Application of HyMethShip Propulsion using On-board Pre-combustion Carbon Capture for Waterborne Transport

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Abstract
The HyMethShip project (Hydrogen-Methanol Ship propulsion using on-board pre-combustion carbon capture) is a cooperative R&D project funded by the European Union’s Horizon 2020 research and innovation program. The project aims to drastically reduce emissions while improving the efficiency of waterborne transport. The HyMethShip system will achieve a reduction in CO₂ of up to 97% and practically eliminate SOx and particulate matter emissions. NOx emissions will fall by over 80 %, safely below the IMO Tier III limit. In this study the HyMethShip concept is introduced and various aspects of the concept development are discussed. Additionally, some issues that might accelerate or hinder the concept application for commercial shipping are presented.

Keywords: Phytochemistry; UPLC-MS; Helleborus Caucasicus; Helleborus Abchasicus.

1. Introduction

Transoceanic shipping is very important for international trade and has high energy efficiency per ton and mile. Much of the transport work occurs close to land and densely populated areas. Emissions of sulfur oxides (SO₃), nitrogen oxides (NOₓ) and Particulate Matter (PM) from shipping have been identified as having a negative impact on health and the environment. Regulations of maritime emissions have been introduced, albeit ones that are less demanding and come into effect much later than those for land-based transport. In 2017 less than 3 % of global CO₂ emissions were attributed to shipping (Figure 1). Due to the efforts in other sectors to reduce CO₂ emissions and the projected growth of global shipping, the contribution of maritime transport to global CO₂ emissions is going to increase significantly. Therefore, the reduction of CO₂ emissions from shipping is becoming an area of interest for various legislative bodies. The EU “White Paper on Transport” from 2011 sets the goal of a 40 % reduction in CO₂ emissions from EU maritime transport in 2050 compared to 2005 [1]. The International Maritime Organization (IMO) adopted a resolution in April 2018 to reduce greenhouse gas emissions by at least 50 % by 2050 compared to 2008 [2]. In order to meet these goals, there is a need to consider new fuels, e.g. natural gas, methanol, hydrogen, ammonia, and innovative technology solutions, like electric propulsion combined with battery storage or fuel cells.

While liquefied natural gas is already used in commercial shipping operations but often seen critical because of the high global warming potential of methane, other alternative fuels, like methanol or hydrogen, are only rarely

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encountered in commercial vessels (e.g. [4]). There are, however, various pilot vessel projects in progress that utilize methanol as the main fuel source and evaluate engine combustion as well as methanol bunkering and storage options [5-9]. Using methanol in engine combustion requires energy intensive post-combustion carbon capture or direct air capture (DAC) in order to significantly reduce CO₂ emissions. Hydrogen combustion does not produce any CO₂ emissions but bunkering and storage on-board the vessel poses various challenges.

**Figure 1. Emissions and development of global transport [3]**

The HyMethShip concept combines the advantages of bunkering the liquid fuel methanol and combusting the carbon-free fuel hydrogen. Using this concept, the HyMethShip project aims to drastically reduce emissions and improve the efficiency of waterborne transport at the same time. Compared to the next best available marine engine technology, i.e. methanol combustion and post-combustion carbon capture, the HyMethShip system is estimated to show more than 40 % higher system efficiency [10]. The HyMethShip system targets a reduction in CO₂ emissions of more than 97 % and will practically eliminate SOₓ and PM emissions. NOₓ emissions will be reduced by more than 80 %, significantly below the IMO Tier III limit.

This article will give an overview of the HyMethShip technical concept, discuss several concept development considerations and outline where interfaces with port infrastructure and rules and regulations demand additional coordination and harmonization. More information on the scope and organization of the project can be found on the project website https://www.hymethship.com/.

### 2. HyMethShip Concept and Project Overview

The HyMethShip concept uses on-board methanol steam reforming with a strong interaction of hydrogen fuel production and hydrogen consumption. The HyMethShip system innovatively combines a membrane reactor, a CO₂ capture system, a storage system for CO₂ and methanol as well as a hydrogen-fueled combustion engine into one system (Figure 2). The hydrogen produced from methanol reforming is burned in a conventional reciprocating engine that has been upgraded to burn multiple fuel types and is specially optimized for hydrogen use.

The HyMethShip system eliminates the need for complex exhaust gas aftertreatment, which is required for conventional fuel systems to achieve equivalent reductions in SOₓ, NOₓ, and PM emissions. The drastic CO₂ reduction is a result of using renewable methanol as the energy carrier and implementing pre-combustion CO₂ capture and storage on the ship. Ideally the renewable methanol bunkered on the ship is produced on-shore from CO₂ captured on-board or from DAC, thus closing the CO₂ loop from the ship propulsion. Bunkering and storing of large quantities of hydrogen fuel can be avoided.

