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CASE STUDY OF HYDROGEN PRODUCTION ON BOARD LNG CARRIER

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ABSTRACT

The present work assesses the performance of hydrogen production plant aboard liquefied natural gas (LNG) carrier via a thermodynamic model written in engineering equation solver software (EES). The raw material for hydrogen production considered is the excess boil-off gas (BOG) generated in liquefied natural gas (LNG) tanks; the produced hydrogen could be used by the propulsion plant and auxiliaries.

The present approach aims to determine the conditions for optimum performance in term of plant thermal efficiency as well as carbon dioxide (CO_2) emissions in order to comply with the long term international maritime organization (IMO) regulations. To this end, the system key parameters, namely reforming temperature, air & BOG temperature at the inlet of combustion chamber and steam to carbon (S/C) ratio are varied and analyzed. As a result, it was found that increasing the reformer temperature increases both the performance of the process and carbon dioxide (CO_2) emissions. On the other hand the steam to carbon (S/C) ratio decreases the hydrogen productivity therefore decreases the thermal efficiency. Preheating the air & bog before entering the combustion chamber raises the efficiency and reduces the CO_2 emissions.

NOMENCLATURE

LHV	Lower heating value (KJ/Kg)
\dot{m}	Masse flow (Kg/s)
P	Pressure (atm)
T	Temperature (K)
W	power (W)
Abbreviations	
BOG	Boil off Gas
EEDI	Energy efficiency design index

EES	Engineering equation solver
GCU	Gas combustion unit
GHG	Greenhouse gas
HEX	Heat Exchanger
HTS	High temperature shift
IMO	International maritime organization
LNG	Liquefied natural gas
LTS (S/C)	Low temperature shift Steam to carbon ratio
SEEMP	Ship energy efficiency management plan
SMR	Steam methane reforming
Ref	Reforming
WGS	Water gas shift
Greek symbols	
η	Thermal Efficiency (%)

INTRODUCTION

Representing 80% of world global trade volumes, the international ship transport is an active and growing economic sector [1] [2]. Consequently, the impact of the shipping industry on the environment constitutes a serious concern, and needs to be addressed rapidly and effectively. In this optic, the IMO has released series regulations limiting the amount of some hazardous emissions, namely NOx, Sox, and PM [MARPOL ANNEX IV] [3], in attempt to incite main players in the shipping industry to find urgent solutions to remedy the drawbacks of the actual marine fleet.

In the same vein, current dual-fuel engines running on LNG suffers from the problem of methane slip, a very potent greenhouse gas, thus, using another alternative fuel such as hydrogen will make a rational solution to this issue.

From different experts' point of view, by the year 2050 the shipping greenhouse gas (GHG) emissions will

experience approximately a 50% reduction compared to 2008[4] level. This is a remarkable achievement by a sector that is and will remain, by far the most efficient mode of transportation.

Numerous studies regarding hydrogen production have been carried out. **M. A. Rosen** [5]. Investigated the thermodynamic performance of an SMR process for hydrogen production and listed the main causes of energy inefficiencies. It was revealed that heat transfer across large temperature differences and the irreversibility associated with combustion are the main reasons for the exergy losses in the reformer. The SMR efficiency may as well be improved using the moderate potential, this later is considered to be a measure of how nearly the performance of the process approximates to the thermodynamic ideal. **Andrew Lutz et al** [6]. Presented a thermodynamic study of hydrogen production via SMR method to determine the maximum efficiency with more realistic estimations. Moreover the comparison between the experimental data and the equilibrium model states that the influence of the temperature is related to the chemical equilibrium. The observed efficiency is lower compared to the equilibrium prediction which indicates a decreased performance due to an incomplete reaction and heat transfer losses. Compared to methane, larger hydrocarbons reforming decreases the thermal efficiency as shown in the global and equilibrium analyses. The efficiency of natural gas is 15% higher than that of reforming diesel fuel. **Adam P. Simpson et al** [7]. Developed a model of the SMR process and evaluated the performance using exergy analysis. The results illustrate the utility of exergy analysis along with instructions for further research and developments regarding hydrogen production via SMR. **A. Bayano et al** [8]. Studied the different aspects of the SMR process in addition to an exergoenvironmental analysis in order to identify the parts responsible for the emissions reduction. As a conclusion, the exergy destruction within the components significantly boosts the environmental impact a matter that can be overcome by improving the component exergy efficiency. **Noureddine Hajjajiet al** [9]. Analyzed and ameliorate an existing SMR process, as a result; higher thermal and exergy efficiencies were observed compared to the original process along with an increase in the hydrogen productivity and reduction in both the unused exergy and greenhouse gas emissions. **Voldsund Mari et al** [10]. Reviewed different technologies of hydrogen production and purification from fossil fuels with CO_2 capture. As a result, improving the hydrogen

