized) engines designed to operate on gasoline. Another 5 to 10% would seem fairly easy to obtain with an engine design fully optimized for methanol's properties when looking at the more extensive data available for ethanol-fuelled engines. Probably even more important for real-world impact is the potential for increased part-load efficiency, since this will affect driving cycle efficiency (both legislated and real-world). Actual numbers are rather limited but seem to point to 25% relative efficiency improvement over gasoline, which however would require engine adaptations so as to better exploit methanol's lean burn characteristics for dethrottling the engine, and thus further reduced pumping losses. However, experimental results are still rather limited so more work would be beneficial, especially exploiting state-of-the-art engine technology (e.g. stratified combustion, highly flexible valvetrains, variable geometry turbines).

## Compression ignition

Looking at methanol's fuel properties, and the extremely low cetane number CN (estimated at CN=3 [Hag77]), it is clear that methanol is naturally suited to SI engines and that use in CI engines is not straightforward. For instance, cold starting can be a challenge. Still, given that most commercial applications use CI engines and that CI engines typically obtain higher efficiencies (peak and part load), several research groups have looked into methanol's use in CI engines [Ver19].

There are several possibilities for burning methanol in CI engines: adding a high cetane fuel to aid with ignition; increasing the temperature around top dead center by e.g. preheating the intake air, using glow-plugs to assisting ignition or increasing the compression ratio; or a combination of these.

Premixing methanol with the intake air and using a small diesel spray (the so-called pilot), i.e. using dual fuel combustion, is the most common approach. In its basic form this only requires the addition of a methanol PFI system so it offers a solution that can be retrofitted. Recent work has shown that the efficiency can either be higher or lower than for base diesel operation [Die19], with relative increases in efficiency up to 12% for higher loads (due to faster combustion and lower heat losses), albeit for a diesel engine with mechanical injection system with fixed injection timing.

Dual fuel approaches can improve the NOx-soot trade-off of diesel engines, but inherently are a compromise as the approach has limits (combustion stability limits at low loads, knocking limits at high loads). Other approaches, with direct injection of methanol, and without the use of a diesel pilot, offer more potential for high efficiency with very low emissions.

Glow-plug assisted combustion was used in a study by Caterpillar back in 1989-1990 where two diesel engine trucks where modified for CI operation on methanol fuel and driven in commercial use for about 60 000 km year around in snowy to hot weather. The engines had fuel systems compatible with methanol and glow plugs installed but where otherwise based on the original diesel engine with the same pistons and compression ratio. Energy consumption was similar to the two reference diesel fuelled trucks while the drivers preferred the methanol trucks due to their better agility and quitter and smother operation. The methanol engines suffered from frequent replacement of glow plugs and the occasional need to replace intake valves [Cat90].

Analogous to ED95, in which ethanol is directly injected as a blend containing 5% of high cetane number ignition enhancer, in a CI engine with increased compression ratio; MD95 has been proposed. This has recently been shown to work, with reduced emissions compared to ED95 [Aak17].

The most attractive concept however is one which uses 100% methanol, i.e. without ignition enhancer. Measurements and simulations have looked into partially premixed combustion (PPC) with methanol, a form of low temperature combustion in which all fuel gets injected before combustion starts. This allows some time for fuel-air mixing, beneficial for hydrocarbons to lower soot formation (this not being of concern to methanol, which does not form soot), and for lowering temperatures so that NOx formation is limited. Preliminary work on an externally charged single cylinder heavy duty engine has shown a peak gross indicated efficiency of 52.8% [Sha17]. The data from this work was used to validate a simulation model that was used to assess the efficiency potential of the PPC concept on methanol [Sve19a,Sve19b,Sve19c]. It was found that, over the investigated load range, the brake efficiency on methanol was on average 5.5% higher relative to gasoline (a fuel that has been proposed earlier as optimal for the PPC concept), with a peak brake thermal efficiency of 47.5% for the 75% load point [Sve19a]. Subsequent work optimized the compression ratio for maximizing the efficiency, finding an increase from the base compression ratio of 17.3 to 21.6 led to an average 1.4 %pt higher efficiency. The peak brake thermal efficiency, again for the 75% load point, increased to 48.2%. Finally, it was checked how sensitive these numbers were to changes in the injection strategy [Sve19c]. The highest efficiencies were reached with fairly early injection timings, which could be a challenge in practice (crevice losses, controllability). Limiting the injection timing to close to top dead center dropped the efficiency, with the effect being strongest for the high load point that was investigated: from 47.5 to 45.3 % for the 75% load point.

These results – but with limited experimental data, and the simulation data that remains to be validated – clearly demonstrate the potential of high efficiency with ultralow emissions. However, more work in this area is warranted.

## Fuel reforming

Reforming of liquid fuel to a gaseous fuel, typically containing hydrogen, making use of waste exhaust heat, has been investigated for different reasons [Tar18]. One target is reducing emissions, either through the benefits of having a gaseous fuel instead of a liquid one; or using the hydrogen-rich gas to more easily regenerate aftertreatment, or reduce NOx emissions by extending the lean limit.

The second target is the more relevant in this report, namely increasing the overall system efficiency. As the reforming reactions are typically endothermic, and are driven by waste exhaust heat, the increased heating value of the reforming products are a form of waste heat recovery. Instead of for instance an organic Rankine cycle, the fuel itself is now the waste heat recovery medium. A heat exchanger in the exhaust is still needed, and a catalyst to promote the reforming reactions, but no additional expander is required.

Methanol is attractive for fuel reforming concepts since it is more readily reformed than other liquid fuels [Ver19]. The thermal decomposition of methanol into carbon monoxide and hydrogen theoretically leads up to a 20% increase in the heating value. Some authors have thus implied that relative efficiency increases of the same order would be possible. However, while the heating value of the reformed stream might increase, there are competing effects. One effect that has been overlooked until recently is the molar expansion ratio decrease. This is the mole ratio of products to reactants, which is much lower for hydrogen compared to methanol. The same is true for CO. As hydrogen and CO are the two main products of fuel reforming, the work potential of the reformed fuel significantly decreases [Szy12]. Recently it was found that the effect negates most of the heating value increase so actual efficiency increases are quite modest [Ngu19a].

Still, there could be advantages for part load efficiency. The increased volume of the reforming products relative to methanol can be used to dethrottle the engine, and the hydrogen fraction allows an extension of the dilution tolerance, so that additional EGR could be used at part load, further dethrottling the engine.

Finally, on-board reforming of methanol has also been proposed for RCCI concepts (reactivity controlled compression ignition). This would enable storing a single fuel, but through reforming obtaining two fuels of different reactivity [Lu11]. These fuels could be dimethylether (DME), a high cetane fuel, and methanol or methanol reformer gas, high octane fuels.

## Perspectives for future high efficiency methanol engines in hybrid and non-hybrid applications

### Engine developments

Stricter emission regulations and fuel efficiency goals; the rapid development of computers that allows more advanced engine control as well as numerical models for engine development; and not least the competition from and integration with electric powertrains; have all led to rapid engine development the last decades, which continues. The interest for research on methanol engines has increased the last decade and although there is still a limited amount of data, already at this stage do methanol engines, show strong potential for high efficiency and low engine-out emissions operation, typically surpassing the equivalent engines fuelled with gasoline or diesel that have been extensively developed and optimized over more than a century.

Considering the currently very small market penetration of methanol engines, research and, especially industry development of combustion engines is primarily directed towards engines running on conventional fuels. These research and development efforts create an improved understanding about combustion engines in general and are valuable, nonetheless, for future methanol engines too.

The Japanese SIP project is one such example, where the target of reaching 50% thermal efficiency, has been achieved for light-duty spark-ignited gasoline engines (51.5%) [SIP19]. These results provide valuable insights about how to reduce various losses (heat losses; e.g. friction, exhaust heat losses etc.) through various measures that can be transferred to SI-methanol engine technologies.

The SIP project success depends to a large extent on “super-lean” operation, something that could be even more suitable for methanol combustion with its well-known extended lean limit operation capability [Ver19]. But, the current advantage in efficiency for light-duty methanol engines over their gasoline fuelled counterparts is expected to diminish as overall efficiency increases, since much of the efforts are directed to mitigate problems with slow combustion rate, knock and exhaust heat, issues that methanol naturally solves, as explained above. The end result is that methanol most likely can provide performance advantages on equally advanced engine technologies, or offer similar performance as gasoline engines with less costly technology.

Considering the promising research results on compression ignition engines running on methanol, further research and also industrial development is relevant. Much of the research on PPC methanol engines at Lund university has been performed on diesel engines with modifications to the fuelling system to tolerate methanol, cold start support, and modifications on control strategies to optimize the methanol operation. This engine hardware setup runs efficiently on a multitude of liquid fuels, such as diesel fuel, gasoline, ethanol, E85, HVO and biodiesel. What varies is primarily the strategies to control the combustion. This fuel-flexibility ranging from high cetane number fuels (diesel type fuels) to high octane number fuels (gasoline, alcohols), which is harder to achieve with spark-ignition engines, poses an interesting opportunity for commercial fleet operators willing to operate on renewable methanol, but not being certain to always find methanol filling stations and thus needing a conventional fuel as back-up. Methanol is currently unavailable at fuel stations on most markets, and introduction will take time.

Similar to spark-ignited engines, there is strong development on compression ignition engines as well. One example is the super-truck programs in the USA where 55% brake thermal efficiency is targeted and achieved [Sup19]. These programs are not limited to reducing losses from the engine itself, but also to investigate and demonstrate the possibility to recover lost heat from the engine and convert that into useful work. Lund university is supporting AB Volvo's activities in the super-truck programs and is researching a new engine concept, the double compression expansion engine, the DCEE, which by more efficiently separated compression, expansion and combustion offers reductions in friction and heat losses [Lam19]. Initial studies suggest a potential for above 56% BTE from the engine alone, on diesel fuel. Considering the discussed beneficial properties of methanol fuel, there is possibly an opportunity for even higher efficiency for a methanol version of the DCEE, and possibly the first ever commercial engine application that surpasses 60% brake thermal efficiency.

## Engine (non-hybrid) applications

Methanol fuel has been used in a large variety of applications ranging from racing engines (high power density, low emissions), to large ship engines (low emissions at attractive price) and the smallest model airplane engines (ease of handling, low emissions). Methanol engines are versatile, powerful and clean.

Although the western world today is a mature market with expected slightly decreasing future sales of cars, car sales in the rest of the world are increasing rapidly. From the current 90 million cars and trucks sold annually (2 million EV´s), most of the increase comes from car sales in countries with developing economies, where there is a demand for low cost cars [IEA19, Aut16]. Considering that methanol engines do not require any unusual or rare materials, there is little challenging the realism of massive scale production of such engines. The beneficial properties of methanol allow more efficient naturally aspirated low cost engines suitable for low cost vehicles, compared to other fuels. There is also substantial knowledge on how to make such engine fuel-flexible and allowing operation on methanol, ethanol and gasoline and blends thereof. Ethanol is currently more readily available on several markets and is also an alcohol with quite similar properties to methanol. Gasoline is a less fuel efficient fuel compared to alcohols but it´s availability guarantees mobility in a transition period towards fossil free transportation.

Most of the small engines used in the world for motorcycles, mopeds, chain-saws, lawn-movers and several other hand-held devices, are also typically based on simple spark-ignition gasoline engine technology. These applications are in several cases suitable for similarly simple spark-ignited methanol/ethanol engines where the low cost, added efficiency and increased power density make sense. However, many of these applications are being replaced with battery electric powertrains, which is especially valuable where exposure to exhausts can be an issue and could lead to negative health effects.

The presented recent research on heavy-duty engines demonstrates that methanol engines are relevant for ships, trucks and long-distance buses. The high efficiency potential is an important factor to reduce overall cost for fleet and vehicle owners, and with the continuous use of such devices (large energy consumption) there is larger interest to implement advanced and costlier technologies, for instance high pressure boosting, to further improve efficiency. Also in this case, there is currently nothing implying the need of unusual materials that could prevent large scale production of these types of ultra-high efficiency methanol engines.

Agricultural-, forestry- and work-machines are excellent candidates for the use of methanol/ethanol engines. Their energy consumption is high due to the high loads they operate at, while the emissions benefits of methanol engines reduces the cost for emission aftertreatment devices. These devices are currently often lacking in existing pre TIER regulations machines anyway, due to long service life of these machines. Considering that these machines work to produce the bio-based feed-stocks, there is not the least a marketing logic that they could run on that biomass too. That methanol has no long term adversary effects at spillage, contrary to diesel fuel, makes implementation all the more sense to avoid long term damage to soil and crops [Cla13]. The sector as such, corresponds to about 10-20% of the energy consumption of road traffic, and is responsible for a much higher proportion regarding emissions of particulates and NOx. The sector depend less on a fuel distribution net of filling stations, which makes the implementation of methanol engines easier.

The shipping sector is already making in-routes towards operation with methanol engines [WMN18]. The main objective has been to meet the introduction of emission regulations at coastal areas, without the need to introduce expensive emissions aftertreatment devices. Other benefits discovered include improved efficiency, cleaner and lower temperature in the machine rooms, and reduce risk at spillages. Stena Line has pioneered the efforts and have gained substantial experience through the conversion and operation of the four on-board engines of the Stena Germanica ferry from diesel fuel to methanol. As emissions regulations continue to be introduced for global shipping, the ship owners need to comply with these by either implementing advanced emissions aftertreatment or by modifying the engines for operation on cleaner fuels, such as LNG or methanol. The latter has also the added benefit to provide a solution for future regulation to reduce $CO_2$ emissions from shipping.

## Hybrid applications

Hybrid drive has gained interest as a means to reduce fuel consumption and emissions, since it offers the ability to recover brake energy and allows the combustion engine to operate at its most efficient and clean operating points [Hyb19]. Another benefit is the capability to operate without tailpipe emissions for a certain distance. These days, hybrid drive typically relies on battery electric storage and an electric drive system. While fully battery electric drive offers attractive features such as reduced local emissions, refined drive and lower noise at low vehicle speeds, there are several question marks regarding availability and environmental impact of battery materials; the time required to build a sufficient charging network and not least the energy sources of the electricity [ECR18, Lee18, IEA18].

As hybrid application adds complexity and expense by having two powertrain systems, these negatives needs to be balanced by improved performance. One example is the current trend where electric vehicles are getting bigger batteries to provide similar driving ranges as combustion engine vehicles. Considering the limited resources on battery materials and also the typical daily driving distance of especially cars, it is possible to electrify transportation many times more, by distributing the limited battery materials over a larger number of vehicles and guarantee the driving distance with small, low cost combustion engines fuelled with renewable methanol only used when driving distance exceeds the battery capacity. Current owners of plug-in hybrids typically report that they run on battery electric alone 90% of the time, with the exception for the limited number of occasions where they visit relatives far away or take the car for the vacation. Unfortunately, all hybrids currently on the market are designed to run on fossil fuels, thus missing an excellent opportunity for very low overall environmental impact a hybrid on renewable fuels would be able to offer. This is possibly all about to change since Toyota is to offer an ethanol-hybrid (E100) for the Brazilian market Q4, 2019 [Reu19, Toy19]. Already since many years a number of Toyota Prius hybrids have at low cost been successfully converted to E85 operation, offering excellent environmental performance. See for instance [BSR10]. Considering that there is much evidence that ethanol engines work well with methanol, the step to introduce alcohol or methanol hybrids is not that long.

Hybrid cars of today are typically designed with a conventional and rather powerful combustion engine. Future hybrids can benefit from a more powerful electric motor and instead a smaller efficient low cost methanol engine (similar to the ones described for low cost cars) to reduce overall cost of the powertrain and offer advantages of the electric drive refinement and renewable fuel´s emissions performance. Indeed, BMW did introduce similar *range extender* concept with their i3 and i8 cars but with gasoline engines [BMW19]. The concept was designed to meet the Californian CARB rules and was initially successful with more than 60 % share sales (i3) and appreciative owners, but due to the small fuel tank and with added battery capacity BMW has decided to stop offering the i3 range extender version in Europe and focus their hybrids efforts to their regular car models. This demonstrates the value of the technology but also the need to make sure the range extender actually also offers range.

For heavier applications where overall operation cost means more, range extender solutions with more powerful electric drive systems, with small batteries and small but efficient range extender engines on renewable fuels will most likely have a strong potential. There are many potential hybrid system layouts that are relevant depending on application (buses, wheel-loaders, trucks, cars, marine vessels, generators, etc).

## Short term obstacles for a wider introduction, from an engine technology perspective

From the above, it is clear that to enable the highest engine efficiencies on methanol, a dedicated engine design is required. As the initial markets (e.g. marine market) currently is rather small (limited number of engines sold to those markets), it can be difficult for engine manufacturers to justify the investment in such dedicated methanol engines. Perhaps synergies can be sought for those manufacturers that are considering the market introduction of dedicated natural gas engines, since these can share some features with dedicated methanol engines (higher compression ratio, variable turbine geometry, higher peak pressure capability, and more).

In terms of required components, the single most important one must be the fuel injection equipment (FIE). Port fuel injectors are available for light and heavy duty applications, but durability remains to be proven. This should fundamentally not be an issue, but experience has shown commercially available injectors that are supposed to be suitable for methanol operation, to fail after only limited running hours. For bigger engines (e.g. medium speed ship engines), there are no commercially available port fuel injectors for methanol currently. Similarly, for direct injection, there is no commercially available FIE for methanol.

# Estimate of the potential for market penetration in medium and long term

## Legislative impact

The development of the market for methanol engines is highly dependent on legislation since renewable methanol currently cannot compete with fossil fuels on price alone. The current directives, in for instance the European Union, have a focus on tailpipe emissions and do not include impact from production of vehicles, fuels or electricity [EC09]. The effect of such directives, is that the benefits with renewable fuels are not accounted for, and that electric drive incorrectly and unreasonably is accounted as zero environmental impact technology, not differentiating, for instance, between electric cars with low or high environmental impact during their production and use. The legislation is reflected in the strategies of the automotive industry that needs to comply with the regulations and business logic, with a high emphasis on developing and marketing electric vehicles and very limited activities on renewable fuels and engines adapted for those. However, the ambitious goals to reach fossil free transportation within the coming decades [EC18] calls for a holistic approach and legislation that is based on life-cycle-assessment (LCA). Such legislation and directives are proposed to be investigated by the European Union 2023 and if implemented will most likely lead to a huge demand on renewable fuels since electrification alone cannot meet the needs for fossil free transportation [IEA18].

## Methanol versus other renewable fuels and electricity

When judging whether methanol can make a significant market penetration compared to other energy sources for transportation, four combined factors are important, namely; functionality, scalability, affordability and sustainability. Covering the aspect of *sustainability*, which currently is the main motivator to replace fossil fuels, methanol can be produced and used in ways that offer very low environmental impact (ref). Partly, due to the simplicity of the methanol molecule, it can also be produced efficiently in several ways from a multitude of sources (forest residue, waste, captured $CO_2$, etc.) which offers both *scalability* and *affordability*. Other renewable fuels can in theory also be produced in large volumes, but the increased complexity of their composition adds in most cases to costly process steps. Molecules simpler than methanol, such as the gases methane and hydrogen, are suitable as fuels and can as electro-fuels be produced at lower cost than electro-methanol (bio-methanol is yet lower cost) but the added cost and complexity of handling gas has to be considered. Hydrogen can be used in fuel-cell cars, with potential for very high efficiency and low emissions, but is currently a technology under development and still very expensive [Wi19].

Vegetable oil fuels, such as FAME biodiesel and HVO (hydro-treated vegetable oil) are already offered on some markets at an attractive price. In Sweden today, above 15% of the consumed road transportation energy comes from HVO (either as blend in diesel or as HVO100). HVO is attractive since it is a sustainable, direct replacement for fossil diesel fuel in diesel engines, but there are no clear additional emissions or efficiency benefits as with methanol [Tun16]. The suitable, sustainable feed-stocks for HVO are also limited and it is not unlikely that HVO, that is approved as a jet fuel, will be prioritized for aviation [EAFO19].

Regarding *functionality* methanol is, as reported, an efficient engine fuel and offers strongly reduced particulate and NOx engine-out emissions. The latter explains the early market penetration as a fuel for maritime applications where expensive emissions aftertreatment systems can be avoided.

The main obstacles for short and medium term market penetration are:

- Proof of long term durability of the fuelling system.
- Fuel standards for neat methanol and various blends of methanol with other fuel components (for instance the E85 similar M56).
- Certification tests for the engine and vehicle manufacturers.