HyMethShip’s overall efficiency entitlement is estimated to be approx. 51% as outlined in Figure 3:

- Methanol bunkered on-board of the vessel and steam are reformed to hydrogen using waste heat from the engine;
- During the reforming process thermal dissociation of water at high process temperatures inside the membrane reformer produces additional hydrogen molecules, resulting in a surplus energy of more than 12 percentage points (CH₃OH + H₂O → CO₂ + 3 H₂);
- The combustion engine operating with an estimated efficiency of 47% generates losses in the range of 60 percentage points based on total hydrogen energy content. About 75% of the engine’s waste heat is used to provide the process temperatures required by the carbon capturing system;
- Due to the methanol reformation the fuel energy available for engine combustion is higher than the methanol energy content that could be used for direct methanol combustion.
Two percentage points of the generated mechanical energy are used to produce electricity for the pumps and auxiliary devices in the carbon capture system.

Within the HyMethShip project the key technology components will be developed and build and tested individually in specifically designed laboratory facilities. The carbon-based membranes, a small-scale membrane reformer and a small-scale carbon capture system will be built early in the project. In parallel the combustion system development will take place using a high-speed single-cylinder research engine. Later the combined system, consisting of full-scale membrane reformer, multi-cylinder engine and full-scale carbon capture system will be validated in an on-shore technology demonstration with an engine in the range of 1 to 2 MW.

The implementation of the propulsion system and the fuel and CO₂ storage systems in a vessel is performed via computer modeling of a use case vessel – a ferry operating in the North Sea / Baltic Sea. The requirements for the implementation as well as for the design of all subsystems are driven by safety regulations and emission legislation. Alternative energy carriers, such as hydrogen and methanol are relatively new to the marine industry and as such specific maritime regulations do not presently exist or are undergoing deliberations at the IMO. Therefore, the HyMethShip project will undertake risk and safety assessments to ensure that the system fulfills all safety requirements for on-board use. It will also take into account the rules and regulations under development for low flashpoint fuels and is expected to contribute to regulatory development in this area. The cost effectiveness of the
system will also be assessed for different ship types and operational patterns using life cycle assessment. A preliminary assessment of environmental and economic impact of various design choices within HyMethShip can be found in [11].

3. HyMethShip Concept Development

3.1. Engine Type and Combustion Concept

The propulsion system of the HyMethShip concept employs a reciprocating internal combustion engine that is already state-of-the-art for marine applications. The engine has to fulfill output power and transient requirements, exhaust emission limits, and safety requirements and needs to interact with the reformer and carbon capture system. For international marine applications the emission limitations contained in the “International Convention on the Prevention of Pollution from Ships” apply. MARPOL Annex VI sets limits on NO emissions with the Tier II / III standards that were introduced in 2008 [12, 13]. NO\textsubscript{x} emission limits are set depending on the engine maximum operating speed. While Tier II limits apply globally, Tier III standards only apply in NO\textsubscript{x} Emission Control Areas (ECA). HyMethShip will fulfill the more stringent NO\textsubscript{x} limits for ECA and target duty cycle NO\textsubscript{x} emissions of less than 2.0 g/kWh. Engine waste heat, particularly from the exhaust gas, will be used for the methanol steam reforming process, adding further demands on the combustion system development. Mixture stoichiometry, compression ratio and combustion phasing will have to be adjusted in order to provide adequate exhaust enthalpy to the reformer. The main energy source for the engine will be hydrogen generated by the methanol reformer but in order to fulfill the redundancy requirements (see Chapter 4.3) the system will be designed to allow operation with a conventional liquid as well. This operating mode can also satisfy vessel power demand during start-up / warm-up of the reformer and the CO\textsubscript{2} capture system.

Currently existing dual-fuel engines for marine propulsion use natural gas as the main fuel source and also allow engine operation with diesel combustion. HyMethShip can employ a similar concept with diesel back-up operation and standard hydrogen operation with diesel pilot ignition. In the latter hydrogen is injected into the intake ports or directly into the cylinder during the intake stroke or early in the compression stroke. A small amount of diesel fuel is injected into the cylinder late in the compression stroke and auto-ignites due to high temperatures of the hydrogen-air mixture. From the ignition centers a flame propagates through the combustion chamber consuming the homogenous hydrogen-air mixture. The diesel fuel fraction depends on the operating conditions and varies between 1 and 5 % in steady-state operation. In order to reliably inject these small quantities of fuel medium speed engines incorporate a pilot injector in addition to the main diesel injector, while for high speed engines wide-range injectors are in development [14].

