BIOMETHANOL
PRODUCTION AND USE AS FUEL

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Table of Contents

ABBREVIATIONS

CI	Compression ignition
EJ	Exajoule
FCV	Fuel cell vehicle
FFV	Flexible Fuel Vehicle
GHG	Greenhouse gas
HTW	High Temperature Winkler
ICE	Internal combustion engine
MSW	Municipal Solid Waste
MW	Megawatt
WGS	Water gas shift reactor

CHEMICAL COMPOUNDS

CH_4	Methane
CO	Carbon monoxide
COS	Carbonyl sulfide
CO_2	Carbon dioxide
DME	Dimethyl ether
HCl	Hydrochloric acid
HF	Hydrogen fluoride
H_2	Hydrogen
H_2S	Hydrogen sulfide
LNG	Liquefied natural gas
MeOH	Methanol
MGO	Marine gas oil
MTBE	Methyl tert-butyl ether
MTG	Methanol-to-gasoline
NaOH	Sodium hydroxide
Na_2S	Sodium sulfide
NH_3	Ammonia
NO_x	Nitrogen oxides
O_2	Oxygen

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ABSTRACT

Methanol is a key product in the chemical industry and an emerging energy fuel, currently mainly produced from fossil sources. Use of renewable methanol produced from biomass, biomethanol, could play an important role in emission reduction for the transport sector. Especially in sectors where the electrification of the power train is difficult. Use of biomethanol results in quite high reduction of greenhouse gas emissions and the physical properties of methanol support a clean and efficient combustion. This report is a brief overview of different aspects of biomethanol production and its use as a fuel with focus on the EU. It is divided in two parts; part 1 focuses on the production of biomethanol and part 2 focuses on use of biomethanol as a fuel.

INTRODUCTION

Methanol is one of the world's largest chemical commodities. It is the simplest alcohol with the chemical formula CH_3OH. It is a light, colorless, volatile, flammable liquid at ambient conditions. Methanol is water-soluble and biodegradable. It is a component in a lot of products and is therefore produced, processed and used in many locations all around the world. Besides being an important chemical commodity, it has now and again been a candidate when developing alternative fuels to the crude oil-based gasoline and diesel fuels. Methanol can be used as fuel, fuel additive or precursor for more complex transportation fuels, or an intermediate for several industrial chemicals such as plastics, textiles, paints etc. The production capacity and demand of methanol have risen rapidly in the past years (see Fig 1). In 2020, around 102 million tons of methanol were produced worldwide[1]. More than 60% of global methanol demand were used in the chemical industry as an intermediate for producing e.g., formaldehyde, acetic acid, and methanol-to-olefine[1]. These chemicals are further processed to products such as paints, plastics and car components. The other 40% were used in the fuel industry as energy carrier, e.g., for pure methanol, methyl tert-butyl ether (MTBE; a fuel additive in gasoline), biodiesel, dimethyl ether (DME) or methanol-to-gasoline (MTG)[1].

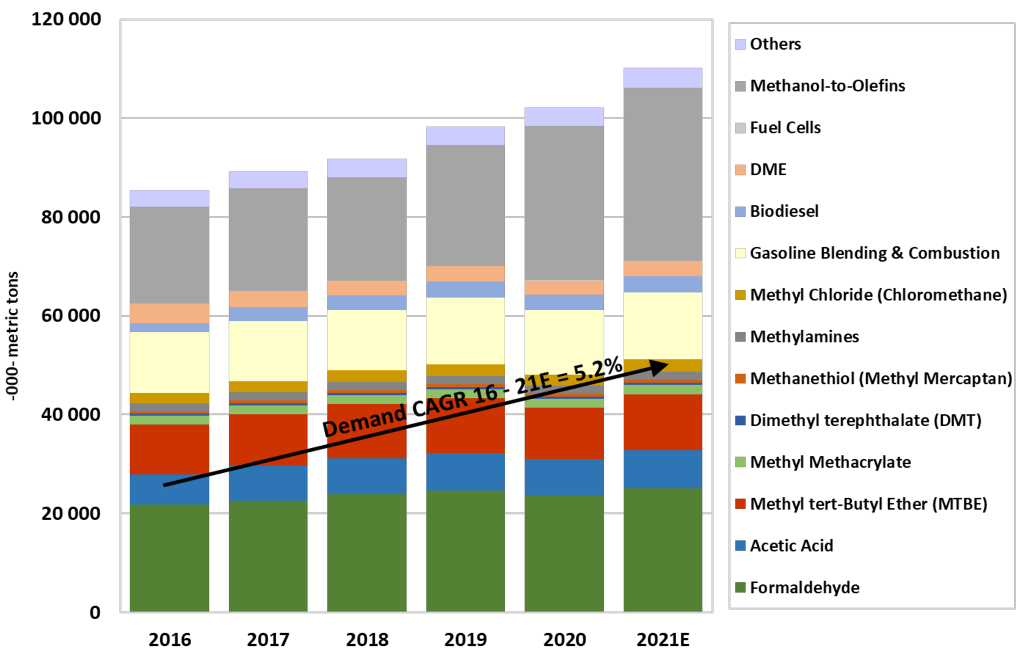

Figure 1. Global methanol supply and demand [1]

