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High temperature fuel cells to reduce CO_2 emission in the maritime sector

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Abstract. Recently the interest in the sustainability of the maritime sector has increased exponentially. The International Maritime Organization (IMO) set as objective the reduction of CO_2 emissions by 2030 by a margin of 40% compared to 2008. Recent studies showed that, according to the ships and the emission mitigation method applied, only 15-25% of CO_2 reduction is de facto needed. Fuel cells represent an answer to meet this regulation. We propose two different solutions: (i) produce with SOFCs instead of engines the minimum power necessary to cut 20% of the emissions, or (ii) reduce the engine power of about 10% balancing the power requirement using MCFCs with CO_2 capture. Using Aspen Plus each solution was investigated. The analysis contemplated LNG steam reforming to produce the H_2 necessary for cell operation and the separation and liquefaction of CO_2. Two case studies were considered comparing existing passenger ships with engines working on HFO and on LNG respectively. Although both solutions showed potential for the reduction of CO_2 emissions respecting the IMO regulations, the SOFC solution requires a major change in the design of the ship, while MCFCs are proposed as an urgent solution allowing ship retrofitting without demanding update.

1 Introduction

The maritime sector has an essential role in the transport of both goods and passengers across the globe. Maritime transport of goods constitutes the most significant fraction of the transportation sector with a 90% share of global trade [1–3]. Accordingly, the naval shipping industry consumes the largest amount of fuel in the transportation sector and generates 3% of the global CO_2 emissions [1]. This fuel consumption is also responsible such for the release into the atmosphere of large amount of greenhouse gases (GHG) and other regulated emissions as nitrogen oxides (NOx), sulphur oxides (SOx), CO, and particulate matter (PM)[2]. In comparison, the transport of passengers generates lower CO_2 emission since the number of vessels employed is significantly lower, however its total GHG emissions have a very high impact at local level especially in port areas [4,5].

Due to this large number of emissions, in the last years, the interest in the environmental sustainability of the maritime sector has increased exponentially. To encourage this effort, the International Maritime Organization (IMO) has set as objective the reduction of CO_2 emissions per transport work by 2030 by a margin of 40% compared to 2008 [2]. Subsequently, it pursues to increase this reduction to 70% by 2050, while also halving the total annual GHG emissions [2]. According to age, design and quality of the ships and considering additional mitigation method such as speed reduction or route optimization, only 15-25% of CO_2 emission reduction is required by the development of new technological solutions.

Fuel cells can provide a valid answer to meet the IMO regulations by allowing the required CO_2 emission reduction. Indeed, compared to the traditionally used internal combustion engines, fuel cells grant a sensibly lower amount of emissions coupled with higher efficiency [6]. Moreover, fuel cells are highly modular thus allowing a smart use of the limited space typical of vessels [7]. For this reason, in literature there have been already different studies that consider the use of fuel cells on ships. Inal et al. [7] studied the substitution in a chemical tanker ship of a 4-stroke diesel engine with 2880 kW output power with an LNG fuelled molten carbonate fuel cell (MCFC) with same output power. The results of their investigation showed that it is possible to effectively reduce GHG emission and particularly CO_2, although more studies on the overall needs of the equipment for a smooth substitution are required. Haseltalab et al. [8] studied the component sizing, energy and power management of solid oxide fuel cells (SOFCs) as the main source integrated into the liquefied natural gas fuelled Power and Propulsion System of vessels. As results they confirmed that the adoption of SOFCs in combination with batteries can effectively address the challenges of the maritime sector in term of emission reductions, despite the need for improvements in the design of the SOFC system to reduce the impact on vessel design and operation. Wu et al. [9] investigated a hybrid proton-exchange membrane fuel cell

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(PEMFC) and battery propulsion system in Matlab for use on a coastal ferry. They showed that the proposed propulsion system can achieve at least a 65% life-cycle greenhouse gas reduction. However, also in this case, more investigation is needed to improve the system. Coupled with this theoretical studies, in the last years also numerous projects have been conducted with practical investigations [6]. Among these, based on the Zemships project [10], a PEMFC power system (maximum power output of 100 kW) was developed for the passenger ship FCS Alsterwasser. The fuel cell system was used to power the propulsion motor directly or charge the lead-gel battery packs that served as a back-up option if the fuel cells failed. The H_2 stored onboard allowed for 2 to 3 days of ship operation. Then, under the FellowSHIP project, the offshore supply vessel Viking Lady was the first to use MCFCs as auxiliary power systems (320 kW for 500 cells) to dual fuel engines propulsor [11]. The system operated for 18 hours [7]. Furthermore, under the METAPHU project, while a conceptual study of a 250 kW SOFC auxiliary power systems using methanol was completed, the practical operation of a 20 kW SOFC unit onboard the car carrier MV Undine were conducted. The SOFC unit was aimed at testing the performance and emissions under real-life conditions onboard a ship and at assessing the maturity of methanol-based technology in the shipping sector [12].

