Is methanol a future marine fuel for shipping?

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Abstract. Methanol as a future candidate marine fuel has drawn enormous attention recently due to its clean combustion and abundance supply from various resources. The study looks into renewable energy sources such as biomass, renewable electricity and carbon capture with their potential to produce methanol. It is found that the productivity of biomass and the electrons generated from renewable means such as solar, wind and hydro are critical to meet the future demand to use methanol as marine fuel, which could be part of the solutions to achieve the goal set by IMO (International Maritime Organization) to reduce global marine GHG (greenhouse gas) emission by 50% in 2050. In order for the shipping industry to adopt methanol as an alternative fuel, enhancement in renewable methanol production technology will play a vital role.

1. Introduction
The ratification of global sulphur cap mandates ocean going ships emit no more than 0.5% and 0.1% sulphur equivalent outside and within ECA (emission control area) areas [1]. It has been bringing in adoption of various compliance technologies, including post-combustion and pre-combustion abatement measures. Switching from high sulphur fuel such as HFO (heavy fuel oil) to low sulphur MGO/MDO, provides an immediate solution at a significant higher cost; while continuing to burn HFO with a SOx scrubber is considered interim measures with short term cost benefit.

Very recently IMO put up a further initiative to achieve a long term reduction of GHG emissions by 50% in 2050 [2], posing a new challenge for marine community to adopt alternative fuels with significantly lower carbon footprint, which basically rules out the use of any fossil-based fuels if no further abatement action is taken.

Fuels are substances that carry energy in a condensed, safe and ready-to-use form. Decarbonizing of the fuels from life cycle perspective is the key to meet the GHG reduction goal. In view of establishing the next generation mainstream marine fuel in the future, a number of candidate fuels have been proposed, some having undergone various stages of developments. Among the candidates, methanol is considered one of the fuels with high potential.

As the simplest form of alcohol, methanol stays at liquid form at ambient temperature and pressure. It easily burns into carbon dioxide and water, emitting no sulphur oxides (SOx) and markedly reduced nitrous oxides (NOx) and particulate matter (PM). Methanol has been used as fuel for a number of successful marine trials [3,4] and commercial projects [5,6], showing compatibility with either spark ignition or compression ignition engines. With estimated 90,000 ocean going vessel in service and 370 million ton/year bunker demand, the shipping industry will possibly open a huge demand of alternative fuels. Assuming 10% of the global fleet switching to methanol, it would lead to a global demand of 80 million ton/year, equalling the entire current world production capacity in 2019 [7].
Methanol has a volumetric energy density of 15.8 MJ/l (lower heating value) comparable to that of liquefied natural gas of 20.8 MJ/l, or half of the value of diesel fuel (36~39 MJ/l), resulting in the fact that a ship must double its fuel storage volume to keep the same endurance. This in turn not only poses critical concern on ship design or retrofitting, but also on the production technology of green methanol at a scale large enough to sustain itself economically.

In view of the future demand of marine methanol, there is a need to look into the feasibility of various sustainable feedstocks as the starting material to produce it, as well as comparing them with other routes of conversions. The study will provide an alternative angle on the future of marine methanol.

2. Methodology
In this study, boundary is set to limit the discussion to renewable or carbon free feedstocks only, which can be in the form of energy or mass. The energy form includes derivatives from solar energy such as solar photovoltaic, solar thermal, wind and hydro. The mass form includes mostly biomass or carbon dioxide capturing from atmosphere.

The energy conversion efficiency from solar radiation, in form of electrons or biomass is considered a critical factor to determine the potential of a feedstock, other factors such as technological barriers and ease of implementation also play important role in the discussion.