Fuel standards are needed to make sure that fuels that are produced and marketed fulfil the criteria agreed upon for use in engines (to guarantee engine performance, cold starting emissions, etc.). For gasoline one commonly used standard is the EN228 while diesel fuel can be marketed according to EN590. Although EN288 allows 3 % methanol within the total allowed 10% oxygenates, there is no standards specifying neat methanol fuel (100 % methanol) or blends containing higher fractions of methanol. Although a neat methanol standard might seem superficial, production of methanol typically incurs fractions of other components, like higher alcohols and other components, that can be expensive to remove. Chemical grade methanol, used on the chemical market, is of high purity (99.99 %) and unnecessarily expensive for use as a fuel. But to define suitable allowances for the composition of a fuel grade neat methanol a standard for such needs to be proposed and verified through engine testing. The standard will also need to specify which test methods that should be used to verify the testing procedures for new produced batches of methanol fuels (or standardized blends). Gasoline is, as an example, tested according to the ASTM D2699 to verify the octane rating, among other tests.

The certification tests are used to determine that an engine or vehicle fulfils all legislated requirements, for instance regarding emissions [EC09]. These tests have over the years become increasingly extensive due to the increased number of factors and operating conditions that are examined and also due to the complexity of measuring the extremely low levels of emissions that modern engines emit (bordering on detection levels and requiring new measurement technologies). These tests demand huge resources from the engine manufacturers, and for obvious reasons challenges the opportunity to certify several fuels and powertrains.

Electric is quickly gaining interest as a mean for propelling transportation. So, a question often raised is whether methanol (and other renewable fuels) have a case compared to electric drive? We have already discussed some of the benefits and challenges above that show that electric drive alone cannot solve the future transportation needs or reduce green-house-gasses, GHG, sufficiently. Another recent report shows that several of the renewable fuels are indeed up to four times more cost effective in reducing GHG from transportation than electric drive even on low-cost, low-GHG electricity from Sweden [Koll19]. Methanol is one of the best candidates in this report.

## Scenarios for future methanol engines

The discussion above indicates that there will be a strong demand for renewable fuels in the future. It is likely that there will be room for a number of different renewable fuels, and little suggests why methanol should not be one of those.

We can make a simple exercise to illuminate a scenario to replace fossil fuels partly with methanol. About 6 billion tons of oil is produced every year of which about 1.5 billion tons are used in transportation [IEA18]. This can be compared to the about 110 million tons of current methanol production capacity of the world, mainly from fossil natural gas, which is about 30 times less than the energy consumed in transportation. We also need to remember that most of this capacity is already used to produce chemical grade methanol for the chemical industry ending up in a multitude of consumer products.

The global transportation sector is also expected to almost double in the coming 20-30 years [WES11]. If we assume that specific transport fuel consumption can be reduced by 30% in that 20-year period, thanks to better coordinated transportation, improved vehicles (with reduced drag and rolling resistance, brake energy recovery and improved engines/energy storage), there is still a net increase of energy needs in transportation. If we make a very optimistic assumption that half of the current oil consumption can be replaced with transportation driven by renewable electricity we still need to cover more than the energy equivalent of 1 billion ton of oil, with other renewable energy sources. If half of that should come from renewable methanol by 2040 (about 2 billion tons annually, due to the difference in heating value) the production will have to double every second year starting with a capacity of 1 million tons in year 2020 (current capacity of renewable methanol is substantially below that).

By considering an introduction of low cost but efficient methanol car engines and a focus on engines for heavier and overall more energy intense applications, following the market penetration potential for such engines based on performances as laid out in this report and the example of methanol fuel production above; there will be a need for around 20 000 methanol compliant engines in 2020 (current gasoline engines are accepted to be used with 3% methanol and do not need modifications), quickly increasing to around 250 000 methanol engines annually by 2026 and planning out at around 40 million methanol engines annually by 2033 to decrease in numbers thereafter. Obviously this is just a simple example, but it still provides ideas about the scales.

Early large scale use of methanol in transportation could be as drop-in up to 3% in gasoline, for use in regular gasoline engines. Considering the similarity between methanol and ethanol (see GEM above) high ratio 56% drop-in of methanol in gasoline could be an attractive way to increase the use of methanol for future vehicles certified for both E85 and M56. M100 (100% methanol) is already used and is likely to grow with captive fleets using dedicated methanol engines, dual-fuel engines or the proposed flex-fuel engines discussed earlier. These are applications within shipping, heavier trucks and agricultural/work machinery. As methanol engine technology matures and renewable methanol production picks up there is potential for an increased number of applications using engines running on 100% or close to 100% methanol. Many of these will be integrated in hybrid applications running large shares of operation on renewable electricity coproduced with renewable e-methanol.

It is not unlikely, though, that electric drive for private cars will still have a huge future public demand due its other benefits, but there is much support for scenarios where renewable fuels and combustion engines will have dominant impact on transportation for the foreseeable future and that there are great opportunities for the world to benefit from both electric propulsion and renewable fuels combined [IEA18].

If we assume that legislation indeed gets LCA based, then challenges to large scale market penetration of methanol engines could be the following:

- Break-through on fast charging or new types of batteries for vehicles – depending less on rare materials, allowing increased production of low cost electric vehicles
- Strong cost reduction of fuel cells – making FC vehicles a cost competitive alternative
- Strong demand for renewable methanol in other sectors

## List of abbreviations

| | |
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| BMEP | brake mean effective pressure |
| CI | compression ignition |
| DI | direct injection |
| EGR | exhaust gas recirculation |
| FIE | fuel injection equipment |
| PFI | port fuel injection |
| SI | spark ignition |
| WOT | wide open throttle |

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# Appendix V: Methanol as motor fuel – Barriers of commercialization

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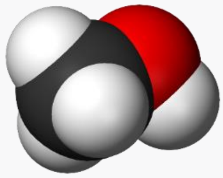

IEA-AMF Annex 56

# Methanol as motor fuel


“ – **$CO_2$ emission was reduced to just 40 g/km.**

M85 has ideal properties for both summer and winter in Denmark.

**Title:**
Methanol as motor fuel

**Prepared for:**
EUDP 2018-I

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May 8th 2019
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## 1. Executive summary

Methanol as motor fuel has regained interest in recent year due to its low price, easy handling and high octane number. Methanol can nowadays be produced from biogas which yields an extremely low Greenhouse Gas emission – easily comparable to those of electric vehicles. According to the latest EU-Renewable Energy Directive, with biogas, it is possible to reach even negative $CO_2$-eqivalent emissions!

Efforts to establish large methanol factory in Denmark with connection to the Danish gas grid are ongoing. Until that happens methanol can easily be imported from Norway. Certificate trading ensures that the methanol is based on Danish biogas.

Methanol is not yet implemented in the Danish transport sector. The current exchange agreement between the fuel companies only allows ethanol to be added to gasoline. However, this barrier can be removed, and 3% methanol be introduced in a new A7 (A for alcohol with 3% methanol and 4% ethanol). A7 can easily and advantageously replace E5 as the current standard gasoline.

In the long term, however, completely new fuels are required. The Danish participants in the project "IEA-AMF Annex 56 Methanol as Motor Fuel" have therefore tested a 105 Octane M85 fuel consisting of 85% methanol and 15% petrol. The pilot car, a Peugeot 107, got a € 100 flex fuel kit installed and its engine performance on 105 Octane M85 went up by 5-7% with all emissions kept in place.

The report finds that methanol can be introduced into the current gasoline infrastructure with very little investment and with no loss of tax revenues. A complete distribution setup is described in the report.

Technical or legislative barriers that need attention are also described in the report.

## 2. Introduction

The Shanxi province has since 2008 had local methanol gasoline standards for M5, M15, M85 and M100. In 2014 the consumption in China of methanol blends with gasoline grew to 7 million tons[1].

The strategy of The European Commission Climate Action is among other things to promote the use of advanced biofuels like 2G-biomethanol. Transport represents almost a quarter of Europe's greenhouse gas emissions and is the main cause of air pollution in cities. The transport sector has not seen the same gradual decline in $CO_2$-emissions as other sectors. Within this sector, road transport is by far the biggest emitter accounting for more than 70 % of all GHG emissions from transport in 2014[2].

Danish Technological Institute and Danish Methanol Association[3] have jointly applied for EUDP support for this preliminary project to pave the way for the use of methanol in the transport sector. July 2, 2018 The Danish Energy Agency announced its support for the project.

The project is part of IEA-Advanced Motor Fuels Annex 56 "Methanol as Motor Fuel" led by the Israeli operating agent, Technion. This report includes the Danish part and focuses on bringing methanol to the short-term market, by overcoming distribution and application barriers.

The report covers the following working packages:

- WP1: Study of barriers to methanol
- WP2: Engine testing with methanol high blends
- WP3: Outline for a National demonstration project
- WP4: Communication and dissemination effort

[1] http://www.methanol.org/wp-content/uploads/2016/06/China-Methanol-Fact-Sheet-1.pdf
[2] https://ec.europa.eu/clima/policies/transport_en
[3] http://danskbiomethanol.dk/profile/home.html

## 3. Vehicle experiments

The purpose of the vehicle experiments was to see if a standard gasoline car would be able to run on methanol.


**Figure 1 Test vehicle equipped with measurement system**

### 3.1. Test setup

The test is focused on engine performance, fuel economy, emissions, noise and drivability.

First the vehicle was tested on standard E5 gasoline. The maximum engine power and torque was measured on a chassis dyno. Then emissions and fuel consumption were measured according to World Light-duty Test Protocol (WLTP) and Real Driving Emission (RDE). Finally, a sample of the engine oil was taken.

The vehicle was then fueled successively with methanol blended gasoline gradually raised in ratio from $15\%_{vol}$ to $100\%_{vol}$ - M15, M25, M50, M65, M75, M85 and M100.

The test vehicle was a Peugeot 107 1.0 68hk from 2008. It has a Toyota/Daihatsu 1KR-FE $998cm^3$ 3-cylinder spark ignition engine with a nominal output of 50 kW. The engine is known from other vehicles such as Toyota Aygo and Citroën C1.

The engine has a cable drawn intake air throttle, a variable valve timing system, knock sensor, crank angle sensor, manifold air pressure sensor and an oxygen sensor. Compression ratio is 10.5:1 which is normal for a naturally aspirated gasoline engine.

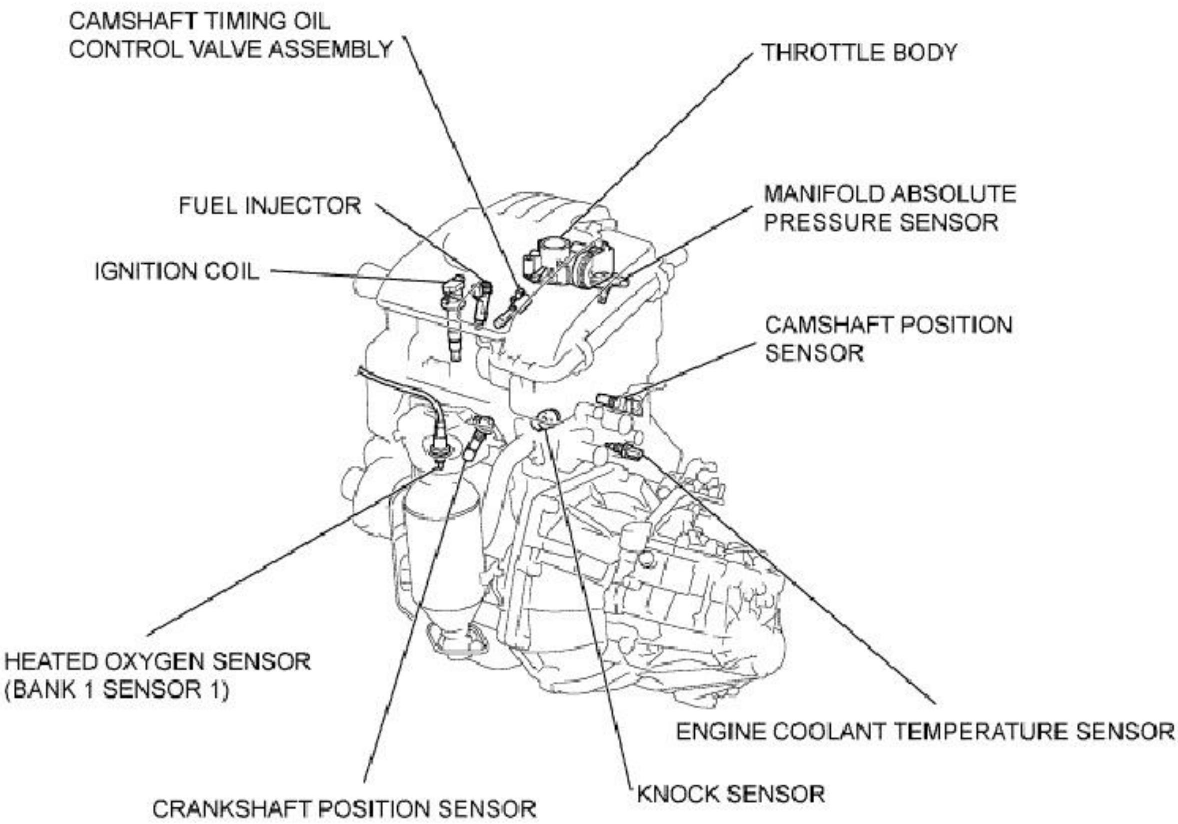


**Figure 2 Main fuel related components on the 1KR-FE engine.**

For the test run Sunoco Racing Methanol has been used. The product complies with the IMPCA METHANOL REFERENCE SPECIFICATIONS.

For the test run 15 vol% 95-octane E5 gasoline has been used. The product complies with the CEN-standard EN228.

For the test run 1 ‰ Redline SI Alcohol has been used. SI-Alcohol is a new additive for alcohol fuels (E85, ethanol and methanol) designed for daily use for so-called FlexiFuel or BioPower engines as well as for Rally / Racing.

## 3.2. Engine control unit and fuel system

The fueling system is an electronically controlled multi-point port injection system with 3 injectors.

It is important to use the right type of connector. The connector type for this vehicle is 'New Toyota' (Type F in Figure 3).


**Figure 3 Fuel rail with 3 injectors (left) - Different types of connectors (right)**

To achieve full engine power and torque with M85 the volumetric fuel delivery must be 74% larger than with gasoline. The original engine control unit (ECU) will accept a certain increase in fuel flow. However, it can result in the ECU issuing a Diagnostic Trouble Code (DTC) which will cause a failure at the vehicle inspection. See Figure 4.

Unofficial reports from French motorists talk about more than 20 000 km of driving with E85 on this engine. However, DTC's are observed after 200 km.


**Figure 4 Max acceleration uphill can cause error. "P0171 System Too Lean Bank 1" and "P0130 O2 Sensor Circuit Bank 1 Sensor1". The errors turn on "Check Engine" light. The diagnostic trouble codes can be cleared with an OBD2 dongle.**

The initial work on the test vehicle in this project showed that the engine could run on any blend up to M100 when the tests were conducted in a warm laboratory environment. The power and torque outputs were normal.

However, when moving to outdoor tests the engine had difficulties starting up and the DTC warning lamp came on after few hours of operation. Even worse, the NOx emissions increased which is attributed to the fact that the engine was running too lean for the 3-way catalytic converter to operate properly. The 3-way catalytic converter requires almost zero oxygen content in the exhaust gas which prohibits lean operation.

To overcome these initial difficulties a flex-fuel conversion kit from Artline International SARL in Lyon, France was installed on the car. See Figure 5. The kit, which is designed for E85, works by prolonging the fuel injection pulses thus increasing the amount of fuel delivered.

Upon installation of the kit the car ran almost perfectly. The maximum power and torque increased about 5% from standard which could be noticed when accelerating. The engine also ran more quietly due to the absence of combustion noise. Cold starting was acceptable, however not completely perfect.


**Figure 5 ETHANOL FLEX E85® Ethanol Conversion Kit. Fully Automatic Digital 3-Cylinders E85 Ethanol Conversion Kit with Cold Start Assist. Made in France.**

## 3.3. Results

In general, the car performed well on M85. In cold weather, the engine starts willingly, but should be kept up for 30 seconds before idling.

### 3.3.1. Engine power

The highest engine power was reached with M85 and the Flex Fuel Kit installed (M85C).

**Table 1 Engine power and torque of Peugeot 107 with gasoline and methanol blends**

| | Max torque [Nm] | at RPM | Max power [kW] | at RPM |
|---|---|---|---|---|
| Gasoline E5 | 97.3 | 3450 | 50.3 | 5900 |
| M15 | 97.9 | 3650 | 52.3 | 5900 |
| M25 | 97.8 | 3600 | 51.5 | 6000 |
| M50 | 97.3 | 3550 | 50.8 | 5950 |
| M65 | 97.1 | 3700 | 51.3 | 6000 |
| M75 | 96.8 | 3650 | 51.8 | 5950 |
| M85 | 97.7 | 3500 | 51.8 | 5850 |
| M85C | 102.3 | 3550 | 53.4 | 5800 |
| M100 | 97.7 | 3650 | 52.5 | 5950 |

The power and torque curves (Figure 6 and Figure 7) revealed a slight problem with the engine's variable valve timing system when running om M100. The system is set to kick in at 3500 RPM and normally this cannot be felt or seen in the curves. However, on M65, M75 and M100, the engine clearly didn't perform right below 3500 RPM and the VVT kick-in was noticeable.

A much smoother power delivery was found on M85. The results turned even better when the Flex Fuel Kit was later installed (M85C).

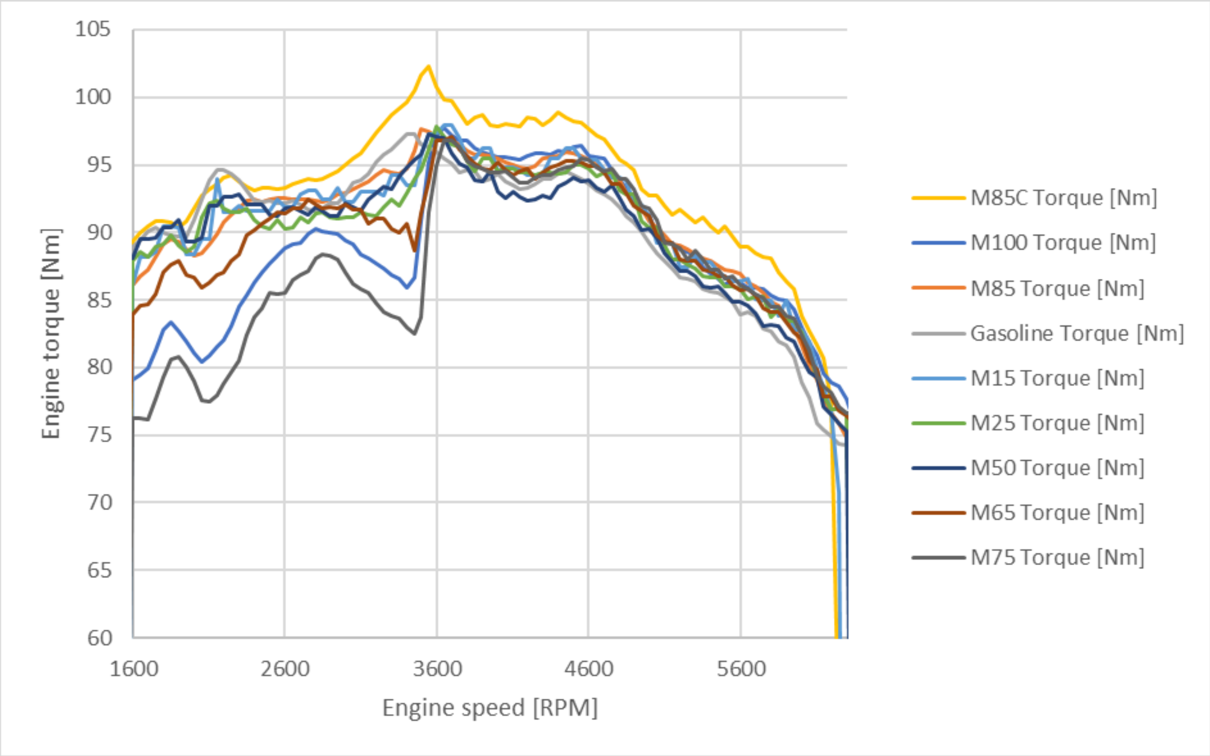


**Figure 6 Torque curve showing VVT kick-in on M65, M75 and M100 at 3500 RPM**

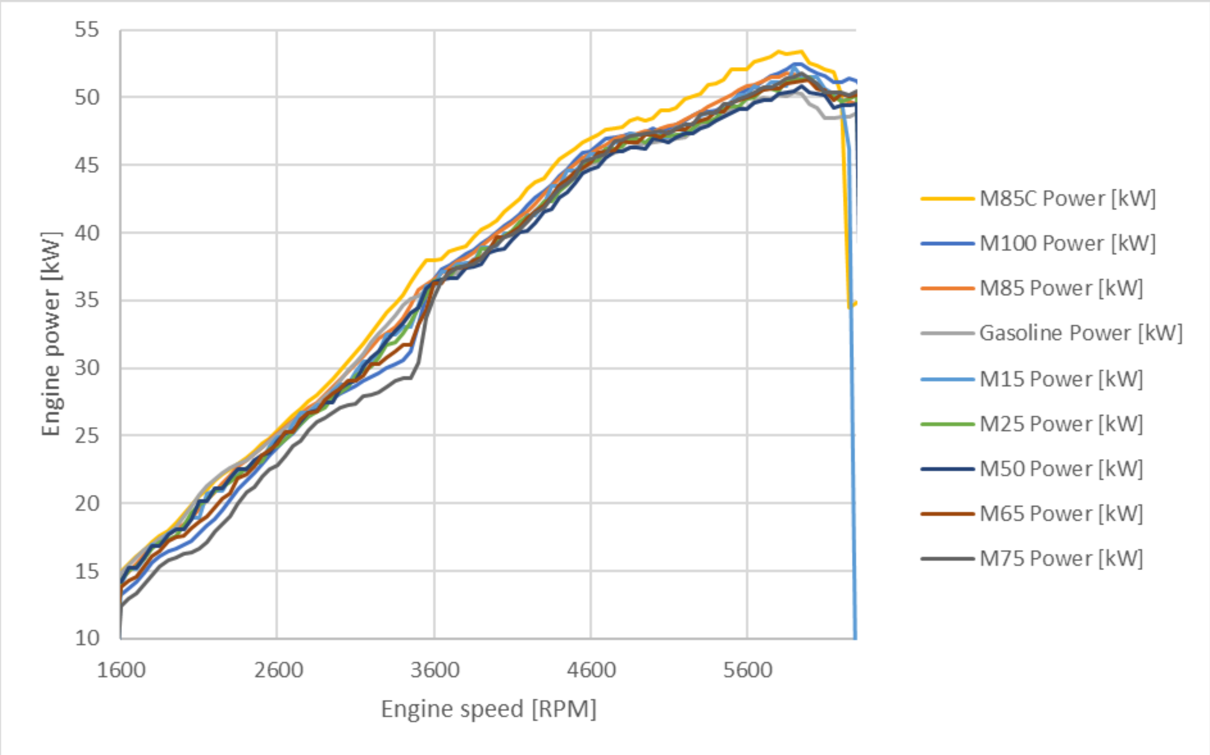


**Figure 7 Power curve showing best overall result for M85C (Flex Fuel Kit installed)**

Overall, a 5% increase in engine power and 7% increase in engine torque was reached. This is a very satisfying result.