However, a complete substitution of the combustion engines with fuel cells may not be easy to apply because the required spaces and costs could be excessive, and existing ships would have to be completely redesigned or put out of use. In this work, the authors propose two different solutions: (i) relying on solid oxide fuel cells instead of engines just the minimum power necessary to cut emissions of about 20%, or (ii) reduce the engine power around 10% while balancing the power requirement using MCFCs for CO_2 capture. Using both solutions two case studies were studied comparing existing passenger ships where engines working on HFO, typical of more traditional ships, and on LNG, currently emerging for emission reduction, are used respectively.

2 Fuel cells

Fuel cells are electrochemical devices that allows the production of electrical power exploiting the electrochemical reaction between a fuel, usually H_2, and an oxidant, usually O_2 [13]. There is a large variety of fuel cells that differ by components and catalyst materials used, charge carriers, operating temperatures, and range of applications [13]. Among these, high temperature fuel cells are considered those type of cells that operate between 500-1200°C. For this reason, compared to low temperature fuel cells (operating temperature 20-200°C), they do not need the use of noble metal as catalysts highly affecting the prices and can work with carbon containing components allowing a more diverse range of possible fuels [6]. They can be divided into two subclasses according to the electrolyte that they use to operate: solid oxide and molten carbonate fuel cells.

Solid oxide fuel cells (SOFCs) use as electrolyte solid oxide materials such as YSZ, GDC, or LSGM. According to the electrolyte materials used and the dopant applied, the temperature range at which SOFCs can operate varies between 1200°C and 500°C. Thanks to the high operating temperature and the Ni based anode catalysts usually used, SOFCs can work also with carbon containing fuels (i.e.: CH_4, CH_3OH) in addition to the commonly used H_2 thanks to internal reforming reactions. As in any other kind of fuel cells, the global reaction that provides energy is the formation of H_2O from reduction of O_2 and oxidation of H_2 at the respective electrodes, as described by Eq. 1 where the subscripts A and C indicate anode and cathode sides.

$$H_{2,A} + \frac{1}{2} O_{2,C} \leftrightarrow H_2 O_{2,A} \qquad (1)$$

Molten carbonate fuel cells (MCFCs) are characterized by the use of a eutectic alkali carbonate mixture as electrolyte of which Li_2/K_2CO_3 and Li_2/Na_2CO_3 are the most common. To both keep the electrolyte in its liquid form and avoid extreme evaporation, they are limited to work in the 580-700°C temperature range. In the specific case of MCFCs, CO_2 serves as an additional reactant with O_2 to form, at the cathode, the carbonate ions (CO_3^{2-}) that function as the anion carrier through the electrolyte and matrix. The total MCFC reaction is thus described in Eq. (2, where the subscripts again refer to anode and cathode.

$$H_{2,A} + \frac{1}{2} O_{2,C} + CO_{2,C} \leftrightarrow H_2 O_{2,A} + CO_{2,A} \qquad (2)$$

This migration of CO_2 from a CO_2 poor stream (cathode inlet) to an enriched stream (anode outlet) allows for MCFC to be used as CO_2 capture tools. The anode inlet constitutes a stream with concentrated CO_2 that can be more easily treated for sequestration.

3 Proposed solutions

As mentioned, the authors propose two different paths to meet new IMO regulation. Both are aimed to reduce CO_2 emission by the necessary percentage which cannot be achieved thanks to conventional ship design and management optimisation, that means around 20%.