3. Discussion
3.1. Methanol production - fossil feedstock
The methanol production process from fossil resources has been developed for almost a century, and currently methanol is produced in large quantity through a two-step catalytic process that involves 1) gasification of carbonaceous feedstock into a gas mixture of carbon monoxide and hydrogen (syn-gas) and 2) converting the as obtained syn-gas into methanol. The process is energy & capital intensive due to the reaction condition and the use of exotic materials to build the reactors. Coal and natural gas are used as the most convenient feedstock to achieve good yield with low cost. The as-produced methanol, when used as a marine fuel, will produce higher life cycle GHG emission than conventional HFO and MGO [8]. The production of fossil-based methanol will keep growing due to the demand from chemical industry or as the feedstock for MTO (methanol to olefin) [9] process. It may also serve as a complementary measure to valorise gas wells that are not well fitted for LNG production [10].

3.2. Methanol production - renewable feedstock
Two streams of feedstock: carbonaceous mass and hydrogen are needed to produce methanol and these are considered renewable if they can be replenished cleanly within an acceptable time scale, be it seconds or years. Methanol produced from renewable feedstock offers great potential to reduce the life cycle GHG emission because the compositional carbons trace back to atmospheric origin. The production process in principle is the same as that of the fossil-based route. The renewable feedstock, mostly derived from biomass are converted into gaseous mixture in presence of steam and oxygen through thermal treatment. It is then purified to remove unwanted contaminants such as tar and acidic gases and reconditioned with steam to have preferable ratio of H₂/CO for methanol production. Figure 1 shows the critical steps of converting biomass into propeller power through methanol route.

![Figure 1 Flow diagram from biomass (crop) to propeller power through methanol route](image-url)
Table 1 World Energy Demand Summary (Mtoe, year 2018) [11]

| Energy demand | Coal  | Oil   | Gas   | Nuclear | Hydro | Biomass & waste | Other renewables | Total energy demand |
|---------------|-------|-------|-------|---------|-------|-----------------|------------------|---------------------|
| Energy demand | 3,778 | 4,488 | 3,253 | 710     | 364   | 1,418           | 289              | 14,301              |

Table 2 Global Installed Capacity of Solar PV, Solar Thermal, Wind and Hydro [12–14]

| Capacity (TW) | Solar PV | Solar Thermal | Wind | Hydro | Total electricity generation |
|---------------|----------|---------------|------|-------|------------------------------|
| Capacity (TW) |          |               |      |       |                              |
| Coal          | 0.398    | 0.472         | 0.600| 1.267 | 7.72                         |

3.3. Solar energy as feedstock

Almost all renewable feedstock can be traced back to incident solar radiation onto the Earth, except for the tidal and geothermal energy coming from the celestial movement and internal heat of the Earth, respectively. Solar energy is abundant; there are 86,000 TW incident onto lower atmosphere and 48,000 TW onto surface respectively, by natural process alone there are 90 TW taken to feed the planet’s photosynthesis, 870 TW to blow wind and 7.2 TW to flow rivers [15]. As a comparison, the global energy demand by human activity in 2018 was 14,301 Mtoe (table 1) or 19 TW year, and the total shipping contributes 250 Mtoe or 0.332 TW year [16], both are seemingly very small fractions out of the enormous solar energy influx.

Solar energy has to be converted into a “mass” form to act as renewable feedstock to produce methanol. Natural photosynthesis is currently the most readily available source to capture carbon as the carbohydrate raw material, whereas the electricity and heat from solar energy have to find their way to become an “energetic mass” such as hydrogen, which needs a further electrolysis step. At present, the four main solar derived energy being harnessed are solar PV (photo voltaic), solar thermal, wind and hydro, and their recent installed capacity is summarized in table 2. When compared to the total capacity of global electricity generation of 7.72 TW [14], it is hard to tell how much surplus or dedicated electricity having the potential to serve as a “feedstock” for methanol production. Nevertheless, future large-scale renewable methanol production would require abundant renewable electricity be readily accessible at reasonable cost. It is worth noting that the offshore wind, with its cumulative installed capacity hitting 0.022 TW (22GW) at the end of 2018 [17], may serve as a potential feedstock of renewable hydrogen, hence the methanol.