### 3.3.2. Fuel consumption

Comparison of the fuels were based on energy content. The difference between E5 and M85 is in the range of ±3 % to either side. Due to the lower calorific value of M85 the consumption is off course higher on a km/l basis. In real driving (RDE) we achieved 11.8 km/l on M85 and 19.8 km/l on E5. Measured energy consumption on dynamometer (WLTP) and real driving (RDE) are seen in Figure 8. The benefit of M85 on the dynamometer could not be replicated on the road, possibly due to temperature differences.

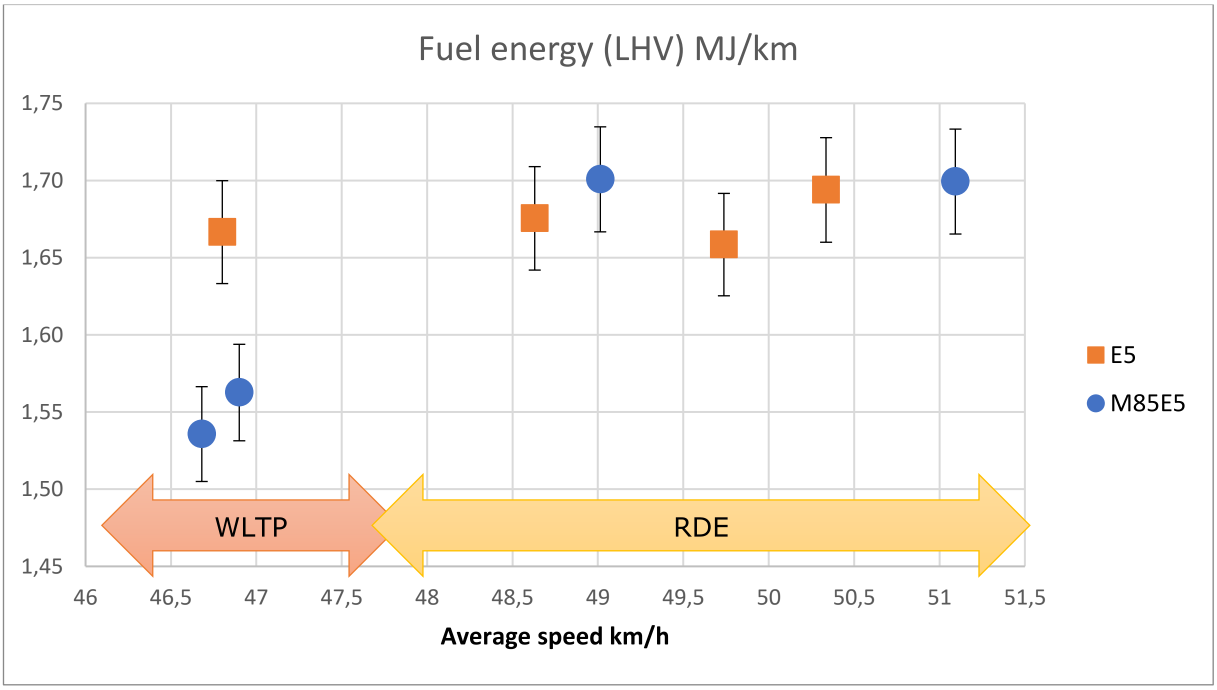


**Figure 8 Fuel energy per distance driven is almost the same on E5 and M85**

### 3.3.3. Noise

It was immediately noticed by the test crew that the engine sound seemed smoother on M85. This can be explained by the fact that methanol burns more uniformly than gasoline due to its homogeneity and high octane number.

To investigate this, without scientific equipment available, two identical cars were placed front-to-front with their engines running (Figure 9). The difference between the E5 gasoline-fueled and the M85 car was clearly audible. Gasoline creates much more irregular combustion noise than M85.


**Figure 9 Sound test on two identical cars, one with gasoline (left) and one with E85 (right)**

A video was captured which demonstrates clearly the difference in engine noise (Motorlyd benzin vs metanol.MOV).

### 3.3.4. Emissions

While running the car without the Flex Fuel Kit it was noticed that NOx emissions were too high as mentioned in Section 3.2. This shown in the table below.

**Table 2 NOx emission is reduced significantly with Flex-fuel kit**

| Route | Fuel | Motor | Tail pipe $CO_2$ g/km | c | Hn | km/h | MJ/km | CO g/km | $NO_x$ g/km |
|---|---|---|---|---|---|---|---|---|---|
| RDE Aarhus | M85 | Standard. | 118,1 | 0,4428 | 23,244 | 51,1 | 1,69 | 0,14 | 2,02 |
| RDE Aarhus | M85 | Flex Fuel | 118,2 | 0,4428 | 23,244 | 49,0 | 1,69 | 0,44 | 0,63 |
| WLTP Dyno | M85 | Flex Fuel | 108,6 | 0,4428 | 23,244 | 46,9 | 1,55 | 0,32 | 0,55 |
| WLTP Dyno | M85 | Standard | 106,7 | 0,4428 | 23,244 | 46,7 | 1,53 | 0,12 | 1,51 |

The table values correspond to the **blue dots** on the following diagrams (Figure 10, Figure 11 and Figure 12). The **orange dots** are gasoline for comparison.

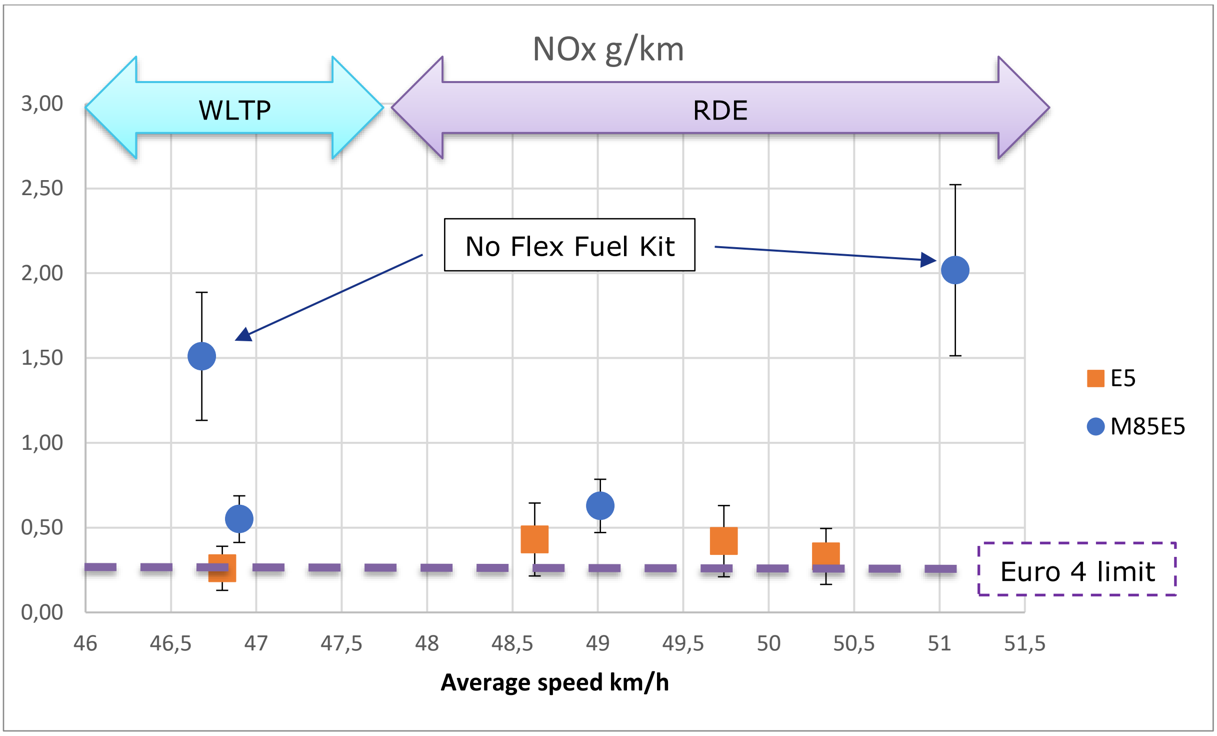


**Figure 10 The two highest NOx values are without Flex-fuel Kit**

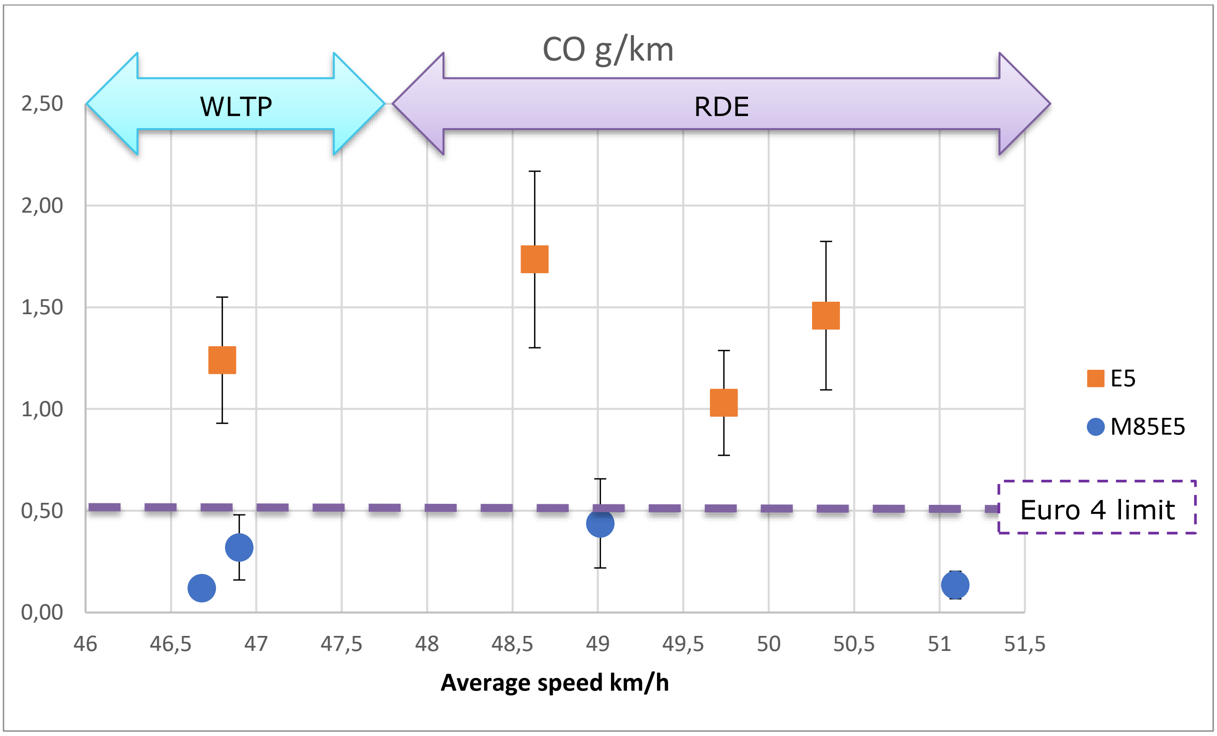


**Figure 11 CO emissions are overall much lower with M85**

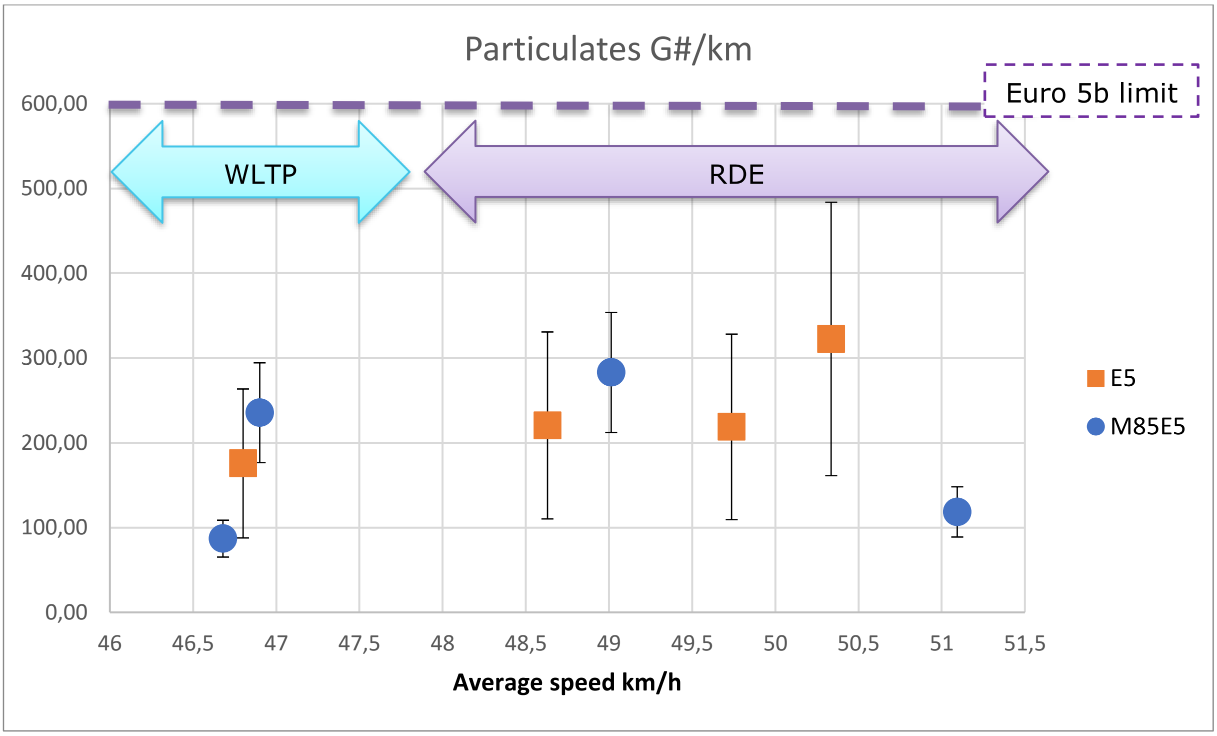


**Figure 12 Particle emissions with E5 and M85 are similar**

Overall the emissions were quite acceptable after the Flex Fuel Kit was installed. CO decreased a lot compared to gasoline while NOx increased a little bit. The vehicle exceeds some Euro emission limits by a factor 2-3. However, that is perfectly normal for a 10-year-old car and even for new cars.

## 3.4. Summary of vehicle performance and emissions

Real Driving Emission (RDE) was measured using mobile equipment (PEMS) under realistic conditions. Power and torque are measured on rolling road Dyno:

**Table 3 Summary of performance with M85 compared to gasoline on Peugeot 107**

| Fuel type | 95 Octane Petrol | 105 Octane M85 |
|---|---|---|
| Air-Fuel Ratio | 14,0:1 | 7,6:1 |
| Fuel energy MJ/l | 32,2 | 18,2 |
| Performance | | |
| Max. power | 68 hk | 73 hk |
| Max. torque | 97 Nm | 102 Nm |
| MJ/km | 1,63 | 1,62 |
| km/l | 19,8 | 11,8 |
| Car efficiency | 15% | 15% |
| Engine efficiency | 25% | 25% |
| Emissions | | |
| CO2, g/km | 118 | 118 |
| CO, g/km | 1,4 | 0,4 |
| NOx, g/km | 0,4 | 0,6 |
| Pn, G#/km | 234 | 259 |

## 3.5. Engine oil

The initial engine oil sample showed an elevated gasoline content which is the result of driving too many short trips. After some weeks of testing with M85 the engine oil was in better shape, primarily because the vehicle had been used more frequently and for longer trips.

There were no signs of unusual wear. The vehicle has covered 2400 km in 4 months on M85.

**Anbefaling**
Olien er klar til fortsat brug.

PRØVESTATUS
NORMALT

**Har du spørgsmål til analysen bedes den kontakte OK på 70121201 eller din lokale distrikschef.**

| | | | |
|---|---|---|---|
| Prøve Nummer | | 1 ** | 2 |
| Analysedato | | 10-09-18 | 16-11-18 |
| Prøven Udtaget Dato | | 04-09-18 | 09-11-18 |
| Rapport Reference | | OK27013 | OK27344 |
| Maskinens Driftstid | | 51265 | 52802 |
| Oliens Driftstid | | 1442 | 2979 |
| Olie Efterfyldt | | - | - |
| Label Nummer | | 031042 | 032003 |
| **Fysiske Tilstand** | | | |
| Viskositet på 40°C | cSt | 54 * | 58 |
| Viskositet på 100°C | cSt | 9.8 | 10.2 |
| Viskositetsindeks | | 169 | 165 |
| Flammepunkt | deg. C | 110+ | 130+ |
| Brændstofindhold | % wt | 3.5 ** | <2.0 |
| Vand | % wt | <0.05 | 0.0743 |

**Figure 13 Oil samples from the test vehicle showed improvement after driving on M85**

## 3.6. IEA work

This report is part of IEA-Advanced Motor Fuels Annex 56, which can be found on http://iea-amf.org.

The active contributors to the annex are Denmark, Finland, Germany, Israel, Sweden and India. Also, China and Canada have supplied useful information.

Israel reported a successful long-term trial of M15 with Fiat vehicles. From China, where methanol is widely used, a M85 fuel standard was received. Canada reported tests on M56 with direct injected engines in IEA-AMF Annex 54 "GDI engines and alcohol fuels".

A collated report from AMF will be available by March 2020.

# 4. Barriers to methanol

Important barriers are illustrated by the following parliamentary question and answer induced by Danish Methanol Association:

Parliamentary question 14 February 2012:

*(1) Will the Commission explain why there is a limit of 3 % for methanol in fuels in the Fuel Directive?*

*(2) Can the Commission also say if it is considering giving it the same treatment as ethanol and raising the 3 % limit for methanol in fuels?*

Answer 28 March 2012 given by Ms. Hedegaard on behalf of the Commission:

*The methanol content of fuel is set at 3 % by the Fuel Quality Directive 98/70/EC. Its use was addressed in the impact assessment associated with the 2009 revision of the directive.*

*If added in a higher percentage, methanol could have damaging effects on vehicles engines. It would also therefore have a negative effect on vehicle warranties, drivability and durability, and have implications for the emissions of such vehicles. Furthermore, adding methanol to petrol raises its vapor pressure which could give rise to air quality problems. Finally, the energy content of methanol is about half that of petrol making it a less efficient fuel additive than ethanol which has about two-thirds the energy content of petrol.*

*The Commission is therefore not considering revising this limit.*

The following sections of the report deals with these concerns and other barriers to methanol.

