10-31-2021

Evolution of the environmental influences of using exhaust gas cleaning systems (EGCS): a case study in Algerian passenger ships

Ahmad Fadhil Hussain Almureeb

WORLD MARITME UNIVERSITY

MALMO – SWEDEN

EVOLUTION OF THE ENVIRONMENTAL INFLUENCES OF USING EXHAUST GAS CLEANING SYSTEMS (EGCS): A CASE STUDY IN ALGERIAN PASSENGER SHIPS

AHMAD –F- HUSSAIN

IRAQ

A dissertation submitted to the World Maritime University in partial fulfillment of the requirements for the reward of the degree of

MASTER OF SCIENCE

IN

MARITIME AFFAIRS

MARITIME ENERGY MANAGEMENT

2021

DECLARATION

I certify that all the material in this dissertation that is not my own work has been identified, and that no material is included for which a degree has previously been conferred on me

The contents of this dissertation reflect my own personal views, and are not necessarily endorsed by the University.

(Signature):

....

(Date): 21-9-2021

....

Supervised by: **Assistant professor Alessandro Schonborn**

Supervisor`s affiliation: **World Maritime University**

ACKNOWLEDGEMENTS

Thanks are to God for what he has given me, and thanks to the government of the Republic of South Korea for allowing me to join the prestigious World Maritime University for my Masters in Maritime Affairs.

My sincere thanks and great gratitude to Professor Alessandra Schönborn, Research Supervisor, for his assistance and wonderful guidance to complete this thesis.

I also thank all the Department of Energy Management professors and lecturers for the information they have given, in addition to Miss Lyndell Lundahl for her follow-up on student affairs.

My sincere thanks and gratitude to my family for their support and encouragement me and their bear the separation for a whole year to make this experience a success.

My sincere thanks to the Iraqi Ministry of Transport and State Company for Maritime Transport in Iraq for nominating me to join WMU.

ABSTRACT

International shipping is one of the most important international transport means, with ships transporting 90% of international trade. Ships usually use internal combustion engines and boilers for propulsion, electricity generation, and various activities onboard, which produce three of the most important pollutants; sulfur oxides, nitrogen oxides, and unburned hydrocarbons, especially methane. Finding solutions to gaseous pollution has become an urgent need, which prompted the International Maritime Organization (IMO) to issue several regulations and guidelines to reduce gaseous pollution, after the clarity of its negative effects on the climate and the health of living organisms. IMO presented three ways that would improve the environmental conditions, and left the choice of compliance method to ship owners to choose according to their working zones; either the use of low-sulfur fuels in certain degrees according to the sailing area, the use of alternative fuels, or the use of the exhaust gas cleaning systems (EGCS), to remove the pollutants from the exhaust before it is released into the atmosphere. This research used three mixed methods to analyse the potential use of EGCS: First, using scrubbers to remove sulfur and nitrogen oxides from the exhaust gases was explored using a literature survey on this topic. Second, the potential for EGCSs, using selective non-catalytic reduction, was investigated using a chemical kinetic modelling study simulating the chemical reactions taking place in the reactor at representative conditions of temperature, pressure, and exhaust gas composition. The simulations showed that it could reduce nitrogen oxides by over 97% as long as it could keep the exhaust gas temperature above 750 Celsius. The selective non-catalytic reduction was considered because of its attractive economic advantages to stakeholders, as well as compelling environmental benefits, ease of operation, and resistance against conditions. Ships can use selective non-catalytic reduction to remove nitrogen compounds in addition to treating methane associated with the use of natural gas as fuel. Although selective non-catalytic reduction technique requires to exist ammonia and a temperature higher than the exhaust temperature to achieve high efficiency in the removal of nitrogen oxides, it is considered a suitable solution for those ships that are rarely sailing at the emissions control areas, especially the supplementary heat can be obtained through an external burner. Third, the oxidation of methane slip emanating from LNG-powered engines was evaluated by simulating the chemical kinetics of methane-oxidation catalysts as EGCS. This was done by simulating the chemical kinetics of gas-phase and surface reactions using a chemical-kinetic simulation. It was observed that high methane oxidation efficiencies over 98% were achieved within a range of temperatures of about 200 Celsius.

Keywords: Sulfur, Nitrogen, Methane, GHG, Environment, IMO, EGCS and Ships**.**

Table of contents

Declaration I

Acknowledgements II

Abstract ……………………..………. III

Table of contents …………….………V

List of tables …………..……….……VII

List of figures …………..………….....VIII

List of graphs IX

List of abbreviations …..........................X

List of chemical formulas XI

Chapter I: Introduction

1.1- Background ………..… 1
1.2- Problem statement …..… 3
1.3- Aims and objectives …..… 5
1.4- Research questions …..… 6
1.5- Methodology ………... 6
1.6- The scope of research.. 6

Chapter II: Literature Review

2.1- Introduction ………..…...8
2.2- Scrubbing of sulfur oxides …...............................….…......9
2.2.1- Types of scrubbers ……...9
2.2.1.1- Dry scrubber …..10
2.2.1.2- Wet scrubber ….......................................…12
- Open-loop ……….......................................……13
- Close-loop ……...15
- Hybrid………................................…………..18
- Washing water ……..…19

2.3- Scrubbing process of nitrogen oxides 21
2.3.1- Selective catalytic reduction SCR …...........21
2.3.2- Oxidation of NO to NO_2 for water absorption ....…22

2.3.3- Selective non-catalytic reduction SNCR 23
2.4- Addressing of methane slip …...24

Chapter III: experimental setting out 26

3.1- Selective Non-Catalytic Reduction of NOx 26
3.2- Oxidation of methane …………...29

Chapter IV: application of chemical kinetic simulation results and parametric analyses 34

4.1- The case study …………………...34
4.2- Nitrogen oxides 35
4.3- Methane slip ……………………….............................44

Chapter V: Conclusion and Recommendations …....................................…50

References: …………...53

List of tables

1- Removal efficiency of different types of scrubbers 10

2- Simulation parameters of NO oxidation......................... 28

3- Experimental parameters of CH_4 oxidation.................... 30

4- The amount of NOx removed... 36

5- The amount of CH_4 removed.. 44

List of figures

1- Basic components of scrubber ………..........................9
2- Types of scrubbers ………………….........................10
3- Couple Systems dry SOx scrubber for marine use ….......11
4- Open-loop scrubber ………………….......................14
5- Closed-loop scrubber ……………….........................16
6- (a) Open-loop mode of hybrid scrubber …….................18
(b) Closed-loop mode of hybrid scrubber …….................18
7- Hydro-cyclone scheme ……….....................................19
8- schematic of the SNCR ……….....................................24
9- Typical exhaust emissions ………...............................27
10- Simulation results of NO oxidation on Python 3.9.2 29
11- Simulation results of CH_4 oxidation on Python 3.9.2 31
12- Simulation results of CH_4 oxidation on Python 3.9.2 at low temperature..33
13- Algiers-Marseille-Skikda-Algeria route 35
14- Reaction path diagram 39

List of graphs

1- (a) NO removal efficiency by SNCR for 8L20 engine ……. 37

(b) NO removal efficiency by SNCR for 12V46 engine …....37

2- (a) NO removal efficiency versus temperature (12V46DF) ...40

(b) NO removal efficiency versus temperature (8L20)...........40

3- NO removal efficiency versus pressure ……….....................41

4- NO removal efficiency versus diameter ……….....................42

5- NO removal efficiency versus NH_3/NO ratio …….................43

6- NO removal efficiency versus length ……….........................43

7- (a) CH_4 oxidation for 9S90ME engine at full load……...........45

(b) CH_4 oxidation for 16V50DF engine at full load…….........45

(c) CH_4 oxidation for 16V50DF engine at 75% load…….........46

(d) CH_4 oxidation for 6L46DF engine at full load……............46

(e) CH_4 oxidation for 6L46DF engine at 75% load……............47

8- CH_4 oxidation versus diameter ……….................................48

9- CH_4 oxidation versus length ……….......................................48

10- CH_4 oxidation versus temperature ……….................................49

List of abbreviations

°C – Degree Celsius

ECA – Emission Control Area

EGCS – Exhaust Gas Cleaning System

GHG – Greenhouse gases

IMO – International Maritime Organization

IPCC - Intergovernmental Panel on Climate Change

LNG – Liquefied Natural Gas

LSHFO – Low sulfur Heavy Fuel Oil

MCR - Maximum Continuous Rating

MDO – Marine Diesel Oil

MGO – Marine Gas Oil

MW-h – megawatt-hour

NOx – Nitrogen oxides

SCR – Selective Catalytic Reduction

SECA – sulfur Emission Control Area

SNCR – Selective Non-catalytic Reduction

SOx – sulfur Oxides

UHC – Unburned Hydrocarbons

UNFCCC – United Nations Framework Convention on Climate Change

WHR – Waste Heat Recovery

WMU – World Maritime University

π - Archimedes' Constant = 22/7

List of chemical formulas

•OH ------- Hydroxide Ion

C ----------- Carbon element

$Ca(OH)_2$ --- Calcium Hydroxide

$CaCl_2$ ------- Calcium Chloride

$CaSO_3$ ------- Calcium Sulphite

$CaSO_4$ ------- Calcium Sulphate

CH_2 ----------- Methylene

CH_3 ----------- Methyl Radical

CH_4 ----------- Methane

Cl ------------- Chlorine element

ClO ----------- Hypochlorite

ClO_2 ---------- Chlorine Dioxide

CO ------------ Carbon Monoxide

$CO(NH_2)_2$ ---- Urea

CO_2 ------------ Carbon Dioxide

H --------------- Hydrogen

H^+ -------------- Hydrogen Ion

H_2O ------------ Water

H_2O_2 ----------- Hydrogen Peroxide

H_2SO_3 --------- Sulfurous Acid

H_2SO_4 --------- Sulfuric Acid

HCl ------------ Hydrochloric Acid

HNCO --------- Isocyanic Acid

HO_2 ------------ Hydroperoxyl Radical (Hydrogen superoxide)

HSO_3 ---------- Hydrogen Sulphite (Bisulphite)

N_2 ------------- Nitrogen

Na^+ ------------- Sodium Ion

Na_2SO_3 -------- Sodium Sulphite

Na_2SO_4 -------- Sodium Sulphate

NaClO --------- Sodium hypochlorite

Na_2CO_3 -------- Sodium carbonate

$NaHSO_3$ ------- Sodium bisulfite

NaOH ---------- Sodium hydroxide

NH_3 ------------ Ammonia

NO ------------- Nitric Oxide

NO_2 ------------ Nitrogen Dioxide

NO_3 ------------ Nitrate

O_2 --------------- Oxygen

OH^- ------------- Hydroxide Ion

PT --------------- Platinum Element

SO_2 -------------- Sulfur Dioxide

SO_3 --------------- Sulfur Trioxide

CHAPTER I

INTRODUCTION

1.1- Background

As a normal result of the remarkable increase in population, the demand for international trade is growing, which is often, transported across seas and oceans, so the concerns of organizations and bodies concerned with the environment and public health increased because ships are considered a source for all kinds of pollution, especially gaseous, which is the subject of this research. The severity of the impact of gaseous pollutants depends on their proximity to places sensitive to their effects (Miola et al., 2010). Although ships emit their exhaust at the open seas away from cities, the exhaust can move with the wind for tens of miles (Viatte et al., 2020). In addition to, the pollution caused by the ports that were built to import and export goods (Miola et al., 2010). The use of fossil fuels in all these activities led to great achievements after it was discovered, and invent the internal combustion engines compared to steam engines. It saved many efforts, time, and money for ship owners and merchants, but it has caused insomnia for many environmental, and health scientists based on differences in the viewpoints of both teams despite the similarity of their goals, which is to serve humanity. This difference led to a struggle to determine priority, especially since environmental and health scientists found that the smoke of power plants contains large percentages of oxides of sulfur and nitrogen as well as carbon particles, which are a source of many diseases and environmental damage. International Maritime Organization, as an organization specialized in maritime affairs; took the initiative with some other governmental and non-governmental bodies and organizations, to put forward a number of regulations and restrictions on ships to follow. In order to preserve the environment and human health, especially after the change in the climate represented by global warming as well as the rise of seawater, which threatens a number of coastal cities.

For decades, flue gases have been released into the atmosphere without treatment neither concern regarding environmental pollution and climate change, nor taking into account the diseases that these gases cause for humans or other living organisms. Due to the obvious negative impact of sulfur and nitrogen components on the life of living organisms and Carbon emissions on the ecosystem. This topic has had the large attention of educational organizations and institutions by encouraging scientific researches and studies to develop development plans and make them more efficient (Acciaro, 2014). Recently, the discharge of these gases has increased in conjunction with industrial development and the increasing human needs for those industries (Bal et al., 2015). The maritime sector, ships, and ports, is one of the sources of gaseous pollution, because of usage of internal combustion engines and steam boilers frequently, either to generate electricity or to propel ships at open seas and for tugs, support boats for mooring and unmooring operations in ports as well as to run the equipment (Wei et al., 2020). Exhaust gas of internal combustion engines and boilers consists of a number of gases; CO_2, NOx, SOx, CO, hydrocarbons, and particulate matter plus methane in LNG-powered engines (Eyring, 2005; Le Fevre, 2018). The percentage of presence of each pollutant varies and depending on the type of engine, fuel type, operating conditions surrounding the engine, such as engine room temperature and engine load (EGCSA, 2012, pp. 6-7).

Exhaust gas components are usually divided into two parts:

- Air pollutants; include compounds of SOx, NOx, CO, unburned hydrocarbons (UHC).
- Greenhouse gases (EGCSA, 2012, pp. 6-7).

Certainly, all of them are harmful to the ecosystem; either on life-organisms causes health problems and premature death, and environmental problems such as acid rain or causes climate change (Corbett et al., 2007).

Although the proportion of carbon dioxide pollution from ships is low, considered an indicator of all emissions, accounting for approximately 2.6% of global pollution (Cames et al., 2015). The 2015 Paris Agreement did not cover it. Still, the task was entrusted to the International Maritime Organization (IMO) as a designated UN body to take the necessary measures to reduce gaseous pollution (Rehmatulla et al., 2017). Therefore, new measures regarding SOx and NOx have been imposed through the IMO initiative strategy of 2018. IMO left the option to comply with regulations for ship owners by following a method that suits them, one of those methods is the use of exhaust gas cleaning systems EGCS (Jiang et al., 2014). EGCS is a system installed on an exhaust pipe to catch the SOx, NOx, CH_4, and particulate matter PM. Axiomatically, like any technology, EGCSs usage involves many technical and operational problems. For example, the lack of continued effectiveness, the resistance of the structure of the system to the chemicals passing through it, especially if the chemicals have a high flow rate and temperature. In addition, the system's needs for raw materials, the availability of these materials. As well as required energy for operation, maintenance is needed to maintain high efficiency such as the time required to clean the injectors or to clean the sludge tank. Moreover, the possibility of its operation by those who work on it, the chemical wastes that are accidentally produced because of work and methods of disposal, the costs involved in all these obstacles and problems (Zhang et al., 2012). Thus the competitiveness of the system in general.

1.2- Problem statement

As a normal result of the growing population and the increasing demand for international trade, where 90% of which is transported by sea (Zhao et al., 2020; Otheitis & Kunc 2015). Mainly, ships use low-speed engines for propulsion and medium-speed engines to generate electricity as well as oil-fired boilers to generate steam. All of these engines and boilers are run by high or low sulfur fuel. Generally, SOx, generated from the burning of sulfur in fuel, while NOx is generated from reaction N2 with O2 in the air but strongly depends on combustion temperature in engine units, about 90% of NOx in the exhaust gas is NO, as for particulate matters (PM) is resulted according to engine condition and fuel specification (Zhou & Wang 2020). As for methane, it is associated with the use of natural gas as a fuel; it slips either due to the presence of enclosed spaces that combustion does not reach, because of the overlap of open valves, or because incomplete combustion (Lighthouse, 2020).