Almost all of the methanol produced today is derived from fossil fuels. Around 65% is based on natural gas reforming, 35% is based on coal gasification, while only <1% is based on renewable sources[2]. To be considered renewable, all feedstocks used to produce the methanol need to be of renewable origin, such as biomass, solar, wind, hydro, geothermal, etc. Renewable methanol produced from biomass, such as forestry and agricultural waste and byproducts, biogas, sewage, municipal solid waste (MSW) and black liquor from the pulp and paper industry is usually called biomethanol. Comparatively, when obtained from carbon dioxide and green hydrogen produced with renewable electricity, it is generally called "e-methanol". Currently, there are only a few facilities for biomethanol production on the market, for example Södra in Sweden.

Biomethanol and e-methanol from renewable sources and processes are chemically identical to fossil fuel based-methanol but result in significantly lower GHG emissions during the entire life cycle. In addition, the use of renewable methanol can reduce dependency on fossil energy imports and stimulate local economies. Several companies are already producing biomethanol and e-methanol across the world. In addition, more companies and institutions have built prototypes and demonstration units or have active R&D in that field. A list of existing and planned renewable methanol facilities and demonstrations are listed in the next chapter.

Renewable transport fuels such as biomethanol could play an important role in combating global warming and air pollution for sectors and regions where the electrification of the powertrain is difficult, e. g. in the shipping sector. Use of biomethanol results in quite high reduction of greenhouse gas emissions[3] and the physical properties of methanol support a clean and efficient combustion. A wide range of resources could be utilized to produce biomethanol, which are summarized below.

PART 1: PRODUCTION OF BIOMETHANOL

There are three main production pathways for biomethanol: gasification, reformer-based (from biogas) and from the pulping cycle in pulp mills. Production routes for methanol from fossil feedstocks are very well proven and much knowledge can be applied when using renewable feedstocks. The gasification and reformer-based production of biomethanol have strong similarities with the production of non-renewable methanol. For these two pathways, methanol production can be divided into the following steps: (1) production of synthesis gas, (2) synthesis of methanol and (3) purification of product. The synthesis gas is a mixture of hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2) and is obtained from a variety of resources.

The syngas generation step is the only step that majorly differs between biomethanol and non-renewable methanol production. Thus, the key to successful production of biomethanol is cost and energy efficient syngas generation from renewable feedstocks. Biomass-based methanol production can also be combined with novel concepts such as e-fuels (Power to Liquids). Including hydrogen from electrolysis can increase the production potential of methanol from a given amount of biomass with > 50%.[4] The three main production pathways are described below.

Gasification-based production

Biomethanol from biomass and MSW can be produced via gasification. Potential biomass feedstocks are forest residues, lignin, black liquor, wood chips, wood pellets etc.[5,6] Gasification involves production of a gas from a solid fuel at elevated temperatures using oxidizing agents such as air, oxygen, steam, carbon dioxide or a combination of these. The temperature lies typically between 600° and 1000°C. The heat for the reactions is provided either by the combustion of a fraction of the feedstock with pure oxygen or an indirect external heat source. The resulting syngas from the gasifier needs to be cleaned and conditioned to meet the requirements for the downstream methanol synthesis process.

The technologies used in the syngas production are similar to, or the same as, the technologies used when using coal, natural gas and heavy residual oil. But there are differences in feedstock preparation. In addition, biomass gasification and gas cleaning steps are still more expensive and less reliable compared to fossil-based syngas production technologies[7]. For most technologies scale-up to full-scale application from advanced demonstration plants remains to be done. Key processes in a conventional methanol plant are pretreatment of feedstock, gasification, water gas shift reaction, gas cleaning, methanol synthesis and purification. Fig 2 shows a general schematic of a gasification-based methanol production. The pretreatment of feedstock, gasification, and gas conditioning/cleaning steps are different when using biomass compared to fossil fuels.

