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Using renewable methanol, PEM fuel cells and on-board carbon capture to reduce well-to-propeller ship emissions

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Synopsis

This paper gives an overview of research that was carried out with the purpose of gaining insight whether renewable methanol, fuel cells and on-board carbon capture can be used to reduce the CO_2 emissions of part of a fleet consisting of various (governmental) work ships, using methanol produced from waste biomass, excess wind energy and recycled CO_2. Since CO_2 is a by-product from steam reforming methanol to hydrogen, this can be captured, liquefied, and stored on board for later use in methanol production. Integrating the necessary systems seemed possible for larger ships using dimensions of currently available systems, although suitable carbon capture systems are not yet available. Using system parameters and operational profile as input, a MATLAB-Simulink model was constructed to calculate the tank-to-propeller emissions, as well as providing insight in required tank dimensions (both methanol and CO_2). In general, the total energy stored on board of larger ships is reduced when using methanol instead of traditional fuel oils, but the reviewed ships are still able to achieve their original operational profile. Smaller vessels require various advancements in order to fit the required systems whilst still being able to store enough fuel for at least a single trip. These advancements can include more compact reformer and fuel cell systems, or class rule changes regarding the dimensions of cofferdams that are to be fitted around methanol tanks. Assuming these advancements are possible in the near future, the total emissions could be reduced significantly, by up to 82% in the originally reviewed case. This means that the net CO_2 emissions are still positive and subsequently a gap in CO_2 supply for methanol production occurs. However, both problems can be tackled simultaneously with further advancements: either by capturing more CO_2 during the various well-to-propeller stages, or by introducing an additional carbon-negative CO_2 source. It could therefore be possible to operate a fleet with net zero CO_2 emissions in the future by using renewable methanol, fuel cells and on-board carbon capture, if feedstock availability is high enough and technological advancements are made.

Keywords: Fuel Cells; Methanol; Reforming; On-board carbon capture; Tank-to-propeller model

1. Introduction: Background of this study

Human activities since the start of the industrial age have resulted in a 1°C rise in global temperature, with a current increase of 0.2°C every decade (Allen et al., 2018). The Paris agreement pushed nations to take action in order to limit the post-industrial temperature increase to well under 2°C, preferably to 1.5°C (UNFCCC, n.d.). Since the emission of greenhouse gases is the main contributor to global warming, the Netherlands adopted a climate law (*Klimaatwet*) with emission reduction targets based on the emission levels of 1990. To conform to this law, the Netherlands needs to emit 49% fewer greenhouse gases by 2030, and up to 95% fewer emissions by 2050. This research was originally carried out for the Rijksrederij, which as part of Rijkswaterstaat and the Dutch Ministry of Transport and Water Management is targeting to achieve fully carbon neutral operation by 2030. Their fleet consists of approximately 100 ships of various sizes and tasks. Therefore, the scope of this research was limited to the resources internally available to Rijkswaterstaat. A model to calculate the tank-to-propeller emissions was set up using ships operated by the Rijksrederij, but will be discussed in this paper in a broader perspective. A (fictional) example vessel is used to illustrate the functionalities of the model.

Fuel cells are interesting for their near-silent operation, clean emissions and the possibility to reach higher efficiencies than combustion engines (Tronstad et al., 2017). Methanol (CH_3OH) is considered as a fuel, since it can be produced renewably as long as renewable hydrogen and carbon sources are available. It has the advantage over pure hydrogen in terms of energy density, ease of handling and safety (Markowski & Pielecha, 2019). As fuel cells need a hydrogen input, methanol needs to be reformed to hydrogen on board. This process also releases a relatively pure CO_2 stream, which could be captured, liquefied, and stored on board, to offload it shore-side for reuse in renewable methanol production (H. Lee et al., 2020). This way, it would be possible to achieve carbon neutral operation.

Author's Biography
Dion Pluijlaar graduated in Marine Technology at the Delft University of Technology in February 2022. During his studies, he mainly focussed on alternative fuels and power systems as a way to aid in the maritime energy transition.
Lindert van Biert is an assistant professor Marine Engineering at the Ship Design, Production and Operations section of the Maritime & Transport Technology department, Delft University of Technology. His research focusses on characterisation, modelling, simulation and application of power and propulsion systems based on fuel cells, and the adoption, storage and bunkering of renewable fuels.