Sulfur and nitrogen compounds are considered hazardous substances to health because their emissions are a major cause of lung, heart, and skin diseases in addition to many types of cancer (Singh et al., 2020; Sofiev et al., 2018; Macagnano et al., 2015). As well as, its impact on the environment, it causes acid rain (Jiang et al., 2014). Therefore, an urgent need arose; either to use fuels that do not contain sulfur or to innovate a new technology to clean and treat the exhaust gas before it is released into the air. That encouraged the production of low-sulfur fuel while nitrogen compounds remained unresolved; in addition, a new problem appeared with using alternative fuels like methane slip that accompanied LNG use, which is considered one of global warming, causes (Schneiter, 2019). That prompting manufacturers to design systems for cleaning exhaust gas from those compounds.

The ways to dispose of these various pollutants require two separate devices. The separate devices are costly and need a large space for their installation, in addition, the energy required to operate them and the subsequent maintenance, operation, and spare parts. Finding a solution for this dilemma by innovating a technology or method to control both SOx and NOx together, is of great importance (Ding et al., 2014). The use of wet oxidation can achieve the goal, by releasing OH radicals from some oxidants such as urea CO(NH2)2 , H2O2 or urea peroxide (CO(NH2)2.H2O2) over surfaces that play the role of catalyst such as hematite. This will lead to high removal efficiency, by small space and low cost. The removal of SOx will be almost 100%, but the removal of NOx is dependent on the decomposition process of oxidants (Ding et al., 2014). Therefore, the choice of oxidizer, control of the degree of oxidation of (NO), and inhabitation of nitrate are the most important problems of simultaneous cleaning (Zhou & Wang 2020).

1.3- Aims and objectives

The main aim of this research is to reduce the amount of sulfur oxides and nitrogen oxides in the atmosphere that are released from international shipping, in addition to treating the methane slippage released from ships powered by LNG. We will try to achieve the desired goal by using an exhaust gas cleaning system with the lowest operational cost and highest possible efficiency.

Due to the aforementioned reasons, it is necessary to collect information about typical operational conditions of ships in order to identify how the emissions resulting from them can be reduced if they use fossil fuels or liquefied natural gas. This work identifies proven methods for SOx reduction from literature and investigates potential ways of reducing NOx and methane emissions from exhaust gases using simulations. SOx reduction methods have been sufficiently covered by the researchers and implemented by industry in the wake of global IMO sulfur regulations from 2020 onwards. This work will therefore focus on studying the selective non-catalytic reduction of nitrogen emissions as well as methane slipped that accompanies the use of

LNG. We will take Algerian passenger ships as research samples as they use dual-fuel engines from Wärtsilä.

1.4- Research questions

- How much the maritime sector generates emission annually and how much percentage of global missions?
- How much EGCS could offer to the maritime sector to save on emission?
- Which onshore industry could benefit from applying EGCS technology in addition to international shipping?
- What is the main problem in using EGCSs?
- What is the best solution for this problem that could apply instead of using a scrubber or low sulfur fuel?
- To what extent do the exhaust specifications after the use of EGCSs comply with IMO standards?

1.5- Methodology

Data were collected through previous researches papers and science articles by google scholar and WMU library as well as from official websites of manufactures, organizations such as IPCC, IMO, UNFCCC, and the official site of Algerian National Company of Maritime Transport of Travelers. The data was analyzed and developed through the simulation, and the creation of a Python program to facilitate obtaining more accurate and realistic results.

1.6- The scope of the research

The paper will explain the role and advantages of exhaust gas cleaning systems and the associated operational problems, then demonstrate the suitability of the results with IMO requirements. The research will not address the financial costs due to the lack of information in literature, and to avoid distracting the search in multiple directions. It will focus on the efficiency of removal and operational problems selective non-catalytic reduction for NOx resulted from ships equipped with medium or high-speed engines in addition to CH_4 resulted from LNG powered spark engines.

CHAPTER II

LITERATURE REVIEW

DESIGN OF EGCSs AND PRINCIPLE OF SCRUBBING PROCESS OF SO_x, NO_x, AND CH_4

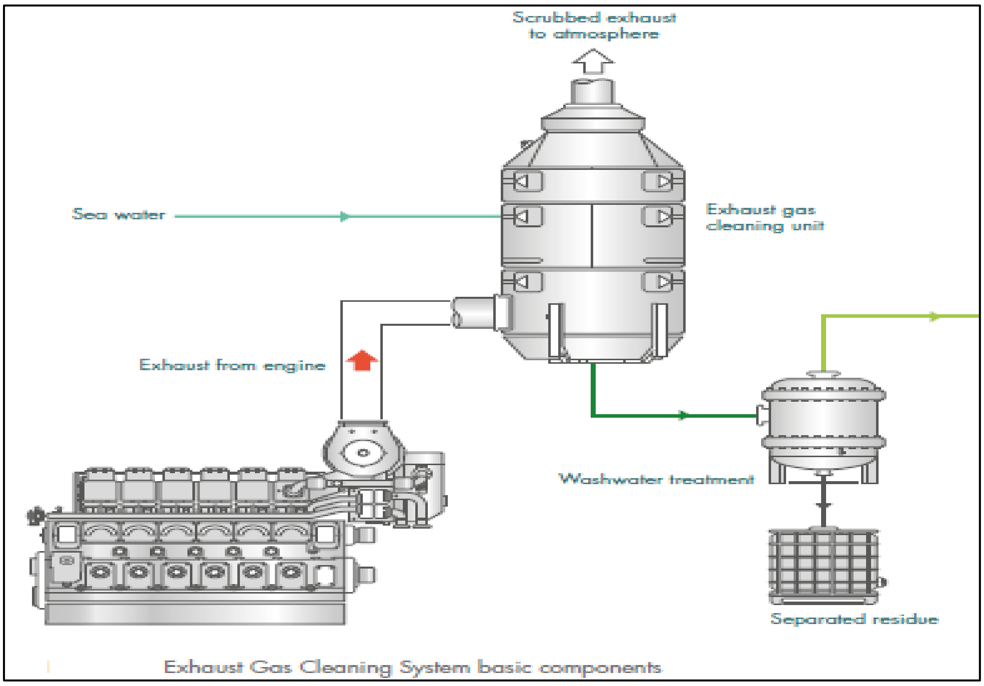
2.1- Introduction

Gaseous emissions from ships in places of congestion, such as ports, straits, and canals, are large if compared to other means of transportation, and their harmful effects increase when using high sulfur fuels. Given the damage that these emissions pose to living organisms, especially humans, the IMO has set out to implement regulations that specify the maximum sulfur content in marine fuels by 0.5% globally and 0.1% in sulfur Emission Control Areas (SECA) (Ji et al., 2020; Thor et al., 2021)., to reduce their negative impacts. Moreover, IMO has also allowed the use of exhaust gas cleaning systems (so-called scrubber), to remaining on the use of high sulfur fuel for those who wish to do from old ships, with severe recommendations for dealing with effluents wash water.

Washing water from exhaust gas scrubbers is characterized by high acidity, as it contains zinc, copper, vanadium, nickel, naphthalene, and fluorine in high Concentration. It caused a clear decrease in water pH in addition, an increase in surface water concentrations, for example, naphthalene and vanadium 189% and 46%, respectively (Teuchies et al., 2020).

An exhaust gas scrubber is a space in which, water is sprayed on the exhaust gas by nozzles before it is released into the atmosphere. It is possible to use one scrubber for more than one engine or exhaust source through multiple inlets, and then there must be a mechanism to separate the sources so that the exhaust does not stream to the ineffective source. Through this scrubbing process, the exhaust gas will be clean of sulfur oxides and some carbonaceous combustion residues. In addition to, nitrogen oxides can remove, if a specific catalyst is used, to convert (NO) which is insoluble in water to (NO_2) that can be easily dissolved in water. This results in chemically polluted wash water, which is more toxic than some marine pollutants which most common in maritime, such as crude oil (Thor et al., 2021).

Figure -1- Basic components of scrubber



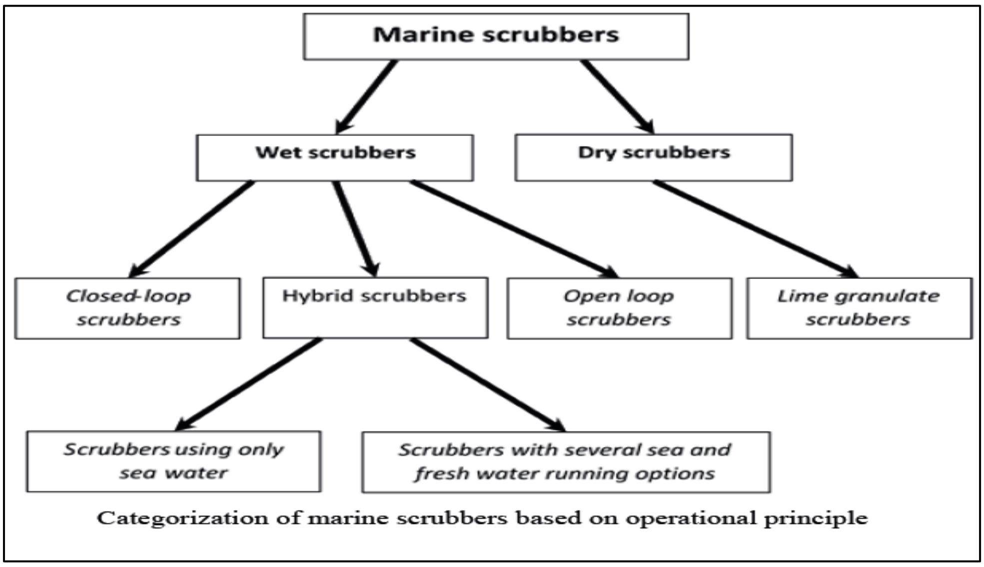
(EGCSA, 2012, pp. 36)

2.2- Scrubbing of sulfur oxides

2.2.1- Types of scrubbers

There are many designs of scrubbers and they all come together in one function figure -2-, which is to remove sulfur and nitrogen compounds and carbon particles from the exhaust gas.

Figure -2- Types of scrubbers



(Lahtinen, 2016)

In general, it is divided into two types; wet and dry, each type has special features and different removal efficiency. Table -1- show the efficiencies of each type based on emission.

Table-1- Removal efficiency of different types of scrubbers

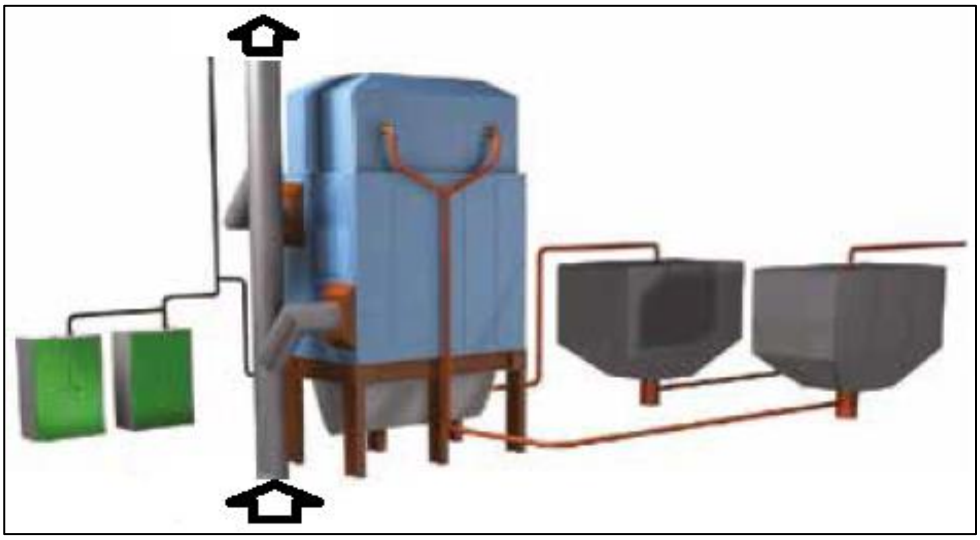
Polutant	Dry	Open-loop (Sea water)	Closed-loop (Fresh water)	Hybrid
SOx	99%	90-95%	99%	98-99%
Nox	No change	3-7%	3-7%	3-7%
PM	85%	80%	30-60%	80%

Source: (Zhang, 2019)

2.2.1.1- Dry scrubbers

The combustion processes, produce exhaust gases containing sulfur dioxide and hydrogen chloride, which must be disposed of to comply with environmental standards. Dry scrubbers are usually used for this purpose, it is a modern mechanism, mostly uses calcium hydroxide $Ca(OH)_2$ as known slaked lime (Helfritch & Feldman, 1984; Stein et al., 2002; Tran, 2017) as shown in figure -3-.

Figure -3- Couple Systems dry SOx scrubber for marine use



(Lloyd`s Register, 2015, pp. 27)

Dry scrubbers are of limited use in the marine sector, the reason is their high need for solid materials of alkaline nature, especially with high mole fractions of SO_2 (1000-2000 ppm) in flue gas (Helfritch & Feldman, 1984).

Reaction results also contain non-reactive quantities of oxidizing materials. Therefore, to increase the efficiency of dry scrubbers, extra oxidizing materials are required.

The chemical reactions process is represented by the following equations:

i. $SO_2 + Ca(OH)_2 \rightarrow CaSO_3 + H_2O$

ii. $CaSO_3 + \frac{1}{2}O_2 \rightarrow CaSO_4$

iii. $SO_3 + Ca(OH)_2 \rightarrow CaSO_4 + H_2O$ (Tran, 2017)

iv. $CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$ (Helfritch & Feldman, 1984)

v. $2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$ (Stein et al., 2002).

The removal process in this type of scrubber depends on the contact of the exhaust gases with calcium hydroxide ($Ca(OH)_2$) inside a reactor whose pressure is under control. The reactor space is characterized by severe turbulence in the movement of the exhaust gas, and this is a contributing factor to the interaction. In addition, the high speed that may reach 3-5 m/sec pushes the reaction products out. Nitrogen components, which are not affected in the spray reactor, will be oxidized to form nitric acid as vapor (Helfritch & Feldman, 1984). Then the mixture enters the multi-cyclone space, which working by centrifugal force to sort out the large particles, and then the gas passes through soft fabric filters to remove the fine particles. The products of removal from large and fine particles transferred through a vibrating belt that separates the impurities transport it to designated containers, while the materials that can reactive returned to the reactor. The effectiveness of the electronic beam reactor depends directly on the radiation intensity, temperature, and humidity of the mixture of gas; it is proportional with the beam and humidity and inversely proportional with the temperature. (Kaiser et al., 2000).

2.2.1.2- Wet scrubber types

As for wet scrubbers, they use either seawater (open loop) or fresh water with chemical additives (closed-loop), for removing sulfur compounds and particles, moreover in hybrid type; both kinds of water are used together.