The first path consists in reducing the power provided by the combustion engines while covering this decrease using a more efficient technology such as SOFCs. The second path adds to this concept the ability offered by MCFCs to capture the excess CO_2 from the engine exhausts. This second path will be slightly more complex because it requires a step of separation and liquefaction of CO_2, but it can also favour the start of a virtuous chain of CO_2 recovery. For both solutions, two case studies will be analysed comparing existing passenger ships where engines working on Heavy Fuel Oil (HFO), typical of more traditional ships, and on LNG (Liquified Natural Gas), currently emerging for emission reduction, are used respectively. Both solutions in both cases will also be studied to determine the additional required fuel for operation at same overall CO_2 emission reduction.

The schematic of how the SOFC fuel cell systems is added to the combustion engines is shown in Fig. **1**. As previously mentioned, the SOFC overall reaction see the oxidation of H_2 to water. This required fuel can be fed either directly or in the form of light hydrocarbons such as CH_4 that due to the high temperature and appropriate catalysts materials can undergo a reforming reaction. Since LNG is already present on ships or of easier storage compared to H_2 [7], the authors decided to use it as fuel. However, as internal reforming fuel cells are more complex to deal with, the authors decided to have the reforming reaction required to produce H_2 before the cell stack. For this scope, water vapour from utilities is mixed with LNG, then they are preheated and sent to a reformer unit. The reformed gas (a mixture of mainly H_2, CO, CO_2 and H_2O) is then cooled and sent to the anode side of the cell as fuel.

For the oxidant at the cathode side, air is used after being preheated.

The anode outlet of the cell is cooled with sea water to favour the separation of water in a subsequent step. The dry current is then sent to a membrane to separate part of the non-combusted H_2. This H_2-upgraded current is sent back to the SOFC inlet. The H_2-deprived current is sent to a burner together with the cathode outlet for combustion. This stream of exhaust is used to heat up the stack inlets and the reforming unit before release in the atmosphere.

The schematic of how the MCFC fuel cell systems is added to the combustion engines is shown in Fig. **2**.

A fraction of the exhausted gases from the combustion engines is used as oxidant at the cathode side of the MCFCs.

Before entering the stack, such exhausts are preheated because in the case of HFO fuelled engines the exhausted gases must be treated to remove sulphur and other pollutants using scrubbers that decrease the temperature to about 30°C, while in the case of LNG fuelled engines the final combustion temperature is usually lower (about 300°C) than the one required for MCFC operation.

As for the SOFCs, also in the case of MCFCs H_2 is the fuel required by the main reactions and can be either fed directly or through light hydrocarbons that can be internally reformed. In similar manner of what presented for the SOFC systems, also in this case the production of H_2 is obtained in an external steam reforming of LNG. The anode inlet production process is like the one previously described for SOFC, however in this case the final reformed gas is cooled down to a lower temperature of 580°C which is suitable for MCFC operation.

As it is done in the SOFC case, after reaction in the cell stack, the anode outlet is cool down using sea water to facilitate the separation of H_2O in a subsequent step and the separation of the H_2. However, in this MCFC case, the CO_2 rich stream (poor in H_2) is sent to a liquefaction system to obtain liquid CO_2. Then, the not liquefied part of the steam and the separated H_2 rich flow rate are sent together with the cathode outlet to a burner where additional LNG is fed to enhance combustion. The cell exhaust is used to warm up the cell inlets and provide heat to the reformer. Eventually, it is released into the atmosphere.

Fuel cell stack sizes, operating conditions and flow rate management have been optimised so that, as result of these overall processes, the total exhaust gas (from combustion engines + cell stack) contains an amount of CO_2 that will respect the regulations set by the IMO.