3.4. Biomass feedstock

Biomass is an organic carbonaceous material originated from plant photosynthesis under sunlight. Out of the global 90 TW exergy flow into photosynthesis, only 1.2 TW goes to traditional agricultural biomass and 0.15 TW to commercial biofuel production [15]. In order to investigate the potential of biomass as a carbonaceous feedstock, it is important to know the productivity of biomass and the land area required.

Biomass is accumulated by plants during photosynthesis, basically there are two main categories including C3 and C4 plants according to the carbon compound assimilated at the very beginning of the photosynthesis. It is frequently suggested that solar conversion efficiency of plants is low compared to photo voltaic cell, however they are in fact comparable before the starting of carbohydrate synthesis [18], the maximum efficiency of solar energy use by plants is 37%, which equals the performance of the very best photo voltaic solar cells under development. It is the plants’ internal chemical process producing carbohydrate that causes the major energy loss, eventually the theoretical maximal photosynthetic energy conversion efficiency is 4.6% for C3 and 6% C4 plants, respectively. The numbers are seemingly low, however, when considering the fact that plants are perennial living organism that maintains a self-standing and propagating structure, it is a trait that no other form of
renewable feedstock could compete. Still, plant biomass is considered one of the best storages of solar energy. From global perspective, tropical terrestrial forests, savannahs and grasslands account for 60% of the total terrestrial land surface metabolism, making them the most productive area of plant biomass [19]. On the other hand, the productivity of ocean-based plant biomass is significantly less [20].

3.5. Biomass productivity

Taken the tropical forest as an example, the gross primary productivity (GPP) ranges between 30 and 40 Mg C ha\(^{-1}\) per year, with an interesting trend to increase with atmospheric carbon dioxide level [21]. A more specific study on Indonesia plantation rain forest reveals that 36.48 ~ 63.55 (dry weight) tons of biomass can be produced per hectare of land per year [22]. Another study on the forest of south East Asia found that productivity varies greatly with tree species. Albizia produces more biomass (18.81 ton ha\(^{-1}\) year\(^{-1}\)) than Eucalyptus (11.76 ton ha\(^{-1}\) year\(^{-1}\)) [23]. Currently plants purposed for energy use has been studied extensively, several candidate species were chosen due to their high productivity and adaptability to various soil and climate conditions (table 3). One should bear in mind that although the most productive C4 plant is able to achieve 80 tons of dry mass per ha year, the yield may drop to half or lesser under more realistic condition. From energy perspective, no demarcation exists to limit the end use of a plant, for example, oil palm is a good producer of both oil and lignocellulose feedstock. A recent study [24] predicts that by 2035 the global biomass potential will reach 150 EJ (or 4.76 TW year), in which 43% and 52% come from agriculture (including energy crops) and forest respectively, the remaining 5% is from waste streams. At this point, the potential of global biomass energy far exceeds the demand from the total shipping of 0.332 TW year.

3.6. Biomass conversion

Biomass conversion to methanol is one of the many options to obtain quality fuels from renewable biomass, which include but are not limited to biodiesel, biomethane and bioethanol. The advantage is that the process is robust and versatile, as almost all parts of various biomass feedstock can be thermally broken down into small molecules such as carbon monoxide and hydrogen, wide range of organic feedstock can be converted.

The present biomass conversion process employing gasification and catalytic synthesis is associated with significant loss. The reported conversion efficiency based on dry biomass varies, values such as 40~50% of a 100 t/day plant using of lignocellulose feedstock [25], 45~57% from wood [26~28], or up to 44% from oil palm residuals [29]. In this study, a conservative yield of 40% is used to for subsequent estimation.