The HyMethShip concept will also allow to utilize a different kind of dual-fuel engine where methanol combustion is used for redundancy. In that case a spark ignition system will be used for hydrogen as well as for methanol combustion. In steady-state hydrogen operation no second fuel is required. There are advantages and drawbacks for both back-up fuel options (Table 1).

Table 1. Methanol vs. diesel back-up operation

| Application | Methanol back-up | Diesel back-up |
|-------------|-----------------|---------------|
| Advantages  | Only methanol tanks required on vessel | Transient capability limited by soot and turbocharger acceleration only to faster transients are possible in diesel operation compared to hydrogen and/or methanol operation |
|            | Transient / maneuvering with methanol fueling with lower (soot) emissions |  |
|            | Lower compression ratio expected to widen operating window and improve performance |  |
|            | Lower emissions in nearly all operating conditions |  |
| Drawbacks  | Transient capability limited by knocking combustion | Methanol and diesel tanks required on vessel & logistic in harbor more difficult |
|            | Energy storage system might be required to address transient power requirements | Compression ratio will have to be a compromise for hydrogen and diesel back-up operation |
|            | Formaldehyde emissions from methanol combustion might require an oxidation catalyst (to be determined) |  |

The advantages of a concept using methanol combustion for redundancy instead of diesel combustion lie in reduced emissions of NO\textsubscript{x}, SO\textsubscript{2} and particulate matter and potentially reduced tank space requirements since no bunkering of diesel is required. The drawbacks could be reduced transient capabilities if knocking combustion occurs and the fact that methanol combustion is not considered an established technology in maritime applications yet and ship operators might be hesitant to accept this new technology. Vessel power requirements, operational patterns and available space will determine which back-up fuel will finally be selected.
The combustion system development for HyMethShip is performed using a single-cylinder research engine before the combustion system will be employed in the full-scale engine in the technology demonstration. The single-cylinder engine operation is investigated with hydrogen, methanol and methanol/hydrogen fuel mixtures [15]. Methanol / hydrogen mixtures are considered in order to evaluate the potential of methanol addition for improved transient performance. Figure 4 illustrates the operating ranges (characterized by ignition timing and boost pressure) for various engine load conditions with either hydrogen or methanol fueling. The methanol operation is shown in the shaded area. Boost pressure requirements for medium load hydrogen operation and high load methanol operation are very similar. Therefore, switching from hydrogen to methanol fueling at a constant boost pressure results in an increase in engine load, et vice versa. This behavior can be exploited if insufficient hydrogen is available during fast load increases or when turbocharger acceleration is limiting a fast boost pressure increase. The engine operating strategy will be finalized in conjunction with the other components of the propulsion system.

3.2. Methanol and CO\textsubscript{2} Tank System

In the HyMethShip concept the CO\textsubscript{2} that is produced on-board the vessel during the methanol steam reforming will be captured, liquefied, stored on-board and discharged in port. The vessel therefore needs to provide storage capacity for liquid carbon dioxide (LCO2) as well as for the energy carrier methanol. Methanol can be stored on-board in tanks similar to the conventional HFO/diesel tanks, although the different corrosion behavior needs to be taken into consideration. Since the flash point of methanol lies below 60 °C, however, compliance with the IGF code [16] is mandatory. CO\textsubscript{2} can be stored in a liquid state at approximately 40 °C and 1 MPa in cryogenic pressure tanks, which is common practice for ships that carry CO\textsubscript{2} as cargo. Since CO\textsubscript{2} is produced at roughly the same pace that methanol is consumed and since storage space in some vessels and applications is scarce it might be desirable to use the same storage space for methanol and CO\textsubscript{2}. This bivalent solution is explored in a modular approach with tanks that carry methanol and CO\textsubscript{2} alternatingly ("B"), a tank that only carries methanol ("A") and a tank that only carries CO\textsubscript{2} ("C").

Figure 5 illustrates the combined tank system and indicates the fluid streams into and out of the tanks during continuous operation of the HyMethShip system when methanol is consumed, LCO2 is produced and gaseous CO\textsubscript{2} needs to be evacuated from or replenished in at least one of the tanks. This system uses components currently available on the market, thereby enhancing the economic feasibility of implementing the system.
A typical full operational cycle for a vessel and its tank system is consisting of the following process steps:

1. Tank preparation for methanol bunkering;
2. Loading of methanol into Tank(s) B and Tank A;
3. Continuous operation with methanol consumption and CO2 production;
4. Tank(s) B preparation for CO2 filling;
5. Discharging CO2 in the bunker port.