## 4.1. Corrosion

As mentioned in Commissioner Connie Hedegaard's reply to Parliament, methanol could have damaging effects on vehicles engines. It would also therefore have a negative effect on vehicle warranties, drivability and durability, and have implications for the emissions of such vehicles.

With reference to countries where methanol is widespread as motor fuel, such as China, and to our own investigations, shown in Chapter 3, the Commissioner's concerns seem to be exaggerated. Additives – like E.M.SH Ng-Tech Super Heavy-Duty Anti-Corrosion & Lubricant Additive – will help keep gasoline engines at work on Methanol/Gasoline Blends. Same with Beraid® 3555M from AkzoNobel.

Alcohol is considered very dry without lubricating properties. Therefore, a lubricant is supplied in a quantity recommended by the lubricant manufacturer.

ASTM D5797 – 17 places demand on the used gasoline blendstock and also mentions "*that unprotected aluminum and an unlined nitrile rubber dispensing hose should be avoided in methanol fuel blend distribution and dispensing systems*". GB/T 23799-2009 – Chinese

M85 Specification - mentions more specifically that "*an effective metallic corrosion depressor and motor gasoline detergent meeting the requirements of GB 19592 should be added*".

On 2010 International Conference on Advances in Energy Engineering a test was reported "*Metal corrosion by methanol and methanol-gasoline has become a key problem for methanol as one of substitute fuels. 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.*"

Corrosion inhibitors (e.g. a combination of cyclohexyldimethylamine, xylene, and ethylbenzene) are widely used in E85.

Innospec Inc. offers as part of their corrosion inhibitors range:

- **DCI-11** for fuel alcohols and a Treat Rate (TR) equivalent to 6-12 mg/l in finished fuels – typical 9 mg/l.
- **DCI-11 Plus** for alcohol fuel blends with TR of 30-86 mg/l blend. Both are registered by EPA as gasoline additives.
- **Biostable E85 G-Plus** – an all in one - containing a lubricant and a TR of 350 mg/l. The product is not registered by EPA, literature is scarce, and the lubricant may be overkill in our Recipe.

Eco-Energy, LLC and Gevo Inc. specify TR min 10 PTB DCi-11 Plus; LINCOLNWAY ENERGY, LLC, NORTH PIPELINE and Magellan Midstream Partners specify min. 6 PTB DCi-11 Plus. 1 PTB (Pounds per thousand Barrels) =2.853 mg/l. A few mention as alternative vendors: Ashland, G E Betz, Midcontinental, Nalco, Petrolite, and US Water Services.

The answer to this problem is that long-term demonstration is needed to convince Europeans that methanol is not harmful to engines. As for warranties this is handled in Chapter 8 of this report.

## 4.2. Vapor pressure

As mentioned in Commissioner Connie Hedegaard's reply to Parliament, vapor pressure is a serious objection.

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.

The vapor pressure of gasoline shall comply with the European Standard EN228. This standard has several ranges for vapor pressure depending on the climate in which the gasoline is used. The exchange agreement in Denmark specifies the following ranges for blended E5:

- Summer **45-70 kPa**
- Spring/fall **45-95 kPa**
- Winter **65-95 kPa**

For Danish raw gasoline, known as BOB (Blendstock for Oxygenate Blending) without ethanol, the ranges are:

- Summer **40-63 kPa**
- Spring/Fall **40-88 kPa**
- Winter **60-88 kPa**

For Chinese and Israeli standards, see section 9.4.

The raw gasoline, BOB, is designed such that when blended with 5% ethanol the vapor pressure matches the requirements of E5. Thus, ethanol increases the vapor pressure.

Methanol lowers the vapor pressure when added in percentages above 82%. This means that M85 will have a lower vapor pressure than the base gasoline.

Should a higher vapor pressure be required then a blend between 70-82% methanol will ensure that.

At 82% methanol the vapor pressure is equal to the base gasoline. See Figure 14.

Unblended methanol M100 has a vapor pressure of only 32 kPa. This is much too low for use in the winter and even too low for Danish summer. This fuel is therefore not desirable for vehicles with indirect injection (port injection). Vehicles with direct injection are on the market but have not yet been tested in this project.

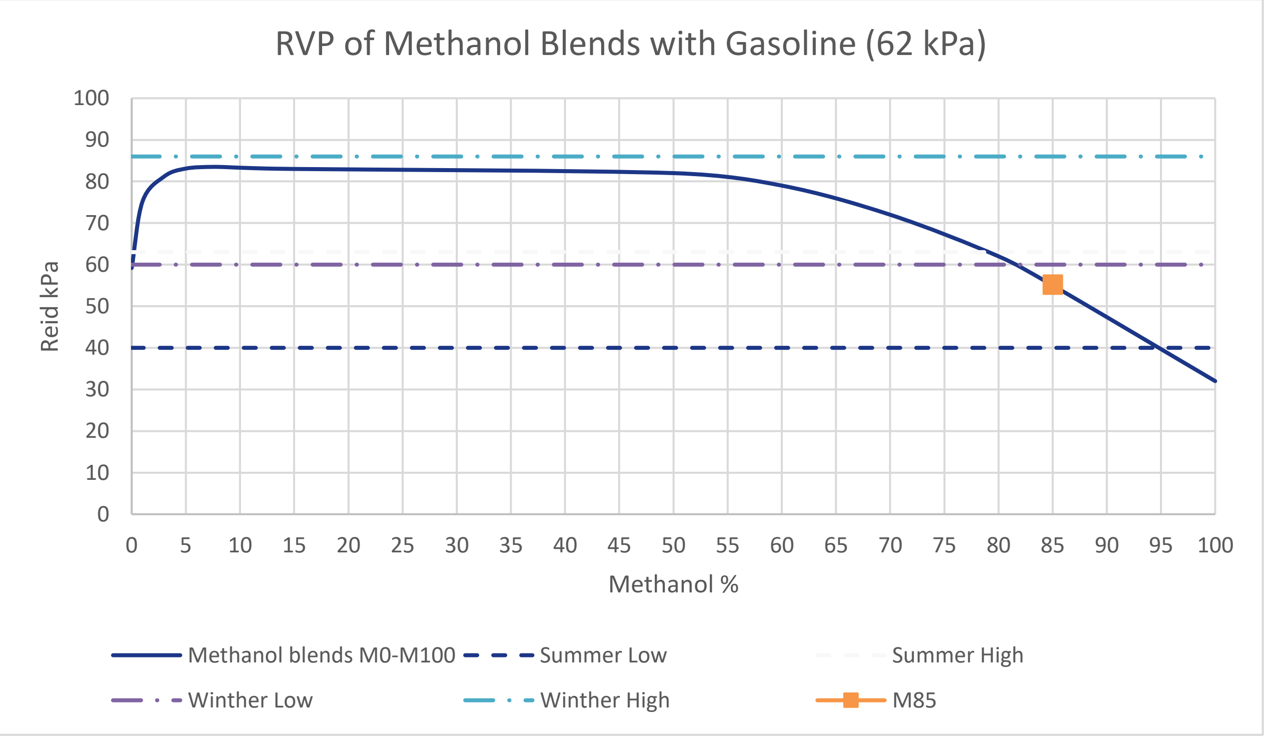


**Figure 14. Combined data for vapor pressure of methanol-gasoline blends. Data Source Methanol Institute for M0-M15; ASTM D5797-17 for M51-M85. Interval between M15 and M51 is unknown.**

ASTM D5797-17 tells the relationship between vapor pressure in a base gasoline, BOB, and the corresponding M85 blend.

y = 0,4357x + 4,0834, where

- y=Vapor pressure [psi] of M85
- x=Vapor pressure [psi] of BOB.
- 1 kPa = 0.145037738 psi.

This is shown in Figure 15.

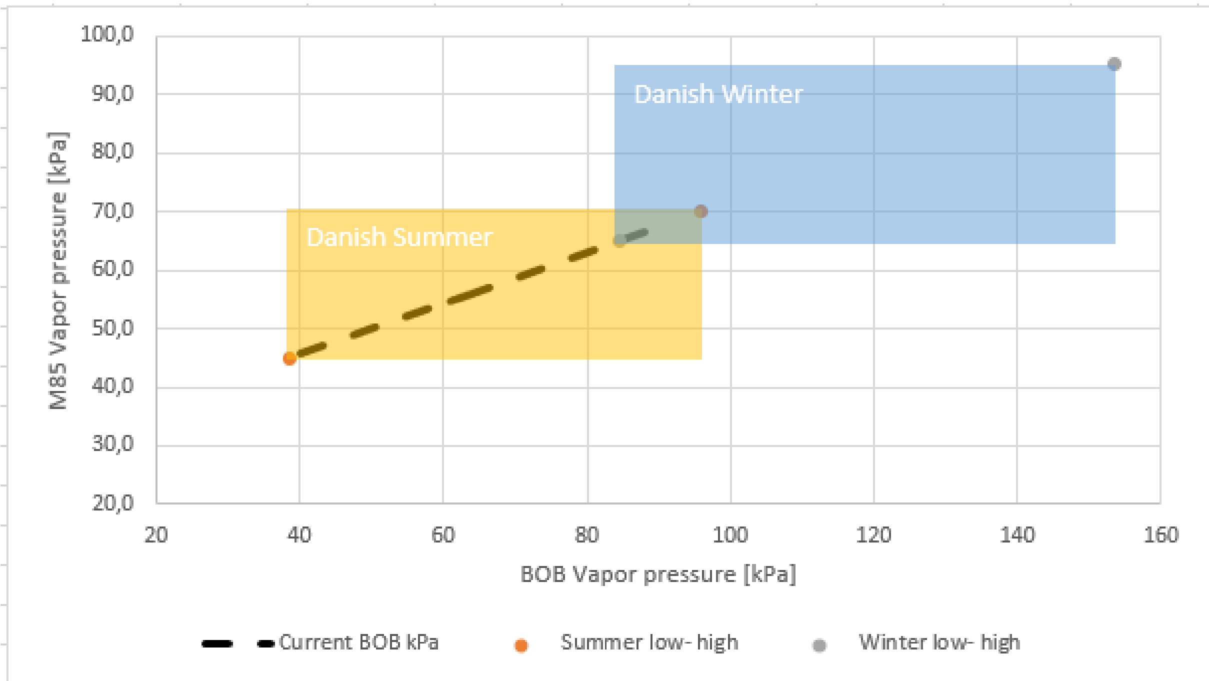


**Figure 15 Resulting vapor pressure in M85 as function of the raw gasoline.**

The Methanol Institute has produced a bulletin on Methanol Gasoline Blends. Methanol has azeotropic effects with the vapor pressure of gasoline. Methanol itself has a low Reid Vapor Pressure (RVP) but RVP increases in blends – most of the increase, however, takes place in blends of up to 3 vol% volume methanol. Refineries may remove some butane as a compensation. The vapor pressure is lowered when lowering the butane content of the BOB.

In conclusion vapor pressure is **not a problem** for high blends of methanol. For low blends it can easily be handled by adjusting the BOB at the refinery. A blend of 82% methanol M82 will result in a neutral vapor pressure. M85 will be good for summer and M70 will probably be perfect for winter in Denmark.

## 4.3. Energy content

As mentioned in Commissioner Connie Hedegaard's reply to Parliament, methanol has a low heating value - it is 16 MJ/l versus 21 and 32 for ethanol and gasoline respectively.

This will affect the driving range of the vehicle, but it can be compensated with more frequent fueling or a larger tank. After all, a larger fuel tank is much cheaper than a larger battery. Furthermore, methanol has an octane rating around 110 - so much higher than gasoline that boost, compression and timing advancement can be increased. This will benefit fuel economy. Due to the high heat of vaporization methanol cools down the intake air and the low air temperature produces more horsepower and torque, so that smaller engines can be used. The potential of high-compression methanol engines was documented by Chinese researchers in 2013[4].

30-40% higher mileage calculated on energy content has been reported by the US EPA[5] – when standard and high compression engines (alcohol engine vs. gasoline engine) are compared. By raising compression ratios in methanol engines from 8.8 to 11.4, FORD engineers in 1981 were able to get about two-thirds as much energy per liter from methanol engines as from gasoline engines[6].

American aerospace engineer Robert Zubrin[7] wrote this in 2011:

*… First, I ran the car on 100 percent methanol. This required replacing the fuel-pump seal made of Viton, which is not methanol compatible, with one made of Buna-N, which is. The new part cost 41 cents, retail. In order to take proper advantage of methanol's very high-octane rating (about 109), I advanced the timing appropriately. This dramatically improved the motor efficiency and allowed the ordinarily sedate sedan to perform with a significantly sportier spirit. As measured on the dyno, horsepower increased 10 percent. With these modifications complete, I took my Cobalt out for a road test. The result: 24.6 miles per gallon.*

*When I first made the bet, many commentators thought that I would aim for high-efficiency performance with high-octane fuel by increasing the compression ratio of the engine (which is how race-car drivers using methanol have done it for the past half-century). However, with modern cars using electronic fuel injection, this is unnecessary. Instead, the necessary changes to the engine can be made simply by adjusting the Engine Control Unit software. Thus, except for switching the fuel-pump seal as noted above, no physical changes to the car were required.*

The mileage reported by Mr. Zubrin as Miles/gal recalculated to Miles/MJ shows 15% better energy mileage on M60 and **23% better energy mileage on M100.**

[4] https://www.sciencedirect.com/science/article/pii/S0196890413003725

[5] An Alcohol Engine will produce 30-40% greater fuel efficiency than a gasoline engine http://www.americanenergyindependence.com/efficiency.aspx

[6] METHANOL WINS FORD COMPETITION https://trid.trb.org/view/174467

[7] Methanol Wins https://www.nationalreview.com/2011/12/methanol-wins-robert-zubrin/
Incl. Table: http://danskbiomethanol.dk/papers/Methanol%20Wins.pdf

**Table 4 Data reported by Robert Zubrin shows great improvement over E10 gasoline**

| | M100 | M60 | E10 |
|---|---|---|---|
| Miles per gallon as reported | 24,6 | 32,3 | 36,3 |
| Miles per MJ - recalculated | 0,41 | 0,38 | 0,33 |

The present study did however not achieve higher energy mileage on M85. The effect of methanol on fuel economy are further described in Section 3.3.2.

## 4.4. Vehicle approvals

Vehicle manufacturers in the EU restrict fuel use to a maximum of 3% methanol, although the same car models are sometimes exported to China without such restrictions. Dedicated Flex Fuel Vehicles are no longer offered on the European market.

The Danish Road Safety Agency (Færdselsstyrelsen) does not currently permit the adaptation of cars to methanol. Only factory adapted FFVs are allowed.

To promote the methanol market the Agency should be allowed to authorize workshops to customize regular car for methanol high blends according to ASTM D5797 - 07 Standard Specification for Fuel Methanol (M70-M85) for Automotive Spark-ignition Engines for cars that are adapted to M85 by the car manufacturer as FFV or by an approved workshop.

One EU member country, France, has already approved the use of Flex Fuel Kits. On Friday 15th December 2018, the French Ministry for Environment and Energy published the bylaw (NOR: TRER1734649A) setting forth the terms to approve Superethanol-E85 conversion systems for petrol-powered vehicles to also use Superethanol-E85. Being subject to less taxation because of its environmental edge, Superethanol-E85 is the cheapest fuel on the French market. This has brought plug and play Flex Fuel Kits on the market. They can be installed by laymen in a matter of minutes virtually without the need for tools. For example, ETHANOL FLEX E85® Ethanol Conversion Kit reportedly allows any gasoline vehicle to run either on Ethanol E85 (also known as Bioethanol) or unleaded petrol 95/98 and save up to 40% of your fuel budget on every tank fill in France.

Such kits have been on the US market for some years - for example, Flex Fuel U.S., original manufactured by Chrysler and approved 2006 by EPA for certain cars. In Sweden, BSR Svenska AB has obtained approval of their kit (SAAB only). The same for StepOne Tech Ltd. in Finland. In France, we find the FlexFuel Company with their DriveCleanBox, Ethanol Flex - E85 Ethanol Conversion Kits from Artline International SARL and now quite a few others. The general working principle is shown in Figure 16.

The kit is an electronical device (piggyback device) to plug in between the injector wires and the injectors. It will expand the injector pulse widths by approximately 30% and it will have the possibility of both running on gasoline and M85. It also adds cold start ability.

Advantages:

- Very low cost
- Easy to install and use
- Has the capability of both gasoline, E85 and M85

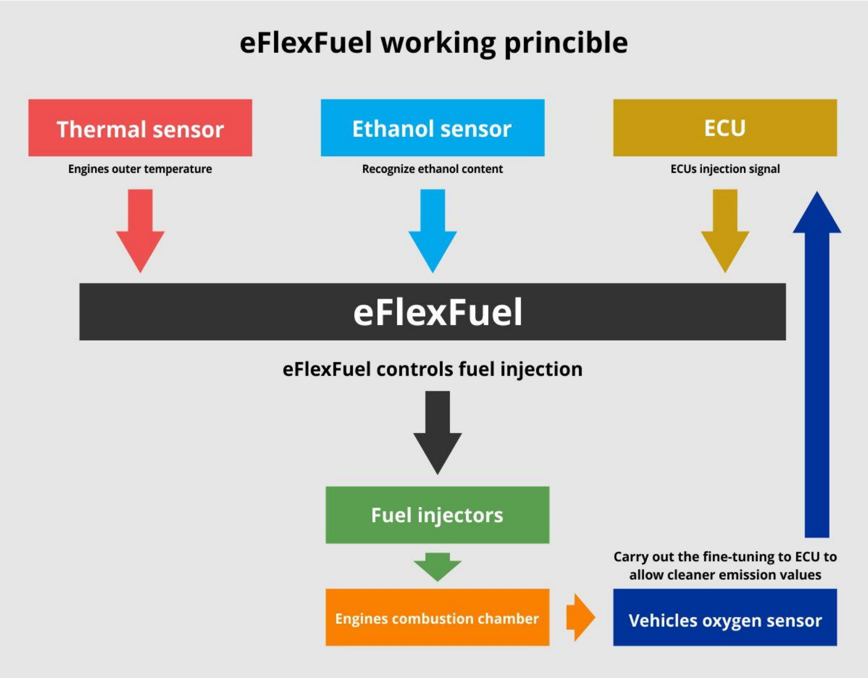


**Figure 16 The eFlexFuel working principle illustrates the application of a Flex Fuel Sensor as well as an exterior thermometer. Some kits are simplified by omitting the Flex Fuel Sensor.**

These kits vary slightly in simplicity with varying installation from a few minutes to a couple of hours. Bosch offers a supplementary Flexstart, a complete Fuel Rail System with pre-heating to improve cold start in frosty weather. Bosch claims their systems are media-resistant for ethanol and methanol applications.

The simplest Flex fuel kit installs as a plug and play device in the vehicles fuel Injection system, by means of rerouting the signal from the Electronic Control Unit (ECU) to the fuel injectors. Takes less than 25 minutes to install. There are no wires to cut or solder. They offer cold starting assistance technology with built in temperature sensor. After installation vehicle will become a Flex Fuel vehicle able to run high alcohol blends and regular gasoline and any blends.

A Fully Automatic Digital 3-Cylinders E85 Ethanol Conversion Kit with Cold Start Assistance Kit "Ethanol E85 3-Cylinders" at 189 € is installed in our test car (see section 3 Vehicle experiments). The kit from Artline International SARL has an integrated cold-start system with an internal temperature sensor, capable of starting the engine in very low temperatures.

## 4.5. Biofuel legislation

In Europe the fuel suppliers are obligated to add 5.75% biofuel measured as energy content. If this is to be fulfilled for gasoline alone it must contain approx. 7%vol ethanol or approx. 11%vol methanol. Both options are, however, in excess of the allowed mixing rate according to EN228, so basically, it's not an option.

European Standards for gasoline (EN 228) and diesel (EN 590) as well as the Fuel Quality Directive (FQD) limits the use of methanol to a maximum of 3 vol%. Gasoline blends with less than 70 vol% gasoline are not covered by the Fuel Quality Directive (FQD) meaning that M30 and higher blends are allowed. Therefore, focus needs to be blends with less than 3% or higher than 30% methanol.