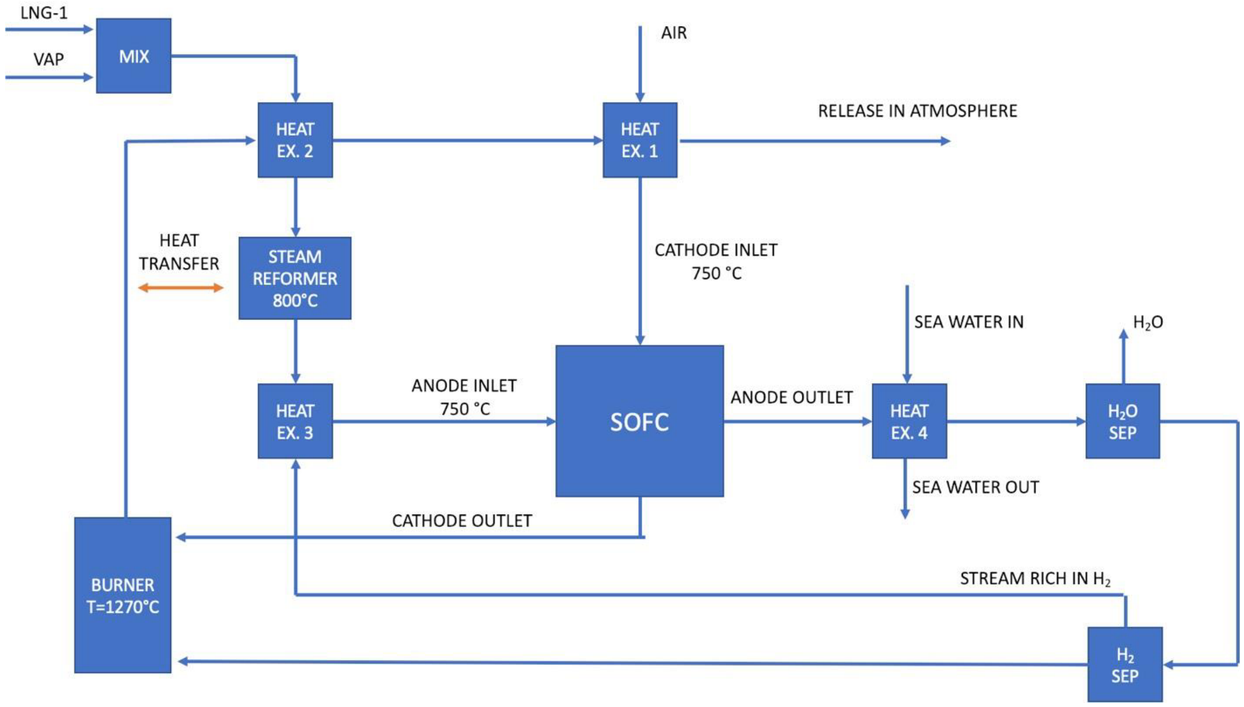

Fig. 1: Schematic representation of the SOFC system downstream the combustion engines.

