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Oxidative Methanol Reforming for Hydrogen-fed HT-PEMFC: Applications in the Naval Sector

Danilo Russo\*, Martina De Martino, Almerinda Di Benedetto, Maria Portarapillo, Maria Turco

Department of Chemical, Materials, and Production Engineering, University of Naples Federico II, P.le V. Tecchio 80, 80124, Naples, Italy.

\*Corresponding Author : danilo.russo3@unina.it

CO2 emissions from marine transport contributes to about 3% of the overall greenhouse gas (GHG) emissions. International regulations and the Paris agreement require to cut them by 50% by 2050. Moreover, the latest International Maritime Organization (IMO) regulations strongly limits SOx emissions. One of the most promising alternatives to conventional fuels is hydrogen, which can meet the environmental targets set by the international community, if coupled with H2-fed PEM fuel cells (PEMFCs) due to their high efficiency. On-board H2 production starting from a suitable liquid source can be competitive compared to compressed/liquid H2. Methanol (MeOH) is a suitable candidate due to: high H2 content, relatively low reforming temperature, absence of sulfur compounds, and the possibility of being obtained from renewable materials. This work investigates the coupling of autothermal oxidative MeOH steam reforming (OSRM) with high temperature PEMFCs (HT-PEMFCs). The latter outperforms low temperature (LT) PEMFCs, concerning resistance to CO poisoning and high operating temperature, allowing an integrated OSMR reactor – HT-PEMFC and energetically self-sustaining system. The integrated system has also been designed considering also MeOH storage tank and the main auxiliary units, and the dimensions appear very interesting for the installation on board of ships, also in terms of emissions.

* 1. Introduction
     1. Emissions in the naval sector

Shipping is a growing source of GHG and one of the main cause of air pollution. The main emissions consist of sulfur dioxide (SO2), carbon dioxide (CO2), black carbon, carbon monoxide (CO), nitrogen oxides (NOx), and particulate organic matter (Rony et al., 2023). Estimated CO2 emissions from shipping account for 2-3% of the total, whereas NOx and SOx from shipping are substantially higher than those from road transport, representing 17-31% of total NOx and 5-10% of all anthropogenic SO2 emissions, respectively. This corresponds to 7-15 Mton of SOx per year (Papadopoulos et al., 2022). According to European Environment Agency, international shipping emits about 3 times more NOx, 12 times more SOx, and 10 times more particulate than aviation. The Environmental Protection Agency (EPA) highlights that emissions from maritime transport contribute to ozone, particulate, and CO levels alterations, with significant health effects, acid rain, eutrophication and nitrification of water. Only 15 of the biggest international ships emit as much as all existing cars. The main shipping emissions grew by a factor of 4 in the second half of the XX century, whereas the number of ships only increased by 3 (Eyring et al., 2005). At this rate, shipping emissions are expected to further increase up to about 3-4 times over the next decades. The actual scenario points out the need in short-medium time of a drastic change in maritime fuels and improvement in energetic efficiency accomplished by the introduction of severe regulations.

* + 1. IMO Regulations

The IMO is an agency of the United Nations, established after the 1948 Geneva International Maritime convention. In 2018, it set a target of 50% cut of CO2 emissions by 2050 concerning 2008 levels (London, IMO 2018). In 2005, through the International Convention for the Prevention of Pollution from Ships, (i.e. MARPOL), the IMO started limiting SOx from ships to improve air quality. The latest IMO 2020 regulation limits the amount of sulfur permitted in commercial ship fuel to 0.5%. The previously permitted level was 3.5% w/w. Ships in Sulfur Emission Control Areas (SECAs) must continue to meet more strict sulfur emission levels of 0.1%. As a result, the IMO expects a 77% drop in SOx emissions from ships. The current regulatory level in a Nitrogen ECA (NECA) is Tier III. Outside of the NECA, Tier II is of application. The allowed NOx levels emissions in Tier III are about 80% less than that Tier I. NECA has been set up in the USA and Canada from 2016, and since 2021, NECA also applies to the North Sea and to the Baltic Sea (Dong et al., 2022).