Each step has its own specificities and particular set of requirements for the tank system. A feasibility study for a combined storage system is performed for all process steps during a full operation cycle and compared to a separate tank solution. Table 2 summarizes the potential complications of a combined tank solution and the mitigation measures that can be taken to avoid these complications.

| Process step                                      | Potential complication                              | Mitigation and/or resulting system and operational requirements                                                                 | Feasible with state-of-the-art technology |
|--------------------------------------------------|-----------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------|------------------------------------------|
| Tank preparation for methanol bunkering          | Flashing of LCO2                                    | Tank pressure control                                                                                                            | Yes                                      |
| Tank preparation for methanol bunkering          | Thermal shock of Tank(s) B inner vessels            | Tank heating by means of ambient temperature gaseous CO2                                                                       | Yes                                      |
| Loading of methanol in Tank B                    | CO2 vapor return to bunker barge not feasible        | Sizing of absorption chiller for peak demand during bunkering; Adjust engine / system operation to meet heat demand of absorption chiller during bunkering | Yes                                      |
| Tank preparation for LCO2 filling                | CO2 contamination of remainder of methanol pumped out of Tank(s) B | Transfer remainder of methanol to separate tank or Tank A                                                                         | Yes                                      |
| Discharging LCO2 in bunker port                  | Duration for discharging prolonging stay in port    | Develop procedures for simultaneous LCO2 discharging and methanol bunkering                                                          | Yes                                      |
| Discharging LCO2 in bunker port                  | Purity requirements of LCO2 grid / reception facility not met | Storage of contaminated LCO2 layers in separate tank instead of discharge (if necessary); Monitor LCO2 purity requirement discussions | Yes                                      |

Although the complications caused by alternating the product to be stored will require extra investment, a higher skilled crew and higher operational costs, there are technical solutions to all issues identified in the feasibility study, leading to the conclusion that the carrying of CO2 and methanol in the same tanks alternatingly is feasible.

### 3.3. Propulsion System

The propulsion system of a vessel cannot be designed independently of the vessel. The available space, legislative requirements regarding the placement of various types of equipment and the allocation of equipment to spaces with various levels of containment protection have to be taken into account. A 3D CAD model of the case study vessel – a ferry operating in the North Sea / Baltic Sea - was developed for visualization and incorporation of system components (Figure 6).
The layout of the vessel propulsion system has to consider steady-state as well as transient performance requirements. The transient performance of the HyMethShip concept is determined by the transient performance of the individual system components – combustion engine, reformer and carbon capture system – and by the interaction between the sub-systems. A high transient capability of the combustion engine is insufficient if the reformer is incapable of delivering the required increase in hydrogen mass flow rate. In an early performance assessment, the transient vessel power requirements are defined for the use case vessel. Figure 7 illustrates the duty cycle of the selected ferry application with a histogram showing how much time the propulsion system operates in the individual load ranges during the selected journey.

![Histogram for engine load on diesel mechanic reference ship](image)

**Figure 7. Case study vessel load spectrum**

A methodology will be developed to assess the transient capability of the HyMethShip concept and evaluate various options for increased transient performance, e.g. buffer batteries, hydrogen buffers and combustion of methanol / hydrogen mixtures. Initial calculations suggest that the concept will best be designed as a hybrid system with full electric propulsion and the combustion engines driving generators. The preliminary size of the battery pack is in the range of 1 to 1.5 MWh. It should be noted that it is rather uncertain if a newly built RoPax will be designed in a similar way as current ones – in view of a probable shortage of fuel with low greenhouse gas emissions it is rather likely that new designs and their operation will have to be made to have significantly lower installed power to use less energy. Since the goal of this project is not to design a new type of ship, but rather a new energy system, current modern designs are used to evaluate the effects of integrating the HyMethShip system. This also reduces the uncertainties since design starts with a known and built systems and modifies it where necessary.

### 4. HyMethShip Transfer from the Lab into the Real World

Before the HyMethShip concept can be used in standard shipping applications there are a number of issues that need to be addressed, including port infrastructures or rules and regulations, but cannot be solved within the project. It is one goal of the project to highlight and evaluate these issues and also work with authorities or classification societies to define a feasible path forward.