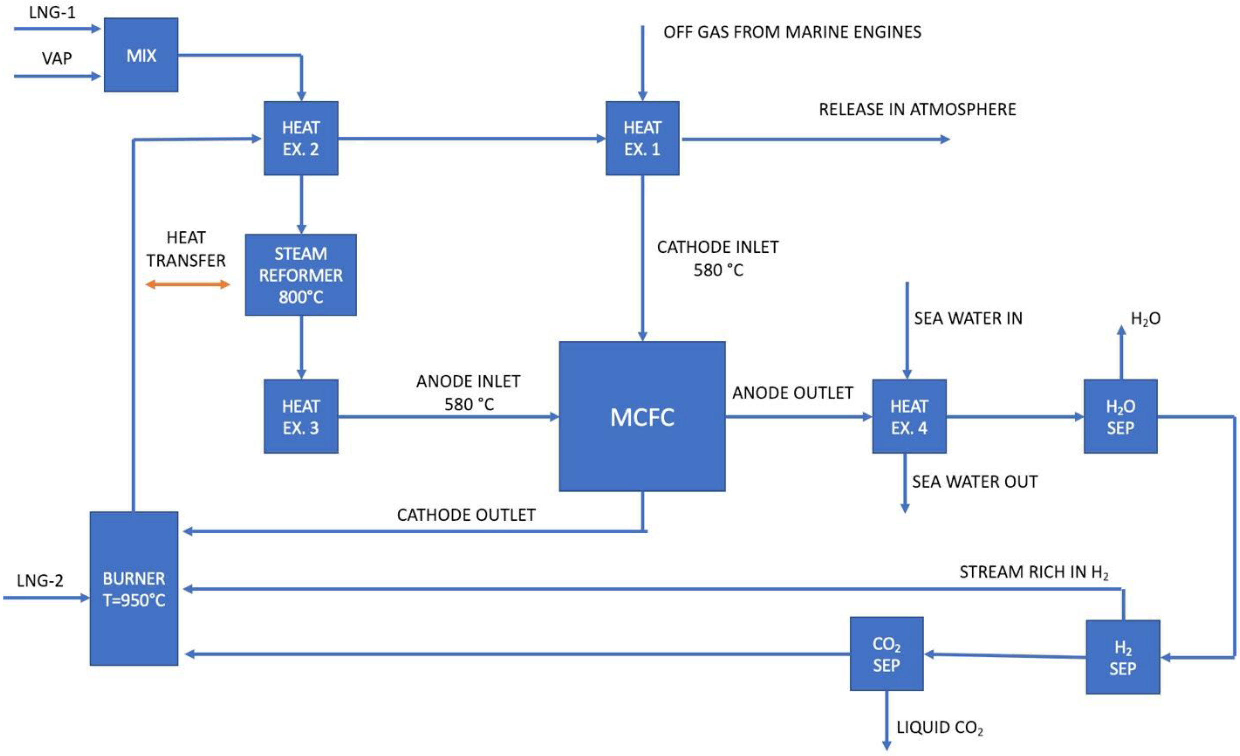

Fig. 2: Schematic representation of the MCFC system downstream the combustion engines.

4 Simulation and results

4.1 Detail of the simulation

To study the feasibility of the proposed solutions, the software Aspen Plus was used for the modelling of the fuel cell systems.

The steam reformer reactor used to produce H_2 from LNG (assumed at 15°C and 1 atm) and steam (available from the ship utilities at 4 bar and 140°C) was simulated using a Gibbs reactor at the pressure of 1 atm and 800°C.

Steam:LNG molar ratio has been guaranteed 3.5:1 to avoid carbon deposition.The reactions are not defined inside of Gibbs reactor but, according to the literature [14], the main reactions assumed are: :

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \tag{3}$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \tag{4}$$

A Gibbs reactor was also used for the simulation of the burner, considered operating with a small negative duty of about -5 kW but slightly different in all the encountered cases. The main reactions supposed for the burning process are the following:

$$CH_4 + 2O_2 \leftrightarrow 2H_2O + CO_2 \tag{5}$$

$$CO + \frac{1}{2}\,O_2 \leftrightarrow CO_2 \tag{6}$$

$$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O \tag{7}$$

The heat exchangers needed to increase the anode and cathode inlet streams to the desired temperature for correct cell operations were set to have both outlet temperature of 750°C in case of SOFC and 580°C in case of MCFC. The heat exchanger that cools the anode inlet is considered to exchange heat with the utilities of the vessels. Instead, the heat exchanger after the mixer of water vapour and LNG prior to the reforming reactor was imposed to have 50°C as difference between the cold and the warm streams. The heat exchanger with sea water at the anode outlet was set to have a gas outlet temperature of 30°C. The following water separation was simulated with a simple flash.

In this initial phase the membrane for H_2 separation was simulated using a simple separator unit imposing the 65% efficiency coupled with 65% purity as per literature [15].

Between the reforming and the exhaust gas coming from the burner there is exchange of heat that has been set to provide 10% heat in excess compared to the total duty required by the reforming reactor.

The separation of the CO_2 was modelled using a separator unit and considering the need of 0.2kWh for the liquefaction of 1 kg of CO_2. The liquid CO_2 is obtained at 25 bar and -40°C.

Finally, for the simulation of the fuel cell stacks a 0D simplified version of the home-made code called SIMFC was used. Developed and tested by the authors, it is based on mass, energy, and momentum balances and is capable to simulate the performance of high temperature fuel cells. The fundamental equations that describe the kinetics of the fuel cells are presented in previous works by the authors for both SOFCs [16] and MCFCs [17–19]. The main operating parameters and evaluated performances of the proposed configurations are reported in Table 1.

Table 1. Main parameters and evaluated performances of MCFC and SOFC in HFO and LNG cases

	HFO Case - MCFC	HFO Case - SOFC	LNG Case - MCFC*	LNG Case - SOFC*
Utilization of CO_2 [%]	85	/	83	/
Utilization of H_2 [%]	76,5	75,5	76,5	75,5
Current density [A/m^2]	1000	5000	1400	5000
Voltage single cell [V]	0,76	0,83	0,76	0,83
Area of single cell [m^2]	1	0,04	1	0,04
Number of cell [-]	1102	22360	2500	105810
Power [kW]	842	3693	2651	17474
*during navigation				

4.2 Heavy Fuel Oil (HFO) case

The reference passenger ship fuelled with HFO uses a main engine with MCR (Maximum Continuous Rating) power of about 11060 kW. For one day its operation time can be divided between navigation (18 hours with engine load of 59%), manoeuvring (2 hours with engine load of 27%) and port operations (4 hours with engine load of 27%). To avoid too stressed operating conditions during manoeuvring and in port, it was decided to act only on the exercise in navigation to meet the overall 20% reduction of the weekly emissions as averaged on all the operation time.