production and CO_2 capture technologies are of high importance to be able to perfectly produce hydrogen while capture CO_2 for transport and storage to move forward to a more promising combustible capable of reducing both transport and industry emissions. **Ignacio Arias Fernandez et al** [11]. Studied the production of Hydrogen through steam methane reforming plant using the excess BOG generated on LNG tankers. Consequently, a maximum plant efficiency of 64%, production of 0.37 Kg/s hydrogen were found favoring the use of the hydrogen as a clean fuel to deal with the new agreements.

In this paper, a thermodynamic simulation of the plant was carried out using Engineering equation solver (EES) software to further investigate the influence of different parameters on the system. The aim of this work is to produce hydrogen from the BOG in its full composition available from ship tanks otherwise burned in GCU with an optimum thermal efficiency and CO_2 emissions.

BOG aboard LNG ships

The large natural gas consumption in the world is driving the LNG maritime traffic to grow [12] [13]. new designed LNG carrier must comply with the IMO regulations, regarding energy efficiency (EEDI) [14] and management plan (SEEMP) [15]. Therefore the shipping industry adopted the idea of producing hydrogen from the BOG generated to feed the propulsion system [16] (Figure1) which lead to a substantial reduction of pollutants since hydrogen is considered as an eco-friendly fuel [17].

Several factors affect the BOG amount to differ during navigation including temperature changes, cargo tank content, sea water temperature, sea condition. The heat ingress is the principal reason for BOG generation, the typical range of the designed natural boil off rates is 0.135-0.15% per day of tanker liquid capacity [18].

In the LNG carrier considered in this study which the characteristics are resumed in table 1, the rate of BOG generation ranges from 0.10 to 0.12 % at a steady-state loaded voyage as illustrate in figure 2 and 0.6-0.10 % in the case of ballast voyage in figure3.

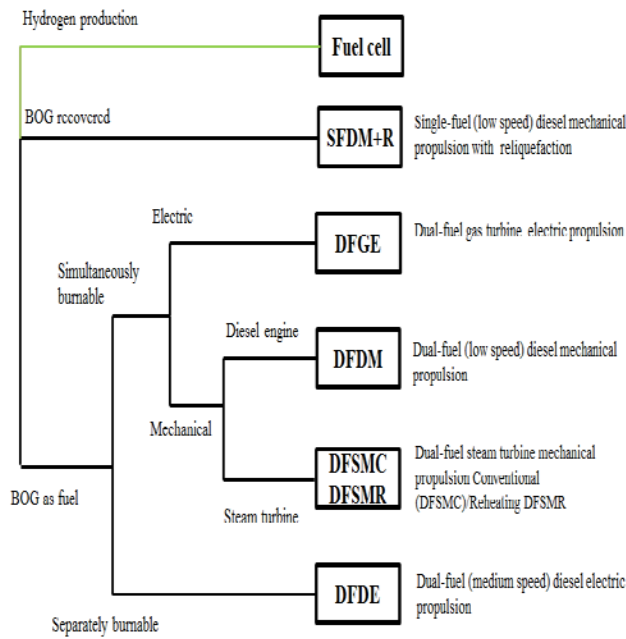


Figure 1. Classification of Propulsion systems for LNG carriers in terms of BOG utilization