All types of wet scrubbers have basic common characteristics such as**:**

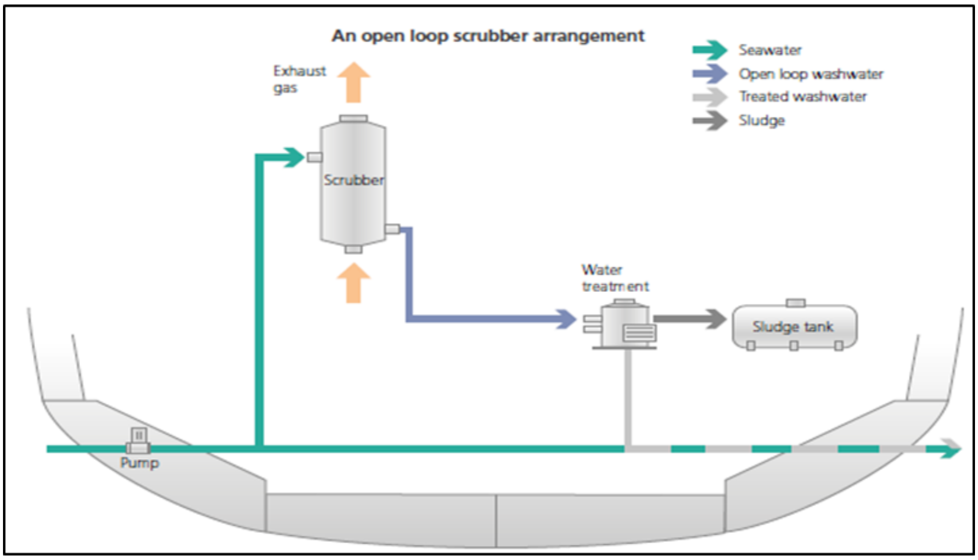
- Providing close contact between the water and the exhaust gas, taking into account not to obstruct the flow of the exhaust gas to prevent the occurrence of backpressure on the engine or the boiler, and this issue carefully considered with boilers**.**
- Due to the noticeable decrease in the exhaust temperature after wet scrubbers, they must be installed after waste heat recovery systems (WHR)**.**

- It is possible to use scrubbers as silencer and sparks catcher**.**
- Wash water treatment plant must be installed after scrubbers and before releasing water overboard**.**
- Residues of washing water must be retained on board ship, then delivered at the ports and not burned by ship incinerator**.**
- The scrubbers can receive the exhaust gases from more than one source, considering that the exhaust does not return to the non-working units and the wash-water treatment plants, as it can work for more than one scrubber (EGCSA, 2012, pp. 35).

- **Open-loop scrubber shown in figure -4-**

Briefly, "Open-loop" scrubbers use seawater directly to clean the exhaust gas, taking advantage of the chemical composition (the natural alkalinity) of seawater to neutralize the acidic sulfur compounds, where seawater is passed through the exhaust gas, then partially treated, and then released to the sea again. This type of scrubber needs about 45 cubic meters of seawater to produce one MW-h when using fuel with a sulfur content of 2.7% (Tran, 2017; EGCSA, 2012, pp. 37).

Figure -4- Open-loop scrubber



(Lloyd`s register, 2015, pp. 19)

Usually, sulfur oxides in exhaust gases from ships are in the form of sulfur dioxide (SO2) with a very small percentage of sulfur trioxide (SO3). Seawater is pumped and sprayed inside the reactor to mix with the exhaust gas without obstructing its flow to avoid the formation of backpressure on the combustion units especially boilers**.** Because of this close mixing, sulfur dioxide and trioxides reacts with alkaline seawater due to the presence of salts in it, resulted hydrogen sulfate and sulfuric acid respectively, according to the following chemical equations:

i. $SO_2 + H_2O \leftrightarrow H_2SO_3$

ii. $SO_3 + H2O \leftrightarrow H_2SO_4$ (EGCSA, 2012, pp. 40)

Then the reaction products will react with salts of seawater ($CaCO_3$ or Na_2CO_3), to form the sulfate according to the following chemical equations:

i. $H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + CO_2 + H_2O$

$Na_2SO_3 + \frac{1}{2}O_2 \rightarrow Na_2SO_4$

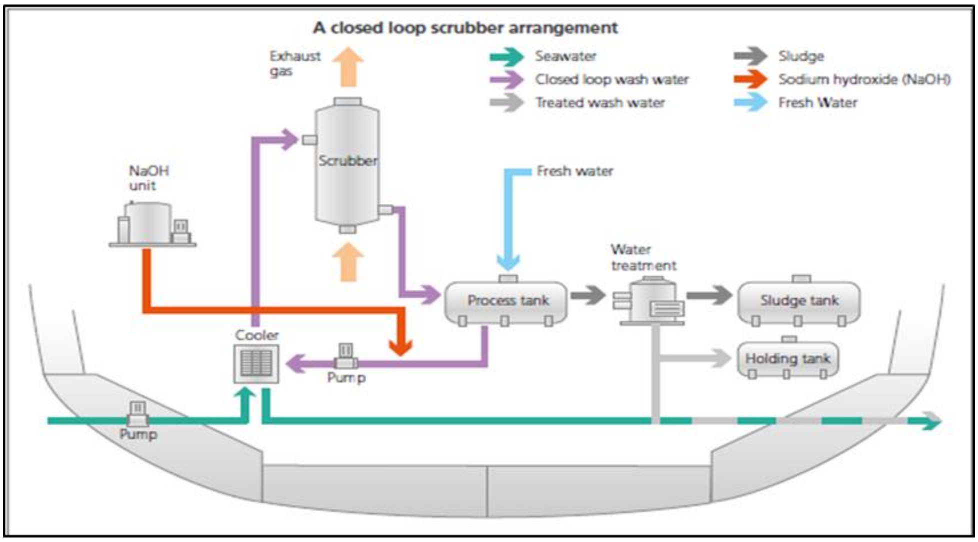
ii. $H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + CO_2 + H_2O$ (Tran, 2017).

Sulfuric acid is neutralized by the alkalinity of seawater because of the bicarbonate it contains. However, the ionization of sulfur dioxide to sulfate quickly decreases as soon as the pH drops after consuming part of the initial buffering capacity and the effectiveness of the whole washing process will decrease. It is worth noting, is the high speed of reaction of sulfur trioxide with water, which produces sulfuric acid, which is also highly attractive to water. According to the above, scrubbers are effective in isolating or neutralizing most of the components, especially when the water flow increases and lowering its temperature in order to the solubility of SO_2 will increase. The total efficiency of open-loop scrubbers is closely related to the chemistry of the water in which the ship operates, as alkalinity is a pivotal factor (Sharif et al., 2021).

- **Closed-loop scrubber shown in figure -5-**

Freshwater is often used in this type of scrubbers (with the possibility of using seawater) after adding some alkaline substances such as sodium hydroxide, to neutralize and remove sulfur compounds. Washing water is recirculated several times after making up for the lack of quantity or alkalinity. The water recirculation rate in this type is much lower than that of "open-loop", which is estimated at 20 cubic meters per MW-h. Typically, part of the washing water is released to the sea after being treated; the amount released outside is estimated by 0.1 to 0.3 cubic meters per MW-h. In addition to, a holding tank may be used to reduce the subtraction process and compensation in the amount of water and additives (Tran, 2017; EGCSA, 2012, pp. 38).

Figure -5- Closed-loop scrubber



(Lloyd`s register, 2015, pp. 19)

Scrubbing is based on neutralizing the acidity of the exhaust gases by the alkalinity of the washing water, so maintaining alkalinity is very important. Since closed-loop scrubbers use a circulating fresh water, therefore an alkaline substance must be added, to perpetuate the reaction. The chemical reaction is summarized by; first, the sulfur dioxide produced by combustion dissolves in water results bisulfite:

$SO_2(aq)+H_2O(l) \leftrightarrow HSO_3^-(aqua\ sol)+H^+(aqua\ sol)$ … (Lahtinen, 2016)

The equilibrium of this process depends on several factors such as the concentration of SO_2 in the wash water, the partial pressure of SO_2, the temperature of the reaction, and the enthalpy of the mixture. Therefore, the use of fresh water in closed-loop scrubbers is not much different from using seawater in open-loop scrubber, except adding some alkaline chemical solutions due to the lack of freshwater for this feature (Lahtinen, 2016). Sodium hydroxide is often used in marine exhaust scrubbers, which has the chemical formula NaOH, known as caustic soda. Caustic soda is available in 50% liquid form that makes it easy to mix with water (Tran, 2017). Second, after adding soda to water, Na and OH ions are produced.

$NaOH(s) + H_2O(l) \leftrightarrow Na^+(aq) + OH^-(aq) + H_2O(l)$ ………..(Lahtinen, 2016)

The chemical reactions will occur in two different directions but their results are similar. It reacts with sulfur dioxide, forming a mixture of sodium sulfite, sodium bisulfite, and sodium sulfate based on their acidity (pH). As for it reacts with sulfur trioxide, is through its interaction with sulfuric acid, which resulted from the reaction of sulfur trioxide with, water that producing Sodium sulfates as well, as shown in the following equations:

Sulfur dioxide reactions

$NaOH + SO_2 \leftrightarrow NaHSO_3$

$2NaOH + SO_2 \leftrightarrow Na_2SO_3 + H_2O$

$2NaOH + SO_2 + \frac{1}{2}O_2 \leftrightarrow Na_2SO_4 + H_2O$

Sulfur trioxide reactions

$SO_3 + H_2O \leftrightarrow H_2SO_4$

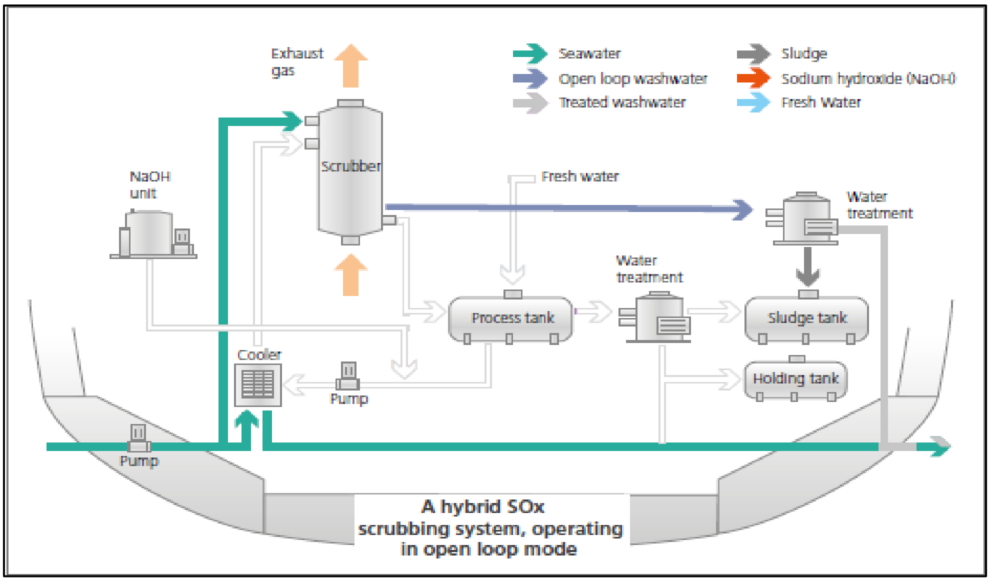
$2NaOH + H_2SO_4 \leftrightarrow Na_2SO_4 + 2H_2O$ (EGCSA, 2012, pp. 41)

The alkalinity of sodium hydroxide enables the washing water to reduce the flow rate to about 20 cubic meters per MW-h, and this is less than the flow rate when using seawater by 55%, so the use of freshwater reduces pumping power as well as the rate of discharging overboard. On the other hand, this system needs a cooler that maintains the temperature of the water in addition to renewing the water's capacity for oxidation (EGCSA, 2012, pp. 41).

- **Hybrid scrubbers shown in figures -6a, 6b-**

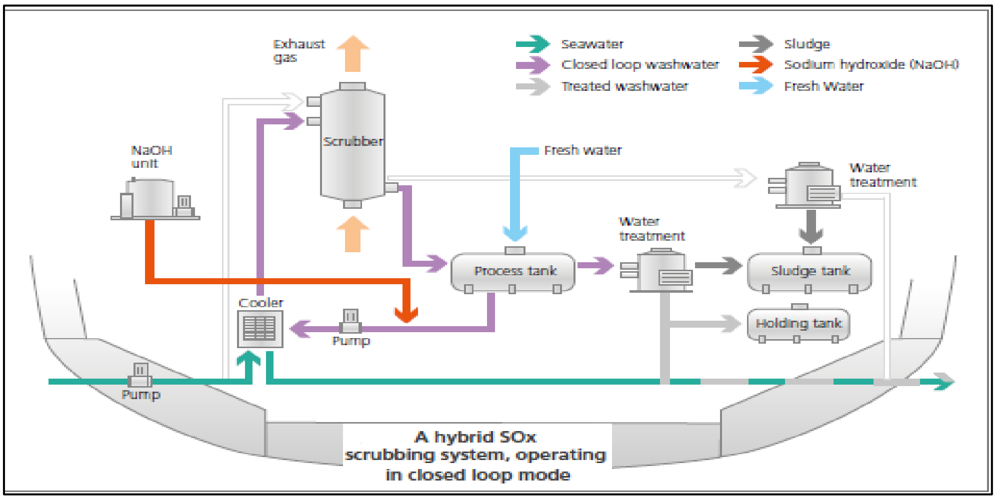
This type of scrubber includes both closed and open loops simultaneously, where seawater (with high alkalinity) is used in the open-loop, while the freshwater used in closed-loop with alkaline chemical additives are used when the alkalinity of seawater is low at the inlet (Tran, 2017; EGCSA, 2012, pp. 38).

