



Scaling Down the Outflow of GHG Emission in Maritime Industry

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Abstract

This paper has described the methodologies used for reduction in greenhouse gases like carbon dioxide [CO₂], methane [CH₄], nitrogen [NO_x] etc. Also, it covers the technologies used all over the globe to capture the carbon [C], which is a major component of greenhouse gases. Moreover, this paper had also elaborated regarding the sustainable marine fuels like the hydrogen [H₂] fuel cells and ammonia [NH₃] as a marine fuel considering its specific energy (amount of energy present per unit mass of fuel expressed in MJ/kg) and energy density (amount of energy present per unit volume of fuel usually expressed in MJ/L), also the various types of biofuels like biodiesel, ethanol (C₂H₆O), E85 [combination of ethanol (C₂H₆O) and gasoline]. Overall, this paper will explain the feasibilities for the reduction of greenhouse gasses emission for the sustainable environment for the future generation. United Nation, European union and other countries has suggested steps to resolve the greenhouse gasses emission, and these steps are briefly elaborated in this paper. At the end this paper will conclude itself by the most feasible means of fuel sources in both environment and economic sustainability in the maritime industry.

1. Introduction

As per the data, the annual air temperature of the globe has increased by 0.3°C to 0.6°C since 1900's. This is due to the trapping of terrestrial radiation by greenhouse gases like CO₂, NO_x etc. The contribution of CO₂ in GHG is 60-65% and it has been said that it may rise by 2°C by the year 2100. That is why the problem of climate change is addressed by the United Nations Framework Convention on Climate Change [UNFCCC] and is majorly recognized as a serious potential threat to the Earth's environment and biodiversity. With the aim of reducing greenhouse gases emissions, many

countries, associations and companies work on different technologies to replace the use of fossil fuels. With the IMO's common ambition to reach net-zero emissions by 2050, the maritime industry is expected to have major shift in fuel usage instead of HFO. The Shipping Industry contributes to about 3% of the total global GHG Emissions. For most of the period in modern shipping, HFO had been used as the primary fuel thanks to its low cost (around 400\$-600\$/ton) and higher energy density (40 MJ/Kg) compared to other fuels [5],[6]. As there is a push for the GHG reductions, alternative fuels

such as hydrogen and ammonia [NH₃], even the biofuel blends like biodiesel, ethanol, methanol, E85 and E10 etc. are being developed for use as fuel in maritime industry. Other methods include CCS [carbon, capture and storage], which captures the carbon from the fuel exhaust, then treated followed by its storage. To control climate change, ammonia [NH₃] can be a good option used as a marine fuel because it is a zero-carbon fuel and is renewable that makes it a support of the energy transition and it has a high energy density, and the cost is low to produce NH₃. [1-5]

2. Carbon, Capture and Storage

As per the data, around 15-35 grams of CO₂ is emitted every kilometer by the ships when she travels. For a reference, a container ship sailing from Port of Singapore to Sharjah Port, it will emit 294 kg CO₂ [per TEU], which directly contributed to GHG. [9]

2.1. Carbon Capturing and Storage

As carbon emissions are inevitable despite efforts to decrease, an alternative viable option is present which allows the carbon to be captured before it enters the atmosphere. By this way, the shipping industry could achieve NET ZERO EMISSIONS. There are two ways to capture carbon dioxide (CO₂),

- Pre-Combustion.
- After Combustion.

2.2. Pre-Combustion

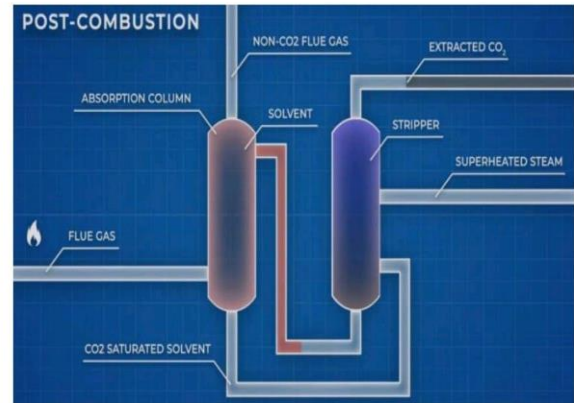
In pre-combustion, the fossil fuel is heated in pure oxygen [O₂], resulting in a mix of carbon monoxide [CO] and hydrogen [H₂]. The carbon monoxide [CO] is reacted with water to produce carbon dioxide [CO₂], which is captured along with hydrogen [H₂]. This extracted hydrogen [H₂] can be compressed and used for generating electricity on board a vessel and then carbon dioxide [CO₂] is stored.