Table1. the case study ship Characteristic

Vessel type	LNG vessel
Load	LNG
LLOYD'S CLASSIFICATION	+100A1Liquefied Gas Tanker. Ship Type2G. Methane (LNG) in Membrane tanks.
Length overall	291.4m
Capacity	169288 m ³
Service speed	19.5 knots
Main Diesel Generators Engines	02 sets x 12V50 DF / 02 sets x 8L50DF
Propulsion power	2 x 13890kw x 72.9rpm
BOG generation (laden state)	0.10%

PROCESS DESCRIPTION

Hydrogen can be produced from several sources such as renewable energies (electrolysis, solar) and hydrocarbons to name a few. Currently the steam methane reforming SMR process is considered as the mainstream method to generate hydrogen; the hydrogen production procedure is divided into three main phases, namely reforming, catalyst and purification as illustrated in Figure 4[9].

The chemical reaction of the natural gas conversion via steam reforming is as follow:

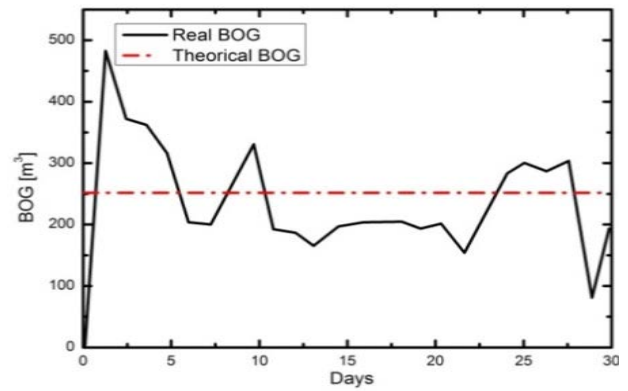


Figure2. Comparison of theoretical and real BOG generation under load conditions

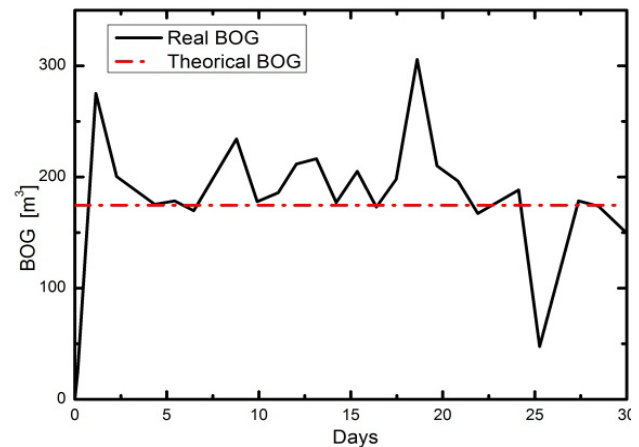
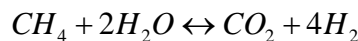
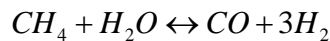
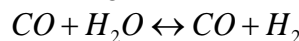


Figure3. Comparison of theoretical and real BOG generation in ballast situation



Since it is an endothermic reaction, reforming process requires a specified amount of heat that must be provided by external source such as boilers, furnaces, hot exhaust gas streams; enabling the raw material (hydrocarbons for instance) to be converted into hydrogen. However, reforming process generates carbon monoxide, carbon dioxide, and unburned hydrocarbons. These reactions are performed at temperature range of 800 to 1000 °C and pressures of 5-20 atm with modern steam reforming nickel-based catalyst [9][19]. To convert CO to CO₂ and H₂ using the H₂O available in the reforming gases via a catalyzer as described by the following reaction:



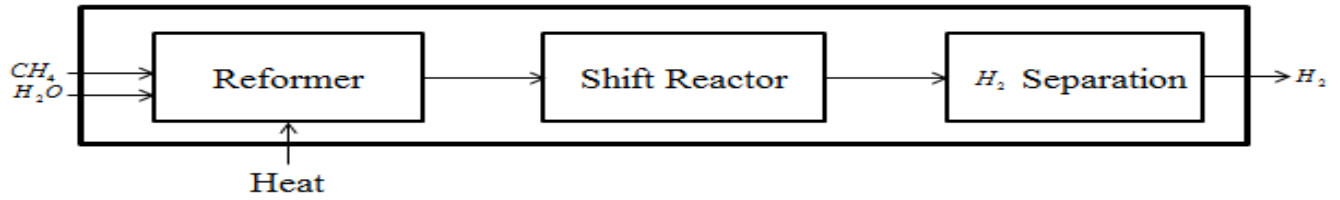


Figure4. Simplified schematic of Steam Methane Reforming process

two reactors used for the previous reaction: high temperature shift reactor (HTS) that operates between 473 and 673 K and low temperature shift reactor (LTS) that operates between 400 and 450K[9][19].

As a final step, the reforming stream enters pressure-swung absorption (PSA) for hydrogen purification. For this end, PSA separates hydrogen from the other chemical substances while condensing water vapor. [20][21][22][23]. It worth noting that hydrogen membrane separation considered in this study offers high end stream H₂ purity (up to 99%) [24].

The BOG obtained is divided into two portions; one supplying the engine and the rest will be taken to feed the hydrogen production plant. The BOG is heated by tail gases stream pre-entering the process than compressed (1-2) (Figure5). Noting that the process is using the BOG in its full composition [25]. The inlet water is pumped to match the pressure of the reforming operation (3-4). The water gas shift reactor (WGS), the produced hydrogen (HEX-4), the reforming gases(HEX-1) and the tail gases (HEX-3) are used to heat the pumped water that will be mixed with methane inside the reformer. The temperature of the reforming gas exiting the reformer drops to 573 K (WGS reaction temperature). The reforming gas is heated by tail gases after exiting the WGS. A temperature drop of Purified hydrogen is observed after it passes through the heat exchangers (HEX-4). Before sending the tail gases back into the furnace(15), the tail gases expand under atmospheric pressure. If it is required, an extra BOG is given to the furnace in order to heat the system. Before sent the stream to the chimney, the tail gases pass through two heat exchangers (HEX-1) and (HEX-2).

ANALYSIS AND MODELLING

Table 2 listed the operating parameters which took the DOE demonstration SMR facility at the city of Las Vegas, NV as a reference [26][27]. The thermal efficiency is a principal parameter for this process. The thermal efficiency is the ratio of the network

output to the heat input [9]. The following equation is used to calculate the thermal efficiency:

$$\eta = \frac{\dot{m}_{H_2} * LHV_{H_2}}{\dot{m}_{CH_4} * LHV_{CH_4} + W_{Compressor} + W_{pump}}$$

Table 2. Operating parameters of the SMR process

Inlet fuel		
CH ₄	87.89	%
N ₂	12.11	%
T	298	K
P	1	atm
Inlet water		
H ₂ O	100	%
T	298	K
P	1	atm
Inlet air		
O ₂	0.21	%
N ₂	0.79	%
T	298	K
P	1	atm
N	5.16	mol/s
Excess air	10	%
Reformer		
T	973	K
P	10	Atm
S/C	4	-
Shift reactor		
T	573	K
P	10	atm
Purification		
T	573	K
P _{H₂}	1	atm
P _{retentate}	10	atm
H ₂ Purity	99.99	%
Others parameter		
η _{s, compressor}	70	%
η _{s, pump}	85	%
Regulator	1/10	-