Figures -6a- Open-loop mode of hybrid scrubber



(Lloyd`s register, 2015, pp. 21)

Figure -6b- Closed-loop mode of hybrid scrubber

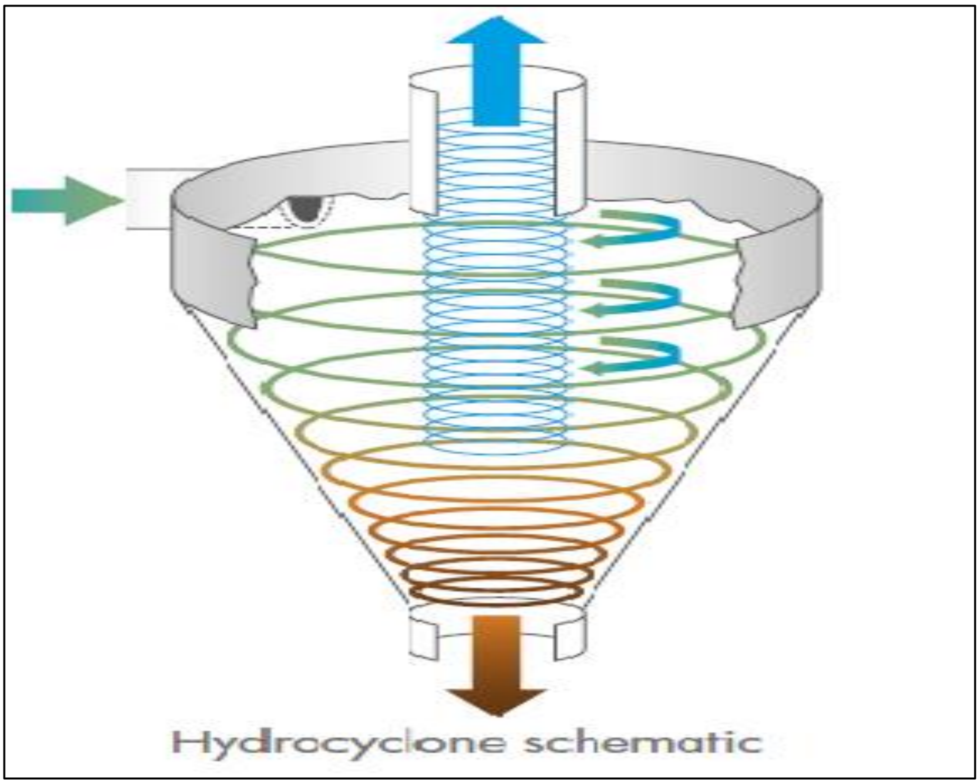


(Lloyd`s register, 2015, pp. 21)

- **Washing water treatment**

After the washing water leaves the reaction space with the exhaust gas, directed to enter into a spiral cylinder to isolate the particles by centrifugal force. So the water carrying the particles will circulate near the circumference (because it is the heaviest) and be directed through the grooves to exit by the bottom hole, while the water free of particles (the lightest) will be in the center of the cylinder and allowed to leave from the top opening as shown in figure -7-

Figure -7- Hydro-cyclone scheme



(EGCSA, 2012, pp. 47)

Wet scrubbers mainly depend on the chemistry of the wash water, whether it is freshwater or seawater (Lahtinen, 2016). The salinity of water of seas varies in accordance with region, like low salinity existing in the Baltic Sea (brackish) while hypersaline water exists in the Dead Sea (Kukkonen, 2019). Therefore, the wash water flow rate needs to be controlled based on the type of loop of scrubber (Endres et al., 2018). Moreover, alkaline substances such as sodium hydroxide need to be added when the alkalinity of seawater decreases or when freshwater is used; to avoid the lack of effectiveness of scrubbers (Tran, 2017). Furthermore, alkalinity is necessary to neutralize the acidity produced due to the dissolution of sulfur compounds in water (EGCSA, 2012, pp. 46). The solubility of sulfur compounds in the wash water is also affected by the water temperature, as a higher temperature reduces the solubility of SO_2 in water. The solubility of sulfur compounds is essential for the function of wet scrubbers, in addition, it leads to a reduction in the pH of the washing water to about 3 (Endres et al., 2018). Because wash water is the working fluid of the scrubber, it must be free of suspended particles (Endres et al., 2018). Moreover, to be treated against chemical changes which resulting from the reactions when it is necessary (Kukkonen, 2019). For example, the pH should not be less than 6.5 within 4 meters from the point of discharge to the sea, or the difference between the inlet and outlet pH not be more than two pH units during maneuvering or crossing (ABS, 2018). These regulations are set out to preserve the ecosystem when using open-loop scrubbers because washing water is more toxic than common pollutants (Thor et al., 2021). In addition, it must be re-effective before can recycle it in closed-loop scrubbers. Usually, as the first stage of wash water treatment, most scrubbers use centrifugal force to separate the impurities and suspended particles in the washing water and collect them in a dedicated tank (EGCSA, 2012, pp. 46). Moreover, in open-loop systems, the concentration of the remaining water is also diluted by mixing it with fresh seawater. For example, mix with the outlet of engine cooling before it is released into the sea. As for closed-loop systems, wash water is reactivated by adding alkaline substances such as sodium hydroxide after the suspended particles are separated. Finally, the sludge collected through the separation mechanisms is handed over to the port facilities, and neither is discharged overboard nor burned by ship incinerator (US EPA, 2011).

2.3- Scrubbing of nitrogen oxides

The removal of nitrogen oxides (NO and NO_2, which are typically grouped under the common term NOx) simultaneously with the removal of sulfur compounds by a single device is the most difficult challenge (Zheng et al., 2014; Ding et al., 2014). At the same time, the use of two technologies simultaneously for the ship has many negative consequences such as the difficulty of operation and maintenance, increased operational costs, or the additional size and weight that replaces the cargo that is supposed to be transported by the ship (MAN Diesel & Turbo, 2011, pp. 5) .

Among exhaust nitrogen oxides, 90-95% of nitrogen takes the form (NO), which is insoluble (Ryu et al., 2020; Zhao et al., 2016). Therefore, it must be either oxidized to a higher valency, such as NO_2 or HNO_2 to increase its solubility in wash water -wet oxidation absorption process- (Liu et al., 2012)., or reduced by a reducing agent to N2 -selective catalytic reduction SCR- (EGCSA, 2012, pp. 16). Therefore, the designers devoted continuous efforts to developing scrubbers, achieving environmental standards and protect the ecosystem. Furthermore, the task would be more challenging if mercury also was a target for removal. For example, removal of sulfur compounds using sodium hydrochloric NaClO as an oxidant is achieved whenever the pH of sodium hydrochloric is increased, while the maximum efficiency of removing nitrogen compounds and mercury when the pH is ranging from 4 to 6 (Byoun et al 2019).

2.3.1- Selective Catalytic Reduction SCR

SCR that transform NOx to N_2 and H_2O, through a catalytic surface and reducing agent like ammonia that can be found from disintegration of urea $CO(NH_2)_2$, that sprayed in exhaust stream (Lloyd`s Register, 2015, pp. 34). The removal efficiency of SCR is proportional to exhaust temperature. Therefore, slow-speed engines still limited use for the SCR, thus is often placed before any WHR systems and after the turbocharger as the highest temperature position of the exhaust gas and sometimes an external heating element is used to increase the catalytic efficiency. Moreover, marine applications sometimes contain a silencer to save the place and weight. The urea solution combines with the water of exhaust and the injected solution, releasing ammonia, which reacts with the nitrogen compounds emitted with the exhaust at the catalytic surface to produce nitrogen and water via the following mechanism.

Decomposition of urea:

- $CO(NH_2)_2 \rightarrow NH_3 + HNCO$
- $HNCO + H_2O \rightarrow NH_3 + CO_2$

Reaction with NOx

- $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$
- $2NO + 2NO_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O$
- $6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$ (EGCSA, 2012, pp. 65)

Removal efficiency of NOx via SCR can reach to 95% especially when used for medium or high-speed engine (Yang et al., 2012).

2.3.2- Oxidation of NO to NO_2 for water absorption

The Oxidation of process, that converts NO to higher valence by the hydroxyl radical •OH which can be provided from the decomposition of some oxidants like Hydrogen peroxide H_2O_2 (Ibrahim, 2016)., sodium persulfate $Na_2S_2O_8$ (Khan & Adewuyi, 2010), sodium hypochlorite NaClO (Byoun et al 2019), in conjunction with using many kinds of iron catalysts such as Fe, Fe-Al and Fe-Ti (Huang et al., 2015). Despite many catalysts being effective for NOx reduction, some of them are typically excluded due to their tendency to produce toxic products like ClO_2 while others may be too expensive. Moreover, the presence of Cl^{-} in wash water is considered the main cause of corrosion in scrubbers (Zhou & Wang, 2020). Typically, the removal efficiency by the oxidation-absorption process for SOx reaches 100%, while the oxidation of NO depends on the decomposition of the oxidizer agent (Ding et al., 2014).

The reaction mechanism of oxidation by H_2O_2 as following:

- $H_2O_2 \rightarrow 2OH$
- $\cdot OH + H_2O_2 \rightarrow H_2O + HO_2$
- $HO_2 + NO \rightarrow NO_2 + \cdot OH$ (Ibrahim, 2016)

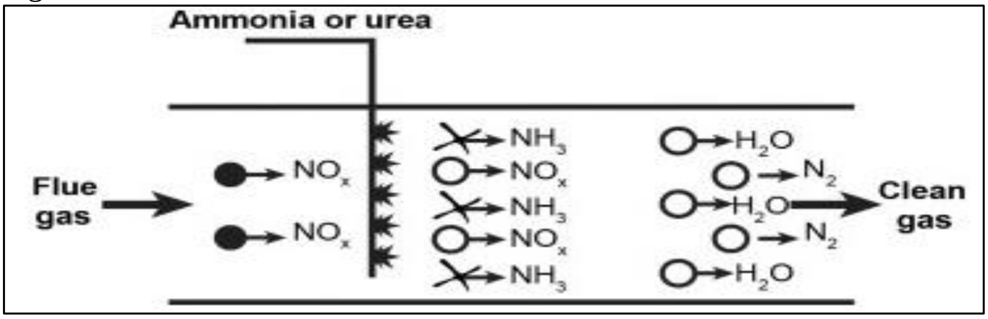
While, the reaction mechanism of oxidation by ClO_2 as following:

- $NO + ClO_2 \rightarrow NO_2 + ClO$
- $NO + ClO \rightarrow NO_2 + Cl$ (Ibrahim, 2016)

2.3.3- Selective Non-Catalytic Reduction (SNCR)

The SNCR technology basis on spreading a reagent such as ammonia or urea in the exhaust duct to react with NO and convert it to N2 and water (Zhou & Wang 2020), which can be released into the atmosphere as air components. The reaction, of course, is affected by many factors, the most important of which are the temperature and the time the materials remain in the reaction space. In addition to the reagent distribution method, the concentration of CO/O2 and the type of fuel, and the nature of the combustion that generates the exhaust. The optimum temperature of the reaction ranges from 870 °C to 1320 °C. The reagent or reductant agent can react with most of the components of the exhaust according to the ambient temperature, therefore the temperature is considered the factor through which it is possible to control and guide the course of the reaction and by which the reaction is considered selective (Sorrels et al., 2019).

Figure -8- Schematic of the SNCR



(Miller, 2017)

The mechanism of SNCR reactions summarizes in one of the following two formulas, depending on the type of reagent, ammonia or urea, both of which react with nitrogen oxide and reduce it to nitrogen and water as shown in the following equations.

- In the case of ammonia

  $2NO + 2NH_3 + \frac{1}{2}O_2 \rightarrow 2N_2 + 3H_2O$

  $2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$
- In the case of urea

  $2NO + CO(NH_2)_2 + \frac{1}{2}O_2 \rightarrow 2N_2 + CO_2 + 2H_2O$

  $2NO_2 + 2CO(NH_2)_2 + O_2 \rightarrow 3N_2 + 2CO_2 + 4H_2O$ (Sorrels et al., 2019)

2.4- Addressing methane slip

In line with the expanding use of LNG in the various sectors, including maritime transport, where the percentage of ships operating with LNG became 13.5% of the global fleet in 2018 (Le Fevre, 2018). Stakeholders are concerned about methane slippage associated with the use of LNG. There are no regulations regarding typical or acceptable values for unburned methane leakage when LNG is used as a fuel. However, most companies pay attention to methane slips by its role in global warming. Methane is described as one of the most important factors of global warming (Schneiter, 2019). In fact, its effect is higher than the effect of carbon dioxide by 25 times within a century

(Lighthouse, 2020). At the same time, the International Maritime Organization presents Liquefied Natural Gas as a promising solution and one of the most important alternative fuels to meet the requirements of reducing air pollution about sulfur and nitrogen compounds (Brynolf et al., 2014). The abundance and cheapness of LNG compared with other fuels and meets the environmental requirements regarding sulfur and nitrogen emissions without techniques or EGCSs. Sulfur content in it is about 0.01%. Thus the emissions of nitrogen oxides will be at Tier III when Otto-cycle engines are used (Bengtsson et al., 2011). Despite the drawback that accompanies LNG use, it is considered one of the preferred types of fuel over traditional marine fuels, both environmentally and economically (Lebedevas et al., 2021). Therefore, different techniques have emerged to address the problem associated with LNG use, which is methane slip. Some of these techniques address the causes of the problem, such as adopting a specific operating cycle or determining a high air/fuel ratio. In contrast, others adopt after-treatment measures like Non-Thermal Plasma technology or catalytic oxidation. Engine manufacturers are racing to produce LNG-powered engines that emit as little methane as possible. For example, MAN reports that its new high-pressure dual-fuel engines involve methane slip of 0.2 - 0.4 g/kWh, while some data indicate the existing engines emiting between 0.9 and 7 g/kWh at the weighted load of the engine; these amounts become double when the engine load is reduced to less than half of the total load (lighthouse, 2020).

CHAPTER III

SIMULATION TEST SETTINGS

Due the SNCR is characterized by low capital and operating costs (Ding et al., 2014). This research will study it in-depth, in two directions; remove nitrogen components from the exhaust gas of traditional fuels and treat methane slippage in the exhaust gas of LNG fuel.

3.1- Selective Non-Catalytic Reduction of NOx

A cylindrical plug-flow-reactor using only for gas-phase chemistry has been developed with different dimensions, to be used for medium and high-speed engines, and for oil-fired boilers. For engines, it should be placed before the turbocharger to take maximum advantage of the temperature and pressure. Likewise, in boilers; it should be placed directly after the combustion chamber for the same cause. The reactor is equipped with ammonia atomizer(s) and an external heating element. It needs at least 750 degrees Celsius for effective operation, and it can be little more than that according to the exhaust mass flow rate. As a result, the reactor can transfer boilers or engines designed to meet the Tier II requirements of nitrogen compounds emissions to Tier III once in operation without further procedures.

To study the oxidation process of nitrogen compounds in exhaust gases. Two different sizes of Wartsila engines were taken as case studies; 12V46DF and 8L20. The first is a dual-fuel engine, the second run by diesel oil only. Both run within temperature ranges of 294C--314C and 355C-385C respectively, as well as 21.5--23.3kg/s and 1.6--3.11kg/s mass flow rate for each, respectively.

Based on the mass of exhaust gas generated by engines at a specified MCR, the exhaust pipe diameter must be determined to achieve a gas velocity about of 35 m/s, which is the ideal value for exhaust velocity to avoid excessive pressure loss (Wartsila, 2015, pp. 7). MAN Company indicates that the exhaust velocity should not exceed 50 m/s to avoid the formation of back pressure on the engine (MAN B&W, 2016, sec 15.03, pp. 1 of 1). While Rolls-Royce suggests that the maximum velocity of the exhaust is 45 m/s to avoid resonance hazards as well (Rolls-Royce, 2016, pp. 2.03). Generally, exhaust velocity is directly proportional to temperature and inversely to the diameter of the pipe. This correlation can be observed by the equations below.

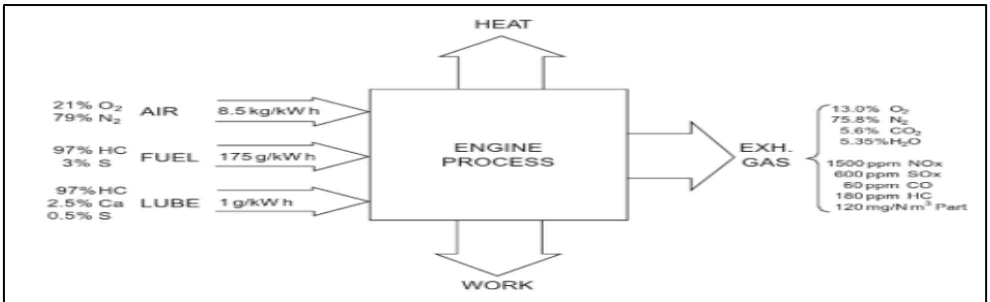
$$\left.\begin{array}{l} V = M / \rho * 4 / (\pi * D^2) \\ \rho = 1.293*273 / (273+T) * 1.015 \end{array}\right] \text{(MAN B\&W, 2016, sec 15.05, pp. 1 of 3)}$$

Where:

- ρ is the density of Exh. Gas in kg/m³
- **V** is the velocity of Exh. Gas in m/s
- **M** is the mass of Exh. Gas at specific MCR in kg/s
- **T** is the temperature of Exh. Gas at specific MCR in °C
- **D** is the diameter of exhaust pipe in m

The length and diameter of the reactor are depend on mass flow rate of exhaust gas, and exhaust gas components percentages were defined as O_2: 13, N_2: 75.8, NO: 0.15 (Woodyard, 2009). As for ammonia, there is a ratio between it and exhaust nitrogen mostly ranging from 0.25 to 3 (Javed et al, 2008).