2.3. After Combustion

The flue gas consisting of CO₂, water vapour, SO_x & NO_x) is passed. Once the column is saturated, a superheated steam at around 120°C passes, which releases the trapped CO₂ and then the remaining gases are treated and sent away. The CO₂ is then stored. With these methods 70-90% of carbon emissions could be prevented from entering the atmosphere. The captured CO₂ could be stored at liquid state with density of 1101 kg/m³ at -37°C as storing in solid state would need to be in -78°C with

density of 1562kg/m³. The captured CO₂ to be stored in series of pressurized cylinders which can be placed in consecutive double bottom tanks thereby utilizing space and helps in increasing the GM (Transverse metacentre) of the vessel. Figure 1 shows Post-Combustion.

Illustration 2: -



Reference: <https://www.energy.gov/fecm/pre-combustion-carbon-capture-research>

Figure 1 Post-Combustion

3. Hydrogen [H₂] As Fuel

Hydrogen is of different types: Grey, Blue, Green, Brown. Grey hydrogen is obtained from Steam Methane Reforming (SMR), while Blue Hydrogen is also obtained the same way, but the carbon produced is captured and stored. Green Hydrogen is obtained by the electrolysis of water by means of renewable energy, which means that in this process carbon dioxide is not produced. Hydrogen as a fuel has higher specific energy compared to other major fossil fuels such as Petrol, Diesel, HFO, Biofuels, etc. with the value of 141.86 MJ/Kg which is 3-4 times higher than other fuels. But hydrogen has a very lower energy density of 10.044 MJ/L in liquid state, which is to be stored at temperatures about -253°C with storage density of 70.85 Kg/m³. While at 69MPa and 681 atm it will have an energy density of 5.323 MJ/L. At this stage it has a storage density of around 38 kg/m³, which means 38kgs of fuel to be accommodated in a 1000L water tank. This is the feasible means of storage for transportation of the fuel as it is not economically and environmentally sustainable to store it in liquid state. Grey hydrogen is currently the most produced as it is commercially viable. But Green hydrogen could be produced onboard with the help of renewable sources of energy such as solar power, which if installed onboard shall

generate electricity to undergo electrolysis process of water, which will break down into hydrogen and oxygen atoms. This hydrogen could be directly used obtain oxygen, which could then be sent to the Main Engine for propulsion, which will help in the capturing of pure carbon dioxide which was described in the Pre-combustion process of Carbon Capture and Storage.

4. Case Study

The Toyota Mirai second-generation variant, a Hydrogen powered car, manufactured and marketed by Toyota, gives a range of 500 kms. It consists of 3 cylindrical tanks with a total volume of 141 litres.

for powering the vessel with electricity by means of fuel cells. The solar power could directly power the vessel with electricity, but with electrolysis, we also It totally weighs 87.5 Kg can hold 5.65 kgs of Hydrogen at 700 bars or 10,000 MPa [1]. As electrolyte technology develops further in fuel cells such as the PEM (Proton Exchange Membrane) Electrolysis, which uses a rigid membrane as electrolyte, the efficiency and purity could be further increased from the existing Alkaline electrolysis method, while also decreasing cost of H2 [9]. Table 1 shows Capacity of Tanks.