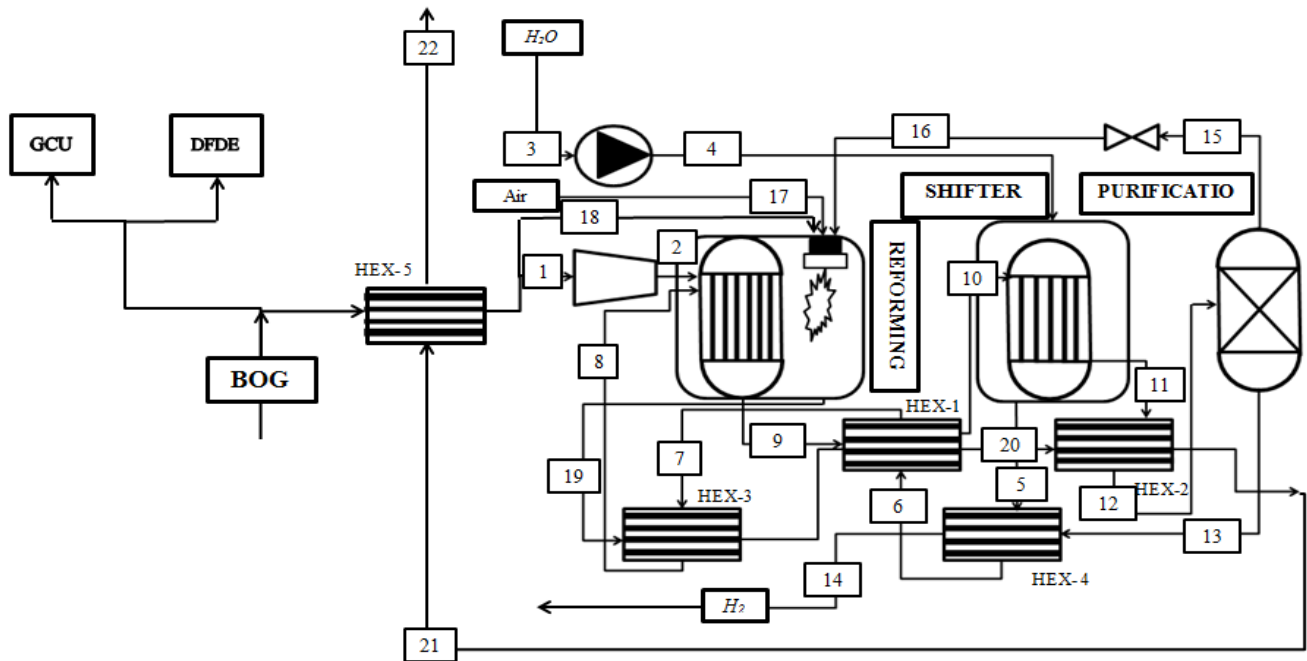


Figure 5. Steam Methane Reforming process

RESULTS AND DISCUSSION

The hydrogen production process described above was simulated by means of a thermodynamic model. The code was written on EES software, wherein the system parameters such as : reforming temperature, air & BOG temperature at the inlet of combustion chamber, and steam to carbon (S/C) ratio were varied to derive their influence on performances of the plant. The results obtained were initially validated with works found in the literature [9].The table below resumes deviations between the current work and Hajajji *et al.* [9]. The results show a minor deviation, and the latter could be attributed to the fact of using different fluid package properties.

	SMR 1			SMR 2		
	Hajajji <i>et al.</i> [9]	Present study	Err	Hajajji <i>et al.</i> [9]	Present study	Err
Thermal efficiency [%]	70.03	70.05	0.03	73.93	74.1	0.23
CO ₂ Emissions [mol/s]	1.194	1.192	0.16	1.130	1.130	0.00
H ₂ production, [mol/s]	2.804	2.804	0.00	2.804	2.804	0.00

-Effect of reforming temperature variation: the hydrogen production rate is examined over a range of reforming temperature from 950K to 1273 K.As illustrated in figure 6, increasing the reformer temperature increases the hydrogen productivity [as Chatelier’s Principle consists] what causes the thermal efficiency to increase.

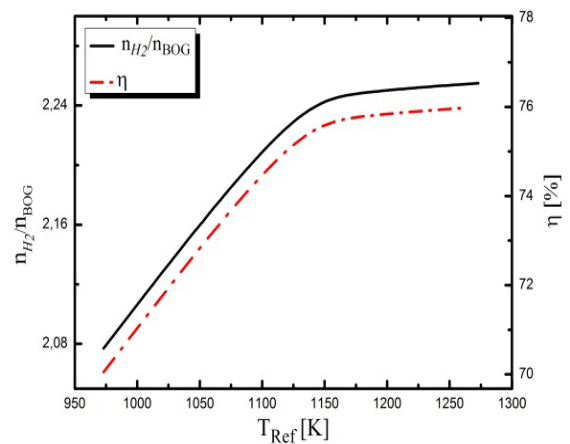


Figure 6.Effect of reformer temperature on thermal efficiency and hydrogen productivity (T_{Ref}= 973 K, T_{Shift}= 573 K, T_{purification}= 723 K, (S/C) ratio = 4, P_{Ref}=10 atm)

- Effect of air temperature variation:

The figure 7 depicts the Evolution of the efficiency of the process and the BOG required for the combustion as a function of the air inlet temperature in which rising the inlet air temperature decreases the BOG required to achieve the desirable reformer's heat what uplift the efficiency from 70 to 74.