* + 1. Fuels in the maritime sector

Common marine fuels are heavy fuel oils (HFO) and distillates. HFO are further classified based on sulfur content as high-sulfur (3.5 %), low sulfur (1.0 %), and ultra-low (0.1%) fuel oil. On the other hand, marine gasoil consists exclusively of distillates, whereas marine diesel oil is a blend of distillates and different portions of HFO (Uhler et al., 2016). As an alternative, Liquified Natural Gas (LNG) contains less carbon per unit of energy than conventional fuels, resulting in lower CO2 emissions. Despite the reduced CO2 emissions, it does not meet the targets set to address climate change, but it contains significantly lower sulfur concentration (Wang et al., 2014).

* + 1. Methanol in the maritime sector

Whether MeOH is a promising future fuel for shipping depends on several factors: its suitability for the maritime sector from a chemical and a technological point of view, global availability of the feedstock, development of the supply chain including infrastructure requirements, and competition with other alternative fuels (Svanber et al., 2018; Liu et al., 2019). Regarding its risk classification, in November 2020, the IMO approved guidelines for the safety of ships using MeOH as fuel as a preliminary act to develop a chapter on MeOH in the International Code of Safety for Ships using Gases or Other low-flashpoint Fuels (IGF Code). MeOH uptake and application as a marine fuel was approved in the IMO Interim Guidelines for Low Flash Point Fuels in November 2020 (II CEN CWA), also regulating MeOH bunkering. To date, 85% of MeOH is be produced from steam reforming of natural gas. However, renewable processes include the production of MeOH from biomasses by biochemical or thermochemical (gasification, pyrolysis) conversion, and e-MeOH from electrolysis, where CO or CO2 are hydrogenated by green hydrogen (Dalena et al., 2018). MeOH may be used as fuel for internal combustion engines or FC operations. The clean-burning properties of MeOH significantly reduce SOx and PM emissions, as MeOH contains no sulfur and no C-C bonds that create particulate matter. MeOH can reduce CO2 emissions by around 10 % when used as the primary fuel. Several projects and applications of MeOH are already in place for combustion engines (Effship, Spireth, Methanol: the marine fuel of the future, MethaShip, LeanShips, proFlash, SumMeth) and FCs (Methapu, the GreenPilot Project, Pa-X-ell and Pa-X-ell2). Together with the recent or ongoing projects, many examples of ships already fueled by MeOH include the Waterford MeOH-fueled fleet, the Stena Germanica, the Creole Sun, the Takaroa Sun, the Mari Couva, the Mari Jone, Mari Boyle, Lindanger, etc. Most of these examples use MeOH or blended MeOH in combustion engines.

* + 1. Hydrogen from methanol for on-board fuel cell systems

H2 strategic role in the next-future energetic transition is crucially linked to FC technologies for clean electric power generation. However, on-board storage in the maritime sector still poses serious challenges: safety, explosibility, low boiling point, and low density in gaseous and liquid states. Currently, commercial H2 is stored as a compressed gas (350 - 700 bar) or liquid at 20 K in cryogenic tanks. The process of H2 pressurization and liquefaction at 20K consumes energy (up to 15% and 30% of LHV, respectively), adding extra costs and strongly contributing to CO2 emissions. Other alternatives include storing H2 in liquid organic carriers, hydrides, and MOFs, which are not considered mature technologies (Usman, 2022). As a result, on-board production of H2 for feeding FC systems through an *in situ* process of a suitable H2 source must be considered an efficient solution for the shipping sector. Such a process should produce H2 in high concentration to obtain high performances of the FCs and with very low CO impurity to avoid poisoning of the FC electrode catalysts (Valdes-Lopez et al., 2020). MeOH appears to be a promising source for on-board production of H2 since it can be stored in liquid form, the absence of C-C bonds does not result in carbon deposits, no sulfur compounds are present, it can be processed at relatively low temperatures and does not produce sulfur compounds and PM (Dagle and Holladay, 2007). H2 can be obtained in one step with the endothermic MeOH catalytic steam reforming (SRM):

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|  | (1) |

SRM has several drawbacks: resulting H2 stream has high impurity levels requiring further purification units (PROx), high energetic input, reactor complexity, difficulty in fast speed variation. Exothermic catalytic partial oxidation can overcome some of the limitations:

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|  | (2) |

Due to the exothermicity of the reaction, no external heating is required, reactor configuration is simpler, and fast start-up is possible. As an alternative, oxidative MeOH steam reforming (OSRM) (reaction 3) is a valuable option (Tang et al., 2015). OSMR is a combination of reactions (1) and (2): by feeding CH3OH, H2O, and O2 (air) in proper amounts, a net reaction enthalpy equal to zero and a potentially autothermal process can be obtained. OSRM has many advantages: (i) can produce H2 with a very low CO content; (ii) does not required external energetic input and is realized at low temperatures (250-400 °C); (iii) easier design of the reactor, with lower volumes; (iv) allows high H2 yield, up to 2.8 mol H2/mol MeOH; the maximum obtainable H2 content in the product gas is 65% at 300 °C when air is used (Turco et al., 2004) according to

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|  | (3) |

* + 1. Catalysts for oxidative steam reforming of methanol

The literature review concerning the catalysts used in the steam, partial oxidation, and autothermal reforming of MeOH reactions shows that the typical catalysts of the discussed processes are copper catalysts supported on different oxides (Al2O3, ZnO, CeO2, MgO, La2O3, SiO2), or mixed oxides (ZnO–Al2O3, CeO2–ZrO2, SiO2–SnO2, Al2O3–CeO2). The reaction of OSRM can be helped by different kinds of catalysts, characterized by noble metals or copper, zinc, nickel, aluminum or chrome oxides. One of the most common choices is a catalytic bed of highly dispersed Cu in the ZnO/Al2O3 matrix (Mosinska et al., 2020 Turco et al., 2004), resulting in high activity

* + 1. Proton exchange membrane fuel cells (PEMFCs) for on-board integrated systems

PEMFC is a mature technology that has been successfully used in several sectors. Low- temperature FCs (LT-PEMFC) work at 50 - 100°C, allowing to meet dynamic power requirements but resulting in high sensitivity to CO poisoning, a complex water management system, and a moderate lifetime. The efficiency of the LT-PEMFC systems is 50-60 %, and excess heat is of such a quality that heat recovery is not feasible (Larminie and Dicks, 2000). More recently, high temperature PEMFCs (HT-PEMFCs) have attracted the attention of researchers and companies worldwide, overcoming some LT-PEMFC limitations. Typical HT-PEMFCs operate at 120-200 °C, allowing for co-generation of heat and power, having high tolerance to CO impurities (up to 4-5 %) and more straightforward system design, and improved electrochemical kinetics. A different electrolyte membrane enables highr temperature, consisting of a temperature-resistant polymer, usually polybenzimidazole (PBI), retaining phosphoric acid (Rosli et al., 2017). The efficiency of a HT-PEM fuel cell is similar to LT-PEMFC, but harvesting more energy from heat recovery can improve overall efficiency of integrated systems (Lee et al., 2020). HT-PEMFC technology was already demonstrated aboard the MS Mariella in Pa-X-ell project with 3 stacks of 30 kW, and in the project MF Vagen, Norway, including a 12 kW HTPEM for small port commuter ferry. A modular 5kW HT-PEMFC is already available by SerEnergy and Fischer eco solutions.

* 1. Methodology
     1. Integrated OSMR – HT-PEMFC for on-board applications: concept

Based on the considerations presented in Section 1, an integrated on-board system can be proposed, as shown in Figure 1. The process diagram is based on the adoption of an OSRM reactor fed by MeOH, water, and air. The outlet stream can be directly used in a HT-PEMFC for the generation of electrical power. The system could be energetically self-sustaining by recovering heat flows from (i) the output reactor stream and (ii) dissipated by the HT-PEMFC to sustain vaporization and pre-heating of reactants.

The overall balance consisted of the preliminary evaluation of four main contributions:

(i) the heat required to vaporize the reagents (MeOH, H2O) and to reach the inlet temperature (120-150°C);

(ii) the heat required to pre-heat reactants to the catalytic bed temperature (i.e. 400 C°);

(iii) the heat that can be recovered from the outlet OSMR catalytic bed temperature (400 C°) to bring it to a suitable inlet temperature for the HT-PEMFC (120-150 °C), that can be used to provide contribution (ii);

(iv) the heat that can be recovered from the HT-PEMFC dissipation, that can be used to provide contribution (i).