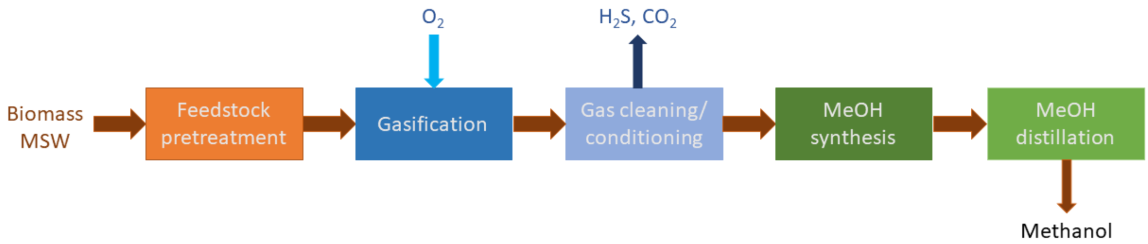

Fig 2. A general schematic of gasification-based biomethanol production

The majority of feedstocks for the biomethanol production plant are solid and thus need to be homogenized before being fed into the gasifier. The challenge to push solids at an even flow rate against pressure, in case of pressurized gasification, has resulted in comparably low pressures in the gasifier of 5-10 bar. In case of liquid feedstock, as with black liquor from pulp and paper mills, the feeding system is simpler and in line with a heavy residual oil feeding system. These feeding systems enable higher pressure in the gasification unit of30-60 bar. The biomass feeding system for pressurized gasification, feedstock grinding, tar concentration in the product gas and handling of ashes are the major technical barriers for biomass gasification[7,8]. The two latter technical issues could be detrimental to subsequent process equipment.

Compared to coal gasification, biomass has higher fuel reactivity, higher organic sulfur-, chlorine- and alkaline content in addition to higher content of produced tars and more CO_2 and CH_2 in the syngas. A few reactor designs have been considered as suitable for biomass gasification which are fixed beds (updraft and downdraft), fluidized beds and entrained flow reactors (for more detailed info see Ref[9]). Among these designs, product gas quality, conversion efficiency, suitability for handling different feedstocks, and investment and running costs differ[10]. Furthermore, pressurized operation is often desirable although it puts additional requirements on the design and operation of a gasifier.

The raw untreated syngas leaving the gasification step needs to be cleaned and conditioned to meet the quality level required by the methanol synthesis step. Aftertreatment is different depending on the type of gasifier, gasification agent, and feedstock composition. Different types of biomass material may also affect aftertreatment requirements because certain feedstocks introduce substances that are unwanted in downstream processes. Most common impurities are particles, tar and methane, COS, chlorine and fluorine components such as HCl and HF, and sulfur components such as H_2S, and CO_2.

Gas conditioning usually includes adjustment of the H_2/CO ratio to around 2 to 1 for optimal methanol synthesis in the water gas shift reactor (WGS)[11]. In case of presence of methane in the syngas, methane reforming is needed to maximize the syngas yield and avoid energy losses in the form of methane leaving the methanol synthesis unit as a purge stream.

Black liquor gasification with downstream synthesis to biofuels has shown gains in energy efficiency and economic performance compared to combustion in a recovery boiler in a Kraft pulp mill[12]. The gained performance is partly due to the catalytic effect of the black liquor, due to the alkali present in high percentage that enhances the gasification reactions. The catalytic activity of the alkali compounds allows for gasification at low temperatures with high carbon conversion and low tar and soot formation. Research has shown that even if the black liquor is diluted with a secondary feedstock, the high reactivity can be kept[13]. Thus, to increase the operational flexibility plus the biofuel capacity of a mill-integrated gasifier, a secondary biomass feedstock could be blended into the black liquor and co-gasified[14]. The secondary biomass feedstock can be pyrolysis liquids[15], residues from biochemical conversion of biomass feedstocks such as crude glycerol from biodiesel production and lignin-rich fermentation residues from lignocellulosic ethanol production.

The key to successful commercialization, from a technological point of view, is to convert the feedstock into a syngas with a quality required by the methanol synthesis technology providers. So far, there is limited long-term operational experience of large-scale plants gasifying biomass or MSW for syngas production for later synthesis into a product. Outside Europe, Enerkem has gasified MSW in Edmonton, Canada at commercial scale since 2015 with a capacity of 100 kt/year(feedstock)[16], which provides valuable experience for other projects. Active gasification-based projects in Europe with focus on biomethanol production are listed in Table 1

Table 1. List of gasification-based biomethanol projects in Europe[17]