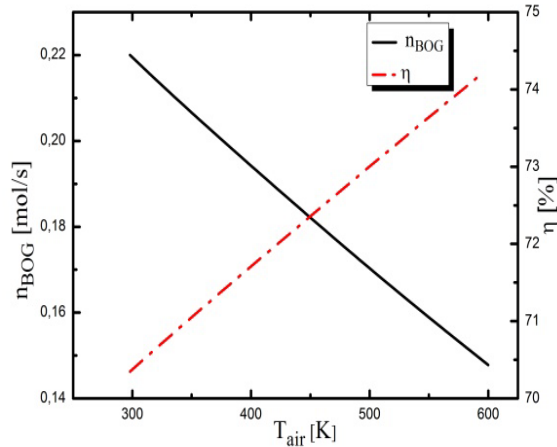


Figure 7.Effect of air temperature on thermal efficiency and hydrogen productivity
($T_{Ref}= 973 \text{ K}, T_{Shift}= 573 \text{ K}, T_{purification}= 723 \text{ K}, (S/C)$ ratio = 4, $P_{Ref}=10 \text{ atm}$)

- Effect of BOG temperature variation:

The fuel masse variations are an indication of the combustion reactants temperature changes, Figure 8 reflects the results of a carried out study about the fuel temperature influence precisely from 298k to 600k. The rise in BOG temperature causes the fuel quantity to decrease which increases the system

performance due to their inverse relationship.

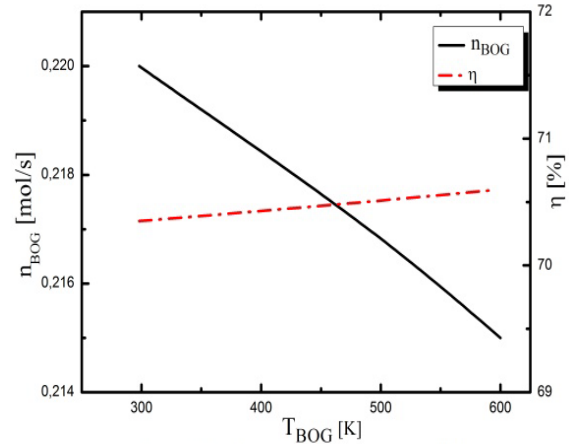


Figure 8.Effect of BOG temperature on thermal efficiency and hydrogen productivity
($T_{Ref}= 973 \text{ K}, T_{Shift}= 573 \text{ K}, T_{purification}= 723 \text{ K}, (S/C)$ ratio = 4, $P_{Ref}=10 \text{ atm}$)

-Effect of reforming temperature and (S/C) ratio variation:

The figure9.Illustrates the effects of changing the reformer's temperature and (S/C) ratio on both efficiency and hydrogen productivity parameters. As it shown above, increasing the temperature increases the hydrogen productivity what increases the efficiency, on the other hand increasing the (S/C) ration decreases the efficiency due to the rise in the heat required for the reformer causing the combustion methane consumption to increase.