#### 4.1. Fuel Supply

For low well-to-wake emissions and a closed CO₂ lifecycle, it is desired that methanol is produced with recycled CO₂, e.g. from HyMethShip, and renewable power. Although the technology for renewable methanol production exists, nowadays the bulk of methanol produced world-wide uses natural gas as a feedstock. Shipping of methanol as cargo is ubiquitous but methanol bunkering as a propulsion fuel is not standard in ports and procedures for safe operation are in development. Methanol bunkering barges are currently not available in most ports making implementation of HyMethShip most likely in applications where the vessel can return to the home port for bunkering.
4.2. CO₂ Discharge

Discharging CO₂ requires that there are CO₂ receptables available in port and preferably even a CO₂ grid that connects the port facilities to methanol production facilities or other industries that use CO₂. This infrastructure is currently not available and therefore assumptions have to be made for the grid specifications, including pressure and temperature, which impact the tank system capabilities of HyMethShip. Furthermore, the possibility to discharge gaseous CO₂ that is released from the tanks during the bunkering procedure needs to be evaluated and taken into account during the tank system design.

4.3. Rules and Regulations

Even more than other industrial installations maritime applications have to adhere to high safety standards. There is, however, no set of rules and regulations available that covers all aspects of HyMethShip for maritime use. In particular the use of methanol and hydrogen as an engine fuel is not covered specifically in any guidelines.

Some guidance can be provided by the IGF Code “International Code of Safety for Ships Using Gases or Other Low-Flashpoint Fuels” [16], that defines international standards for vessels not covered by the IGC Code [17] and by the “Draft Interim Guidelines for the Safety of Ships Using Methyl/Ethyl Alcohol as Fuel” that was published in 2018 [18]. The IGF code is geared to meet the requirements for natural gas as fuel and provides mandatory provisions for the arrangement, installation, control and monitoring of machinery, equipment and systems using low-flashpoint fuel to minimize the risk to the ship, its crew and the environment. Other safety requirements for marine engines (EN 1679-1:1998), machinery (ISO 12100) or pressure vessels (Directive 97/23/EC) are not applicable to hydrogen operation or specifically exclude maritime applications from their scope. In order to guarantee a safe design of HyMethShip and compliance with the functional requirements of the IGF Code risk-based techniques are used in hazard identification and hazard and operability studies. Insights of these studies can also be used to improve the new guidelines being crafted over the next years.

The IGF Code demands redundancy of fuel supply and specifies that fuel supply systems shall be arranged with full redundancy and segregation all the way from the fuel tanks to the consumer, so that a leakage in one system does not lead to an unacceptable loss of power of the vessel. The HyMethShip system will fulfill the redundancy requirements by allowing the engines to operate on a conventional liquid fuel that is supplied directly from the tank to the engines.

Last but not least the acceptance of the HyMethShip concept for commercial shipping will depend on economic feasibility. The advantage of near-zero greenhouse gas emissions comes at the cost of increased system complexity. Any future regulation putting a price on carbon dioxide will directly impact the life cycle cost comparison with conventional propulsion systems [11] and therefore the economic viability of HyMethShip.

5. Conclusion

The HyMethShip concept combines the advantages of bunkering and storing the liquid fuel methanol on-board the vessel and burning the carbon-free fuel hydrogen in an internal combustion engine that is a well proven technology in maritime applications. The proposed system has the potential to drastically reduce greenhouse gas emissions as well as pollutant emissions of ship propulsion systems. The combustion of hydrogen and methanol was validated in a single-cylinder research engine. The final combustion system design will depend on the particular vessel requirements, like transient performance or space considerations, and can incorporate a diesel-type or a gas-type combustion engine. The feasibility of a combined tank system for methanol and CO₂ was evaluated and the tank system design as well as the propulsion system design are on-going. The uptake of the concept in commercial operations will not only depend on the system capability but also on port infrastructure, methanol production as well as future regulations.

6. Nomenclature

| Abbreviation | Description |
|--------------|-------------|
| CAD          | Computer-Aided Design |
| DAC          | Direct Air Capture |
| HFO          | Heavy Fuel Oil |
| LCO₂         | Liquid carbon dioxide |
| NOₓ          | Nitrogen oxides |
| RoPax        | Roll on / roll off / passenger vessel |
| SO₂          | Sulfur oxides |
| CO₂          | Carbon dioxide |
| ECA          | Emission Control Areas |
| IMO          | International Maritime Organization |
| MCR          | Maximum Continuous Rating |
| PM           | Particulate Matter |

* This document is now finalized and was approved by IMO in November 2002 during MSC102.
7. Declarations

7.1. Data Availability Statement

The data presented in this study are available on request from the corresponding author.

7.2. Funding

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7.3. Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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