Figure -9- Typical exhaust emissions



Typical exhaust emissions from a modern low-speed diesel engine

(Woodyard, 2009).

By using the Cantera 2.5.1 chemical kinetic software tools implemented in the Python 3.9.2 programming language with reactions mechanism of Yaml after some modifications such as insert equations of density and velocity (Krishna, 2018). The length of the reaction tube, ammonia ratio, and the ambient temperature were changed within many tests, also the diameter of the reactor -exhaust pipe- was changed, taking into account the permissible gas velocity limits. Generally, the length of the reaction tube and the velocity of exhaust gas directly affect the time of the reactions (Javed et al., 2008), in addition, exhaust gas velocity has an obvious effect on the quality of mixing the oxidizer spray with exhaust gas before entering the reaction tube. The reactor simulated with quantities of exhaust gas identical to what is generated by the engines of Wartsila type 12V46 and 8L20LF at full load. The mass flow of exhaust gases for each was 27.4 and 3.11 kg/sec, respectively (Wartsila, 2019, pp. 3-17; Wartsila, 2013, pp. 14). At 3 NH_3/NO ratios, 97% of NOx removed as shown in table -2-.

Table -2- Simulation parameters of NO oxidation

Wartsila	T - °C	M - kg/s	D - m	V - m/s	P - bar	L - m	NH_3/NO	Removal Eff	Load
12V46DF	750	27.4	3	11	1	3	3	97.0%	100
8L20	750	3.11	1.5	5	1	1.5	3	97.0%	100

Source: created by author

Figure -10- Simulation results of NO oxidation on Python 3.9.2

```
Python 3.9.2 (tags/v3.9.2:1a79785, Feb 19 2021, 13:44:55) [MSC v.1928 64
bit (AMD64)] on win32
Type "help", "copyright", "credits" or "license()" for more information.
>>>
= RESTART: E:\dissertation sources& data_statistics\SNCR\Ahmad script
12V46DF.py =
velocity 11.067934786283361
area 7.0685834705770345
dia of tube 3.0
pressure 405300.0
length 3.0
temperature 1023.0
exhaust mass 27.4
CanteraWarning: NasaPoly2::validate:
For species HOCHO, discontinuity in h/RT detected at Tmid = 1000.0
       Value computed using low-temperature polynomial:  -
40.3603591666667
       Value computed using high-temperature polynomial: -
38.1678611841666

0.0015800844025871722
4.942400210065004e-05
eff 0.9687206569347023
>>>
== RESTART: E:\dissertation sources& data_statistics\SNCR\Ahmad script
8L20.py =
velocity 5.025003968662956
area 1.7671458676442586
dia of tube 1.5
pressure 101325.0
length 1.5
temperature 1023.0
exhaust mass 3.11
CanteraWarning: NasaPoly2::validate:
For species HOCHO, discontinuity in h/RT detected at Tmid = 1000.0
       Value computed using low-temperature polynomial:  -
40.3603591666667
       Value computed using high-temperature polynomial: -
38.1678611841666

0.0015788466931340385
4.649064024862698e-05
eff 0.9705540503388895
```

Source: created by the author

3.2- Oxidation of Methane

In recent years, a significant increase in the use of LNG as a marine fuel, for other types than LNG tankers (Lighthouse, 2020). Therefore, a model of exhaust gas of LNG-powered engines will be tested by a script program from the Cantera 2.5.1 chemical kinetic software tools implemented in the Python 3.9.2 programming language, adopting a reactions mechanism of YAML after some modifications such as insert equations of density and velocity. In addition to, the circumstances of reaction are readjusted to achieve the best results, such as the dimensions of the reactor and reaction temperature, taking into account the exhaust velocity to be within the permissible limits.

The simulation was carried out on two different sizes of Wärtsilä's engines, which are 16V50DF and 6L46DF with their operation parameters (Wartsila, 2019, pp. 3-17; Wartsila, 2019, pp. 3-1). In addition to, a hypothetical engine with violent operating conditions that were taken from a slow-speed MAN engine for the test. They were examined and tested under the various expected engine conditions and according to the operating information published by the manufacturer. Exhaust gas compositions percentages were assumed as CH_4: 2.3, CO_2: 2.3 (Bengtsson et al., 2011), and O_2: 13, N_2:75.8 (Woodyard, 2009). Through simulation tests that based on the amount of gas flowing and its temperature, the length of the reactor was set to be 3 meters and its diameter of 3 meters also. In order to meet the environmental requirements even it use for the big size engines, with an oxidation efficiency up to 97% or more, while maintaining the exhaust velocity below 35 m/s for the reasons mentioned previously. Table -3- shows results.

Table -3- Simulation parameters of CH_4 oxidation

Engine	Load %	Mass kg/s	Temp °C	P - bar	L - m	D - m	velocity m/s	η
Wartsila 16V50DF	100	24.5	401	1	3	3	6.5	97%
	75	19	445	1	3	3	5.3	96%
Wartsila 6L46DF	100	11	367	1	3	3	2.7	97%
	75	8.3	409	1	3	3	2.2	96%
hypothetical		120	231	1	3	3	30	99%

Source: created by the author

Figure -11- Simulation results of CH_4 oxidation on Python 3.9.2

```
Python 3.9.2 (tags/v3.9.2:1a79785, Feb 19 2021, 13:44:55) [MSC v.1928 64
bit (AMD64)] on win32
Type "help", "copyright", "credits" or "license()" for more information.
>>>
= RESTART: E:\dissertation sources&
data_statistics\Methane\surf_pfr1_Ahmad.py =
    distance        X_CH4        X_H2        X_CO
    0.000000     0.022955     0.000571     0.000001
  3000.000000     0.000767     0.000002     0.000000
velocity 6.520281950392688
diameter 3.0
length 3.0
temperature 401
mass flow 24.5
efficiency 0.9665807233943753

= RESTART: E:\dissertation sources&
data_statistics\Methane\surf_pfr1_Ahmad.py =
    distance        X_CH4        X_H2        X_CO
    0.000000     0.022676     0.000736     0.000000
  3000.000000     0.000580     0.000002     0.000000
velocity 2.77979682254978
diameter 3.0
length 3.0
temperature 367
mass flow 11
efficiency 0.9744112544386583

= RESTART: E:\dissertation sources&
data_statistics\Methane\surf_pfr1_Ahmad.py =
    distance        X_CH4        X_H2        X_CO
    0.000000     0.015542     0.003179     0.000000
  3000.000000     0.000124     0.000001     0.000000
velocity 23.880981793723112
diameter 3.0
length 3.0
temperature 231
mass flow 120
efficiency 0.9920114709392387
```

Source: created by the author

Reactions mechanism by (Quiceno et al., 2006)

1- H_2 + 2 PT(S) => 2 H(S)

2- O_2 + 2 PT(S) => 2 O(S)

3- CH_4 + 2 PT(S) => CH_3(S) + H(S)

4- CH_4 + PT(S) + O(S) => CH3(S) + OH(S

5- CH_4 + PT(S) + OH(S) => CH_3(S) + H_2O(S

6- H_2O + PT(S) => H_2O(S)

7- CO_2 + PT(S) => CO_2(S)

8- CO + PT(S) => CO(S)

9- 2 H(S) => H_2 + 2 PT(S)

10- 2 O(S) => O_2 + 2 PT(S)

11- H_2O(S) => H_2O + PT(S)

12- CO(S) => CO + PT(S)

13- CO_2(S) => CO_2 + PT(S)

14- C(S) + O(S) => CO(S) + PT(S)

15- CO(S) + PT(S) => C(S) + O(S)

16- CO(S) + O(S) => CO_2(S) + PT(S)

17- CO_2(S) + PT(S) => CO(S) + O(S)

18- CO(S) + OH(S) => CO_2(S) + H(S)

19- CO_2(S) + H(S) => CO(S) + OH(S)

20- CH_3(S) + PT(S) => CH_2(S) + H(S)

21- CH_2(S) + H(S) => CH_3(S) + PT(S)

It is worth noting that can reduce the diameter of the reactor if the system is installed at a point of the exhaust pipe or for another engine with a low temperature where the diameter can be 2.5 meters for the same amounts of exhaust gas at a temperature of 200 degrees Celsius without affecting the removal efficiency as shown in figure -12-. Thus, the reaction mechanism selected meets the requirements of majority engines at different operating conditions and sizes.

Figure -12- Simulation results of CH_4 oxidation on Python 3.9.2 at low temperature.

```
Python 3.9.2 (tags/v3.9.2:1a79785, Feb 19 2021, 13:44:55) [MSC v.1928 64
bit (AMD64)] on win32
Type "help", "copyright", "credits" or "license()" for more information.
>>>
= RESTART: E:\dissertation sources&
data_statistics\Methane\surf_pfr1_Ahmad.py =
    distance        X_CH4         X_H2         X_CO
    0.000000     0.021690     0.001778     0.000000
  3000.000000     0.000312     0.000008     0.000000
velocity 32.273441109802945
diameter 2.5
length 3.0
temperature 200
mass flow 120
efficiency 0.985626524764873
```

Source: created by the author

CHAPTER IV

APPLICATION OF CHEMICAL KINETIC SIMULATION RESULTS AND PARAMETRIC ANALYSES

4.1- The case study

"Entreprise Nationale de Transport Maritime de Voyageurs (ENTMV)"

National Company of Maritime Transport of Travelers / Algeria

Tassili II is one of the Algerian ferries, its details are shown below. Mainly, she sails in the Mediterranean, between registry port Alger and European countries. The company operates its ships in four routes with three European countries, Spain, France, and Italy. Each round trip consists of three ports, two Algerian and one European. We chose the France route that consists; Algiers-Marseille-Skikda-Algeria because the departure and arrival dates for the month of July /2021 are announced on The Company's website (Algerie ferries, 2021).

Ship name: Tassili II

Owner: Algerian Government

Capacity of passenger: 1320

Capacity of vehicle: 300

Capacity of eco armchairs: 600

Speed: 12.6kn

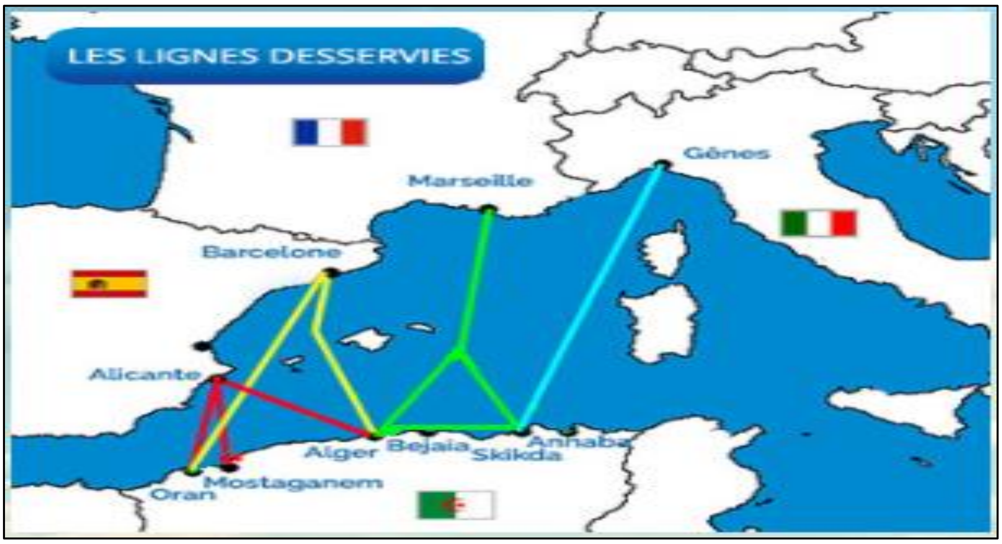
Length: 146.6m

Width: 24m

Main engine: Wartsila 12V46 (12600kw) * 2

Auxiliary engine: Wartsila 8L20 (1600kw) * 4

Figure -13- Algiers-Marseille-Skikda-Algeria route (green



(Algerie ferries, 2021).

According to the program prepared for July/2021, the ship will sail for 161 hours on round trips among three ports, Algiers-Marseille-Skikda. Based on this program, the ship will release the number of nitrogen oxides at diesel operation mode, and methane will be slipped at LNG operation mode. Both modes` emissions will be calculated from the main and auxiliary engines, according to actual running hours for a year, considering that the operating program is constant for ten months per year and the remaining two months are for maintenance and expected repairs. Thus, the main engines will record 161 hours per month for each (322 hours for both). In comparison, the auxiliary engines will record 161 hours for two engines, in addition to 559 hours distributed among all auxiliary engines without specifying (881 hours for all). The 559 hours present the period of the ship’s stay in the ports, assuming that the ship sails with two main engines at full load and two auxiliary engines at full load also, while only one auxiliary engine during the port period.

4.2- Nitrogen Oxides

According to the specifications of the Main and Auxiliary engines, the total amount of nitrogen oxide emitted during ten months - an operational year -

amounted to 416258 tons. As for the quantities removed by the non-catalytic oxidation system, according to the average efficiency of 97% as shown in graphs 1a, they amounted to 403770 tons. It is noted that this amount of reduction in nitrogen oxides emissions transferred the ship's performance to meet the requirements of the emissions control areas ECA. In other words, it achieved at least the minimum of Tier 3 of the regulations of the International Maritime Organization.

Table -4- The amount of NOx removed

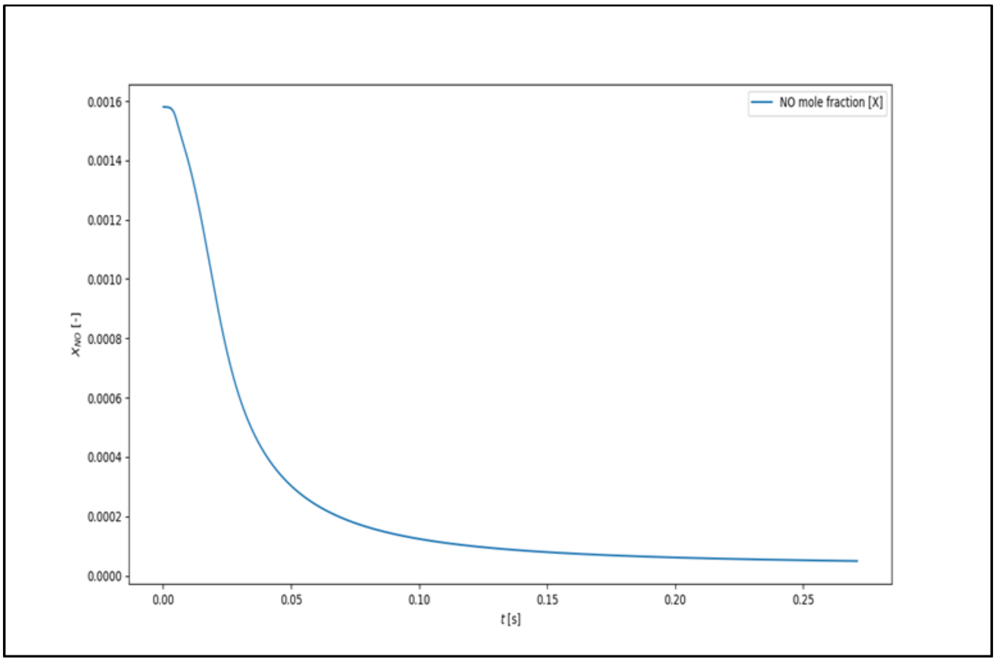
Nitrogen oxides		
Engine	NO emitted (t/y)	NO Removed (t/y)
M/E	317621	308092
A/E	98637	95678
Total	416258	403770

Source: created by the author

Due did not obtain the amounts of nitrogen oxides emitted by the shipping industry in recent years, the amounts of nitrogen components emitted in 2001 were adopted as a baseline, taking into account the increase in the global fleet and by comparing the increases of the amounts of carbon dioxide (Clarkson report No. 901834) starting from 2001 to 2021.