There are currently two certification systems for bioenergy. Energinet.dk issues green certificates. These certificates are not recognized by the EU, which only recognizes certificates (Proof of Sustainability) under the Renewable Energy Directive (RED). It drives the price of bio methanol unreasonably.

To promote the methanol market Energinet.dk should meet EU requirements so that the market is aligned with one certification system only.

Rules for transport in the gas and electricity networks, respectively, are significantly different.

Certified biomethane from waste and residues injected into the grid may be withdrawn as a corresponding amount of natural gas anywhere at no cost and the methanol will be recognized as second generation fuel.

Wind power cannot be "moved" in a similar way and methanol from electricity is not recognized as advanced bio fuel. This is a significant trade barrier preventing use of wind power as "liquid electricity" for transportation.

## 4.6. Competition from ethanol

Significant research means have been spent on lignocellulosic ethanol in Denmark and for years ethanol was the fuel of choice for researchers in Denmark.

Oxygen bearing liquids (oxygenates) are often added to gasoline to enhance octane rating and for a more complete combustion. Ethanol is the leading oxygenate added to gasoline in most countries. In Denmark, oil companies have agreed to use only ethanol as an oxygenate. This is partly to avoid the use of MTBE, which is harmful to ground water. Furthermore, national exchange agreements on fuels require a uniform product specification.

These agreements are, however, also a barrier for the use of methanol for transportation in Denmark.

The prevalent mixture today is E5, which has a bio content of 3.35% energy. This blend is in line with EN228.

One could increase the bio content by adding bio methanol together with ethanol. The limit for methanol is 3%$_{vol}$ and furthermore, the oxygen content may not exceed 3.7%$_{m}$.

This exact limit is reached with 3%$_{vol}$ methanol and 4%$_{vol}$ ethanol. This blend has a bio content of 5,6% energy. The blend can be obtained by adding 3%$_{vol}$ methanol to the existing E5 gasoline. However, the vapor pressure would probably go too high for summer operation as shown in Figure 14.

An alternate route is to increase ethanol content to 10%$_{vol}$. This gives a bio energy content of 6.8% which is more than the methanol blend. Also, the oxygen content is just below 3.7%$_{m}$. The vapor pressure would not increase.

Due to these regulations it may seem easier for fuel companies to go for added ethanol content rather than adding methanol.

However upcoming regulations might change this. From January 1, 2020, Danish law enforces the EU RED II directive which will change the biofuel obligation to include at least 0.9 energy% advanced biofuel in transport fuel. Since advanced methanol is cheaper than advanced ethanol, this law may bring bio methanol into play.

Ethanol absorbs water and gets corrosive to pipelines and should therefore preferably be mixed at local terminals. Gasoline refilling stations have fiberglass and corrosive-resistant plastics and road tankers are protected likewise. The refineries therefore also offer a Blend stock for Oxygenate Blending (BOB) which does not contain ethanol.

To open the market for low-blend methanol it would be beneficial to have the Danish BOB adjusted so that it, in terms of vapor pressure etc., accommodates low-blends with up to 3 vol% methanol.

## 4.7. Wind energy subsidies

The wind industry could potentially benefit from the methanol market if methanol is produced as an electro fuel (see section 9.2).

However, the business case for methanization and conversion of the energy and carbon dioxide to methanol is weak because the power is subsidized and thus cannot be acquired profitably. This prevents the use of Danish wind power for use as a methanol feedstock.

To benefit the methanol market RED-Certified wind energy should be supplied to the electric grid and taken out anywhere for any purpose with a certified documentary track, which is used today for biogas. This path is not allowed today.

# 5. Blending, storage and handling

Fuel logistics involves large investments in port-, dispensing and blending facilities etc. However, proper storages for methanol already exist in Denmark (Figure 17). Some fuel stations will need a protective coating inside the storage tanks, but this can be done in connection with a planned 5-year inspection at an estimated cost between EUR 1,100-2,700 per station.


**Figure 17 One of two Methanol tanks – each 2.500 $m^3$ - owned by Nordalim A/S, Port of Aarhus. The tanks are ISCC certified as warehouse for bio methanol traded by New Fuel A/S.**

The gasoline blendstock is a liquid hydrocarbon component suitable for use in spark-ignition engine fuels such as conventional gasoline blendstock for oxygenated blending (CBOB), and reformulated gasoline blendstock for oxygenate blending (RBOB).

When gasoline is added the usual $5\%_{vol}$ bioethanol, the blend is sensitive to moisture and must therefore be stored and transported in dry environments. This is the reason why some fuel companies choose to do the blending themselves close to the end user, to avoid moisture problems. The readymade E5 bland can also be taken directly from the refinery, but it will need protection from moist onwards from there.

Methanol blends are much more stable in that sense.

Methanol is toxic like most other fuels. Both bitterant and odorant is therefore added to M100 fuel methanol as a precaution. The M85 blend, however, is denatured by the gasoline so it cannot be ingested by mistake.

The Methanol Institute has created the Methanol Safe Handling Manual[8] to address both common and technical questions related to methanol handling, storage and transport.

[8]http://www.methanol.org/wp-content/uploads/2017/03/Safe-Handling-Manual.pdf

Methanol can be used in different blends together with gasoline. The most promising blends are A7, M15, M56, M85 and M100. These are described below.

## 5.1. A7 vs E5

Danish gasoline usually contains 5 vol% ethanol. It is not enough to meet the requirement of 5.75% calculated as energy. However, a blend with 3 vol% 2G-biomethanol and 4 vol% 1G-bioethanol satisfies the requirement of 5.75 energy%, because 2G-biomethanol counts twice. The ethanol also acts as cosolvent.

M3E4 or catchier A7 (A for Alcohol) complies with EN 228 for gasoline and no test is required on the vehicle.

Except for a minor adaptation of an existing storage tank to methanol, the infrastructure is completely in place all the way from refinery to our service stations and our gasoline cars.

Commence sales of A7 replacing the current E5 gasoline can begin right away. The methanol may be added at the refinery and the ethanol by the oil company or both can be added by the oil company by using a pre-mixed blend of methanol and ethanol with a ratio of 3:4 vol%.

The refinery would need to adjust vapor pressure by removing butane from the BOB.

## 5.2. M15

M15, a mixture of $15\%_{vol}$ methanol and $85\%_{vol}$ gasoline, is popular because modern cars can usually run it without engine changes. In China, M15 is the largest utilization of methanol and Israel has recently concluded promising M15 tests.

In long term, long distance trials 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 stop-start system (shown in Figure 18).

The trials also revealed that the car could run on gasoline with up to $20\%_{vol}$ methanol.


**Figure 18 The production ready Fiat 500M15 - November 2016**

Sadly, M15 is not allowed in the EU. Only fuels with less than 3 vol% and more than 30 vol% methanol are allowed.

## 5.3. M56

Flex-fuel vehicles, which have been widely used in Sweden, are designed to run on 85%$_{vol}$ ethanol (E85). E85 in flex fuel vehicles is a well proven solution. For these vehicles a natural starting point would be M56, M85 or M100.

The equivalent methanol blend which gives the same air-to-fuel ratio as E85, is M56. This blend is presently undergoing tests by IEA-AMF 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 flex-fuel vehicles are no longer produced in Europe but can be bought second hand in Germany or Sweden. E.g. 2014 VW Golf VII 1,4 TSI MultiFuel BMT, shown in Figure 19. (more are available on https://bilweb.se/sok/bensin-etanol).


**Figure 19 The legacy VW Golf Multifuel – winner of 2016 MAAF Auto Environmental Award**

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 rather high. Good for winter but not for summer in Denmark.

## 5.4. M85

Dedicated M85 vehicles are not available on the market today. Instead, a vision of an M85 car is shown in Figure 20.

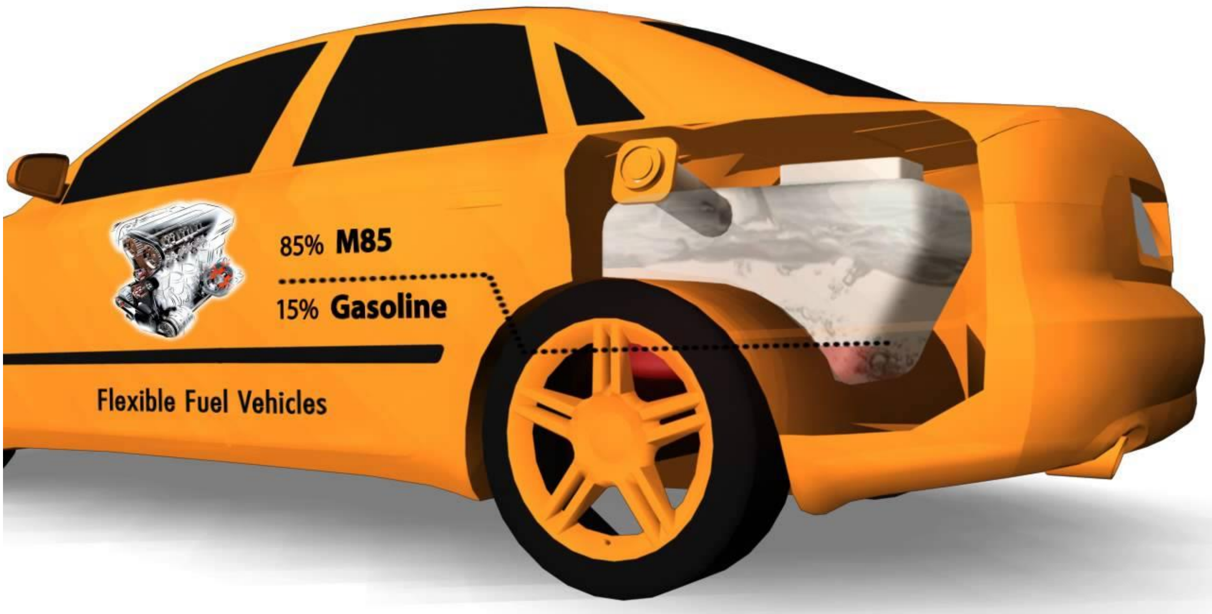


**Figure 20 Vision of a M85 vehicle**

M85 has a bio energy percentage of 73.5%. There is no increase in vapor pressure compared to base gasoline.

High blends require adaptation of the engine and since this adaptation does not cost more at a higher content of methanol, the M85 appears to be an obvious choice. There is an ASTM standard that does not give rise to cold weather problems and which has an excellent driving economy. The ASTM D5797-17, Standard Specification for Methanol Fuel Blends (M51–M85) for Methanol-Capable Automotive Spark-Ignition Engines is adopted as Danish Standard (DS). The standard allows vehicles to achieve cold-start and improve the visibility of methanol flames.

It is a goal to have the ASTM definition further reviewed, tested and recognized in Denmark.

GB/T 23799-2009 Methanol Gasoline (M85) for Motor Vehicles is a national standard of the People´s Republic of China. The Chinese standard is close to the previous ASTM D5797-2007 with few deviations. Among other things, a note is added: "effective metallic corrosion depressor and motor gasoline detergent meeting the requirements of GB 19592 shall be added".

In order to use M85 a gasoline engine must give a 70% higher injected fuel amount per engine revolution. It might therefore be convenient to begin with a E85 compliant vehicle, which has larger injectors as standard. However, ordinary gasoline cars can also be fixed to run on M85.

It is quite probable that many car models can be programmed through the OBD-connector, also known as ECU flashing. Swiss company Flashtec SA offers this kind of services. They did however not respond to our enquiries.

Complete engine control units from VEMS, Megasquirt, AEM, ECU Master etc. can be bought from Danish company QualiTec in Ringkøbing. They can be configured in various ways. QualiTec offered to do the complete conversion at a reasonable fee.

This study points to all legal forms of modification, including authorized ECU flashing, provided the acceptance of Danish road authorities (see section 8).

## 5.5. M100

It is also possible to run on neat methanol M100, but this can result in cold-starting issues because the vapor pressure is much too low for Danish winter. It may be that cold-starting issues are eliminated on newer vehicles with direct fuel injection but is remains to be verified. A new factory-built methanol car is available from Chinese manufacturer Geely. It's called Emgrand M100 EC7 1,8 127hp. This model runs now in a trial fleet of six car on Iceland. Geely Emgrand M100 EC7 uses gasoline at cold-start to avoid problems.


**Figure 21 Geely Emgrand 7 with and engine for 100% methanol**

Due to the cold-starting issues and the need for a denaturant/odorant M100 is not seen as favorable.

## 5.6. Use of cosolvents

During the 1980s and through much of the 1990s, most gasoline in Western Europe contained a small percent of methanol, usually 2-3%, along with a cosolvent alcohol. Ethanol will work as a cosolvent with an optimal methanol-to-ethanol ratio of 3:4 vol%.

Cosolvent alcohols like ethanol, propanol or butanol are normally added to methanol blends to provide water tolerance or phase stability in colder areas. With water tolerance and corrosion inhibitor protection, methanol gasoline blends have safely been shipped just like gasoline. Cosolvent alcohols also provide reduction in the vapor pressure in methanol blends.

For high methanol content fuels such as M85, phase separation is not a problem because of the large capacity of methanol to absorb water[9]. Thus, M85 does not need a cosolvent.

[9] Use of Methanol as a Transportation Fuel, Methanol Institute, Nov. 2007 http://www.methanol.org/wp-content/uploads/2016/06/Methanol-Use-in-Transportation.pdf

# 6. Stakeholders

Part of this project is to identify major stakeholders in the Danish region. As stakeholder we define someone with a positive interest in methanol fuels.

The stakeholders can be mapped in the following categories.

## 6.1. Methanol producers

Worldwide, there are over 90 methanol producers with a combined annual production capacity of about 110 Megatons per year. This methanol is almost entirely fossil based.

For bio-methanol, agriculture is a key player because this is where solar energy is naturally captured. Livestock farming can convert some of this energy into food products. The rest is bound in waste such as straw and manure. This is the part that the EU Commission allows for use in advanced (2nd generation) biofuels.

Biogas producers are the next link in the chain. They are spread throughout the country, thus reducing road transport of biomass. They are represented by "FORENINGEN BIOGASBRANCHEN".

The actual factories that can convert methane to methanol are a necessary link in the chain. For example, New Fuel A/S is ISCC EU approved as a methanol producer and uses Statoil's plant at Tjeldbergodden in Norway for this purpose. This plant has a capacity close to one million tons methanol a year. Methanol is dispatched from the factory at Tjeldbergodden to Warehouse in Port of Aarhus.

A plan for a 1,000 ton per day bio-methanol factory in Aarhus exists and is currently seeking co-investors. The placement of the factory is shown on the map in Figure 22.

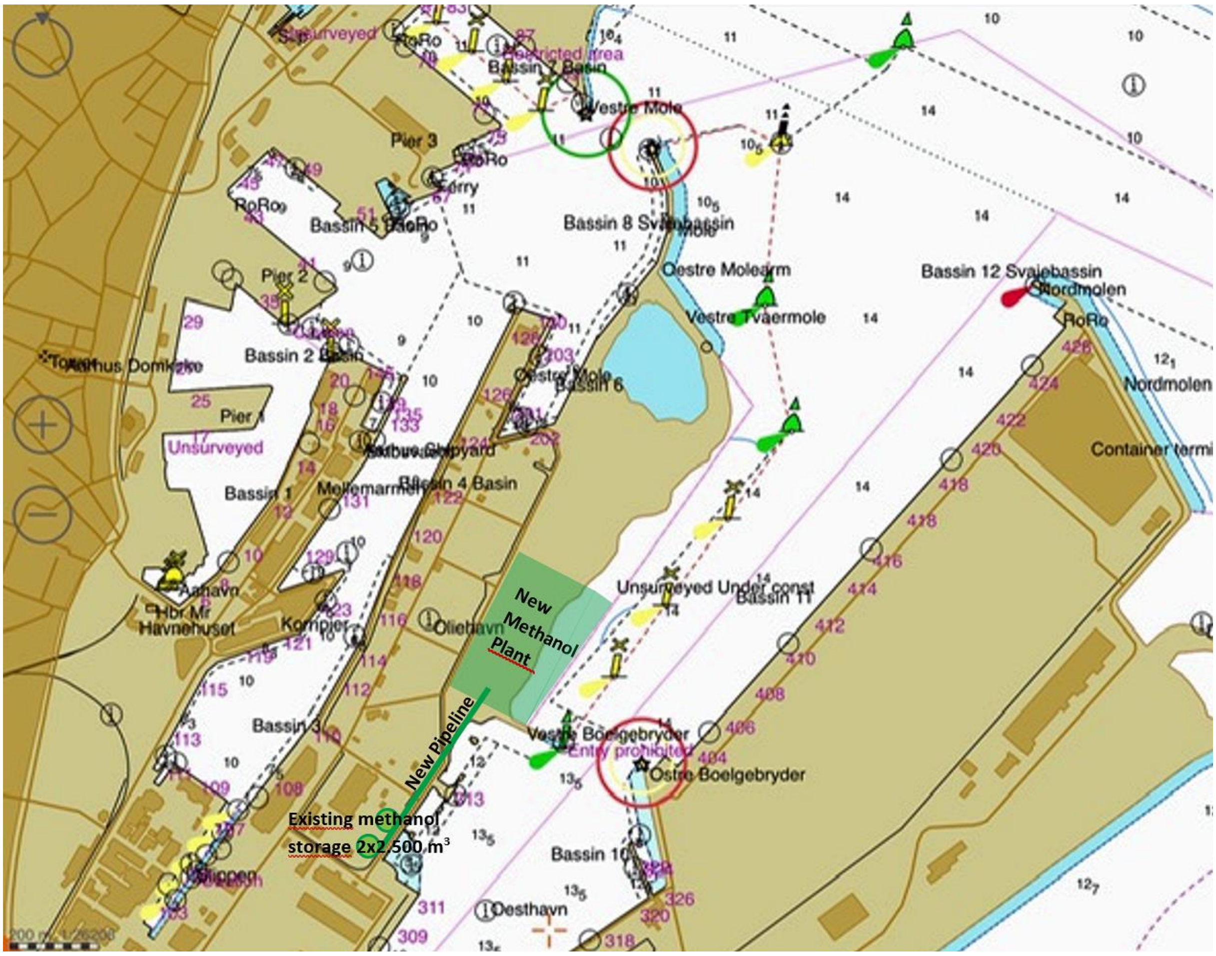


Figure 22 Location for a 1 kton/day methanol plant in Aarhus

## 6.2. Refineries.

Refineries play an important role because the vapor pressure and other quality parameters of the gasoline blend needs to be controlled. This is done easily by reducing the content of butane in the raw gasoline. However, it can only be done at the refinery. Denmark currently has refineries in Fredericia and Kalundborg located perfectly for in-shipping of methanol.

Danish Fuels Industry Association (Drivkraft Danmark) is an independent business association for the Danish petroleum & gas companies representing a major part of the Danish petroleum & gas retailers as well as the refineries.

## 6.3. Traders, shippers and retailers

Gas traders are usually also shippers approved for gas transport by energinet.dk. There is a list of Biomethane Certificates Account Holders available at https://energinet.dk/Gas/Biogas/Liste-over-kontoindehavere. Some biogas becomes RED-certified and thus useful to produce RED-certified biomethanol. This amount is increasing.

New Fuel A/S shipped the very first shipload of bio methanol made of Danish biogas on August 23, 2018 (see Figure 23).


**Figure 23 Bomar Quest en route from Tjeldbergodden to Port of Aarhus with methanol.**

## 6.4. Car owners

Car owners may be looking for alternatives to electric vehicles due to the cost of purchasing, lack of appropriate charging space or because they need towing capacity for e.g. a caravan. Methanol offers the convenience of a liquid fuel, improved engine torque and less combustion noise compared to gasoline.

The automotive industry seems to have little interest in renewable fuels. Therefore, new flex fuel compliant cars are hard to find. When converting existing vehicles, it would most likely mean that the original warranty is void. Thus, it would be advisable to draw up an insurance policy for the vehicles against technical break down related to the fuel. This approach was used successfully in a former project 'Biodiesel Danmark' and can be done similarly with M85.

# 7. Nationwide distribution plan

The authors of this report have suggested a complete path for methanol fuel in Denmark (Figure 24). The main feedstock for the methanol will be Danish Biogas.

Danish biogas is produced and purified locally and injected into the European gas grid as biomethane. Certificates are then transferred to a methanol factory, also connected to the European gas grid, and the methanol is returned to Denmark by ship. This part of the process is already in place.

Methanol shipments are currently coming from Tjelbergodden in Norway via Aarhus Port but should in the future be landed directly at the Shell Marine Terminal in Fredericia, which is connected by pipelines to the refinery. The refinery will then handle the blending and final quality assurance. The eastern part of the country can be serviced through the refinery in Kalundborg.