2. Tank-to-propeller model

A MATLAB-Simulink model was constructed to aid in calculating CO_2 emissions for a ship equipped with methanol reformers and fuel cells. In this model, data from Excel files is read and processed by MATLAB. The input data includes the ship's operational profile and specific data on fuel cells and reformers, like fuel consumption and power output. The Simulink model is then used to translate the input parameters to output parameters, which include emission data on both a trip and yearly basis. These output parameters are again handled by MATLAB to be visualised in figures. For the purposes of this paper, an example vessel (EXV) is used as input.

2.1. Input

The main input data files contain the operational profile of one or various ships. The different ships can be called upon using the main MATLAB script. The same holds for fuel cell and reformer data: different systems present in the input files can be called upon by changing an input variable. The different ships can also have different electrical systems, for which provisions are also made in the input data files.

The operational profile is structured as follows: a ship can have one or multiple main tasks, each corresponding to a different trip type. Each main task can have multiple sub tasks, representing different operational modes during a single trip. For every sub task, two different power levels are present: average power and maximum power. Each power level has a corresponding time parameter, indicating how long the ship spends using that specific power level. Different annual operational times are taken into account when calculating the yearly time spent per power level. The operational profile of the example vessel is listed in Table 1. The power demand listed is the power demand from both propulsion systems and auxiliary loads. This ship is normally in stand-by mode, with emergency operations only necessary during some of the trips. Therefore, a reserve fuel capacity for emergency operations is always necessary on top of the minimum fuel capacity dictated by 14 days of stand-by mode. Provisions for this type of operational profile are made in the model.

Table 1: Operational profile for example vessel (EXV)

Main task	**Subtask**	P_{max}	$T_{P,max}$	P_{avg}	$T_{P,avg}$
Emergency	Fast mobilisation	5000 kW	2 h	2000 kW	3 h
Emergency	Emergency operation	10000 kW	18 h	5000 kW	25 h
Stand-by	Mobilisation	3000 kW	20 h	1500 kW	64 h
Stand-by	Stand-by	800 kW	52 h	400 kW	200 h

The Simulink model converts the operational profile parameters to vectors, with each line corresponding to a different average or maximum power level. This enables total fuel consumption and output data to be calculated by summing the elements of each output vector. The fuel cell data input is a table relating power output to (hydrogen) fuel consumption. The reformer data is similar, with produced hydrogen flow related to the reformer efficiency (which will form the basis of the methanol demand flow).

2.2. Electrical system

For the purposes of the specific ships that were reviewed, the following electrical system is assumed. Fuel cell systems provide unregulated DC power, which is converted to DC power with a constant voltage using a DC/DC converter for each unit. This is fed into a DC switchboard, to distribute DC power throughout the ship. Since AC electric motors are assumed, a DC/AC converter is used, feeding into an AC switchboard. From here, the power is converted to the right frequency for the AC electric motors driving the propellers via gearboxes.

The model provides support for different electrical systems with different efficiencies by having variable inputs for each different ship present in the main input files. For the electrical system described above, the total electrical efficiency is used to convert the required propeller power to the required power from the fuel cell outputs:

$$P_{FC} = \frac{P_{prop}}{\eta_{DC/DC} \cdot \eta_{DC/AC} \cdot \eta_{AC/AC} \cdot \eta_{emAC} \cdot \eta_{GB}} \tag{1}$$

2.3. *Fuel cells*

The fuel cell sub model converts the power demand to a hydrogen demand. The fuel cell efficiency can be calculated from this hydrogen demand, the lower heating value of hydrogen and the fuel cell power:

$$\eta_{FC} = \frac{\dot{m}_{\mathrm{H}_2} \cdot LHV_{\mathrm{H}_2}}{P_{FC}} \tag{2}$$