To improve the efficiency of conventional biomass conversion, an effective way is to introduce hydrogen gas directly into the gaseous mixture from biomass gasification, which immediately makes up the hydrogen shortage due to the less favourable H/C ratio of carbohydrate-based biomass. As a result, a simulated plant integrating woody biomass and water electrolyser is able to achieve methanol exergy efficiency of 72% and total energy efficiency of 96% when waste heat is utilized [36]. This also opens the opportunity to incorporate renewable electron with biomass to achieve satisfactory methanol output if a dedicated land area is a limiting factor.

| Plant species | Miscanthus | Sugar Cane | Oil Palm | Diesel Tree | Creeping river grass (Echinochloa polystachya) | King grass (Pennisetum americanum xP.purpureum) |
|---------------|------------|------------|----------|-------------|-----------------------------------------------|-----------------------------------------------|
| Biomass productivity (ton ha\(^{-1}\) year\(^{-1}\)) | Lignocellulosic | 13~44 (dry) | 79 (wet)* | 21.3 (dry) | 39~40 (dry) | - | 80 | 28~79 |
| Fatty acid triglyceride | - | - | 4~5 | 12,000 liters | - | - |
| References | [30] | [31] | [32] | [33] | [34] | [35] |

* water content of fresh sugar cane is 73%
3.7. Renewable carbon capture and conversion

Methanol production from carbon dioxide hydrogenation is a one-step reaction by the equation:

\[ \text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H = -49.16 \text{ kJ/mol} \]

To provide infinite carbon feedstock, non-biological carbon capture from air is the choice of future renewable methanol production. Until very recently, the carbon dioxide concentration from air has reached 414.42 ppm from Mauna Loa Observatory, Hawaii [37], however it is an extremely low concentration away from practical level. Direct air capture (DAC) of CO\(_2\) by conventional scrubbing process has to be applied with high energy penalty. An estimated cost of $100 to 200 to capture one ton of CO\(_2\) from air is still considered expensive [38].

Despite of the gaps, carbon capture and hydrogenation is a promising way to produce methanol offshore, where concentrated wind electricity can be more readily accessible.

3.8 Techno-economic perspective of methanol production from biomass and renewables

At present, methanol production from renewable feedstock is more costly than from fossil feedstock due to the higher capital and operational expenditure. As a powerful tool, techno-economic analysis has been used intensively to understand the feasibility of bio/renewable methanol for existing or future scenarios. It was found that the price of electricity and biomass [39], the capital of the plant and the production capacity are sensitive factors to determine the production cost of methanol [40, 41]. Starting from lignocellulose feedstock, the outcome of several studies shows a quite close range around $20 per gigajoule when the production cost is expressed on energy basis [36, 39, 40, 41, 42, 43]. It should be noted that methanol produced from carbon capture and hydrogenation is still the most expensive at a cost of $ 33.8 per gigajoule [36]. The cost reduction over long term is expected to build on technology breakthroughs that may seal the significant gap between the cost of green and fossil methanol.

Future implementation of large capacity plant may create challenges on biomass collection and logistic due to the dispersed nature of their primary production. However, it is believed that future opportunities may arise from distributed or decentralized smaller scale production facilities [41], and rural production may be considered due to its positive social effect [40].

3.9 Other alternative biomass conversion routes

Without diverging into the “extractive” renewable biomass such as sugar, fatty acid triglyceride and protein, the discussion is focused on the lignocellulose-based plant biomass that forms the majority of total biomass potential. Modern day use of biomass usually starts from gasification to break down bulky plant tissue into small molecules by either thermal treatment or anaerobic fermentation in presence of bacteria. The product from thermal gasification is a mixture rich in hydrogen, carbon monoxide and carbon dioxide, which is a versatile precursor to produce a number of gaseous and liquid fuels. The fermentation process however produces a gas mixture mainly of methane and carbon dioxide, or under particularly controlled condition contains significant amount of hydrogen [44].

The gasified biomass can be used in gaseous form such as cleaned bio syn-gas, bio-methane or bio-hydrogen; or go through further catalytic conversion to produce liquid fuels. However, deeper processing is always associated with further energy loss from the raw biomass input, a conversion route with lesser steps is preferred.