The complete distribution chain is seen below.

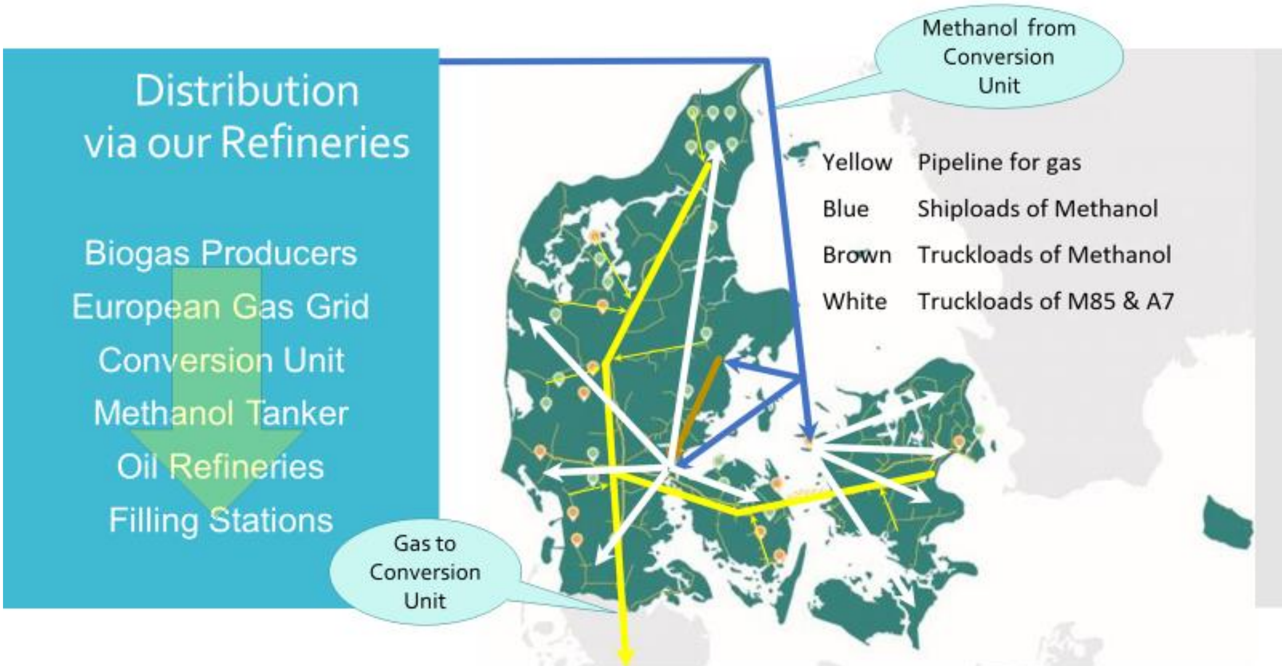


**Figure 24 Nationwide distribution plan for M85**

Smaller oil companies do not currently have storage suitable for methanol and should therefore leave this to refineries. Unlike ethanol that is too corrosive to mix at the refinery and therefore must be blended with gasoline immediately before being shipped to filling stations, mixing with gasoline at the refinery is a good option for methanol. This may of course change in the very long term, when gasoline is no longer used.

The main product shall be M85, which is adjusted between 70 and 85% methanol to account for seasonal changes in Denmark, according Figure 14. The reasons for choosing M85 is covered in section 5.4.

A7 may be produced in parallel using ethanol-methanol blended at the refineries or imported ready to use. Ready to use 4:3 alcohol blends may replace the ethanol used in E5 today.

For local distribution of methanol or methanol blends there are two possible strategies. The preferred one is to use the existing 92-octane infrastructure so that the refinery simply delivers a methanol blend instead of the previous 92-octane gasoline. The blend is then transported with road tankers as it is done today. The changes would be minimal apart from sealings made of flouro-elastomers or polyurethane, which will have to be replaced.

Another strategy is to introduce blender pumps, which blend the methanol and gasoline in any ratio. This enables both A7, M30, M85 and M100 at the same dispenser (Figure 25). It should be left to the local gas companies to decide whether they want readymade blends or use blender pumps.


**Figure 25 Vision of an alternative fuel dispenser**

## 8. Outline for a national demonstration project

Part of this project 2018-2019 was to identify topics for a larger demonstration project in 2019-2022. Based on the identified stakeholders, technologies and barriers, a national demo project is outlined. Inspiration is taken from past successful projects such as Bio-diesel Danmark and B5NEXT which have had real impact on the national fuel strategy.

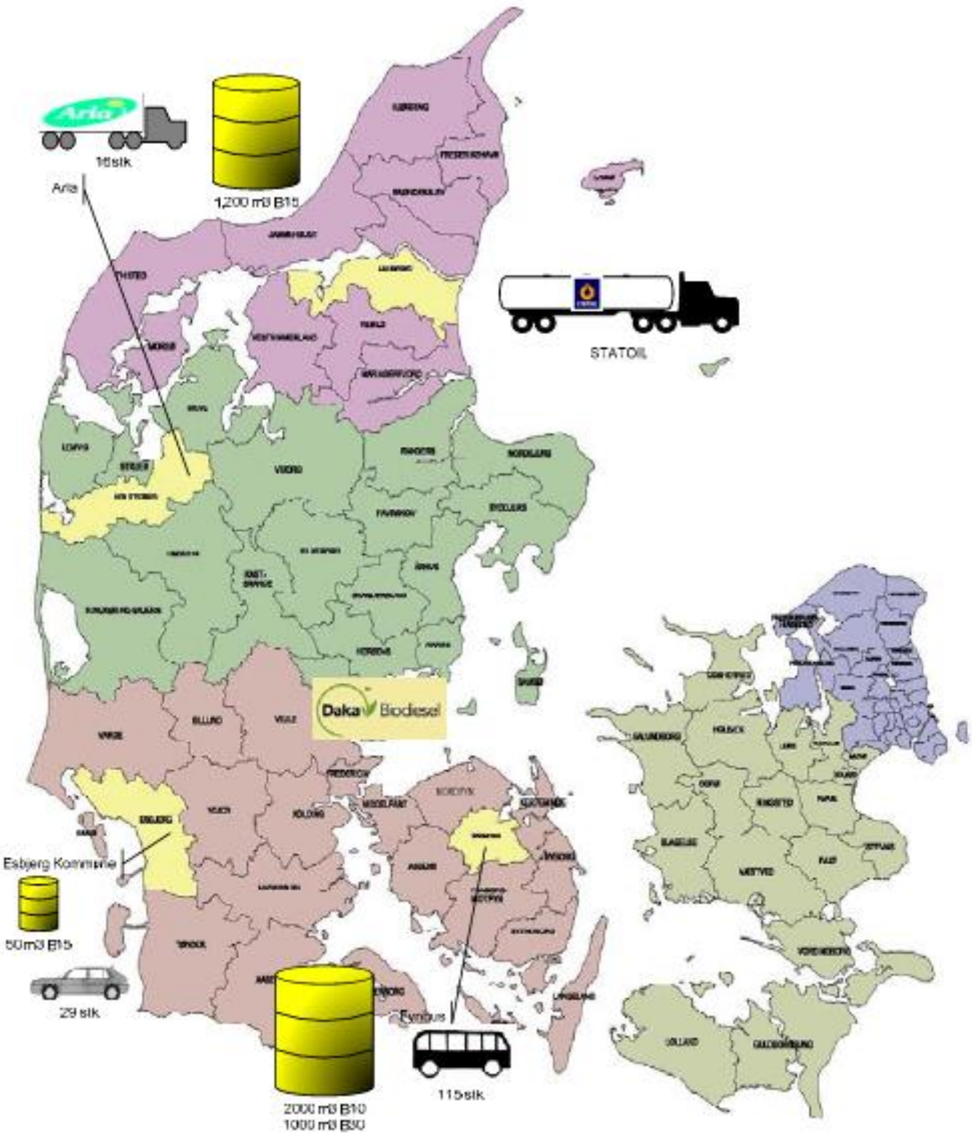


**Figure 26: Outline of the 2010 national biodiesel project (SAE 2010-01-0474)**

With the well-proven test of a M85 test car, the pilot project needs to plan a fleet trial for the coming year. Also, for M85, the infrastructure is more or less in place. A fleet trial, however, will identify any shortcomings and how to remedy. The trial will show people and not least the government that we have enough renewable energy from wind and biomass to produce methanol for transport – if only the barriers are removed.

At one and the same time a maximum number of car brands are tested, and their numbers are set to minimize measurement uncertainties. These numbers are determined by statistical assessment of previous trials. The scope is narrowed as required by financial resources. A long-term fleet trial is preferably conducted with over 100 cars and for at least one year.

Since the 92-octane gasoline was removed from the market in Denmark, there are extra pumps available. A setup as shown in Figure 27 can be used for M85 – possibly using currently vacant 92-octane petrol pumps.


**Figure 27 A refueling pump for Propel Fuels alongside traditional gasoline pumps in Citrus Heights, California.**

## 8.1. Organization

FDM and oil companies are supposed to assist identifying interested participants. Applications are also made to municipalities and companies that previously have shown green initiatives.

Non-FFVs are fitted with a Flex Fuel Kit, which will be removed after the end of the test. The kit used in the test car was purchased in France. Other kits are tested including a Chinese kit specifically designed for methanol.

Car manufacturers are requested to assist in specifying the cars that can use the 105 octane M85 with the least possible changes and which may advantageously install a Flex Fuel Kit.

An engine examination is performed before and after testing. Bell Add is offering such service. One Dyno metering for each car on E5 and M85 is part of the examination. DTI cooperates with workshops with equipment and interest in following and documenting the test.

For each participant, insurance against machine damage attributable to the fuel is written.

Oil companies are requested to provide a smaller number of pumps for M85 – possibly by changing some 92 octane pumps to 105 octane M85. NPS A/S. Nordic Petrol Systems estimates a cost of DKK 20,000 per tank for cleaning and conversion of existing ground tank and pump as well as an approx. DKK 10,000 for reprograming, so it is only can be used by participants.

Malte Fuel & Wash, Sweden offers a mobile tank station with 5 m3 tank, dispenser and a Codab registration system with online registration. The installation cost is approx. 450,000 per piece exclusive VAT.

In workplaces 330 l portable tanks with 12-volt pumps and dispenser can provide additional access for refueling. 50-100 l portable trolleys provide convenient loading on construction sites.

Mixing and distribution is left to the refinery as the immediate best solution. Alternatively, mixing can take place in the road tanker serving the filling stations

There are very few Real Driving Emission (RDE) measurements of vehicles and their efficiency - including electric cars. Inspired by the so-called Diesel Gate Scam, a standard test under real-life conditions has been developed. Therefore, an RDE measurement of comparable cars on electricity and M85 is performed - for example a VW UP in electric and M85 version. This will give the government a qualified basis for environmental policy in this area. Results from the trial fleet will contribute further to this decision basis.

## 8.2. Tentative budget

A Fleet trial with 100 cars a 25.000 km a year ~ 2½ million km will require 31.800 l E5 gasoline and 1.2 GWh biogas for making biomethanol (212.000 l).

**Table 5 Indicative budget for at large fleet trial in Denmark (1 kr. = 0.13 EUR)**

| | |
|---|---|
| Fuel on-cost 2 kr. per liter gasoline equivalent | kr. 250,000 |
| Mechanical insurance for 100 vehicles, 30 months | kr. 360,000 |
| Technical examinations and oil probes | kr. 300,000 |
| Vehicle conversions | kr. 350,000 |
| Dyno tests | kr. 150,000 |
| RDE tests | kr. 650,000 |
| Storage & blending facilities at refinery | kr. 500,000 |
| Gasoline pump conversions | kr. 300,000 |
| Hosting an IEA meeting | kr. 80,000 |
| Travel cost | kr. 200,000 |
| Administration and reporting | kr. 1,500,000 |
| | |
| Total project expenses | kr. 4,640,000 |

# 9. Methanol Handbook

This chapter provides information on production, GHG balances, cost and taxation of methanol fuels. It also contains reference to methanol fuel standards and information on electric cars for comparison.

## 9.1. Raw material and potential quantities

Methanol is made from a wide range of feedstocks. In Denmark it is practical to produce methanol from biogas and wind energy (Figure 28).

Denmark's biogas potential is substantial due to the large stock of farm animals, about 14 million cattle and hogs.

**Figure 28: Two sustainable feedstocks for bio methanol are biogas and wind power**

Until 2014, biogas was mainly used in gas engines for electricity and heat. This form of utilization, however, is stagnating and the gas is instead upgraded to biomethane that can be injected into the gas grid. According to the European Biogas Association and the EU Commission, biogas plants that upgrade to biomethane for injection into the grid will grow 15x between 2015-2030. This forecast growth is driven by a new EU directive (RED II), that will require minimum renewable sources in the heating and cooling markets and limit the use of energy crops for production of biofuels and favour the use of waste-derived biofuels in the transport sector. As a result, the next phase of market growth will favour plants using waste as a feedstock, producing biogas direct to grid.

This trend is shown in Figure 29.

Green Gas Denmark has estimated that the Danish Gas grid could be running entirely on green gas by 2038. By then the capacity for biogas should be about 72 PJ/year. Figure 29 illustrates this by the crossing of the line "DK total gas consumption" with the area "Biogas potential".

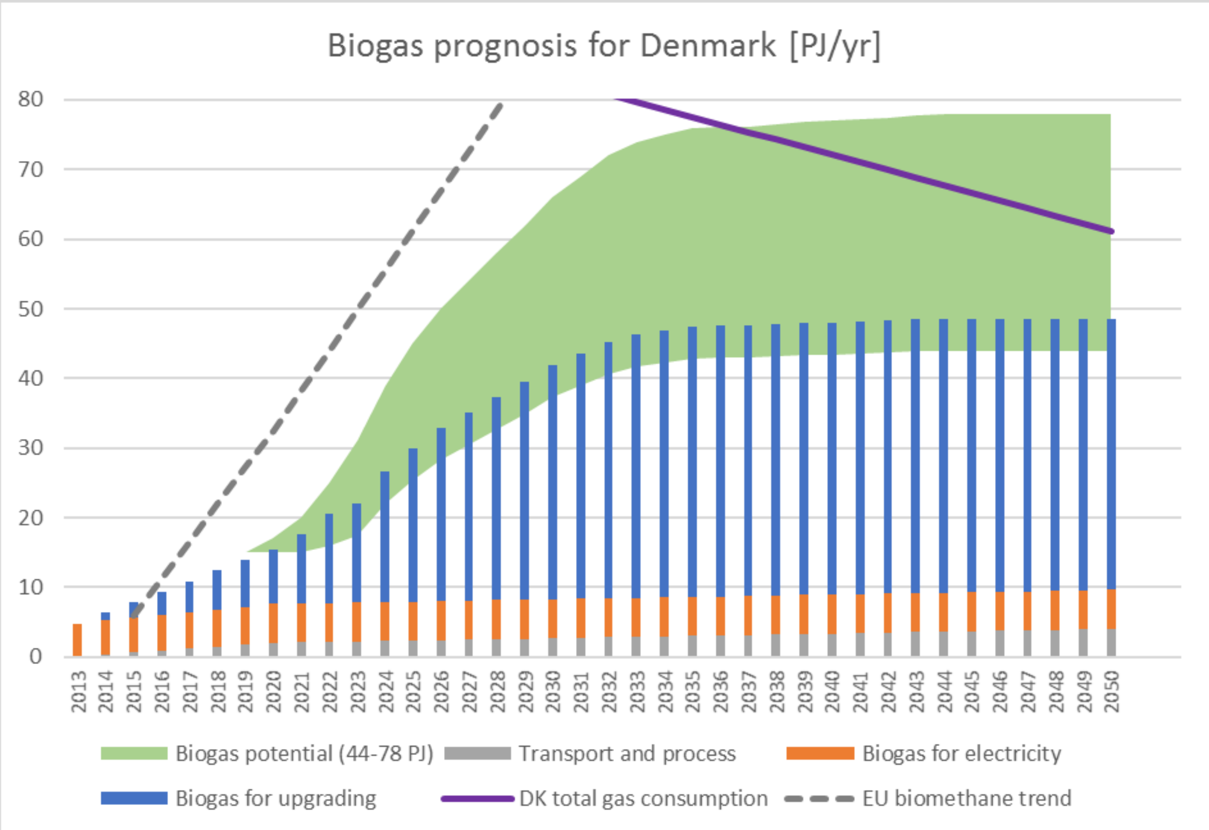


**Figure 29 Biogas potential and growth rates based on collated information from Green Gas Denmark, Danish Energy Agency, European Commission.**

This estimate agrees with "Biogas in Denmark - Status, Barriers and Perspectives" prepared by the Danish Energy Agency February 2014. It states that the maximum technical biogas potential based on Danish biomass resources can be estimated between 44 and 78 PJ depending on the time perspective and the amount of energy crops. In Figure 29 the interval between high (78 PJ) and low (44 PJ) scenario is marked as the green area.

The Danish Biogas Taskforce has for the analysis of the use of biogas in the future energy system used a slightly more conservative biogas potential of 48.6 PJ. This is within the green area in Figure 29.

For illustration the European biomethane trend is included as a dotted line in Figure 29. It is based on a prediction from European Biogas Association and the European Commission, that EU biomethane production will grow 15 times from 2015 to 2030. Applying this trend to the Danish 2015 production sees an even higher increase than any other estimates. Thus, EU is very optimistic about biogas potential.

Assuming the potential in Denmark is 48.6 PJ and 9.6 PJ is used for other purposes, there is 39 PJ biogas available for methanol production. This yields 30 PJ of methanol plus some useful heat.

On top of this, there is an additional potential of methanized wind energy. Statistics Denmark reported a production of 13,000 GWh wind energy in 2014 ~ 47 PJ wind energy, enough for 28 PJ methanol.

Denmark has about 1.64 million gasoline cars consuming a total of 1.8 million m3 petrol per year, corresponding to 58 PJ.

One car thus consumes approximately 10,000 kWh per year. One PJ fuels about 28 000 cars for one year.

The Danish biogas-methanol potential thus corresponds to 0.8 million cars. Wind power adds potentially another 0.8 million cars. The estimates are summarized in Table 6.

**Table 6 Potential number of cars to be fueled by methanol from renewable sources**

| Estimate | PJ wind | PJ biogas | PJ methanol | MWh methanol | Number of methanol cars |
|---|---|---|---|---|---|
| Available bio methane | | 39.0 | 30.0 | 8,336,763 | 833,676 |
| Available wind | 47.0 | | 28.0 | 7,777,778 | 777,778 |
| | | | | | |
| Wind and biogas combined | 47.0 | 39.0 | 58.0 | 16,114,540 | 1,611,454 |

Table 6 shows that there is enough potential to fuel every gasoline car in Denmark with methanol from wind and biogas in 2035.

## 9.2. Conversion to methanol

Conversion can be done as Gas-to-Liquid or Power-to-liquid as illustrated in Figure 30.

In the case of Gas-to-liquid, manure and waste biomass from farms is transported by road to biogas digesters. The biogas is then purified to biomethane and trough a short pipeline injected into the gas grid. The European gas network can be regarded as a container capable of receiving gas from many sources and from which gas can be taken in many places for many purposes. When gas is taken by a production facility and converted to methanol, it is transported by ship, road tanker or rail wagon to a Warehouse and distributed to an end-user.

Production facilities for methanol abroad can be used, as the EU Commission recognizes the transport of biogas in the European gas network as illustrated in Figure 33. When the gas is first injected into the gas network, it loses its identity, but an EU-certification system ensures a documentary track.