As the total emission of the ship without any modification are of about 538 t week^{-1} that can be divided between 479 t week^{-1} during navigation and 59 t week^{-1} during port operation and manoeuvring, to achieve the 20% weekly reduction, the cell stacks have to reduce the navigation CO_2 emission to 372 t week^{-1} as it is shown in Fig. *3*-A. Fixing this value, calculations have been made to evaluate the SOFC and MCFC stack requirements, the percentage at which the engines should work, and new fuel requirements.

As shown in the graph Fig. *4*, in the case of SOFC, it was determined that to meet such requirements the stack must provide a total energy output of about 66.5 MWh day^{-1}, that can be provided using 45 modules, each made of 500 cells having area of 0.04 m^2 and working with a current of 5000 A m^{-2}. This quite small size of each single cell is dictated by the current technological state of the art.

In these conditions, the engine must provide 50.5 MWh day^{-1}, which means that the engine would work with a load of about 25% (total maximum energy provided is of about 199 MWh day^{-1}).

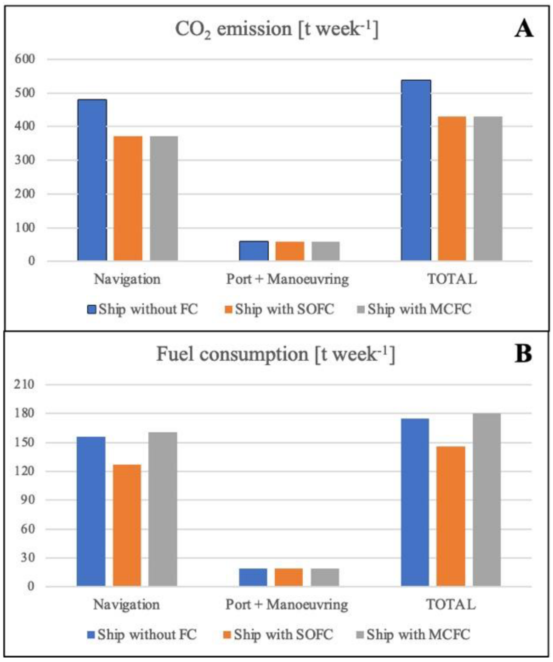

Fig. 3: Weekly CO_2 emission (A) and fuel consumption (B) of the HFO fuelled ship using the traditional combustion engine only, and the engines integrated with an SOFC or an MCFC system.

In such operating conditions, as shown in the graph B of Fig. *3*, the fuel consumption of the systems considering both the HFO fed to the engines and the LNG fed to the stack decreases of about 16.6%. However, since the engine would need to work at 25% of its total load, this solution does not seem practical for retrofitting on this kind of ship. In fact, it is usually desirable to not operate the combustion engines with load lower than 40%, while it can be accepted just for short periods of time such as during manoeuvring or port operations. So, in this case, it would be preferable to substitute the engines with smaller ones to avoid excessive losses or directly substitute the engines with an opportune SOFC stack.

In the case of MCFC, as shown in the graph Fig. *4*, it was determined that to meet CO_2 emission requirements the stack must provide a total energy output of about 15 MWh day^{-1} that can be provided using 2 modules, each made of 550 single cells having area of 1 m^2 and working with a current of 1100 A, according with the technology state of the art. In these conditions, the engine must provide 105 MWh day^{-1}, which means that the engine would work with a load of about 52.8%. Of this power, it is to be noted that about 3 MWh day^{-1} are needed for the liquefaction of CO_2, and this explains why thy energy required in this case is slightly higher than in the other cases. In such operating conditions, as shown in the graph B of Fig. *3*, the fuel consumption of the systems considering both the HFO fed to the engines and the LNG fed to the stack increases of about 3.2%.