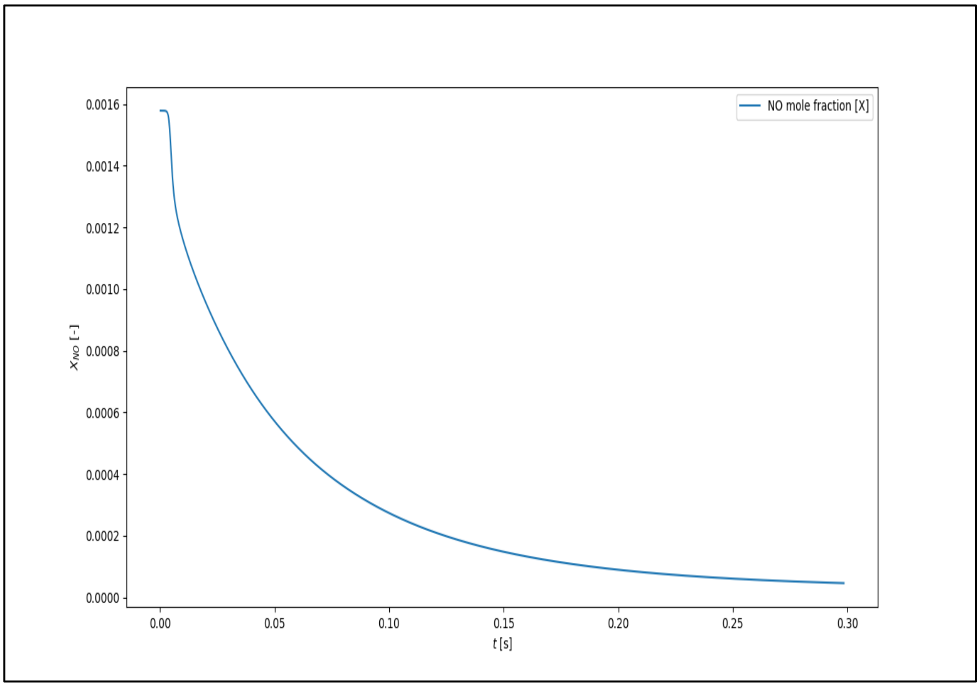
The amount of nitrogen emitted in 2001 was 6.87 million tons (James and Corbett, 2003); therefore, the amount of NOx that will emit in 2021 is 7.71 million tons. Thus, based on the efficiency achieved 97% as shown in graph 1a and 1b, NOx that this system can remove will be 7.48 million tons, as for remaining NOx will be 0.23 million tons.

Graph -1a- The oxidation of NO at M=27.5kg/s, T=750°C, L=3m, D=3m, $NH_3/NO=3$, η =97%



Source: created by the author

Graph -1b- The oxidation of NO at M=3.11kg/s, T=750°C, L=1.5m, D=1.5m, $NH_3/NO=3$, η =97%



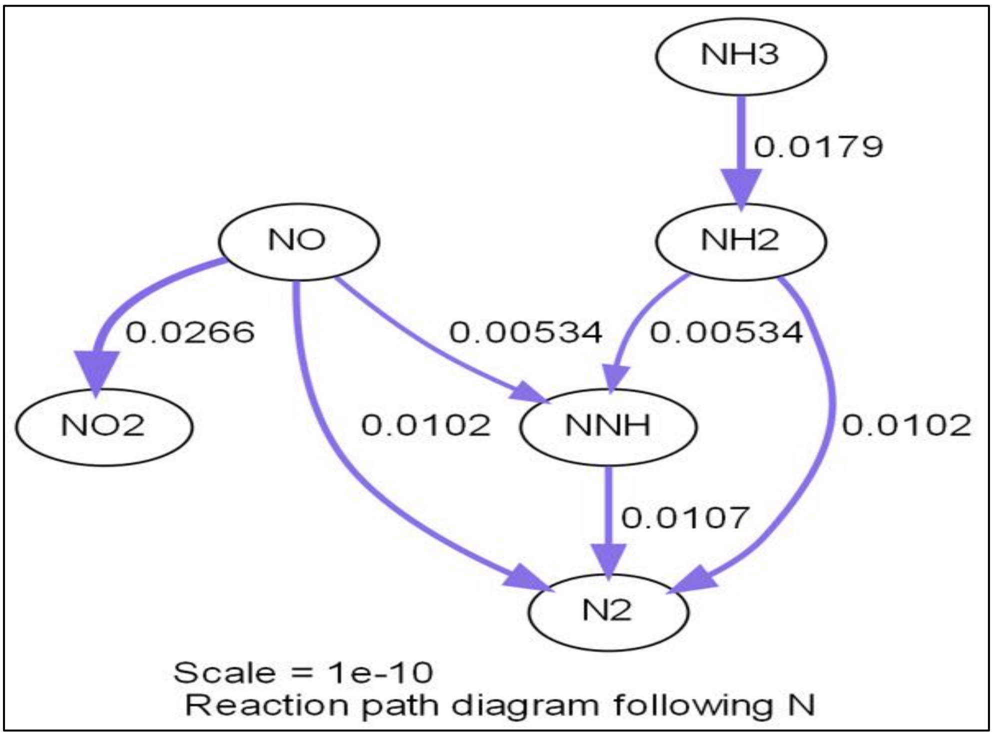
Source: created by the author

Through simulation tests, it has been observed that the system can be manufactured in different dimensions to suit various types of engines and boilers. Table -2- shows two different sizes in lengths and diameters. Thus all operation parameters differ depending on the power plant or in other words, depending on the amount of exhaust gas to be cleaned. It was also noted that the reaction needs high temperatures more than the exhaust temperature. For example, the 8L20 engine from Wärtsilä required 750°C -365°C more than exhaust gas temperature to remove 97% of NO as shown in graph 1b.

In addition to, the process is affected by the residence time, which is a function of diameter, length, and temperature as well. Therefore, the SNCR is suitable for high-temperature power plants for some extent.

Figure -14- is plotted by Python program 3.9.2 to shows the reaction pathway starting with NH3 decomposition and ending with NO reduction. In addition to noting the importance of the ratio of NH3/NO. The products of the reaction are N2 and NO2, both of which have high water solubility. Thus, it confirms the efficiency of the system.

Figure -14- Reaction path diagram



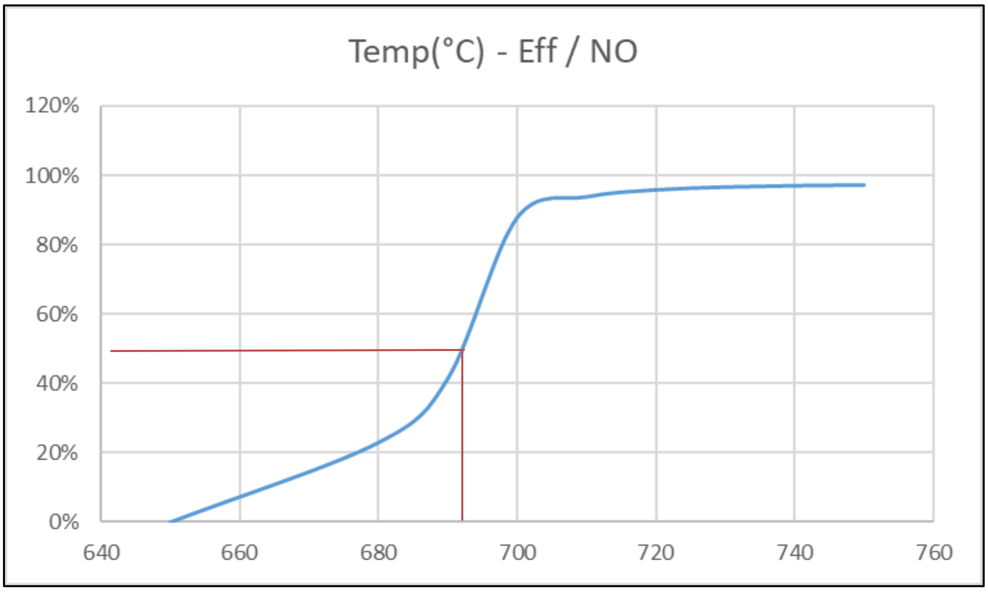
Source: created by the author

The graphs -2a, 2b- show how temperature affects the reaction course and the efficiency in general, as it is considered the pivotal player in this reaction. The red line indicates the *light-off* * temperature, usually set mainly according to the mass of gas passing through the reactor, then other parameters such as the NH3/NO ratio, diameter and length of the pipe, and pressure. Thus, for example, the light-off temperature of the Wartsila 12V46DF engine that generates 27.4 kg/s of the exhaust is 692 Celsius. In comparison, it is 676.5 Celsius for the Wartsila 8L20 engine that generates 3.11 kg/s at the same dimensions and parameters.

---

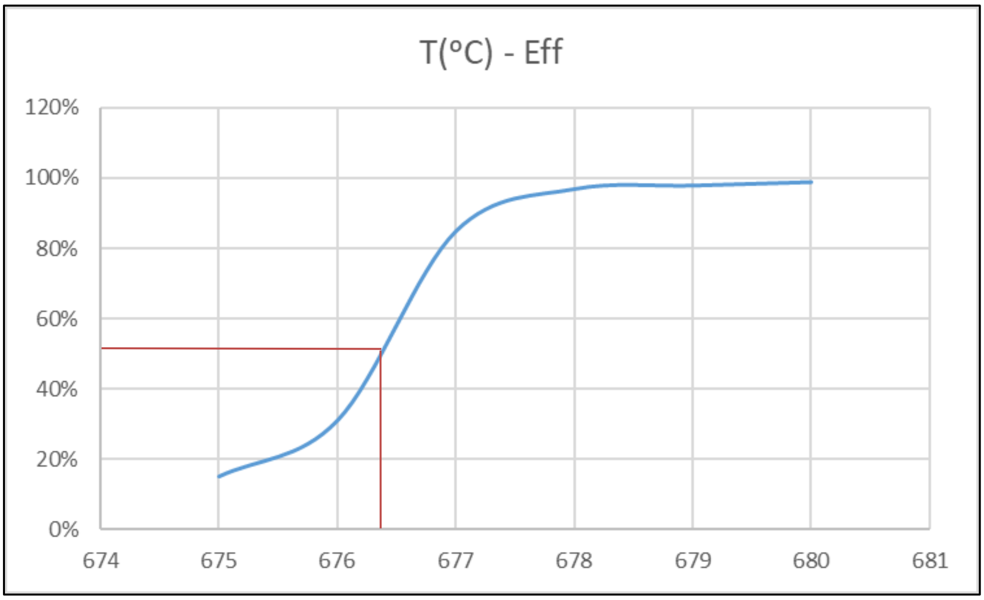
*_It is the lowest temperature at which the reaction begins, and sometimes 50% is considered the starting point of the reaction instead of zero (“Catalytic Converter”, 2021).

Graph -2a- The effect of temperature on reaction and the light-off temperature at constant the other parameters; D=3m, L=3m, P=1atm, $NH_3/NO=3$ (12V46DF)



Source: created by the author

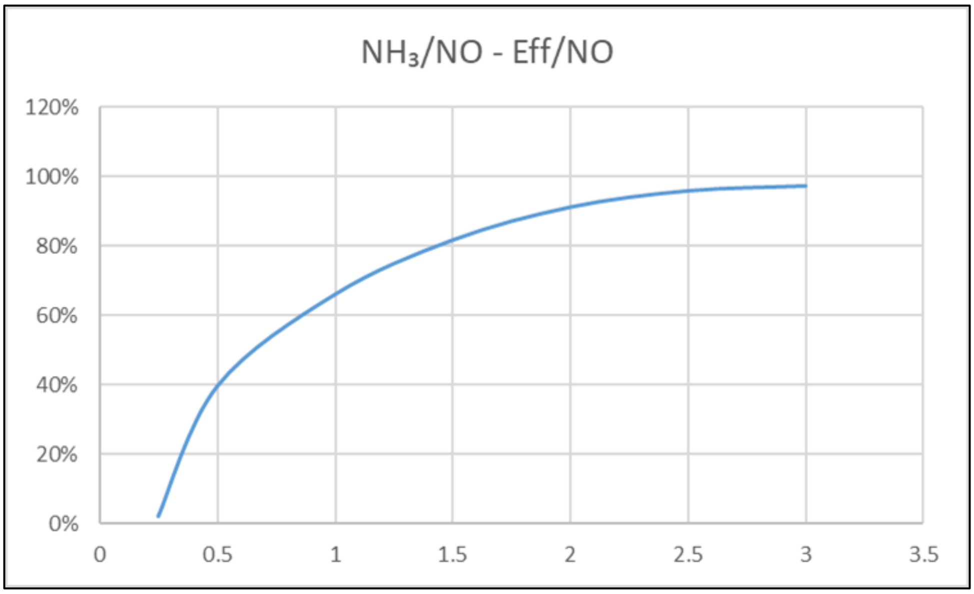
Graph -2b- The effect of temperature on reaction and the light-off temperature at constant the other parameters; D=3m, L=3m, P=1atm, $NH_3/NO=3$ (8L20)



Source: created by the author

The amount of ammonia released into the exhaust stream is determined by the amount of nitrogen oxides emitted by the exhaust. The ratio of NH/NO affects the oxidation process no less effectively than the effect of temperature, as shown in graph -3-. Therefore, even the decrease in temperature can be compensated by an increase in the percentage of ammonia, provided that the drop does not reach the point of the light-off temperature referred to previously.

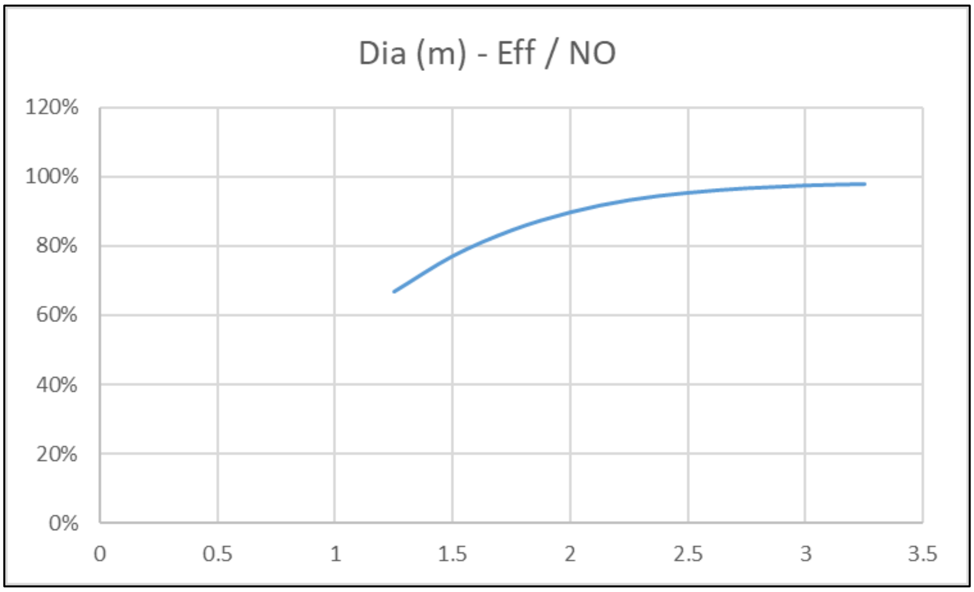
Graph -3- The effect of NH_3/NO ratio at constant the other parameters; D=3m, L=3m, P=1atm, T=750°C



Source: created by the author

The diameter of the reactor follows the temperature and the ratio of NH_3 / NO in terms of affecting the efficiency, as increasing the diameter reduces the velocity of the gases and thus increases the reaction time. Hence, it is possible to compensate for some of the lack of heat or the amount of ammonia by increasing the diameter of the tube. Graph -4- shows the relationship between diameter and efficiency.