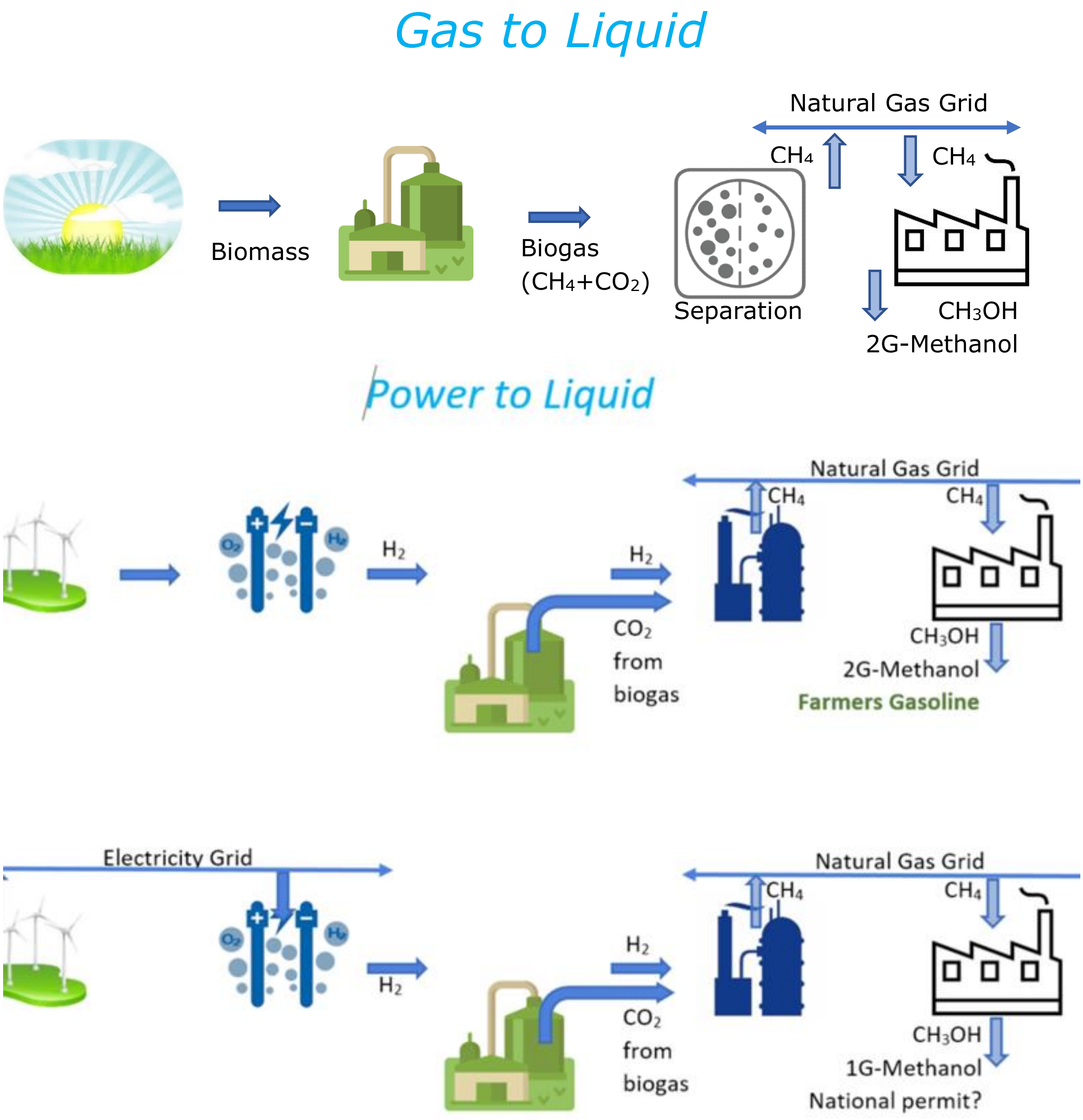


**Figure 30 Illustration of gas-to-liquid and power-to-liquid methanol production methods**

Energinet.dk owns the overall distribution system for both electricity and gas in Denmark. Permits to use the national gas grid are in place. New permits are needed to use also the national electricity grid, as shown in the bottom example in Figure 30.

Most industrial methanol is manufactured from methane by the ICI Low-Pressure Methanol Synthesis Process. Conversion efficiency of 69,3% is reported by the 2400 ton per day Methanol Plant at Tjeldbergodden, Norway, commissioned in 1997[10].

[10] http://newfuel.dk/ne/CU2%20WMC%201998%20without%20color%20frontpage.pdf

For power-to-liquid, The MeGa-StoRE project reports a yield of 600 $m^3$ methane (21,5 $GJ_{LHV}$) from 10 MWh (36 GJ) electricity. The methane may be converted to 748 kg (14,9 $GJ_{LHV}$) methanol – an overall efficiency of 41.3 $\%_{LHV}$. For motor fuels, only lower heating values LHV are relevant.

Electro fuels (methanol) may also be manufactured by hydrogenating carbon dioxide captured from air, fermentation exhausts or flue gases with unreported efficiencies.

Other examples of conversion efficiencies are:

**Example 1: Power to hydrogen**

The process is realized by electrolysis, $H_2O \rightarrow H_2 + ½O_2$ (Data from HyProvide A6).

| | |
|---|---|
| Power consumption for a 250kW stack: | 972 MJ/h |
| Hydrogen Production 60 $Nm^3/h$ or 5.4 kg/h | 648 MJ/h (LHV) |
| Electrolysis Efficiency at LHV and HHV | 66.7 $\%_{LHV}$ |

**Example 2: Hydrogen to methane**

The process is done by a Sabatier reactor using $CO_2$ from e.g. biogas, $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (Data from MeGa-StoRE).

| | |
|---|---|
| Hydrogen consumption 2400 $m^3/h$ or 8,4 $MW_{HHV}$: | 25.6 $GJ_{LHV}$ /h |
| Methane production 600 $m^3/h$ or 6,6 $MW_{HHV}$: | 21.4 $GJ_{LHV}$ |
| Sabatier efficiency | 83.6 $\%_{LHV}$ |

**Example 3: Methane to methanol**

This process has two steps. Steam reforming, $CH_4 + H_2O \rightarrow CO + 3H_2$ followed by Syngas conversion, $CO + 2H_2 \rightarrow CH_3OH$ (Data from 1998 World Methanol Conference).

| | |
|---|---|
| Methane consumption 28.74 $GJ_{LHV}/t_{methanol}$ | 2.977 $GJ_{LHV}$/h |
| Methanol production 103.6 t/h | 2.062 $GJ_{LHV}$/h |
| Methane to methanol efficiency | 69.3$\%_{LHV}$ |

**Example 4: Hydrogen to methanol**

This process uses hydrogenation of $CO_2$. (Data from Chemical Engineering Transactions Vol 29, 2012).

| | |
|---|---|
| Hydrogen consumption 2.3 kt/yr | 31.4 $GJ_{LHV}$/h |
| Methanol production 1kt/yr | 22.7 $GJ_{LHV}$/h |
| Hydrogenation efficiency | 72.3% |

**Example 5: Power to methanol**

This process also has two steps. Electrolysis followed by $CO_2$ hydrogenation, $3H_2 + CO_2 \rightarrow CH_3OH + H_2O$ (Data from CRI Iceland).

| | |
|---|---|
| Hydrogen production by electrolysis 800 t/yr | 66.7%$_{LHV}$ |
| $CO_2$ hydrogenation 5.5 kt/yr | 72.3%$_{LHV}$ |
| Power to methanol efficiency | 48.2% |

A summary of conversion efficiencies are shown in Table 7.

**Table 7 Summary of conversion efficiencies**

| | | Input GJ/h LHV | | | Output GJ/h LHV | | | |
|---|---|---|---|---|---|---|---|---|
| | | Electricity | Hydrogen | Methane | Hydrogen | Methane | Methanol | Efficiency |
| Example 1 | Electrolysis | 0.972 | | | 0.648 | | | 66.7% |
| Example 2 | Sabatier | | 25.8 | | | 21.5 | | 83.2% |
| Example 3 | Tjelbergodden 1998 | | | 2,977 | | | 2,064 | 69.3% |
| Example 4 | CO2 hydrogenation | | 31.4 | | | | 22.7 | 72.3% |
| Example 5 | George Olah 2015 | 18.7 | | | | | 9.00 | 48.2% |

Examples 3 and 5 are shown in Figure 31 and Figure 32.

**Figure 31 Gas-to-Liquid, Tjelbergodden Plant in Norway, commissioned in 1997. Capacity 1000 mill. liters per year**

**Figure 32 Power-to-Liquid, George Olah Plant in Svartsengi, near Grindavik, Iceland, 2012. Capacity 5 mio. liters per year.**

## 9.3. Certification

An increasing proportion of Danish biogas (Figure 29) is being RED-certified and hence suitable for green second-generation biofuel in the form of bio methanol.

Biogas used for transportation as "Liquid Gas", must be produced from waste and residues and upgraded to natural gas quality and RED-certified. Otherwise the product is of no interest to the market.

In Denmark two EU accredited inspection and certification companies operate, which have obtained their certification system recognized by EU (see Figure 33). These are ISCC System GmbH and REDcert International Pvt Ltd. Both act through partnerships with designated certification bodies. The third certification company RSB is currently not operating in Denmark.


**Figure 33 European RED certification bureaus of which 2 operate in Denmark**

The emission savings for certification are found using a tool provided by Biograce [11]. The BioGrace greenhouse gas (GHG) calculation tool has been recognized as a voluntary scheme by the European Commission.

A current example of RED-certified bio methanol, branded as 'Farmers Gasoline' in Denmark, is shown in Figure 34.

[11] http://www.biograce.net/home

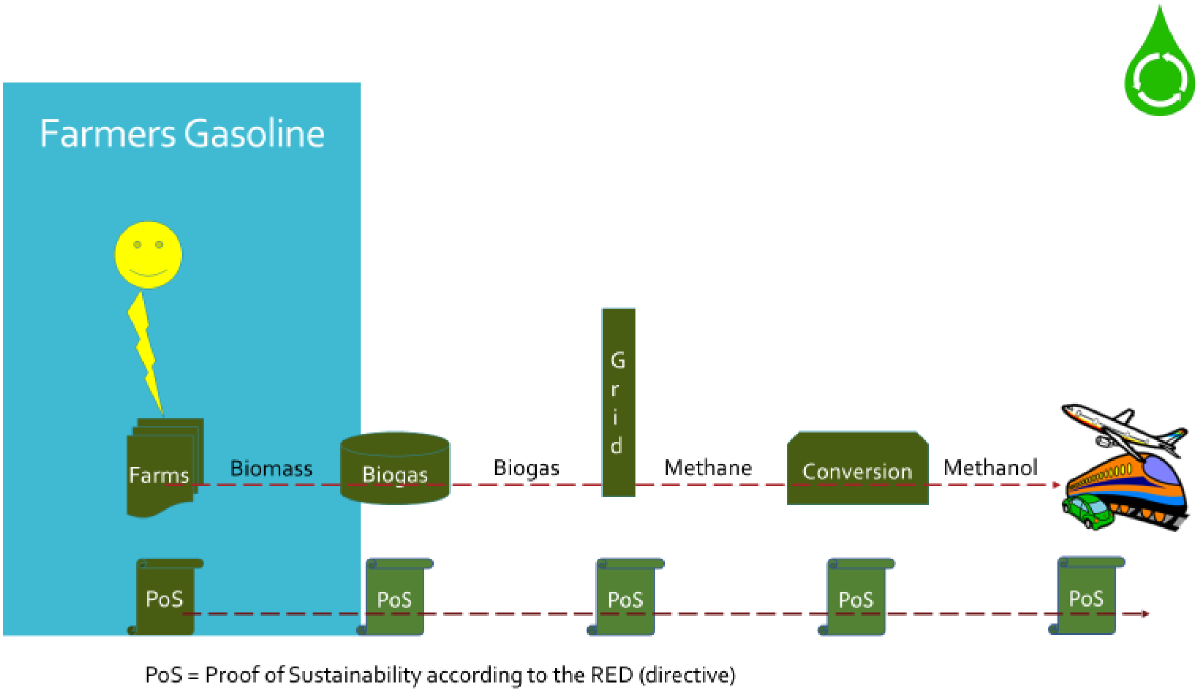


**Figure 34 Certification pathway for 'Farmers Gasoline' ISCC EU certified bio methanol**

Decentral collection of biomass and conversion to biomethane saves transport. Placement of methanol plant 'Conversion' can be central and given a profitable capacity of a few thousand tons of methanol per day.

Profitability could be increased by concurrent use of wind power for central electrolysis. This would allow the use of both oxygen and hydrogen from the electrolysis - but it requires regulatory changes.

Under ISCC EU and European legislation (FQD) the following power-to-liquid pathways will be possible:

1. $CO_2$ from biogas processed using electricity from renewable sources
2. $CO_2$ from fossil sources (non-biological origin) processed using electricity from renewable sources

The direct supply of renewable electricity (without grid connection) will be possible.

For the off-taking of electricity from the grid, national obligations shall probably be considered. As a first step this can be certified under ISCC, if certain requirements will be fulfilled (e.g. double-accounting of the renewable electricity is excluded).

Until more favourable rules for using wind power are introduced, Denmark may continue to use the pathway illustrated in Figure 34.

The crucial RED II-directive is implemented according to the timeline below:

- 13/11/2018: Provisional agreement passed by the EU Parliament
- 03/12/2018: Final approval by the EU Council (Member States)
- 21/12/2018: Publication in the official journal of the EU

- February 2019: Delegated act on EU ruling for high and low iLUC biofuels
- 30/06/2021: Deadline for transposition into national legislation in Member States

## 9.4. Methanol fuel standards

There are 3 methanol fuel standards of major interest. These are the American ASTM standard for M85, the Chinese counterpart GB/T, also for M85, and finally the Israeli standard for M15. The standards are compared in the table below.

For Denmark, it is recommended to use ASTM International Designation: D5797 – 17; Standard Specification for Methanol Fuel Blends (M51–M85) for Methanol-Capable Automotive Spark-Ignition Engines. This specification is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is under the direct responsibility of Subcommittee D02.A0.02 on Oxygenated Fuels and Components. The specification is also adopted as Danish Standard.

**Table 8 Summary of methanol fuel standards**

| Property | ASTM 1 | ASTM 2 | ASTM 3 | GB/T 23799 | SI 90 M15 |
|---|---|---|---|---|---|
| Methanol incl. higher alcohols $\%_{vol}$ | > 84 | > 80 | > 70 | 84..86 | 10..17 |
| Higher alcohols $\%_{vol}$ | < 2 | < 2 | <2 | < 2 | < 10 |
| Hydro carbons $\%_{vol}$ | 14..16 | 14..20 | 14..30 | 14..16 | < 54 |
| Vapor pressure kPa | 48..62 | 62..83 | 83..103 | < 78 Winter<br>< 68 Summer | 50..80 Winter<br>45..65 Summer |
| Lead mg/l | < 2,6 | < 2,6 | < 3,9 | < 2,5 | < 5 |
| Sulphur mg/kg | < 160 | < 200 | < 300 | < 80 | < 10 |
| Phosphorus mg/l | < 0,2 | < 0,3 | < 0,4 | < 2 | |
| Acid mg/kg | < 50 | < 50 | < 50 | < 50 | |
| Gum washed mg/100ml | < 5 | < 5 | < 5 | < 5 | < 5 |
| Gum unwashed mg/100ml | < 20 | < 20 | < 20 | < 20 | |
| Chlorides mg/kg | < 2 | < 2 | < 2 | < 2 | |
| Inorganic chloride mg/kg | < 1 | < 1 | < 1 | < 1 | |
| Water $\%_{wt.}$ | < 0,5 | < 0,5 | < 0,5 | < 0,5 | < 0,2 |
| Appearance | Bright and clear with no particles visible | | | | |
| RON | | | | | > 95 |
| MON | | | | | > 85 |
| Density kg/m$^3$ | | | | | 720..775 |
| Oxidation, min. | | | | | > 360 |
| Oxygen $\%_{wt.}$ | | | | | < 9 |
| Copper- corrosion | | | | | Class 1 |

## 9.5. Recipe for M85

105 octane M85 is a mixture of:

- 85 volume percent methanol
- 15 volume percent gasoline
- Q.S. (a suitable amount) lubricant
- Q.S. (a suitable amount) anti-corrosive additive

For winter driving in Denmark it may be practical to reduce methanol content to 70%. This will ensure a higher vapor pressure as indicated in Table 8. A higher vapor pressure helps cold starting in general.

The methanol shall comply with the IMPCA METHANOL REFERENCE SPECIFICATIONS issued by International Methanol Producers & Consumers Association, Avenue de Tervueren 270 Tervurenlaan - 1150 Brussels – Belgium. The specification limits water to max 0,100 % w/w acc. to ASTM E1064-12 and limits purity on dry basis to min 99.85% w/w acc. to IMPCA 001-14.

For a lubricant and anti-corrosion additive there are several options, e.g. Redline SI-Alcohol.

In M85 there is no need for a co-solvent or ignition improver.

## 9.6. Properties of methanol blends

Table 9 shows the properties of each fuel component. The numbers are based on the RED Directive GHG emission 26 g $CO_2$ /MJ for 1G-ethanol from wheat (with straw combustion for CHP) and 5 g$CO_2$ / MJ 2G-methanol from waste wood. As stated in the RED Directive, the greenhouse gas emission varies for biofuels with the raw material and process/pathway used. For 1G ethanol, the default value thus varies between 24 and 70 g $CO_{2eq}$ / MJ. For 2G methanol, the emission varies between 5 and 7 g $CO_{2eq}$ / MJ.

There is no pathway for biogas in the current RED. Biograce standard values can be used instead.

**Table 9 Base data for biofuels and gasoline**

| | Density | LHV energy | Bioenergy | Advanced bio | Oxygen | Carbon | Energy | Range | WtW CO2 | WtW CO2 |
|---|---|---|---|---|---|---|---|---|---|---|
| Component | g/l | MJ/l | %LHV | %LHV | %m | %m | MJ/km | km/l | g/l | g/km |
| Ethanol 1G | 0.794 | 21.3 | 100% | 0% | 35% | 52.2% | 1.68 | 12.7 | 553 | 44 |
| Methanol 2G | 0.793 | 15.8 | 200% | 200% | 50% | 37.5% | 1.68 | 9.4 | 79 | 8 |
| Gasoline | 0.745 | 32.9 | 0% | 0% | 0% | 85.0% | 1.68 | 19.6 | 2757 | 141 |

Energy consumption per km is obtained from the Real Driving test in Chapter 3. Taxes are Danish rates as of September 2018. Based on the information in Table 9 the blends can be characterized.

**Table 10 Properties of typical European E5 gasoline**

| | Content | LHV energy | Bioenergy | Advanced bio | Oxygen | Carbon | Energy | Range | WtW CO2 | WtW CO2 |
|---|---|---|---|---|---|---|---|---|---|---|
| Component | %vol | MJ/l | %LHV | %LHV | %m | %m | MJ/km | km/l | g/l | g/km |
| Ethanol 1G | 4.8% | 1.0 | 100% | 0% | 1.8% | 2.7% | 1.68 | 0.6 | 27 | 44 |
| Gasoline | 95% | 31.3 | 0% | 0% | 0% | 80.7% | 1.68 | 18.6 | 2625 | 141 |
| 95 octane E5 | 100% | 32.3 | 3.16% | 0.00% | 1.77% | 83% | 1.68 | 19.3 | 2651 | 138 |

It is apparent from Table 10 that E5 does not meet present biofuel obligations in the EU. The bio energy content is only 3.16% whereas the obligation is 5.75%. This means that biofuels must be added elsewhere to compensate, e.g. in the diesel sector.

A7 on the other hand, as seen in Table 11, complies with both the present and the 2020 biofuel commitment. It is therefore an excellent successor to E5.

**Table 11 Properties of 95 octane A7**

| | Content | LHV energy | Bioenergy | Advanced bio | Oxygen | Carbon | Energy | Range | WtW CO2 | WtW CO2 |
|---|---|---|---|---|---|---|---|---|---|---|
| Component | %vol | MJ/l | %LHV | %LHV | %m | %m | MJ/km | km/l | g/l | g/km |
| Ethanol 1G | 4% | 0.9 | 100% | 0% | 1.5% | 2% | 1.68 | 0.5 | 22 | 44 |
| Methanol 2G | 3% | 0.5 | 200% | 200% | 1.6% | 1% | 1.68 | 0.3 | 2 | 8 |
| Gasoline | 93% | 30.6 | 0% | 0% | 0% | 79% | 1.68 | 18.2 | 2564 | 141 |
| 95 octane A7 | 100% | 31.9 | 5.63% | 2.97% | 3.07% | 82% | 1.68 | 19.0 | 2588 | 136 |

**Table 12 Properties of 105 Octane M85**

| | Content | LHV energy | Bioenergy | Advanced bio | Oxygen | Carbon | Energy | Range | WtW CO2 | WtW CO2 |
|---|---|---|---|---|---|---|---|---|---|---|
| Component | %vol | MJ/l | %LHV | %LHV | %m | %m | MJ/km | km/l | g/l | g/km |
| Methanol 2G | 85% | 13.4 | 200% | 200% | 43% | 32% | 1.68 | 8.0 | 67 | 8 |
| Gasoline | 15% | 4.9 | 0% | 0% | 0% | 12% | 1.68 | 2.9 | 414 | 141 |
| 105 octane M85 | 100% | 18.3 | 146% | 146% | 42.9% | 44% | 1.68 | 10.9 | 481 | 44 |

The M85 based on 2nd generation methanol has a $CO_2$ emission of only 44 g/km. This corresponds to the emission of an electric car with the Danish electricity mix.