Name of gasification technology/ owner	Location	Type of gasifier	Heating principle	Feedstock	Project phase	Plant capacity	Project, reference	Notes
Enerkem	Tarragona, Spain	Bubbling fluidized bed	Directly heated via partial combustion with O_2	Non-recyclable waste from municipal, industrial, commercial and institutional sectors	In development, pending final investment decision	Feedstock: 400k ton waste Output: 220M liter per year	Ecoplanta, [16,18]	Uses externally produced H_2 to adjust the H_2/CO ratio instead of WGS [19]
	Rotterdam, the Netherlands			non-recyclable MSW	Engineering	Feedstock: 340 kton waste Output: 220M liter per year	W2C Rotterdam[20]	
HTW/ Thyssenskrup	Hagfors, Sweden	Bubbling fluidized bed	Directly heated via partial combustion with O_2	Forest residues	Planning	Output: 100 kt per year	Värmlands-Methanol[21]	
	Gidara Energy, Amsterdam, the Netherlands			Non-recyclable MSW, wood waste	Planning, in operation in 2023		Advanced Methanol Amsterdam[22]	
NextChem	Eni refinery in Livorno, Italy	Fixed bed, updraft	Directly heated via partial combustion with O_2	Non-recyclable municipal- and industrial waste, mainly plastic and dry waste	Engineering	Output: 115 kt per year	MyRechemical [23,24]	To be integrated with JM's syngas to methanol process[25]
	LowLands Methanol, Rotterdam, The Netherlands			MSW/ waste wood	Planning	Output: 120 kt per year	Renewable Methanol[26]	Uses externally produced H_2 to adjust the H_2/CO ratio instead of WGS [19]
Bioliq/ KIT/ Air Liquide	Karlsruhe, Germany	High pressure entrained flow	Directly heated via partial combustion with O_2	A liquid energy mixture (Biosyncrude): Pyrolysis oil+ pyrolysis char	Operational	5 MW_{th} feed	Bioliq[27]	Produces gasoline via DME (via methanol)

Reformer-based production from biogas

Biogas is formed from anaerobic breakdown of organic material by microorganisms and is mainly composed of CH_4 (50-75 %) and CO_2 (25-50 %)[28]. Other compounds of biogas are H_2O, O_2 and traces of sulfur, H_2S and NH_3. The amount of CH_4 depends on the type of organic material decomposed (amount of fats and carbohydrates). Typical feedstocks for biogas production are manure and water treatment sludge, the organic fraction of waste from households and industry, residues of crop production (e.g.., straw) plus energy crops including maize and grass silage.

Production of biogas has increased in the EU, boosted by the renewable energy policies, economic and environmental benefits. Europe has an established and mature biogas market. In 2018, more than half of the biogas production in the world was located in Europe with production of 30.9 billion m^3 with an energy equivalent of 0.71 EJ[29]. Currently, the main use for biogas is local heat and electricity generation, which requires minimum upgrading. In 2019, the installed power capacity using biogas as feedstock was 10500 MW[19] in Europe. A small percentage of the produced biogas (around 3% in 2019[19]) is used for upgrading to biomethane for injection into the natural gas grid in Europe. Biomethane is currently used as a co-feed with natural gas in existing methanol production facilities in some locations, such as by BASF in Germany and OCI/BioMCN in the Netherlands. Co-feeding biomethane with natural gas offers reduction of GHG emissions compared to traditionally produced methanol[30].

For biogas reforming to syngas (or for distribution in the existing natural gas network), upgrading and cleaning of the biogas is required. The upgrading process includes removal of CO_2 and the cleanup process involves removal of toxic and corrosive components. For example, biogas from manure contains high amounts of H_2S that can cause corrosion in the upgrading and reforming stages and catalyst degradation[31]. The upgraded biogas is occasionally referred to as biomethane as the concentration of CH_4 is high. Fig 3 shows a general schematic of the biogas-based biomethanol production. As presence of CO_2 has shown to reduce energy consumption[32] , a process design with possibility of purging the CO_2 separated into the synthesis stage is also included. Another alternative is the "dry reforming" process which replaces a part of the steam with CO_2 for methane reforming. This concept has been developed by Linde at pilot scale[33].