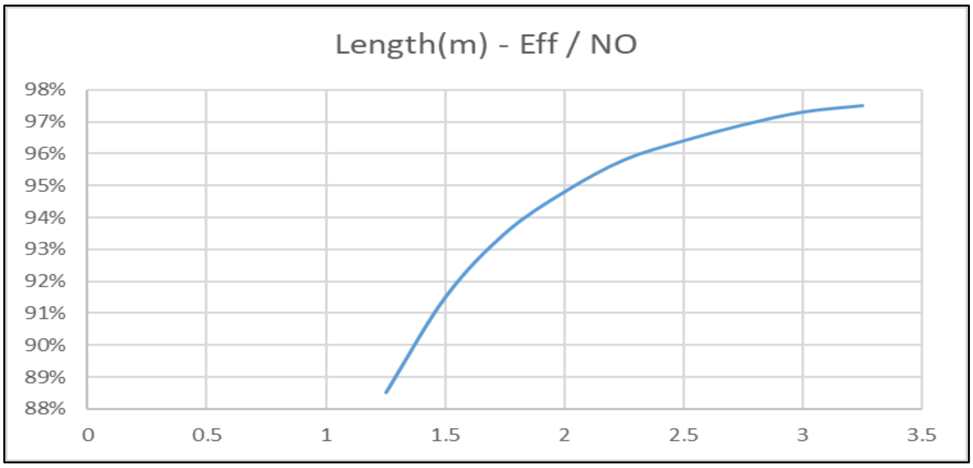
Grapf-4- The effect of diameter at constant the other parameters; $NH_3/NO=3$, L=3m, P=1atm, T=750°C



Source: created by the author

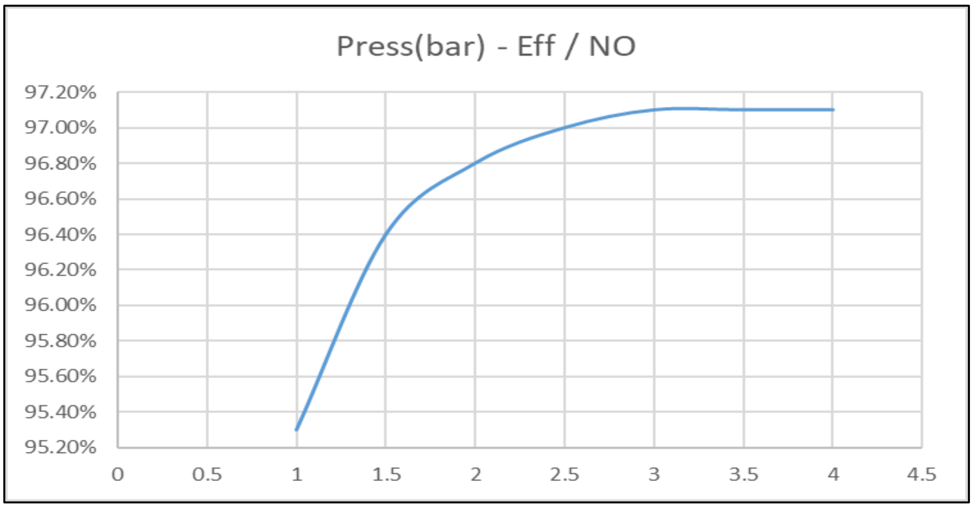
As for the reactor length and the pressure, they have a negligible effect on the reaction in direct proportion and are limited range to a certain extent, and they have no impact outside their respective scope. Therefore, length and pressure influence can be neglected, as an increase in pipe diameter by half a meter can be equivalent to the rise in pressure of 3 bars. Graphs -5, 6- show these relationships.

Graph -5- The effect of length at constant the other parameters; $NH_3/NO=3$, D=3m, P=1atm, T=750°C



Source: created by the author

Graph -6- The effect of pressure on reaction at constant the other parameters; D=3m, L=3m, T=725, $NH_3/NO=3$



Source: created by the author

Although the reactor needs a power source to operate the heating elements, for example, the Wratsila engine (8L20) needs 415 degrees Celsius in addition to the exhaust temperature, as well as the need to add ammonia throughout its operation. It is able to change the exhaust specifications of ships' engines designed to meet the requirements of Tier II of the IMO regulations to Tier III that is, allowing them to sail within the emissions control areas. This in itself is beneficial for ships that frequent the control zones at spaced intervals since the reactor will remain switch off as long as the vessel is outside the emissions control areas. As for the energy required to raise the exhaust temperature to the required temperature, can install an external burner at the front of the reactor, and the amount of fuel is determined according to the engine load. The presence of the burner can also oxidize some unburned hydrocarbons (Lighthouse, 2020).

4.3- Methane slip

Referring to product guides of Wartsila engines, the total methane, which will slips from Tassili engines during a year (3220 hours for main engines and 8810 hours for auxiliary engines), is 9574 tons. Therefore, the quantity converted to friendly environment compounds by the non-catalytic oxidation system at 98% efficiency is 9382 tons as shown in table -5-.

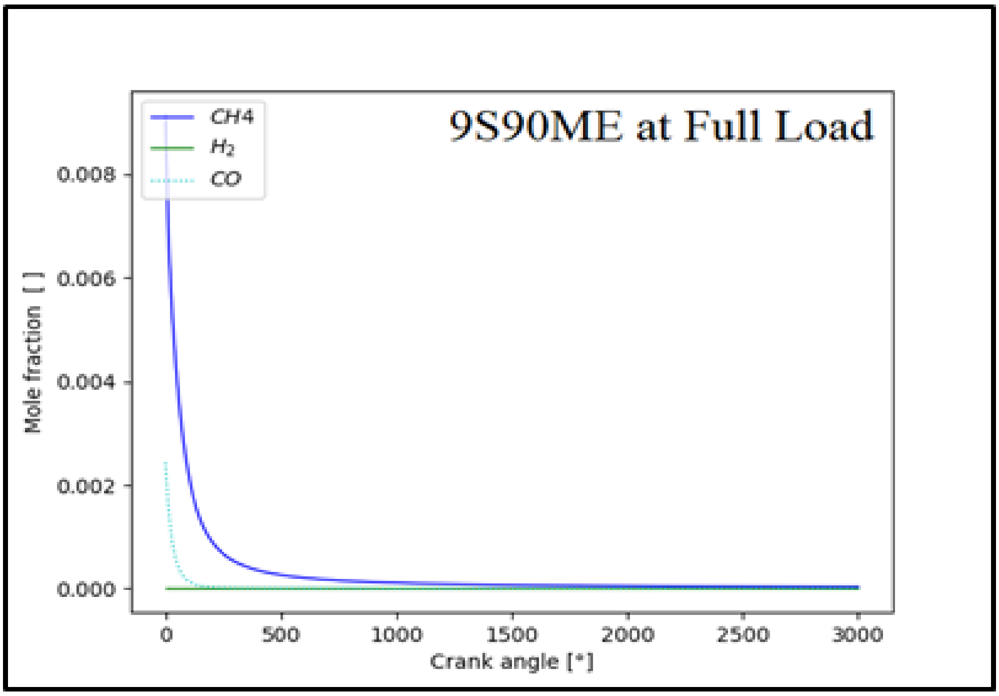
Table -5- The amount of CH_4 removed

Methane slip		
Engine	CH_4 (t/y)	CH_4 Removed (t/y)
M/E	7305	7159
A/E	2269	2223
Total	9574	9382

Source: created by the author

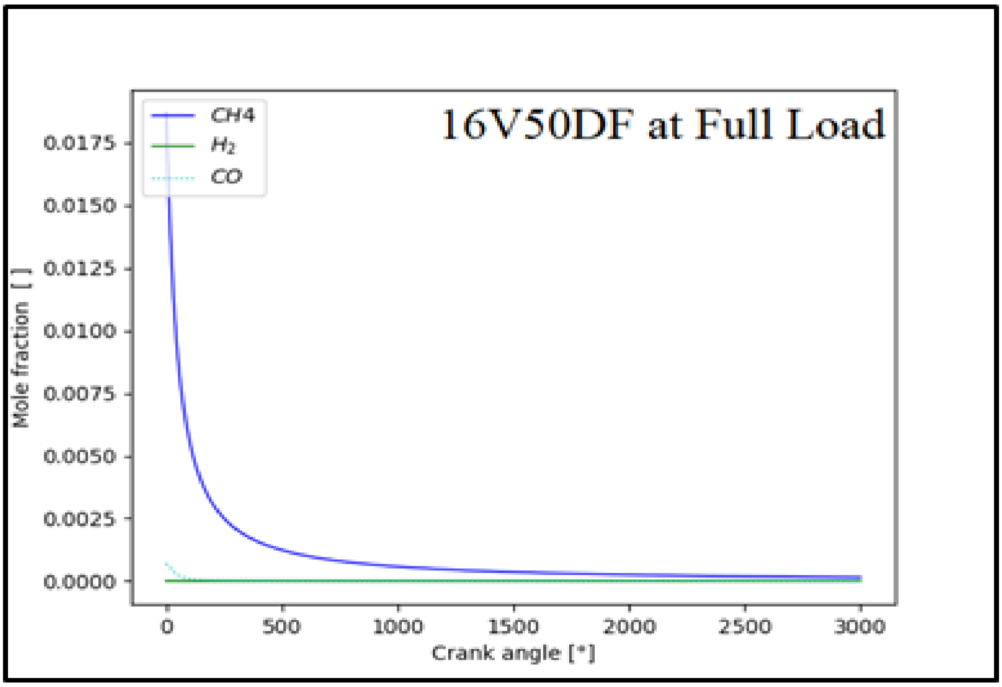
Simulation experiments achieved high-efficiency rates that can reach 98%, especially if the reactor is placed after the waste heat recovery systems (WHR) to increase the efficiency of WHR and avoid the gas velocity increase due to high temperature. Graphs 7a, 7b, 7c, 7d, and 7e show removal efficiencies achieved for 9S90ME of MAN, 16V50DF, and 6L46DF of Wartsila.