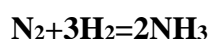
Table 1 Capacity of Tanks

FOR TANKS WITH 70 Mpa								
INTERNAL VOLUME	L	64.9	52	25.3	230	202	176	458.5
TANK MASS	kg	43	36.7	22.6	136	118	100.9	243.8
HYDROGEN STORAGE CAPACITY	kg	2.6	2.1	1	9.4	8.2	7.2	18.8
TANK TO FUEL WEIGHT RATIO		16.5	17.4	22.6	14.46	14.39	14.01	12.96
RANGE 12.96-22.6								
S.E/E.D RATIO		24.9	24.7	25.3	24.46	24.6	24.4	24.3
RANGE 24.3-25.3								
*[Various scales of hydrogen tank with 70MPa capacity. With the Tank to Fuel weight ratio, and Specific Energy to Energy Density ratio (S.E/E.D), it could be concluded that the lower the value, more efficient it is, also considering ship's carrying capacity]								

Reference : <https://www.toyota.co.jp>

5. Ammonia [NH3] As a Fuel

Ammonia (NH3) is a chemical compound which is mainly used for manufacturing fertilizers such as ammonium nitrate, urea, and ammonium sulfate, but also being developed as a source of fuel for transportation. It has lesser energy density and specific energy than Hydrogen, with the value of 11.5 MJ/L and 18.6 MJ/Kg respectively. But it does not produce greenhouse gas as it does not contain the carbon atom and is also stable compared to Hydrogen as it has a boiling point of -33.34°C which is far more compared to Hydrogen, so it requires less energy to be stored in its liquid form (-35°C) Ammonia is produced from Haber’s Process which involves the capture of Hydrogen and Nitrogen and produced because of this combination.



So, Ammonia should be relatively costlier than Hydrogen fuel considering capturing both Hydrogen and Nitrogen, but it is still less expensive than Hydrogen as the transportation and storage cost of Hydrogen outweighs the production and storage costs of Ammonia. A ton of Ammonia costs 600\$ to 800\$ per ton while in comparison to Hydrogen’s 3\$ to 8\$ per kg i.e. minimum of 2000\$ to 3000\$ per ton. Table 2 shows Specific Energies and Energy Densities of Selected Fuels. emerging as a promising alternative fuel due to its carbon-free combustion and potential for large-scale energy storage. With an energy density of approximately 18.6 MJ/kg, it can serve as an efficient hydrogen carrier while leveraging existing infrastructure with minimal modifications. Unlike conventional fossil fuels, ammonia burns without emitting CO2,

making it a sustainable option for reducing greenhouse gas emissions. It can be produced through the traditional Haber-Bosch process or via green methods using renewable energy. Despite

challenges like high ignition temperature and NO_x emissions, advancements in combustion technology and catalysts are making ammonia a viable.

Table 2: Specific Energies and Energy Densities of Selected Fuels

FUELS	SPECIFIC ENERGY (MJ/kg)	ENERGY DENSITY MJ/L
LIQUID HYDROGEN	141.86	10.044
HYDROGEN GAS (69 Mpa @ 25°C)	141.86	5.323
HYDROGEN GAS (1 atm)	141.86	0.01188
PETROL	46.4	34.2
DIESEL	45.6	38.6
ETHANOL	30	24
E85	33.1	25.65
E10	43.54	33.18
METHANOL	19.7	15.6
LIQUID AMMONIA	18.6	11.5
LNG (-160°C)	53.6	22.2
BIODIESEL OIL	42.2	33

*[The above mentioned values are given against Higher Heating Value (HHV) and the values vary with testing conditions]