* + 1. Integrated OSMR – HT-PEMFC for on-board applications: self-sustainability

The different energetic contributions are summarized in Table 1, assuming a stoichiometric inlet composition, for a temperature range on inlet streams in the range 120-150°C and a produced electrical power of 1 kW. As one can see, recovered heat is greater than the one required by vaporization and pre-heating, and so the system can be considered self-sustaining even for lower efficiency of heat exchangers that is much higher than value of OSRM process. When liquid H2 is considered, about 20%-30% of the energy content of H2 is required for its liquefaction, corresponding to 1.3-2.0 tonCO2/tonH2. Such evaluation underlines the importance of MeOH coupled with OSRM process as an efficient way for on-board H2 storage, at least in short-medium term (Dalena et al., 2018)



Figure 1: Flow diagram of the integrated OSMR/HT-PEMFC system with heat recovery

Table 1: Heat contributions to evaluate system self-sustainability to produce 1 kW of electric power

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| T inlet (°C) | Q (i), kJ/s | Q (ii), kJ/s | Q (iii), kJ/s | Q (iv), kJ/s |
| 120 | 0.14 | 0.09 | -0.115 | -1.0 |
| 150 | 0.15 | 0.08 | -0.103 | -1.0 |

* 1. Results
     1. Design, sizing, and safety considerations

The reactor design was performed by assuming an electric power of 1 kW. In agreement with the literature data, the efficiency of the HT-PEMFC of 50% was considered. The power coming from H2 feed can be evaluated by

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|  | (4) |

According to reaction 3, a stoichiometric inlet molar composition was assumed: 43.5% MeOH, 34.8% H2O, 4.3% O2 and 17.4% N2, in agreement with literature H2O/MeOH feeding ratios which do not deviate much from the stoichiometric one The volume and mass of the catalyst were calculated using kinetic data reported in the literature (Turco et al., 2004; Wu et al., 2012). In particular, we referred to Cu/ZnO/Al2O3 catalysts derived from a hydrotalcite precursor since they provided high hydrogen yield (up to the stoichiometric one), high selectivity, and low by-products (i.e. CxHyO, CH4, CO) formation (Turco et al., 2004). In particular, CO is less than a few hundred ppm at optimized conditions. Based on literature data, MeOH conversion rate = 1.7-2.5⋅10-4 mol s-1 g-1cat, H2 production rate = 2.0-3.5⋅10-4 mol s-1 g-1cat the following conditions were considered: T = 350–400 °C; GHSV = 0.6-1.2⋅105 h-1. Hence, the mass and volume of required catalyst were calculated. The calculated volume was multiplied by a factor of 10 to take into account the necessary catalyst dilution to ensure quasi-isothermal operating conditions. Results are summarized in Table 2, assuming an apparent density of 1 g cm-3.

Table 2: Mass and diluted volume of catalyst required to produce 1 kW of electric power

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| T, °C | mcat, kg | Vcat,diluted L |
| 350 | 0.240 | 0.240 |
| 400 | 0.042 | 0.042 |

Sizing a fixed bed reactor was done by optimizing some parameters like as: section diameter to length ratio, particles diameter, void fraction, velocity, and consequently pressure drop. Such parameters are correlated. Therefore reciprocal influence must be considered. The most established influence on the void fraction is the tube to particle diameter ratio. This dependency is more pronounced for low diameter ratios, typically < 10. The tube to particle diameter ratio is expressed in an equivalent sphere diameter for particles other than spheres. Most correlations available in the literature (Benyahia et al., 2005) concerns mono-size spherical particles, with a smaller number concerning cylindrical particles. Therefore, in order to obtain a first evaluation of section, length, velocity, flow conditions, and pressure drop, the following cases are considered with D/L reactor ratio from 1 to 2, particle diameter in the range 0.5-1.5 mm, void fraction between 0.3-0.5 and sphericity factor between 0.7-0.9.

The results can be summarized as follows: (i) For D/L = 2, higher adiabatic conditions can be ensured, but laminar flow is established. In this case a well-distributed flow of reactants in the bed cannot be ensured; (ii) For D/L = 1, acceptable adiabatic conditions can be supposed and in a transient flow regime with higher homogeneity of reactants distribution in catalytic bed; (iii) In no analyzed condition turbulent conditions were found; (iv) In all conditions, the pressure drop is acceptable and in the range 50-10000 Pa; (v) the Reynold number is not affected significantly by the sphericity factor. In first approximation the following volumes of the different systems of the plant can be supposed, for one kWel and ten days of autonomy.