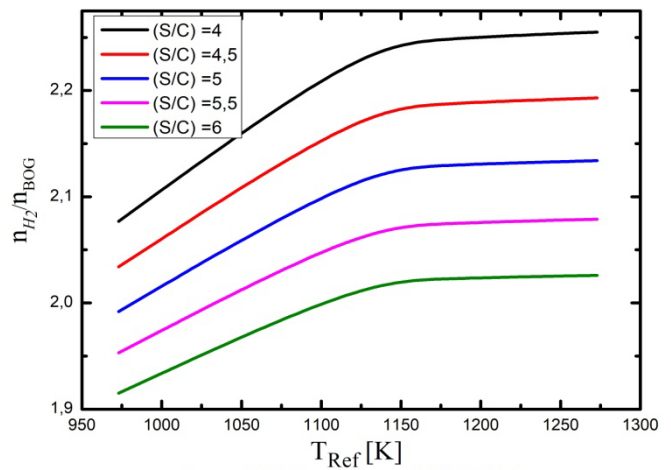
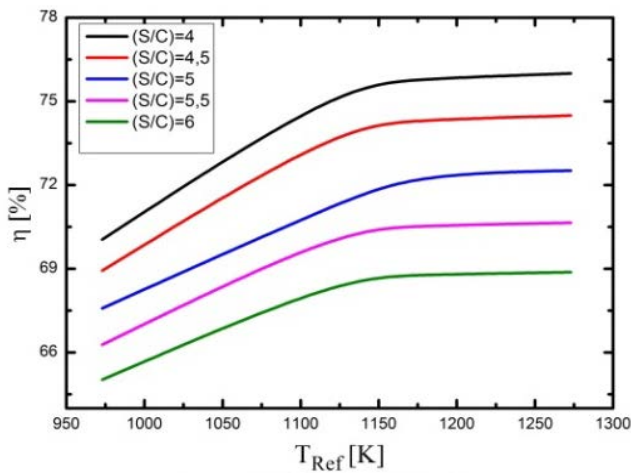


Figure 9. Effect of reforming temperature and (S/C) ratio on both: (a)- Thermal efficiency and (b)- Hydrogen productivity
($T_{Shift}= 573 \text{ K}, T_{purification}= 723 \text{ K}, P_{Ref}=10 \text{ atm}$)

CONCLUSIONS

In this study, the excess BOG in its full compositions generated on board LNG carriers is used for the hydrogen production process rather than dispense it in the GCU, an appealing solution to achieve shipping emissions reduction to be better in line with the International Maritime Organization (IMO) long term regulations.

The hydrogen production thermodynamic analysis suggests the followings:

The variation of reforming temperature, air & BOG temperature at the combustion chamber inlet and steam to carbon (S/C) ratio are used to improve the plant's performance.

Setting the process's reforming temperature and (S/C) ration to 974 K and 4 respectively will significantly boost the plant efficiency from 70% to 74% once the air is preheated before entering the combustion chamber in addition to a CO₂ emissions reduction

Preheating the BOG before entering the combustion chamber increases the plant efficiency from 70% to 70.6 %

The line of research, which may be undertaken from this work, is:

Integrating the CO₂ capture system within SMR process system to obtain blue hydrogen,