Although the exact relationship differs for different fuel cell systems, fuel cells in general have their most efficient working point at a low power output. Therefore, it is interesting to look at the number of systems that are operational at the same time. For example, if the required system output is 1000 kW, with 2000 kW being installed, a higher efficiency can be achieved by operating all systems at 50% capacity, rather than half of the systems at 100% capacity. The trade-off is the fuel cell lifetime: in the former scenario, the total number of "fuel cell hours" is twice as high as in the latter. With fuel cells having limited lifetime (van Biert et al., 2016), the higher efficiency scenario leads to systems having to be replaced sooner, leading to higher investment costs. However, higher efficiency equates lower fuel consumption, and thus lower fuel costs. Balancing the efficiency and lifetime ultimately comes down to price levels and priorities of the owners and operators. The model can handle different fuel cell system inputs, including low and high temperature PEM fuel cells, the former of which were used in the case studies, as these have a smaller footprint area (van Biert et al., 2016).

The model has a built-in selector for deciding the number of online systems at the same time, which can be modified towards higher efficiency or longer lifetime at wish, or kept variable. The variable mode can be used to calculate the most cost-efficient operational number of fuel cells. In Figure 1 this is used to show the lowest fuel cell (investment) costs and methanol costs if more power is installed than required by the operational profile. It also shows the average efficiency at which the total costs are lowest. The take-away from this particular figure is that with the assumed price points (€800 per tonne of methanol, €2500 per kW fuel cell systems decreasing to €1000 per kW over 30 years), it is not cost efficient to install more power than required. Different price points can be inserted into the model to analyse different cost scenarios.

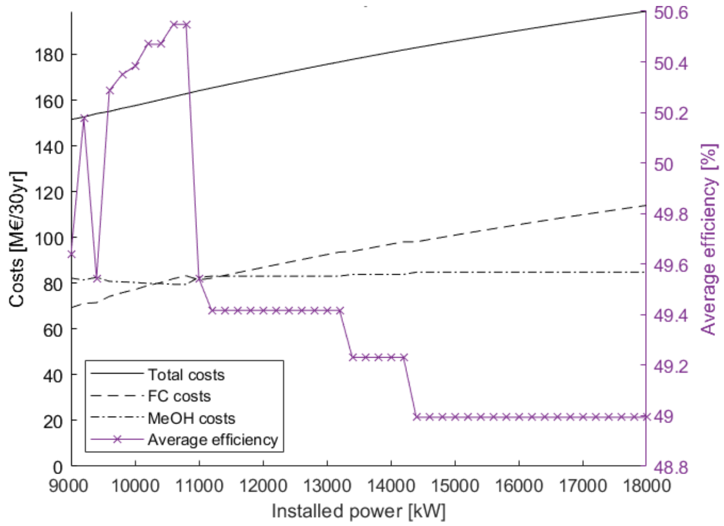

Figure 1: Example of model output showing costs and average efficiency if more power is installed

2.4. *Reformer systems*

The reformer system sub model has as input the hydrogen flow as demanded by the fuel cell system. This is converted to a methanol demand by using the main steam reforming reaction equation:

$$\mathrm{CH_3OH} + \mathrm{H_2O} \leftrightarrows 3\mathrm{H_2} + \mathrm{CO_2} \tag{3}$$

However, besides the main reaction, other reactions occur, including the production of CO. From manufacturer's data it is concluded that the CO levels are low enough for LTPEM fuel cells to operate without the risk of CO poisoning. The same data source provides an efficiency number of 80%, which is assumed constant for every level of hydrogen production, as no other data points were found. Thus, the number of simultaneously operational reformer systems is calculated as the minimum required, each operating at as high a capacity as possible, to reach as few total operational hours as possible. This is analogous to the fuel cell sub model with the balance towards prolonging system lifetime. If reformer systems were used with non-constant efficiency levels, the same trade-offs as in the fuel cell sub model can be made. Besides methanol demand, demand for deionised water and the amount of produced CO_2 by reforming methanol are calculated in this sub model.