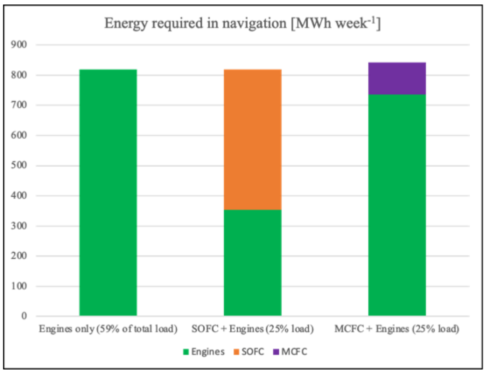

Fig. 4: Total daily energy required by the HFO fuelled ship during navigation using traditional engines only, and the engines integrated with an SOFC or an MCFC system.

4.3 Liquified Natural Gas (LNG) case

The reference passenger ship fuelled with LNG uses two main engines with total MCR power of about 30880 kW. For one day its operation time can be divided between navigation (15.5 hours with engines load of 78%), and manoeuvring as well as port for which only one of the two engines is used (8.5 hours with engine load of 50%). In this case, it was possible to reduce the emission of both phases to achieve a reduction in total CO_2 weekly emission of 20%.

As shown in the graph A of Fig. 5, the total emission of the ship without any modification are of about 1656 t week^{-1} that can be divided between 1398 t week^{-1} during navigation and 258 t week^{-1} during port operation and manoeuvring.

As only the final emission reduction value of 20% is known, the desired result was achieved through iterative calculations.

In the SOFC case it was determined that a stack made of 212 modules using 500 cells having area of 0.04 m^2 and working with a current of 5000 A m^{-2} during navigation and the same stack using only 20 modules during port operation and manoeuvring are suitable for achieving the desired CO_2 emission reduction. When the vessel is in navigation, the stack will provide a total energy of about 271 MWh day^{-1} with the engines that would consequently need to provide 102.5 MWh day^{-1}, which is about 21% of the total load (around 479 MWh day^{-1}). When the vessel is manoeuvring or doing port operation, the stack will provide a total energy of about 13.6 MWh day^{-1} with the engines that would consequently need to provide 52 MWh day^{-1} which is about 40% of the total load (around 131 MWh day^{-1}). Both these results are shown in graphs A and B of Fig. *6*. Under these operating conditions, the emission are reduced to 1084 t week^{-1} (22%) during navigation and 242 t week^{-1} (6%) during manoeuvring and port operation, for a total of about 1325 t week^{-1} that corresponds to the desired 20% reduction, as shown in graph A of Fig. 5. As in the previous case with ship fuelled with HFO, as shown in Fig. 5, the total fuel consumption, which in this case is represented only by LNG, is reduced of about 8.8%.

Also in this case using an SOFC stack the reduction target is achievable, but the load of the engines results too low, so that a retrofitting approach seems not suitable.

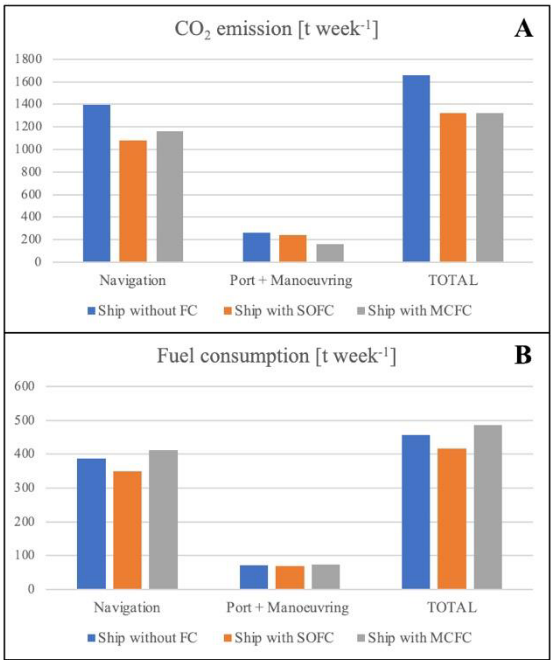

Fig. 5: Weekly CO_2 emission (A) and fuel consumption (B) of the LNG fuelled ship using the traditional combustion engine, and the engines integrated with an SOFC or an MCFC system.