Study about different hydrogen storage systems on board LNG ships

Different technologies to inject hydrogen in different propulsion systems

KEYWORDS

Hydrogen production, BOG, Steam Methane Reforming, Energy efficiency

REFERENCES

1. J. Rodrigue, C. Comtois and B. Slack (2006). The geography of transport systems, Routledge.
2. Concawe (2016). Marine Fuel Facts.
3. IMO. Resolution MEPC.203(62), Amendments to the annex of the protocol of 1997 to amend the international convention for the prevention of pollution from ships, 1973, as modified by the protocol of 1978 relating thereto (Inclusion of regulations on energy efficiency for ships in MARPOL Annex VI), MEPC 62/24/Add. 1, London: International Maritime Organization; 2011.
4. IMO. Low Carbon Shipping and Air Pollution Control. Available online: <http://www.imo.org/en/MediaCentre/HotTopics/GHG/Pages/default.aspx> (accessed on 11 March 2019)
5. Rosen MA. Thermodynamic investigation of hydrogen production by steam-methane reformation. *Int J Hydrogen Energy* 1991; 16(3): 207–17.
6. Lutz A, Bradshaw R, Keller J, Witmer D. Thermodynamic analysis of hydrogen production by steam reforming. *Int J Hydrogen Energy* 2003; 28:159–67.
7. Simpson AP, Lutz AE. Exergy analysis of hydrogen production via steam methane reforming. *Int J Hydrogen Energy* 2007; 32:4811e20.
8. A. Boyano, A.M. Blanco-Marigorta, T. Morosuk, G. Tsatsaronis. Exergoenvironmental analysis of a steam methane reforming process for hydrogen production *Energy* 2011; 36:2202-2214.
9. Nouredine Hajjaji, Marie-Noelle Pons, Ammar Houas, Viviane Renaudin. Exergy analysis: An efficient tool for understanding and improving hydrogen production via the steam methane reforming process. *Energy Policy* (2012); 42:392–399.
10. Voldsund Mari, Jordal Kristin, Anantharaman Rahul. Hydrogen production with CO₂ capture. *Int J Hydrogen Energy* 2016; 30:1–24
11. Ignacio Arias Fernández, Manuel Romero Gómez, Javier Romero Gómez, Luis M. López-González. H₂ production by the steam reforming of excess boil off gas on LNG vessels. *Energy Conversion and Management* 2017; 134:301–313.
12. IEA, 2004, Security of Gas Supply in Open Markets, LNG and Power at a Turning Point.
13. U.S. Energy Information Administration, Annual Energy Outlook; 2022.
14. IMO. Resolution MEPC.212 (63) Guidelines on the method of calculation of the attained energy efficiency design index (EEDI) for

- new ships. MEPC 63/23, London: International Maritime Organization; 2012a.
15. IMO. Resolution MEPC.213 (63), Guidelines for the development of a ship energy efficiency management plan (SEEMP), MEPC 63/23, London: International Maritime Organization; 2012b
 16. Ignacio Arias Fernández, Manuel Romero Gómez, Javier Romero Gómez, Álvaro Baaliña Insua. Review of propulsion systems on LNG carriers. *Renewable and Sustainable Energy Reviews.*, volume 67, january 2017, pages 1395-1411.
 17. Hydrogen forecast to 2050. *Energy Transition Outlook 2022*(DNV).
 18. Gómez J Romero, Gómez M Romero, Bernal J Lopez, Baaliña Insua A. Analysis and efficiency enhancement of a boil-off gas reliquefaction system with cascade cycle on board LNG carriers. *Energy Convers Manage* 2015; 94:261–7.
 19. Ari Minkkinen, Fabrice Giroudiere and Jerome Colin Gas to hydrogen power process. 16/13-16 June 2006. Lyon France .
 20. Warmuzinski, K., Tanczyk, M., 1997. Multi-component pressure swing adsorption. Part I modeling of a large scale PSA installation. *Chemical Engineering and Processing: Process Intensification* 36, 89–99.
 21. Voss, C., 2005. Applications of pressure swing adsorption technology. *Adsorption* 11, 527–529.
 22. Ribeiro, A.M., Grande, C.A., Lopes, F.V.S., Loureiro, J.M., Rodrigues, A.E., 2008. A parametric study of layered bed PSA for hydrogen purification. *Chemical Engineering Science* 63, 5258–5273.
 23. Majlan, E.H., Wan Daud, W.R., Iyuke, S.E., Mohamad, A.B., Kadhum, A.A.H., Mohammad, A.W., 2009. Hydrogen purification using compact pressure swing adsorption system for fuel cell. *International Journal of Hydrogen Energy* 34, 2771–2777.
 24. Adhikari, S., Fernando, S., 2006. Hydrogen membrane separation techniques. *Industrial & Engineering Chemistry Research* 45, 875–881.
 25. E. Querol , B. Gonzalez-Regueral, J. García-Torrent, M.J. García-Martínez. Boil off gas (BOG) management in Spanish liquid natural gas (LNG) terminals. *Applied Energy* 87-2010: 3384–3392.
 26. Lutz A. IV.C.2 Power parks system simulation. DOE Hydrogen Program; 2004 Progress Report.
 27. Wait MF. R&D of a PEM fuel cell, hydrogen reformer, and vehicle refueling facility (Las Vegas Energy Park). Presented at the 2005 hydrogen and fuel cells merit review meeting, Washington, DC, May; 2005.