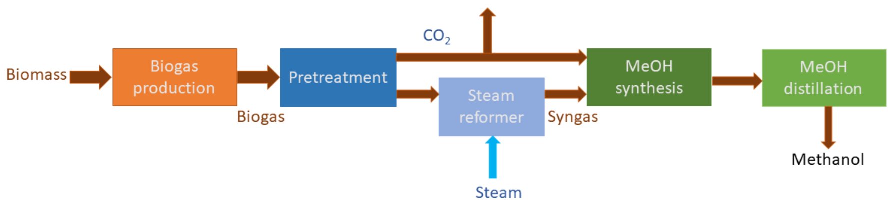

Fig 3. A general schematic of reformer-based biomethanol production

Production from the pulping cycle in pulp mills

During the conversion of wood into wood pulp, methanol is formed in the digester, where wood chips react with a liquor containing sodium hydroxide (NaOH) and sodium sulfide (Na_2S). The methanol is referred to as "raw methanol" and contains several impurities and is usually used as an internal fuel to produce heat and power. The amount of methanol produced depends on the type of the wood and the pulping process[34]. Recently, treating and upgrading the raw methanol to a salable grade methanol has been developed. A pulp mill in Mönsterås, Sweden owned by Södra[35] uses the methanol purification process A-Recovery+[36] developed by Andritz to produce commercial grade biomethanol. The plant has a capacity of 5250 t/y[37]. According to the International Renewable Energy Agency (IRENA), 220 000 t/y of biomethanol could be produced in Europe if all pulp mills would apply the method used by Södra[37].

PART 2: BIOMETHANOL AS A FUEL

The use of methanol in the fuel industry has increased rapidly since the mid-2000s. Methanol can be used as a fuel either directly or in a blend with gasoline. It can also be used to produce biodiesel, DME and MTBE. Biodiesel can be produced by reacting methanol with vegetable oils (e.g., rapeseed oil) or animal fats and it can be used as a blender or replacement for diesel. Biodiesel can be blended with conventional diesel and used as a vehicle fuel. Direct use of methanol as a fuel has grown from less than 1% of the global methanol consumption in 2000 to more than 14% by 2021. [37]

Methanol has some advantageous properties in terms of its use in internal combustion engines, such as a high octane number. This means that it can be used as an additive or substitute for gasoline. The high knocking resistance and high heat of vaporization of methanol results in higher thermodynamic efficiency than gasoline-fueled engines. Owing to its molecular structure (no carbon-carbon bond and bounded oxygen) use of methanol will result in lower soot formation. Lower combustion temperature of methanol results in lower NO_x emissions. Unfavorable properties of methanol such as low energy content, corrosivity, seal-swelling properties and viscosity necessitates some adjustments in the fuel system: larger fuel tank, pumps and injectors with higher flow rates and methanol-compatible seals. Methanol has around half of the volumetric energy density of gasoline and diesel. This will result in reduction of driving range of the vehicle, but this can be compensated, in addition to a larger fuel tank, by more frequent fueling or more efficient combustion engines. The low ignition quality and the high evaporation enthalpy of methanol requires substantial adjustments in the combustion process. In addition, incomplete combustion of methanol results in formation of pollutants such as formaldehyde and formic acid.[38,39]

Historically, methanol has been a candidate to substitute conventional crude oil-based fuel. Use of methanol received great attention during the oil crises in the 1970s[40]. Fossil-based methanol was widely tested both, as a blending component and as pure fuel in small and large test fleets in many developed countries in the 1980s and 1990s. The potential to reduce air pollution was also a driver at the time. This was boosted by the ban on lead in gasoline and the most interest was in California (USA).[38] Due to the lack of refueling infrastructure, Flexible fuel vehicles (FFV) were developed instead of dedicated methanol vehicles.[41] FFVs able to run on methanol or gasoline were developed by Ford and Volkswagen in the 1980s and tested in California. Although the methanol FFV program was technically successful the interest in methanol diminished by the late 1990s as a result of decreasing gasoline prices and rising methanol prices.[38] In addition, technological advances such as catalytic converters, direct fuel injection, etc. dramatically reduced the emission issues associated with gasoline. At the same time, ethanol gained more attention compared to methanol.

Despite the diminishing interest in methanol-powered vehicles in developed countries, China has recently laid focus on methanol as a transport fuel, mainly to reduce its dependency on imported fuel and reduce air pollution. Several Chinese automotive manufacturers produce methanol-powered cars, trucks, vans and buses which can run on M85 (85% methanol, 15% gasoline), M100 (pure methanol) along with methanol/gasoline blends with lower methanol content [42].

Methanol can also be used in diesel engines but more significant modifications, compared to gasoline-engines, are required.[43] This is mainly due to the low cetane number of methanol[38]. There are a few possibilities for using methanol in compression ignition (CI) engines: premixing methanol with the intake air and adding a fuel with high cetane number to improve the ignition, addition of ignition improver or installation of glow plugs[38] etc. Currently, using dual fuel combustion i.e., premixing methanol with the intake air and using a small diesel spray (pilot diesel) is the most common approach. This approach only requires the addition of a methanol performance fuel injection (PFI) system and allows retrofitting[43].