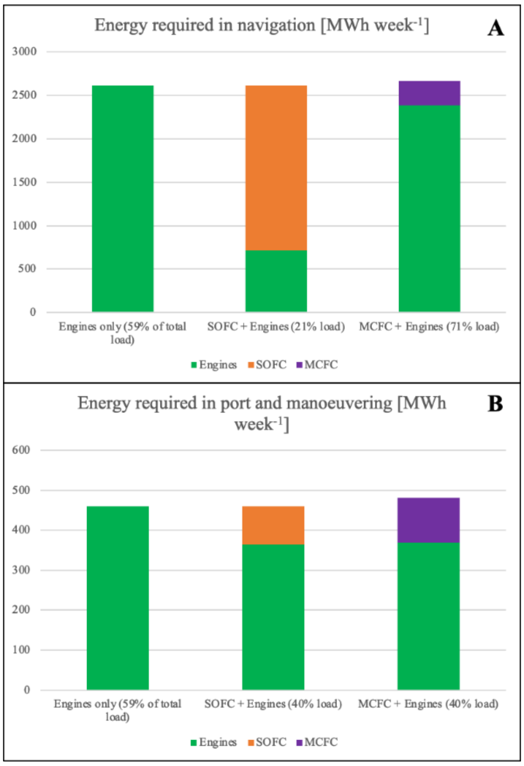

Fig. 6: Total daily energy required by the LNG fuelled ship during navigation (A) and during manoeuvring and port activities using traditional engines only, and the engines integrated with an SOFC or an MCFC system.

In the MCFC case it was determined that a stack made of 5 modules using 500 cells having area of 1 m^2 and working with a current density of 1400 A m^{-2} during navigation and the same stack using 1000 A m^{-2} during port operation and manoeuvring are suitable for achieving the desired CO_2 emission reduction. When the vessel is in navigation, the stack will provide a total energy of about

41.1 MWh day^{-1} with the engines that would consequently need to provide 340.5 MWh day^{-1}, which is about 71% of the total load (around 479 MWh day^{-1}). Of this amount 8 MWh day^{-1} will be used for CO_2 liquefaction. When the vessel is manoeuvring or doing port operation, the stack will provide a total energy of about 16.1 MWh day^{-1} with the engines that would consequently need to provide 52.7 MWh day^{-1} which is about 40% of the total load (around 131 MWh day^{-1}). Of this amount 3.2 MWh day^{-1} will be used for CO_2 liquefaction. Both these results are shown in graphs A and B of Fig. ***6***. Under these operating conditions, the emission are reduced to 1163 t week^{-1} (16.8%) during navigation and 161 t week^{-1} (37.7%) during manoeuvring and port operation, for a total of about 1324 t week^{-1} that corresponds to the desired 20% reduction, as shown in graph A of Fig. 5. As in the previous case with ship fuelled with HFO, as shown in Fig. 5, the total fuel consumption, which in this case is represented only by LNG, increases of about 6.2%.

5 Conclusions

In this work, the authors presented a new approach for the mitigation of CO_2 emission in the maritime sector by coupling high temperature fuel cells and combustion engines with the aim to minimise the impact on the traditional ship design.

To study the feasibility of this proposal, the author investigated two systems: one coupling combustion engines and SOFC stacks to provide the required power, and one coupling combustion engines and MCFC stacks to provide the required power as well as to segregate the produced CO_2.

Both systems were studied considering two passenger ships operating with combustion engines fuelled using either LNG or HFO.

The results of the study showed both the solutions have potential for the reduction of CO_2 emissions respecting the IMO regulations.

Nevertheless, the SOFC solution resulted not suitable for simple ship retrofitting, as it would involve a too extreme reduction of the working load of the engines (about 20% during navigation) thus requiring either the substitution of the engines with smaller ones or a complete substitution of the engines with SOFC stack of appropriate size.

On the over hand, the simulation showed that an MCFC stack can be effectively used to reduced CO_2 emission while maintaining the same combustion engines operating at reduced load. Although this solution involved a higher fuel consumption (3.2% in the HFO fuelled ship case and 6.2% in the LNG fuelled ship case), its benefits make it interesting for more detailed investigation using more detailed modelling (i.e.: 2D or 3D model of the cell stack) and focusing more the attention on the energy balance for better integration with the utilities of the ship.

Thus, MCFC is proposed as a valid solution to mitigate the CO_2 emissions with a ship retrofitting policy which allows urgent and efficient actions and follows the energy transition phase.

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