Converting lignocellullos biomass to methane and hydrogen are considered alternative routes. Biomethane from either anaerobic digestion or biomass gasification exhibits similar efficiencies (62–65%) to retain the energy from raw forest residues [45]; in another study when fermentation is used to produce bio methane, an average productivity of 4,000 Nm\(^3\) ha\(^{-1}\) a\(^{-1}\) is used to estimate across EU-25 agricultural area using energy crop rotation, with good individual example reaching 7,500–10,200 Nm\(^3\) ha\(^{-1}\) a\(^{-1}\) on maize plantation [46], which shows competitive energy yield to methanol route.

Gasification to hydrogen follows a similar route, high temperature thermochemical conversion is currently the predominant pathway due to its established process understanding and equipment design.
The yield of hydrogen on dry biomass weight basis is relatively low, reported values vary from 8–13% via steam gasification of saw dust [47], or 12.6–17.1% from pyrolysis oil [48]. Practical issues such as gasifier design, cost of biomass, hydrogen storage and distribution infrastructure are still the main barriers that make hydrogen less competitive to methanol in the near term. However, from long term perspective, biohydrogen will play a key role during the transition towards a clean and sustainable energy future, in which biomass gasification will become a dominant technology [49].

3.10. Methanol as future marine fuel
The adoption of methanol as a maritime fuel shall be viewed from a long-term horizon. From energy perspective methanol is convenient end carrier of all sunlight derived energies, be it in mass form (all biomass) or quantum form (electricity). Assuming there is dedicated land based energy crop plantation, they will have a potential of 16 tons methanol per hectare per year, taking the high side lignocellulose productivity of miscanthus and oil palm as example. If methanol (LHV: 19.9 MJ/kg) is used as an alternative fuel to replace 50% of world bunker demand (HFO with LHV 39 MJ/kg), it would require a global production capacity of 362.5 million ton, or 22.6 million hectares of dedicated land use, or 0.46% of the total agricultural land on earth [50].

There has been a number of commercial ships and development projects using methanol as fuel or being under test trials. Seven new build chemical tankers of Waterfront Shipping, Marinvest and MOL are running on dual fuel methanol engines, each of 10 MW in total power. The Stena Germanica of Stena Lines has been retrofitted with 24 MW total power to run on methanol/diesel dual fuel mode. There are several upcoming projects such as Leanship, Methaship, Green Maritime Methanol Consortium and the HyMethShip, all aiming at overall GHG reduction by adopting green methanol fuel. From practical point of view, there is no major technical barrier to convert or build a new engine and fuel system to use methanol. At the same time, marine safety provisions, fuel standard, emission profile of methanol are still being developed along with knowledge gained from existing trials.

Fossil based methanol will, in short term offer the marine community a clean solution for reduced SOx, NOx and PM emission, as well as helping to establish good understanding to use methanol in larger scale in future. The renewable methanol production from land-based plants will have to undergo significant improvement, achieving efficient use of renewable feedstock before they become reliable sources of supply. Eventually methanol used as marine fuel will be produced from carbon dioxide hydrogenation, preferably assisted by the electricity from offshore wind farms.

4. Conclusion
Renewable methanol production plays critical role in determining if it is feasible as an alternative marine fuel in the future. Sunlight is the origin of the renewable feedstocks such as plant biomass and electrons for renewable methanol production. It is expected that plants with high photosynthesis efficiency, i.e. high annual accumulation of biomass has the higher potential. Renewable electrons, on the other hand, are a source of hydrogen to be combined with either carbonaceous biomass or carbon dioxide to produce methanol. Direct air capture of carbon dioxide provides the ultimate carbon source for renewable methanol production, which relies on further cost reduction of the capturing technology and the renewable electricity generation. It is anticipated that further enhancement in renewable methanol production technology is needed to enable global adoption of methanol as a marine fuel.

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