However, the most attractive concept could be the one using pure methanol without any ignition enhancer which needs further research.

In addition to its use in conventional internal combustion engine (ICE) vehicles, Methanol can also be used in advanced hybrid and fuel cell vehicles. In such cases, methanol is reformed on board of the vehicle to hydrogen, which then is fed to the fuel cell to charge the batteries in an electric vehicle (EV) or to deliver direct propulsion in a fuel cell vehicle (FCV)[44]. Using methanol eliminates the need for costly on-board systems for safely storing and transferring hydrogen gas at high pressure (350-700 bar) in FCVs. Methanol reforms at a temperature that is low enough to utilize the low-grade exhaust heat, even at low loads. This makes methanol very attractive regarding waste heat recovery in ICEs. On-board methanol reformers to drive FCVs have been demonstrated by several car manufacturers in the 1990s and 2000s.

Currently, interest in the use of methanol in the marine sector is growing which is motivated by tightening emissions legislation. The International Maritime Organization has set new regulations to reduce the sulfur content of marine fuels and NO_x emissions in the emission-controlled areas (e.g., coastal areas). This has led to new technologies being tested to meet the new regulations. In addition to aftertreatment systems, which allow the continued use of heavy fuel oils, the shipping industry has been looking into alternative fuels, among which methanol is a primary candidate. Currently, more than 40 ships in operation or on order are using methanol[45]. Methanol is sulfur-free and when burned produces almost no particulate matter and low amounts of NO_x.

Several demonstration projects have investigated the use of methanol for shipping[39]. Among which the Stena Germanica ferry conversion and the Waterfront Shipping tanker vessels are most notable (shown in Fig 4). Stena Germanica is a 1500 passenger ferry (50000 t, 32000 horsepower) operating between Sweden and Germany which was retrofitted to run on methanol. The marine diesel engines were upgraded with injectors to allow direct injection of methanol and Marine gas oil (MGO). Methanol is the main fuel but there is the option to use MGO as backup[46]. The retrofitting took less than 3 months. The Waterfront shipping vessels run with two-stroke engines using separate direct injection of methanol MGO or heavy fuel oil. A few measurement data from these engines presented by the manufacturers show compliance with emission regulations and efficiencies similar to the efficiency on diesel fuel[39]. Also, Maersk has ordered 8 ocean-going container vessels running on biomethanol and e-methanol that are planned to be in operation in 2024 and 2025[47]. The vessels will have a dual-fuel engine setup, running on methanol and traditional low-sulfur fuel. In order to secure enough carbon-neutral methanol for the operation of these vessels, Maersk is focusing on collaborations to ramp up the methanol production. A complete list of projects involving the use of methanol as marine fuel can be found in reference[39]

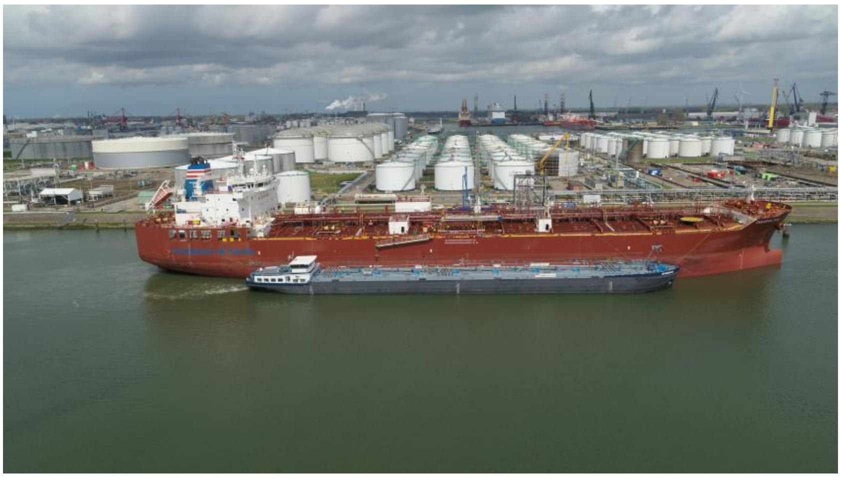

Figure 4. a) Methanol-powered ferry Stena Germanica, operating between Gothenburg (Sweden) and Kiel (Germany) [46]
b) Methanol-powered ocean-going vessel by Waterfront shipping [48]

For use in aviation, direct use of methanol is not favorable due to its low volumetric energy density. But methanol can be converted to kerosene-type aviation fuels[49]. Conversion and upgrading of methanol to jet fuel and other hydrocarbons consists of several process steps such as DME synthesis, olefin synthesis, oligomerization and hydrotreating. Another option is to use methanol for advanced hybrid planes that use a combination of fuel cell and battery to run turbofans or turboprops[50].