Table 3: Mass and diluted volume of catalyst required to produce 1 kW of electric power

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| HT-PEMFC  Volume, L | Reactor  Volume, L | MeOH/H2O  Tank Volume, L |
| 3-4 | 0.84-1.26 | 131 |

The reactor volume has to be considered 2 or 3 times the volume of the catalytic bed already evaluated, considering the void fraction, heat exchanger, and auxiliary equipment. The volume of the HT-PEMFC takes into account some commercial data. MeOH/H2O tank volume has been evaluated considering the density of 0.87 kg/l for 64% w/w solution at 25°C. Finally, it is necessary to assess whether the feeding conditions are safe concerning flammability problems. Oxidizing-fuel mixtures can ignite only if their composition is contained within the flammability limits that vary from mixture to mixture. In this specific case, there is a lack of data on which the molar composition of the mixture is 43% MeOH, 35% H2O and 22% air. For MeOH in air, the LFL and the UFL are around respectively 8.6 % and 36%. The presence of inert gases (N2, CO2, etc.) significantly lowers the upper flammability limit of the fuel, without significantly modify the lower one. In particular, H2O contained in the feeding stream, has an inhibiting effect on the progress of the flame front, allowing for safe operations of the reactor.

* + 1. Evaluation of CO2 emissions: comparison of MeOH with traditional H2 storage adoption

The CO2 impact from using MeOH as a H2 storage technique compared to compressed/liquid hydrogen must also consider the MeOH production process (from biomass, green H2, or fossil sources). The production of renewable MeOH allows for mitigating CO2 emissions, but could only be practicable in the mid-term. Bio-MeOH from biomasses currently only accounts for about 7% of the total MeOH production, and the cost is significantly higher than that of MeOH from natural gas. In 2020, the global bio-MeOH market value was 53 million USD and it is expected to reach 251.1 million USD by the end of 2026; this could lead to a significant cost reduction. MeOH produced from green H2 (so called Power-2-Methanol) is CO2 neutral. Demand for green electricity is expected to rise significantly in the following decades. Adoption of MeOH from green H2 for shipping will only take place if regulations allow MeOH to qualify as a renewable fuel of non-biological origin. The evaluation of CO2 emissions must consider the use of fossil MeOH nowadays. Over 95% of H2 is produced by steam reforming (or partial oxidation) of fossil feedstocks, such as natural gas or naphtha. CH4 steam reforming is a multi-stage and energy intensive process: this is a penalty jointly affecting the use of MeOH as a H2 source and compressed or liquid H2 storage (Vancoillie et al., 2012). Methane Steam Reforming process gives an overall H2 yield of 4 molH2/mol CH4: CO2 emissions deriving from the mere CH4 to CO2 conversion amounts to about 7 tonCO2/tonH2. However, the significant energetic contributions required for the compensation of reaction enthalpy and reactor heating, varying with H2O/CH4 feeding ratio, must be also considered according to a Well-To-Tank approach. Therefore, total CO2 emissions can amount up to about 12-15 tonCO2/tonH2. MeOH is produced by reaction of syngas from SRM. MeOH synthesis is not energy expensive since it is an exothermic reaction typically carried out at 200-300°C and 100-150 atm. Therefore the energy consumption is mainly due to the syngas compression from 20-30 atm up to 150 atm. CO2 emissions coming from the process can be evaluated, considering that the OSRM can be performed in autothermal conditions. Thus a rough evaluation of the CO2 impact deriving from MeOH synthesis and subsequent OSRM can be up to about 1 tonCO2/tonH2.The deriving CO2 impact should be compared to that from the current H2 storage techniques, that should result in up to about 2 tonCO2/tonH2 .

* 1. Conclusions

Comparison in terms of emissions and present regulations show that MeOH can be a promising and safe fuel for the shipping sector. Specifically, integration of catalytic oxidative methanol steam reforming with high temperature fuel cell, is demonstrated to be a suitable technology for on-board clean electric power generation. A first energetic evaluation shows that the system can be fully self-sustaining, since the heat required for vaporization and pre-heating can be fully recovered from the reaction products and FC dissipation, whereas the reactor has a net-zero enthalpy, when proper conditions are adopted. A preliminary sizing of the storage tank, catalytic reactor, and FC system per unit electric power suggests that a safe, efficient, and convenient on-board implementation can be possible. However, the risk assessment of the water/methanol storage system is planned in order to fully ascertain the safe applicability of the integrated OSRM-HT-PEMFC system. The main limitations of the proposed system may be associated with the resistance to chemically aggressive humid and brackish atmosphere and to mechanical stresses, such as vibrations and oscillations. Future investigations will have to address these aspects for a safe and efficient technological implementation.

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