2.5. *Fuel consumption*

The amount of methanol and water that are consumed producing hydrogen were calculated in the reformer sub model. These figures can then be converted to figures per trip and per year, by multiplying it with the time vectors based on the operational profile. The figures per trip result in minimum tank size requirements for methanol and deionised water, the figures per year can be used to calculate the amount of methanol that needs to be produced. Additional fuel consumption due to liquefaction of captured CO_2 is not yet taken into account in this model.

2.6. *Emissions and carbon capture*

The reformer CO_2 output can either be captured and stored on board or emitted into the air. Based on the HyMethShip project a capture rate of 97% is assumed (Wermuth et al., 2020). This project is developing a system where membrane reactors are used to reform methanol (where steam reforming and membrane separation of hydrogen and CO_2 happen in a single stage), and subsequently capture CO_2 to be stored on board. The assumed capture rate means that at least 3% of all CO_2 is emitted into the air. The model uses a variable input for CO_2 storage tank size, and if the tank size limits are exceeded the excess CO_2 is also included in the emissions. By analysing this output, this data can be used for design consideration between extra tank space and total CO_2 emissions. In the example vessel, as seen in Figure 2, the extra CO_2 tank space is only required in trips where the emergency fuel reserve is used, and thus installing more CO_2 storage has a relatively minimal effect on the total yearly CO_2 emissions.

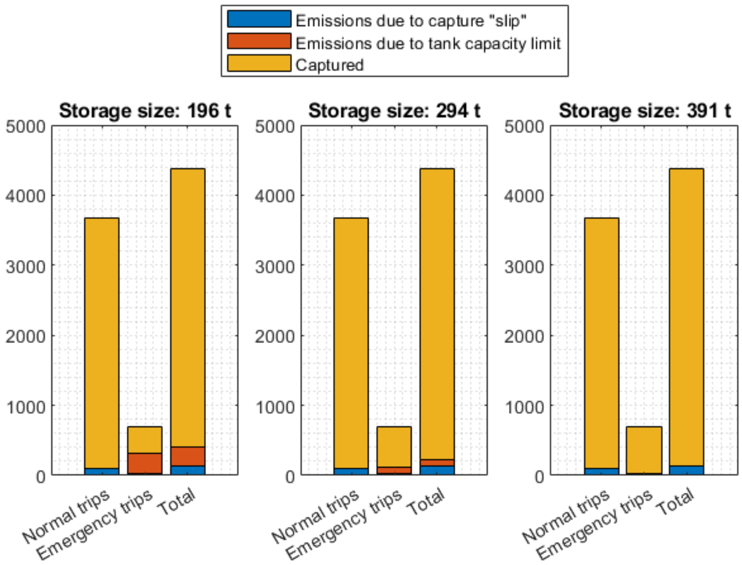

Figure 2: Yearly CO_2-emissions of the EXV for three different CO_2 tank sizes

2.7. *Model limitations*

The model has some limitations. Due to time constraints and lack of system data, the energy consumption of liquefying CO_2 was not included. Battery systems, which can be used to increase fuel cell lifetime by acting as a buffer during severe load changes, are also not considered. Lastly, some aspects of the model are not fully variable, especially when considering ships with very specific operational profiles. However, modifications can be made to accommodate this.

2.8. *Impact on on-board integration*

In the original research, three different ship types were selected as the subject for a case study. The goal of the case study was twofold: to show if the vessels are able to be converted to use methanol, fuel cells and on-board carbon capture, and to calculate the annual CO_2 emissions if such a conversion were to take place. For the former, spatial integration was considered using the general arrangements of the vessels. For the latter, the previously constructed tank-to-propeller emission model was used. The model also provided some insight into the required systems (therefore being used in the integration), including tank sizes and installed power. This paper will not discuss the on-board integration in detail, but general findings will be stated.

It was found that with the current dimensions of fuel cell and reformer systems, it seemed possible to convert the larger vessels (between 50 and 70 metres in length). However, the current requirements for methanol tanks to be outfitted with 900 mm cofferdams (DNV GL, 2020) means that in for example smaller patrol vessels a lot of space is required for fuel storage. Therefore, not enough space is available for the fuel cell and reformer systems. Advances in more compact systems and possible reduction of required cofferdam dimensions could make it viable in the future. Even then, it is probably necessary to install any CO_2 capture and storage systems on deck. In the larger vessels, tank capacities of methanol, deionised water and CO_2 can be sufficiently large for a single trip, although this does mean that bunkering fuel and offloading CO_2 will be required more often than currently.