This type of hybrid planes will have advantages such as reduced emissions and noise with 40-60% reduction in energy use[37]. This type of aircraft is considered suitable for regional flights[37].

As methanol is already a globally available commodity with distribution and storage capacity in place, a transition from liquid fossil fuel derived products to methanol would be desirable. Millions of tons of methanol are transported to diverse and scattered users by ship, rail and truck. It can also be transported through pipelines. Methanol refueling stations for cars, buses and trucks are essentially identical to current gasoline or diesel filling stations, requiring very little change in consumer habits. In most cases the same tanks can be used with minor changes to the refueling lines, gaskets, etc. Cost of methanol filling stations are expected to be the same as a gasoline/diesel station, cheaper than liquefied natural gas (LNG) stations and much cheaper than hydrogen refueling stations[38] Methanol bunkering for ships is also easy and clean. As methanol is liquid at atmospheric pressure, it can be stored much like bunker fuel. Methanol is already available in many ports around the world. This results in low infrastructure cost to store methanol[51].

REFERENCES

1. Methanol Institute. MMMMSA Global Methanol Supply and Demand Balence: 2016 - 2021E. https://www.methanol.org/methanol-price-supply-demand/ (2021).
2. Dolan, G. Methanol: Emerging Global Energy Markets. in *16th Annual State of the Energy Industry Forum* (2020).
3. Chaplin, A. G. Renewable methanol-An Analysis of technological potentials in light of the EU biofuels policy objectives of Greenhouse Gas Savings, Security of Supply and Employment. (2013).
4. Landälv, I. *Methanol as a Renewable Fuel-a Knowledge Synthesis*. https://f3centre.se/sv/ (2017).
5. Carvalho, L., Lundgren, J., Wetterlund, E., Wolf, J. & Furusjö, E. Methanol production via black liquor co-gasification with expanded raw material base – Techno-economic assessment. *Applied Energy* **225**, 570–584 (2018).
6. Carvalho, L. *et al.* Techno-economic assessment of catalytic gasification of biomass powders for methanol production. *Bioresource Technology* **237**, 167–177 (2017).
7. Morandin, M. H. S. *Methanol via biomass gasification, Thermodynamic performances and process integration aspects in Swedish chemical cluster and pulp and paper sites*. (2015).
8. Heyne, S. L. T. M. M. *Biomass gasification-A synthesisi of technical barriers and current research issues for deployment at large scale*. (2013).
9. Molino, A., Chianese, S. & Musmarra, D. Biomass gasification technology: The state of the art overview. *Journal of Energy Chemistry* **25**, 10–25 (2016).
10. Siedlecki, M. On the gasification of biomass in a steam-oxygen blown CFB gasifier upgrading: technology background, experiments with the focus on gas quality and mathematical modeling. (2011).
11. Hannula, I. K. E. *Liquid transportation fuels via large-scale fluidised-bed gasification of lignocellulosic biomass*. (2013).
12. Landälv, I. W. L. *Building up the future, cost of biofuel* . (2017).
13. Lundgren, J. C. L. W. E. F. E. O. J. B. P. A. G. *Methanol production via black liquor gasification with expanded raw material base*. (2017).
14. Jafri, Y., Furusjö, E., Kirtania, K., Gebart, R. & Granberg, F. A study of black liquor and pyrolysis oil co-gasification in pilot scale. *Biomass Conversion and Biorefinery* **8**, 113–124 (2018).
15. Bach-Oller, A., Kirtania, K., Furusjö, E. & Umeki, K. Co-gasification of black liquor and pyrolysis oil at high temperature: Part 1. Fate of alkali elements. *Fuel* **202**, 46–55 (2017).
16. Enerkem. Facilities and projects. https://enerkem.com/company/facilities-projects/ (2021).
17. ETIP Bioenergy. Production Facilities Database. Production Facilities (2021).
18. Enerkem. Carbon recycling. https://enerkem.com/process-technology/carbon-recycling/ (2021).
19. IRENA; Methanol Insititute. *Innovation Outlook: Renewable Methanol*. (2021).

20. Enerkem. W2C Rotterdam project. https://enerkem.com/news-release/w2c-rotterdam-project-welcomes-shell-as-partner/ (2019).