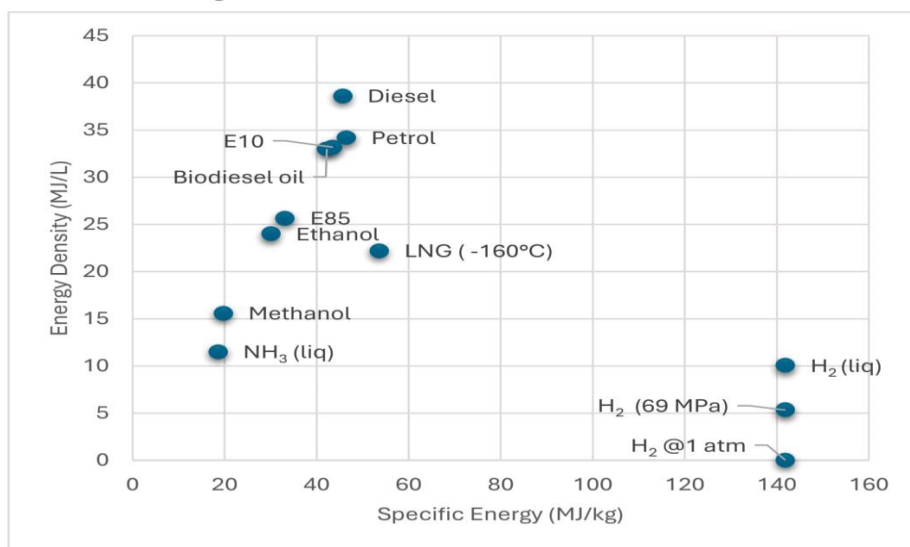
Reference : https://www.engineeringtoolbox.com/fossil-fuels-energy-content-d_1298.html

6. Biofuels as Marine Fuel

Biofuels are fuels obtained from fermentation of Bio products such as corn, sugarcane, and other biowastes by mainly using yeast and other processes. Biofuels are now widely used in transportation in many countries including The United States, Brazil, European Union in blend with other petroleum products such as Petrol and Diesel [7]. Depending on the composition of the blend we

have E5, E10, E15, E25, E85, E90 and many other blends, among which the most used blend is E15 (Crude Petroleum-85% and Ethanol-15%) [3]. E85 (Ethanol-85% Gasoline-15%) is also being widely used in road transportation and its notable use include motor racing, where many motor racing series have adopted it to reduce their GHG Emissions [4]. Figure 2 Graph of an Energy Density

Graph - 1



Reference: From Table (2) of this document

Figure 2 Graph of an Energy Density

Ethanol [C₂H₆O] has a boiling point of 78.23 C which makes it a stable fuel, while its storage density is 785 Kg/m³ and its specific energy being 26.8 MJ/Kg. While in comparison, the E85 fuel has a specific energy of 33.2 MJ/Kg which implies that the fuel with more ethanol blend tends to have lower specific energy. Also, higher blends don't tend to perform better during cold starts in winter conditions, which is not a problem on ships as the fuel is anyways preheated before entering the combustion chamber [2]. Ethanol blends generally have higher octane rating (around 109) than normal gasoline which gives additional power. With specific design of engines, we can achieve higher thermal efficiency, raised torque, and better specific fuel consumption to operate with the ethanol blends. Methanol [CH₃OH] which has a boiling point of 64.7°C, while its storage density is slightly higher than its counterpart with 792 Kg/m³ and its specific energy being 22 MJ/Kg. Similarly, methanol also has a higher-octane rating of nearly 108 which allows for higher compression ratios and therefore allows the engines to run more efficiently. Methanol is also cheaper to produce compared to production of ethanol (which involves energy intensive process) thanks to the Steam Methane Reforming Process, but significant efforts and investments are also made to obtain methanol from biomass.

Conclusion

Reducing GHG Emissions in maritime industry requires many alternatives and efforts to implement it as IMO has ambitions to reduce net zero emissions in the fore coming decades. It requires the feasibility of the use of such alternatives. Hydrogen as a fuel has higher specific energy but very much lacks in Energy density, which needs more energy to store it, which otherwise may require huge tanks to hold it which is not economical to carry onboard as cargo loading capacity cannot be compromised for Shipping liners. While for Ammonia, it has lesser Energy density and specific energy than the other mentioned fuels but has a benefit of not producing any greenhouse gas and needs lesser energy to store, compared to hydrogen. It is on its development phase to be used as fuel as technology develops. Biofuels, which are blends of alcohol and petroleum products, act as Net-Zero Carbon fuel as it has absorbed CO₂ during its living phase as plants and

combusted therefore releasing the CO₂ back into the atmosphere. For CCS, the market plays a major role, whether there is a demand for CO₂. Otherwise, capturing won't make sense economically as the cost of capturing needs to be offset by selling it. The costs of these alternatives can come down only with mass adoption and production and huge investment in infrastructure to compete with the bunker fuels.

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