3. Well-to-propeller emissions

The tank-to-propeller analysis provides a methanol demand and possible availability of recycled CO_2. Methanol production requires both CO2 and hydrogen sources. In order for this methanol to be considered renewable, these feedstocks need to be renewable as well. Since not all CO_2 can be recycled from on-board, additional carbon sources are necessary for methanol production. A well-to-tank analysis is performed for various feedstocks. Together with the tank-to-propeller analysis, this can be used to calculate the total well-to-propeller emissions of a certain fleet. To account for the (CO_2) losses that occur during both methanol production and CO_2 capture on board, some proposals are given to close these gaps.

3.1. Methanol supply

In this project, methanol is produced on-shore as an intermediate carrier of hydrogen, before reforming it back to hydrogen on demand for use in fuel cells. Methanol production itself requires hydrogen and carbon sources. The well-to-tank analysis focuses on the methanol supply part of the whole system, including the conversion of hydrogen into methanol using carbon sources. The potential methanol feedstock sources are constrained by the original scope of the research, but can serve as potential pathways for any user that has these feedstocks available. Three main sources were considered for producing methanol renewably: excess wind energy to produce green hydrogen, waste biomass, and recycled CO_2 from on-board carbon capture. Three possible pathways were identified to produce methanol from the available feedstocks: two pathways using biomass as main carbon source (producing bio-methanol), and one pathway using only recycled CO_2 (producing green methanol). The pathways are visualised in Figure 3. Green methanol can be produced by hydrogenating recycled CO_2, which uses hydrogen that is in turn produced using excess wind energy. As not all CO_2 can be captured on-board, additional CO_2 sources are necessary. If waste biomass is available, this can be directly gasified into bio-methanol (without producing hydrogen). However, if waste biomass is mono-fermented (a process producing biogas), a CO_2 stream is created, which can substitute the recycled CO_2 in the hydrogenation process. As the CO_2 originates from a biomass source, we also call the produced methanol bio-methanol. The production processes are discussed below.

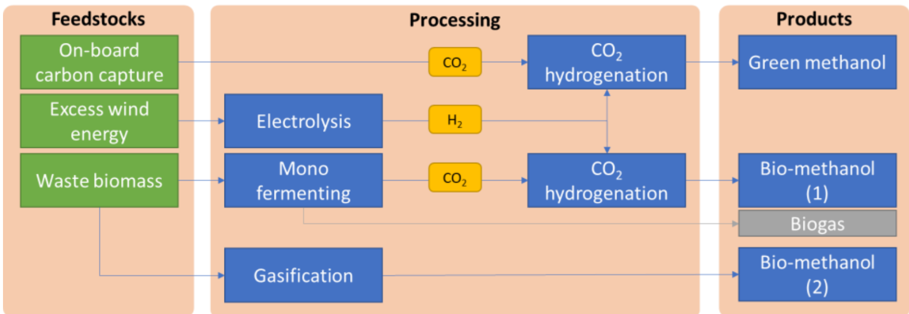

Figure 3: Different pathways to produce renewable methanol

Regardless of the source of CO_2, CO_2 hydrogenation involves the following main chemical reaction:

$$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O \tag{4}$$

Two side reactions also occur, the reverse water gas shift (RWGS) reaction and hydrogenation of carbon monoxide (B. Lee et al., 2020):

$$CO_2 + H_2 \leftrightarrows CO + H_2O \tag{5}$$

$$CO + 2H_2 \leftrightarrows CH_3OH \tag{6}$$

Looking at these reaction equations, it is clear that not all CO_2 is converted to methanol. A standard CO_2 hydrogenation process yield factor is 0.81 (Nieminen et al., 2019), which is defined as the ratio between actual production and theoretical maximum production if all CO_2 could be converted to methanol. Following this ratio, approximately 0.59 tonnes of methanol can be made from every tonne of CO_2.