21. Värmlandsmethanol Ltd. Methanol from wood - an excellent fossil free motor fuel! (2017).

22. Gidara Energy. Advanced Methanol Amsterdam. https://www.gidara-energy.com/advanced-methanol-amsterdam (2021).

23. NextChem. Waste to Chemical. https://nextchem.it/what-we-do/technologies/waste-chemicals (2021).

24. Eni. Eni and Maire Tecnimont sign agreement to introduce new technology that transforms non-recyclable waste into hydrogen and methanol. Eni and Maire Tecnimont sign agreement to introduce new technology that transforms non-recyclable waste into hydrogen and methanol (2020).

25. NextChem. press release NextChem's MyRechemical and Johnson Matthey team up to commercially develop waste-to-methanol technology. press release NextChem's MyRechemical and Johnson Matthey team up to commercially develop waste-to-methanol technology (2021).

26. LowLands Methanol. Renewable methanol, Sustainable, Clean & Essential for the Energy Transition. https://www.renewablemethanol.com/technology/ (2021).

27. Zimmerlin, B. K. T. E. M. D. N. Status of the bioliq®-process at KIT. in *International Seminar on Gasification* (2016).

28. Wellinger, A. M. J. B. D. *The biogas handbook*. (Woodhead publishing, 2013).

29. World Bioenergy Association. *Global Bioenergy Statistics 2020*. (2020).

30. BASF. BASF produces methanol according to the biomass balance approach. https://www.basf.com/global/en/media/news-releases/2018/11/p-18-370.html (2018).

31. Pedersen, T. S. R. Technical and Economic Assessment of Methanol Production from Biogas. (2012).

32. Hansen, J. et al. *GreenSynFuels*. (2011).

33. Linde. Recycling CO_2 – the efficient way. https://www.linde-engineering.com/en/about-linde-engineering/success-stories/recycling-co2.html (2021).

34. Zhu, J. Y. , Y. S.-H. , L. P. H. , C. X.-S. Methanol formation during alkaline wood pulping. *TAPPI Journal* (2000).

35. Södra. Södra first in the world with fossil-free biomethanol. https://www.sodra.com/en/se/om-sodra/pressrum/press-releases/sodra-first-in-the-world-with-fossil-free-biomethanol (2020).

36. Andritz. *Biomethanol - Forming a circular bioeconomy at pulp mills*. (2021).

37. IRENA; Methanol Institute. *Innovation Outlook: Renewable Methanol*. (2021).

38. Schröder, J. ; W. K. , Müller-L. F. ; B. W. ; A.-S. P. ; L. M. S. *Methanol as Motor Fuel Summary Report*. (2020).

39. SGS INSPIRE. *Methanol: Properties and Uses*. (2020).

40. Olah, G. A. P. G. K. S. *Beyond Oil and Gas: The Methanol Economy*. (Wiley-VCH, 2009).

41. Nichols, R. J. The Methanol Story: A Sustainable Fuel for the Future. *Journal of Scientific & Industrial Research* 62, (2003).

42. Zhao, K. *A Brief Review of China's Methanol Vehicle Pilot and Policy*. (2019).

43. Verhelst, S., Turner, J. W., Sileghem, L. & Vancoillie, J. Methanol as a fuel for internal combustion engines. *Progress in Energy and Combustion Science* 70, 43–88 (2019).

44. Kumar, P., Dutta, K., Das, S. & Kundu, P. P. An overview of unsolved deficiencies of direct methanol fuel cell technology: factors and parameters affecting its widespread use. *International Journal of Energy Research* 38, 1367–1390 (2014).

45. DNV GL. Current uptake of alternative fuels and technologies in shipping. *Altenrative Fuels Insight* https://afi.dnv.com/Statistics (2021).

46. Stenaline. Stena Line launches the world's first methanol ferry. https://news.cision.com/stena-line/r/stena-line-launches-the-world-s-first-methanol-ferry,c9748162 (2015).

47. Maersk. Maersk accelerates fleet decarbonisation with 8 large ocean-going vessels to operate on carbon neutral methanol. A.P. Moller - Maersk accelerates fleet decarbonisation with 8 large ocean-going vessels to operate on carbon neutral methanol (2021).

48. Waterfront shipping. Waterfront Shipping takes leadership role in demonstrating simplicity of methanol bunkering to marine industry. https://www.waterfront-shipping.com/news/2021/05/waterfront-shipping-takes-leadership-role-demonstrating-simplicity-methanol-bunkering (2021).

49. Wang, W. C. & Tao, L. Bio-jet fuel conversion technologies. *Renewable and Sustainable Energy Reviews* 53, 801–822 (2016).

50. Soloveichik, G. Electrified future of aviation: batteries or fuel cells? in *arpa-e* (2018).

51. Andersson, K. ; S. C. M. *Methanol as a Marine Fuel Report*. (2015).