## 9.7. Cost and taxation

Price fluctuations over time and origin makes it difficult to calculate comparable consumer prices. Figure 35 shows the historical price fluctuations.

The Ethanol price is indirectly affected by oil prices but most directly by US corn prices.

Methanol price is driven up by the Chinese market for transportation fuel. The large gas discoveries in the US and Canada, however, have attracted new methanol mega-plants with the capacities of 5-10 kt per day, which could reverse the price trend. Large quantity buyers typically get 15-20 % off the list price.

For bio-methanol there are no price listings, but most often it is sold at the quarterly Methanex or ICIS price plus a bio-premium. The surcharge is justified because bio methanol is a 2nd generation fuel counting twice in the EU RED national obligations.

The Danish energy tax for petrol in 2019 is 4.339 DKK per litre petrol. Biofuels are taxed relatively to their energy content. In the same period, gasoline attracts a $CO_2$ tax of DKK 0.421 per litre, while biofuels are exempted from $CO_2$ tax.

The use of methanol and bio methanol is tax-neutral according to current regulations. I.e. that the state tax revenue is unchanged.

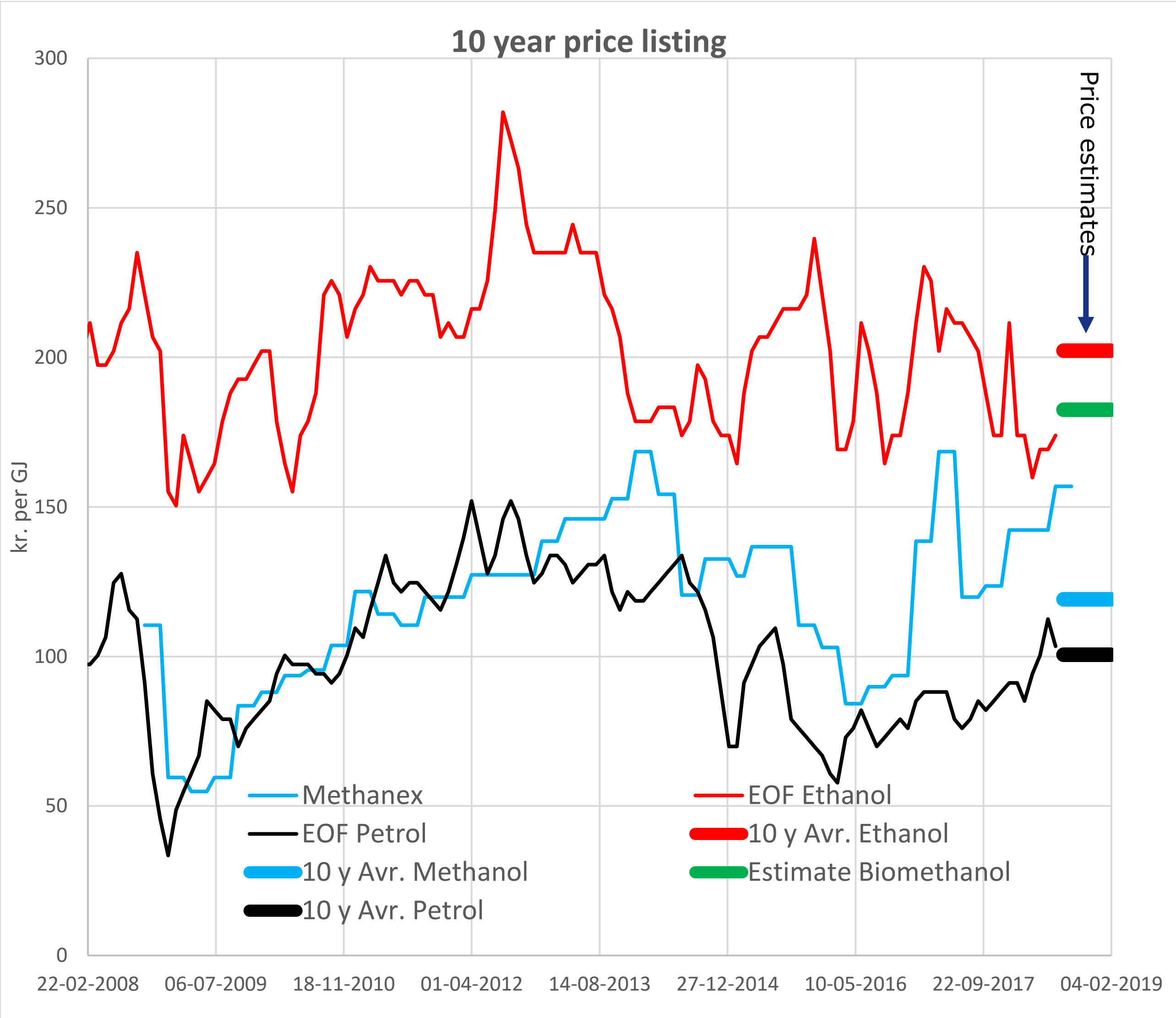


**Figure 35 Estimated cost of petrol, ethanol and methanol based on historical price listings (EOF and Methanex). The estimates at the far right will be used for further cost calculations**

Based on the fuel prices in Figure 35 and test performance (19.3 km/l) of the city car, the total cost to the consumer including taxation and VAT can be calculated. This is done in Figure 36.

| | Content | Energy tax | CO2 tax | Total tax | Fuel cost | Surcharge | Product cost | Pump price | Consumer cost |
|---|---|---|---|---|---|---|---|---|---|
| Component | %vol | kr/l | kr/l | kr/km | kr/l | kr/l | kr/l | kr/l | kr/km |
| Ethanol 1G | 100% | 2.81 | 0 | 0.222 | 4.30 | 0.85 | 7.96 | 9.95 | 0.79 |
| Methanol 2G | 100% | 2.08 | 0 | 0.222 | 2.98 | 0.63 | 5.69 | 7.12 | 0.76 |
| Gasoline | 100% | 4.34 | 0.42 | 0.243 | 3.31 | 1.32 | 9.39 | 11.73 | 0.60 |

| | Content | Energy tax | CO2 tax | Total tax | Fuel cost | Surcharge | Product cost | Pump price | Consumer cost |
|---|---|---|---|---|---|---|---|---|---|
| Component | %vol | kr/l | kr/l | kr/km | kr/l | kr/l | kr/l | kr/l | kr/km |
| Ethanol 1G | 4.8% | 0.13 | 0 | 0.011 | 0.21 | 0.04 | 0.38 | 0.48 | 0.04 |
| Gasoline | 95% | 4.13 | 0.40 | 0.231 | 3.15 | 1.25 | 8.94 | 11.17 | 0.57 |
| 95 octane E5 | 100% | 4.27 | 0.40 | 0.24 | 3.36 | 1.29 | 9.32 | 11.65 | 0.61 |

| | Content | Energy tax | CO2 tax | Total tax | Fuel cost | Surcharge | Product cost | Pump price | Consumer cost |
|---|---|---|---|---|---|---|---|---|---|
| Component | %vol | kr/l | kr/l | kr/km | kr/l | kr/l | kr/l | kr/l | kr/km |
| Ethanol 1G | 4% | 0.11 | 0 | 0.009 | 0.17 | 0.03 | 0.32 | 0.40 | 0.03 |
| Methanol 2G | 3% | 0.06 | 0 | 0.007 | 0.09 | 0.02 | 0.17 | 0.21 | 0.02 |
| Gasoline | 93% | 4.04 | 0.39 | 0.226 | 3.08 | 1.22 | 8.74 | 10.92 | 0.56 |
| 95 octane A7 | 100% | 4.22 | 0.39 | 0.24 | 3.34 | 1.28 | 9.22 | 11.53 | 0.61 |

| | Content | Energy tax | CO2 tax | Total tax | Fuel cost | Surcharge | Product cost | Pump price | Consumer cost |
|---|---|---|---|---|---|---|---|---|---|
| Component | %vol | kr/l | kr/l | kr/km | kr/l | kr/l | kr/l | kr/l | kr/km |
| Methanol 2G | 85% | 1.77 | 0 | 0.189 | 2.53 | 0.54 | 4.84 | 6.05 | 0.64 |
| Gasoline | 15% | 0.65 | 0.06 | 0.037 | 0.50 | 0.20 | 1.41 | 1.76 | 0.09 |
| 105 octane M85 | 100% | 2.42 | 0.06 | 0.23 | 3.03 | 0.73 | 6.25 | 7.81 | 0.73 |

**Figure 36 Cost and taxation of methanol blends**

## 9.8. GHG emissions from Biogas

Waste-derived renewable energy is focus of RED II EU regulation from 2020. Biogas solves an important waste issue because it reduces the methane emissions from farm manure. Upgraded biogas utilizes existing European gas grid which has received over €400 billion of investment.

As stated by the European Biogas Association (EBA) as per 22 November 2018:

*"Manure if left untreated will emit methane and nitrous oxide emissions as well as a number of other air pollutants or GHG precursors such as ammonia. Instead, if the organic content of livestock manure decomposes in the absence of oxygen in an anaerobic digester, it will decompose into a gas mixture richer in methane. This so-called biogas can be captured, cleaned and combusted for energy production. However, the way in which the biogas is produced – in particular the inputs to the digestion process in the form of type of manure and eventual additional biogenic material such as crops or food waste – can have significant impacts on the efficiency and cost of the process. A by-product is "digestate", a nutrient-rich substance that is usually used as fertiliser. Other options exist to reduce manure emissions but do not produce usable energy: Storage management, air filtering and circulation, composting, nitrification-denitrification treatment, acidification, solid separators and artificial wetlands all shown potential to reduce greenhouse gas emissions from manure."*

The EU RED directive (2009/28/EC of 23 April 2009) on the promotion of the use of energy from renewable sources) - **ANNEX V** set out rules for calculating the greenhouse gas impact of biofuels, bioliquids and their fossil fuel comparators.

The Directive currently only mentions wood methanol. Biogas to methanol is not specified in the directive and may therefore be calculated using the Biograce tool.

Biograce can use a default value for biogas and the EU RED directive specifies 3 such values for biogas based on municipal waste, dry manure and wet manure respectably. Danish biogas is practically only certified with default value - a relatively high value. This is because there is not yet a market for biogas with individually calculated emissions.

This means that the calculated emissions from the production of biomethanol can range from below 5 to as much as 26 g$CO_{2eq}$/MJ using present default biogas values.

The EU has continuously assessed the $CO_2$ emissions from different fuels and, in its latest proposal for a new directive, sets out the $CO_2$ emissions for biogas to be as low as -100 g$CO_2$ / MJ, as shown in Table 13.

**Table 13 CO2-emissions of typical bio methane-derivatives /COM/2016/0767/.**

| Biomethane production system | Technological option | Typical greenhouse gas emissions g $CO_{2eq}$/MJ | Default greenhouse gas emissions g $CO_{2eq}$/MJ |
|---|---|---|---|
| Biomethane from wet manure | Open digestate, no off-gas combustion | -22 | 22 |

| | | | |
|---|---|---|---|
| | Open digestate, off-gas combustion | -35 | 1 |
| | Close digestate, no off-gas combus-tion | -88 | -79 |
| | Close digestate, off-gas combustion | -103 | -100 |

As seen in Table 13, biogas carefully manufactured by state of the art, really has no GHG emission. Conversion to methanol is associated with a low greenhouse gas emission and even the waste heat from the conversion is made useful. This makes biomethanol an extremely promising liquid fuel for transport.

## 9.9. Comparison of EV and methanol car

In Denmark, the government's plan is to ban all sales of new petrol and diesel cars by 2030 and only allow electric cars or other forms of "zero-emission" cars. However, electric cars also cause $CO_2$ emissions.

Emissions of $CO_{2eq}$ produced by an electric car is based on local footprint of local electricity plus the car manufacturing.

The local footprint of electricity in Denmark is very low, 200 g/kWh ~ 56 g CO2eq/MJ as shown in Figure 37. By comparison, Biograce states for "Electricity EU mix LV" 129 g CO2eq/MJ.

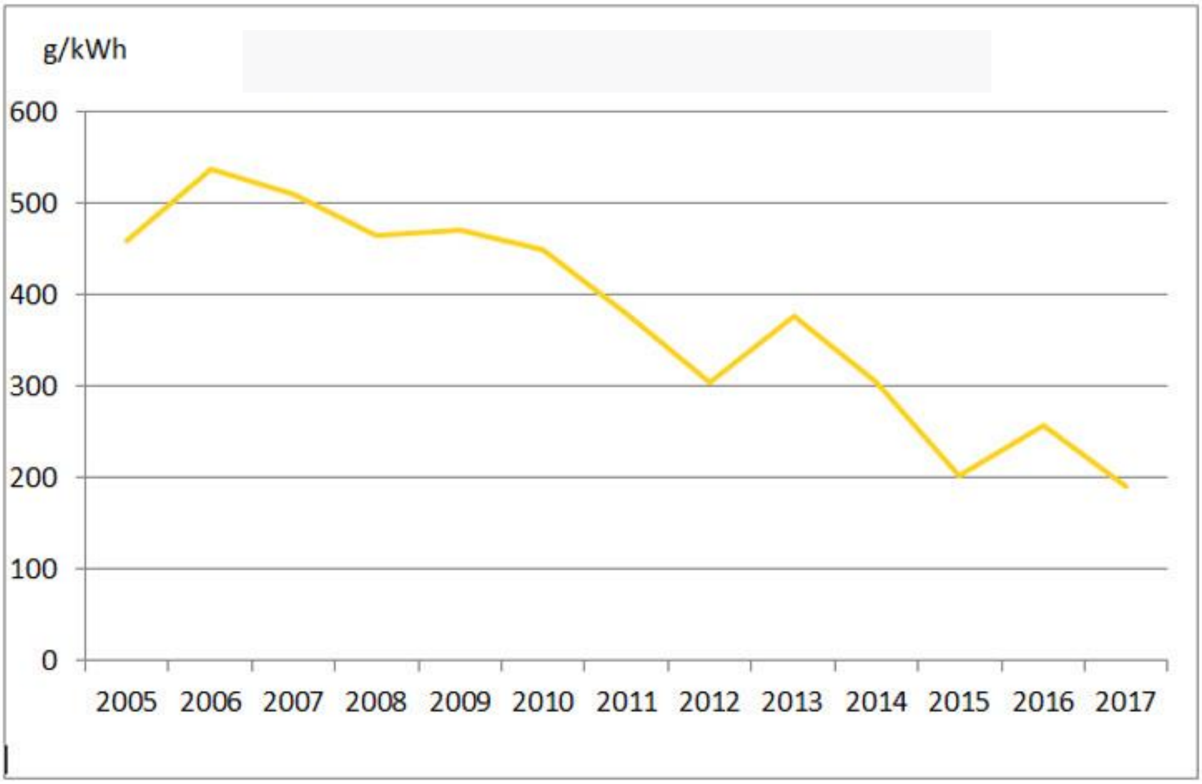


**Figure 37 Development in $CO_2$ emissions per kWh consumed in Denmark**

Due to the relatively large $CO_2$ footprint of manufacturing batteries however, methanol cars still make a strong case in comparison.

The LowCVP (Low Carbon Vehicle Partnership), established in 2003, is a public-private partnership that exists to accelerate a sustainable shift to lower carbon vehicles and fuels and create opportunities for UK business. Nearly 200 organizations are engaged from diverse backgrounds.

LowCVP starts their News Release, 8th June 2011 "*LowCVP study demonstrates the increasing importance of measuring whole life carbon emissions to compare vehicle performance*" saying

> ELECTRIC and hybrid cars create more carbon emissions during their production than standard vehicles – but are still greener overall, according to a new report.
>
> For example, a typical medium sized family car will create around 24 tonnes of $CO_2$ during its life cycle, while an electric vehicle (EV) will produce around 18 tonnes over its life. For a battery EV, 46 % of its total carbon footprint is generated at the factory, before it has travelled a single mile.

**Table 14 LowCVP estimated emissions in vehicle production (tons CO2e)**

| | |
|---|---|
| Standard gasoline vehicle | 5.6 |
| Hybrid vehicle | 6.5 |
| Plug-in hybrid vehicle | 6.7 |
| Battery electric vehicle | 8.8 |

Based on a 150,000 km life cycle we find from Table 14:

Emission <u>during manufacture of an EV</u> 8,8 * 1.000.000 /150.000 = 58,7 g $CO_2$/km

Emission <u>during manufacture of an FFV</u> 5,6 * 1.000.000 /150.000 = 37,3 g $CO_2$/km

To these manufacturing figures driving emissions must be added. LowCVP find that an EV generates 65 g$CO_2$ per km with a 500 g/kWh electricity mix. With the Danish mix of 200 g/kWh that translates to 26 g$CO_2$ per km. The Danish Climate Counsil uses 35 g/km to account for production of wind turbines etc. We shall use 32,5 g/CO2/km.

Using Real Driving Emission (RDE) measurements from Chapter 3, we find:

- Emission driving a city car on E5: 130 $gCO_2$/km
- Emission driving a city car on M85: 40 $gCO_2$/km
- Emission driving a city car on M100: 8 $gCO_2$/km
- Emission driving an EV: 32,5 $gCO_2$/km

Summing up

- Life cycle emission of a city car using E5 (37,3+130) = 167,3 $gCO_2$/km
- Life cycle emission of a city car using M85 (37,3+40) = 77,3 $gCO_2$/km
- Life cycle emission of a city car using M100 (37,3+8) = 45,3 $gCO_2$/km
- Life cycle emission of an EV (58,7+32,5) = 91,2 $gCO_2$/km

A car on M100 thus emits from cradle to grave about half as much $CO_2$ as an electric car, when the methanol is produced from biogas.

Even an M85 car emits less CO2 than an electric car, as shown in Table 15.

**Table 15 Life cycle comparison of gasoline, electric and methanol vehicle**

| | E5 | M85 | Electric |
|---|---|---|---|
| Emission in production of vehicle | 5.600 kg $CO_{2eq.}$ | 5.600 kg $CO_{2eq.}$ | 8.800 kg $CO_{2eq.}$ |
| Emission driving 150.000 km | 19.650 kg $CO_{2eq.}$ | 5.250 kg $CO_{2eq.}$ | 6.000 kg $CO_{2eq.}$ |
| Life cycle emission | 25.250 kg $CO_{2eq}$ | 10.850 kg $CO_{2eq.}$ | 14.800 kg $CO_{2eq.}$ |
| Fuel and energy pathway | Corn fermentation and natural gas in CHP | Wet manure from open digestate with off-gas combustion | From Danish grid |

# 10. Dissemination

Information about this project is available on the following websites:

https://www.iea-amf.org/content/projects/map_projects/56

http://danskbiomethanol.dk/profile/home.html

A contribution to AMFI Newsletter was sent on Jan. 11th, 2019.

As newsletter, two publications were made. One short information sheet and one folder describing the project in more detail. See "CityCarSheet" and "CityCarFolder".

Physical meetings/workshops were held with several Danish stakeholders,

- Shell Refineries on 31/8-2018
- Scantune on 21/9-2018
- Port of Aarhus on 28/9-2018
- Circle-K on 8/1-2019
- Nordic Green on 15/3-2019
- EWII on 22/10-2018
- NGF Nature Energy 15/11-2018
- Dansk Folkeparti 27-11-2018
- Danish Transport and road safety agency on 7/3-2019

Discussions and mail correspondence about this project were also held with several stakeholders,

- Go'on
- FDM
- Scania
- Drivkraft Danmark (Fuel Suppliers Association)
- The government's Commission for Green Transition of Passenger Vehicles
- KL - Local Government Denmark
- City of Aarhus
- City of Skanderborg
- City of Copenhagen

A presentation suitable for a webinar was developed but not deployed. The Transportation Innovation Network TINV was used to create further national interest in the topic.


**Figure 38 Magnetic advertising sign for test vehicles says: "We drive on M85 Methanol made from Danish Biogas"**


**Figure 39 Magnetic sign on test vehicle in public traffic**

## 11. Recommendations for the future

Due to the extremely low conversion cost and low life cycle GHG emissions it is recommended to continue work on methanol fuelled cars as a supplement to electric cars.

A continued effort is needed to convince decision makers, vehicle suppliers and the general public that methanol fuel is as safe and practical as gasoline.

For future work some key aspects should be addressed:

- Demonstrating M85 in a much larger number of vehicles
- Obtaining a general approval of a Flex Fuel kit in Denmark
- Software conversions (ECU flashing) as alternative to flex fuel kits
- Using Direct Injection engines for better cold start
- Establishing physical production of bio-methanol in Denmark
- Removing the barriers mentioned in this report

The authors of this report welcome all Danish stakeholders to make contact in order to establish broader collaboration on future methanol fuelled cars.