Biomass gasification involves producing a syngas (consisting of mostly CO and hydrogen, and a smaller amount of CO_2) directly from biomass, which is then synthesised into methanol as follows:

$$CO + 2H_2 \leftrightarrows CH_3OH \tag{7}$$

$$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O \tag{8}$$

The work of Liu et al. (2020) mentions a (dry) mass conversion factor of 0.57, meaning that for every tonne of dry biomass, 0.57 tonnes of methanol can be produced.

If CO_2 is recycled using on-board carbon capture, it is considered a carbon neutral feedstock for methanol synthesis in this research, as this stays within the system. CO_2 stemming from biomass is considered carbon negative, as it is extracted from a process where it would otherwise be emitted into the air and subsequently introduced into the system from outside. Any carbon-negative CO_2 entering the system this way can compensate CO_2 emissions elsewhere in the system. The result would be a neutral CO_2 balance with net zero emissions.

3.2. Total CO_2 cycle

In the original research, given the feedstock availability and assumptions made in future technological advancements, a reduction of 82% of well-to-propeller CO_2 emissions could be achieved. A diagram showing the lifecycle of all CO_2 sources and emissions (not to scale) that were included in this study is found in Figure 4. Here, it becomes apparent that CO_2 losses in any part of the system lead to both emissions and a production gap. Net zero CO_2 emissions can be achieved multiple ways: either by reducing the losses, or by introducing an alternative negative CO_2 source. Regarding the former, production losses could be reduced by performing carbon capture during methanol synthesis (which is outside the scope of this project), and exhaust losses could be reduced by increasing the capture rate on board of the fleet. Since part of the CO_2 source is considered carbon negative, these losses do not need to be eliminated completely in order to reach carbon neutrality: total losses equal to the amount of "carbon-negative" CO_2 (the biomass-derived CO_2) are allowed, although alternative CO_2 sources would still be needed to overcome the production gap. In this regard, reducing emissions even further would allow for the fleet to sail carbon negative.

If the aforementioned losses can not be reduced enough, there are still options to reach carbon neutral operation. Since a production gap exists in the case of net positive CO_2 emissions, additional CO_2 is necessary. If this CO_2 is derived from a carbon neutral source (e.g., an increased waste biomass source or Direct Air Capture), this essentially connects the emitted CO_2 with the production input, thereby closing the CO_2 system again, and reaching net zero CO_2 emissions. However, this would also increase the required wind derived electricity.

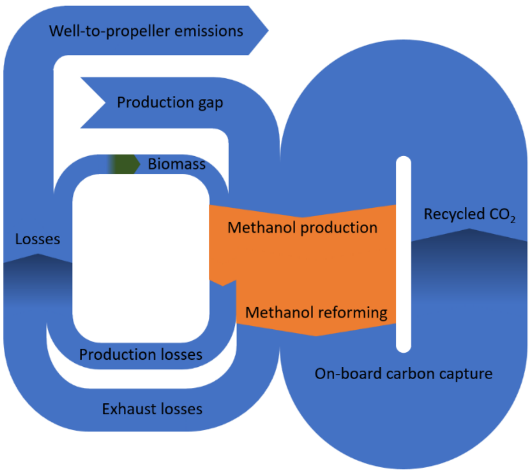

Figure 4: Total CO_2 cycle (not to scale)

4. Conclusion

In conclusion, it is possible to use a combination of fuel cells, reformers, and on-board carbon capture to reduce the overall well-to-tank emissions of a certain ship or fleet. Within the scope of the original research, a reduction of 82% well-to-propeller CO_2 emissions was projected. In a general sense the possible reduction is constrained not only by the vessel characteristics and operational profiles, but also by feedstock availability and technological advancements, especially regarding on-board carbon capture. However, even considering the assumptions made in this research, additional measures are necessary in order to reach net zero CO_2 emissions. This can be achieved by either reducing the emissions during methanol synthesis and on board, or by introducing another carbon negative CO_2 source such as from additional waste biomass or from Direct Air Capture.

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