Graph -7a- CH_4 oxidation at M=120kg/s, T=350°C, P=1bar, L=3m, D=3m, η =98%



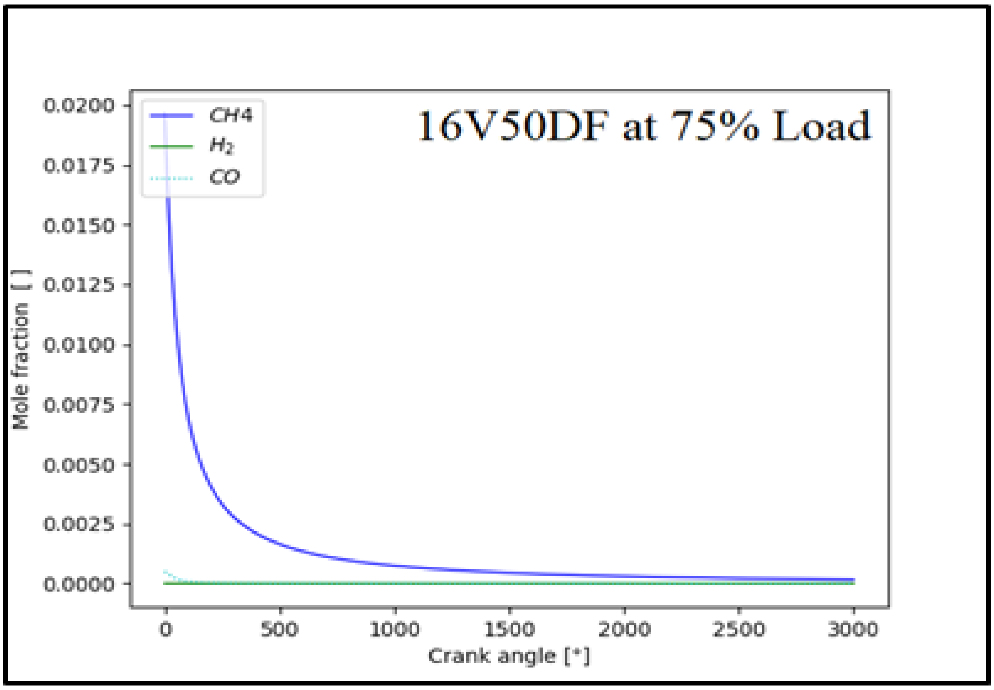
Source: created by the author

Graph -7b- CH_4 oxidation at M=24.5kg/s, T=401°C, P=1bar, L=3m, D=3m, η =97%



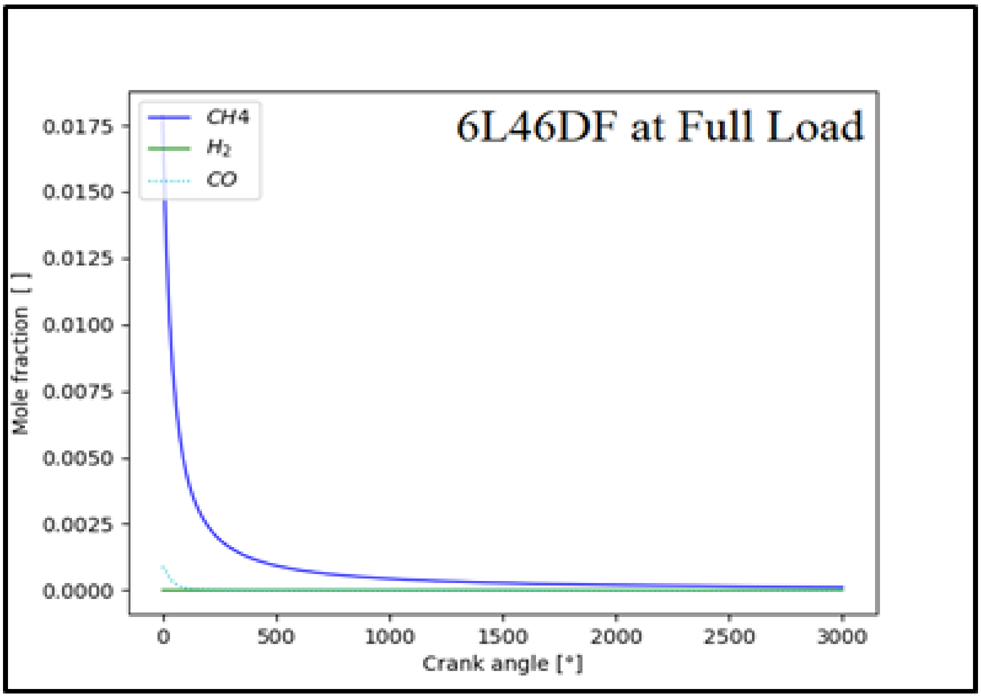
Source: created by the author

Graph -7c- CH_4 oxidation at M=19kg/s, T=445°C, P=1bar, L=3m, D=3m, η =96%



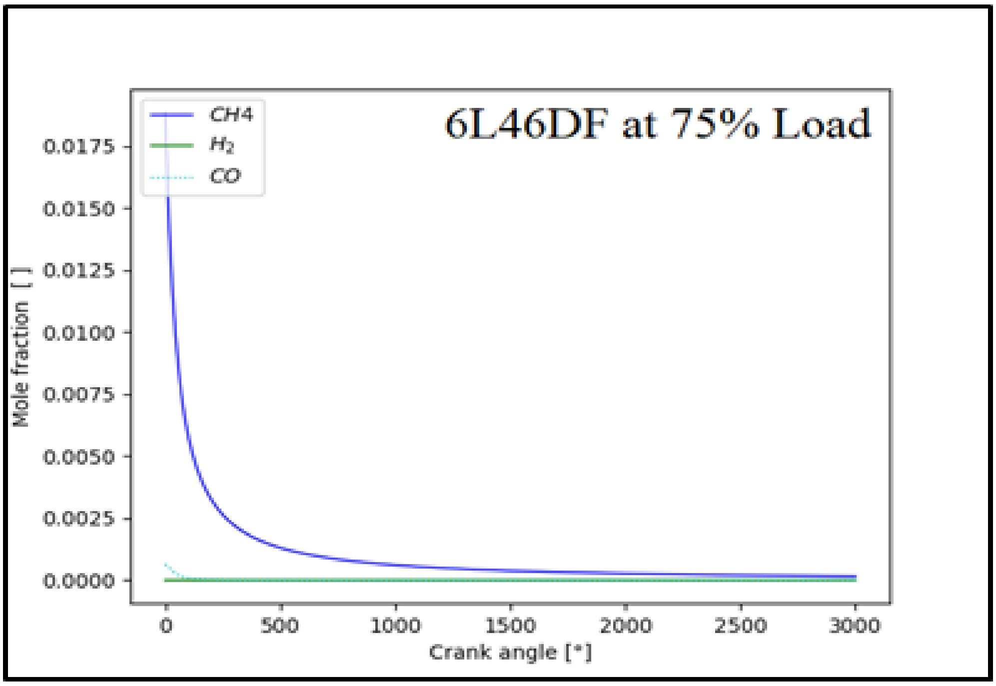
Source: created by the author

Graph -7d- CH_4 oxidation at M=11kg/s, T=367°C, P=1bar, L=3m, D=3m, η =97%



Source: created by the author

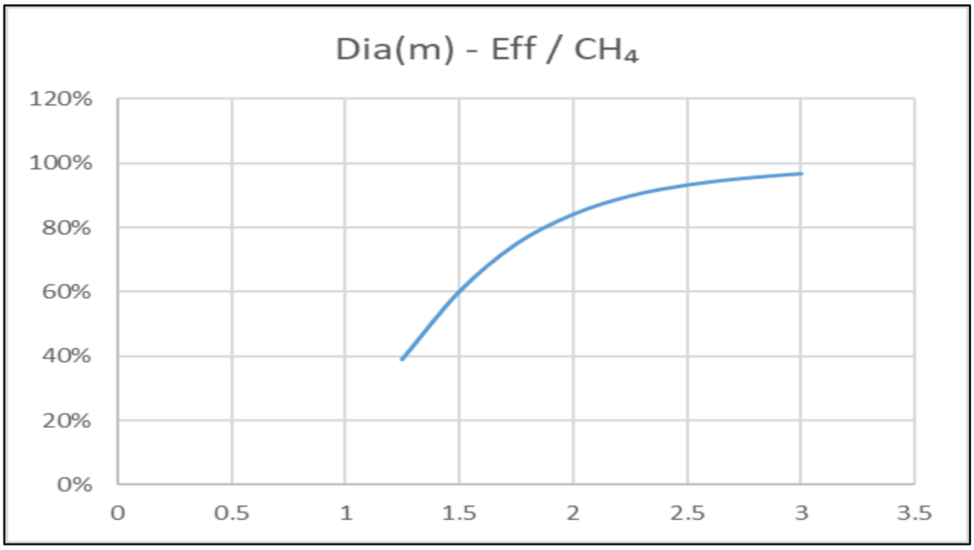
Graph -7e- CH_4 oxidation at M=8.3 kg/s, T=409 °C, P=1bar, L=3m, D=3m, η =98%



Source: created by the author

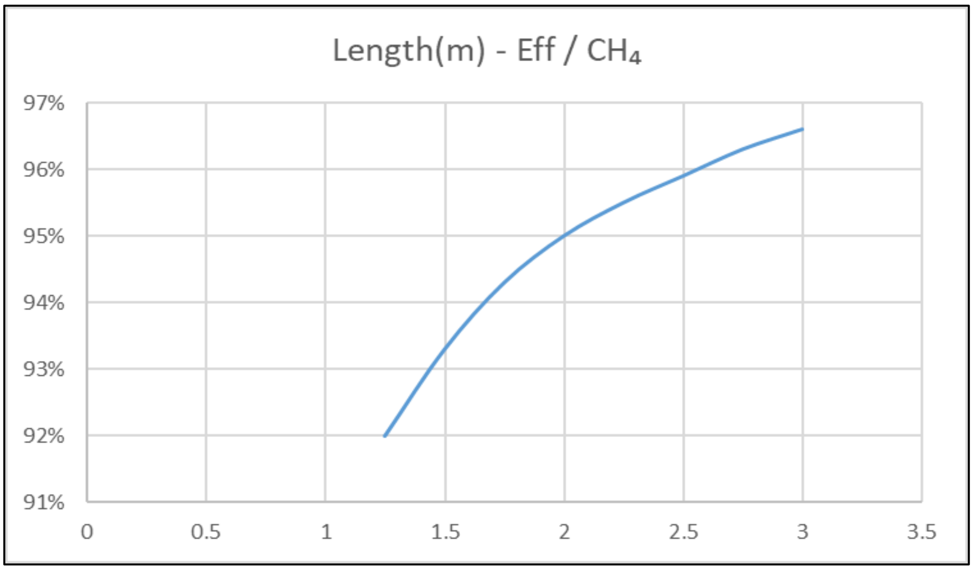
It seems clear through the simulation experiments conducted on two different sizes of the Wartsila engines and a hypothetical engine of MAN. The reaction mainly depends on the time during which the exhaust stays in the reaction space. The graphs below show the relationship between the methane oxidation efficiency and the reaction parameters of an engine that emits 24.5 kg of exhaust gases per second. The pipe diameter is the most influential player as the efficiency decreased from 96.6% to 84% and then to 39%, with a decrease of 1 meter each time, graph -8- . In contrast, the exact value of the reduction in the length of the reactor caused the efficiency to be reduced from 96% to 95% and then to only 92%, graph -9-. The difference in effect occurs because the increase in the diameter decreases the velocity of the gases and increases the reactor volume, that is, the increase in the amount of gas per time unit and increases its residence. Therefore, the diameter of the reactor is a pivotal factor in this reaction process, as providing more time to complete the reaction in the presence of its fundamental elements. Graph -8- shows the effect of the diameter change on the efficiency with all other parameters held constant.

Graph -8- The effect of diameter on the methane oxidation process at, L=3m, T=401°C, M=24.5kg/s, P=1bar



Source: created by the author

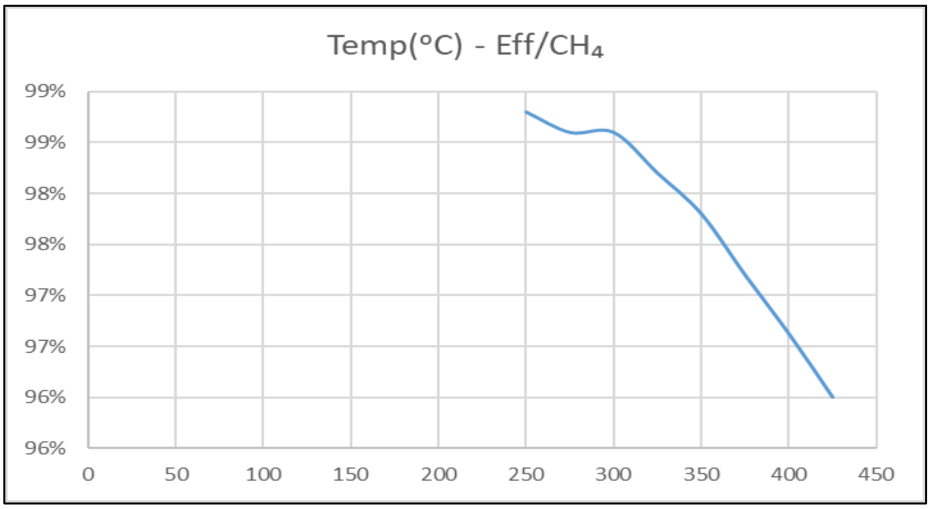
Graph -9- The effect of length on the methane oxidation process at M = 24.5kg/s, T = 401°C, D = 3m, P = 1bar



Source: created by the author

The temperature usually affects the quality of chemical reactions, and the proportion between them often is direct (Basile et al., 2001). In this reaction, because the reactants are gaseous and have directional movement, the temperature has another effect that causes an increase or decrease in its velocity by changing the gas's density. In other words, the temperature changes the residence time, which is very important to complete the interaction. Graph 10 clarifies the inverse proportion between the efficiency of oxidation and temperature, indicating the importance of the time factor for this reaction, which exceeds the importance of temperature for the reaction mechanism itself.

Graph -10- The effect of temperature on the methane oxidation process at M = 24.5kg/s, L = 3m, D = 3m, P = 1bar



Source: created by the author

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

One of the priorities of this modest research is to shed light on the gaseous pollution arising from the use of marine fleets of various types of engines and fuels, which often reflect negatively on the environment and human health. The most pollutants that have attracted researchers' attention are sulfur compounds, nitrogen, mercury, and suspended particles, and the list goes on for chemists. In conjunction with the growth of international maritime trade, which was accompanied by an obvious increase in the volumes of goods and consequently an increase in the sizes of ships and their engines, in other words, an increase in their consumption of fuel, which leads to pollution of all kinds. The Environmental Protection Committee of the International Maritime Organization has issued some standards and regulations for ships regarding pollution by sulfur compounds and nitrogen compounds as well as greenhouse gases, left the door open for stakeholders to choose the method of compliance; as the use of low-sulfur fuels, the use of alternative fuels or the use of exhaust cleaning systems. Each method is accompanied by advantages and disadvantages, depending on the type and age of the ship, its operation zone, the imposed laws, and the volume of services available in the ports it frequents. The first way is the use of low-sulfur fuel is the fastest solution that can be followed by existing ships of all kinds and does not require any modification or change in the ship's hull or engines except for a cleaning process for the fuel system and tanks. This procedure can be implemented during the normal consumption of old fuel. Low-sulfur heavy fuel (LSHFO) is not available enough because of the old specifications of current refineries, so it is replaced by light fuel of one of the two types MDO or MGO. both of which are more expensive than heavy fuel (380cST) by about 300 US dollars per ton and most European countries suffer a shortage of it for cars (Lloyd`s

Register, 2015, pp. 9). The second solution, which is a promising solution because it gets rid of sulfur and nitrogen compounds almost completely, is the use of alternative fuels such as natural gas, petroleum gas, and biofuel. LNG is one of the most important of these alternatives. It is available and cheap compared to fossil fuels if the energy content is neglected. LNG is characterized by good combustion characteristics, its sulfur and nitrogen emissions are very low, where the SOx emissions are less by 90-95%, meaning that it meets the requirements of emissions control areas. Natural gas is also characterized by a lower carbon content by 20-25% compared to conventional fuels, and any methane leakage must be avoided to maintain this advantage (MAN Diesel & turbo, 2011, pp. 3). The use of LNG as fuel for ships is faced by the lack of infrastructure for storing and bunkering. In addition, the existing ships need a major modification, including the development of tanks that suit the storage conditions of LNG, as well as modifying the engine. As for the environmental aspect, the use of natural gas involves a significant slip of methane, as it is one of the most important greenhouse gases and more influential than carbon dioxide in this field. The third option to comply with the requirements of the Environmental Protection Committee is the use of exhaust gas cleaning systems EGCSs. These systems are divided in terms of their mechanism of action into two main parts: dry, which are limited in use on ships, the wet, which are the most famous, used in three different mechanisms -open, closed, or hybrid loops- were previously detailed. These systems are specialized in removing sulfur compounds and some suspended particles. Another section of EGCSs specialized removing of nitrogen oxides and the treatment of the slipped methane associated with the use of liquefied natural gas. Both of which depend on the principle of chemical reactions with conditions and factors that differ from one type to another. In addition, there are methods that can be followed to reduce nitrogen oxides such as recirculating part of the exhaust and entering it into the combustion chamber, including water in the combustion mixture either with fuel or directly to the cylinder, reducing the mean effective pressure of combustion. It is noted that all of them adopt the principle of lowering the combustion temperature to reduce the chance of nitrogen reacting with oxygen to produce NOx, which depends mainly on temperature. By these systems, it is possible to continue using high-sulfur fuel, but they are characterized by their high weight and the consequent change in the ship's stability, especially since its position is high in relation to the main deck of the ship, not to mention the recovery time and the remaining lifespan of the ship.

The noted from the foregoing that getting rid of all harmful emissions simultaneously is very difficult, and it cannot be achieved without sacrificing other aspects of profitability; Investment or operational or both together, throughout the next period of the ship's life, where the problem is to enhance the absorption of NO in water (Zheng et al., 2014). Therefore, we believe that it is better for existing ships to adopt low-sulfur fuel, as it involves operational losses that represent the difference between its price and the price of conventional fuel. As for the ships that will be built, they may choose based on their operating area, primarily; Either the adoption of EGCS with one of the modern technologies that reduce nitrogen emissions, or the adoption of an engine running by LNG with the adoption of a non-catalytic oxidation reactor to treat methane leakage, which was discussed in this research. Especially since the achieved efficiency is up to 99% by SNCR, at the same time the high costs of some materials used in the SCR such as palladium, rhodium, and platinum (Lighthouse, 2020)., and concerns about the use of ammonia, a chemical that is environmentally unfriendly (Zhang et al., 2012).

REFERENCES:

ABS, (2018, July). Advisory on Exhaust Gas Scrubber Systems. https://ww2.eagle.org/content/dam/eagle/advisories-and-debriefs/exhaust-gas-scrubber-systems-advisory.pdf

Algerie ferries, (2021). Fleet international marine transport. *Fleet Algeria ferries. https://algerieferries.dz/index.php/tassili-ii*

Bal, F., & Vleugel, J. M. (2015). Container ship calls: Triple throughput without an increase in marine CO2, NOx and PM10 emissions? *European Transport-Trasporti Europei, 58 (5), 2015*.

Basile, F., Fornasari, G., Trifiro, F., & Vaccari, A. (2001). Partial oxidation of methane: Effect of reaction parameters and catalyst composition on the thermal profile and heat distribution. *Catalysis Today*, *64*(1-2), 21-30.

Bengtsson, S., Andersson, K., & Fridell, E. (2011). A comparative life cycle assessment of marine fuels: liquefied natural gas and three other fossil fuels. *Proceedings of the Institution of Mechanical Engineers, Part M: Journal of Engineering for the Maritime Environment*, *225*(2), 97-110.

Brynolf, S., Magnusson, M., Fridell, E., & Andersson, K. (2014). Compliance possibilities for the future ECA regulations through the use of abatement technologies or change of fuels. *Transportation Research Part D: Transport and Environment*, *28*, 6-18.

Byoun, S., Shin, D. N., Moon, I. S., & Byun, Y. (2019). Quick vaporization of sprayed sodium hypochlorite (NaClO (aq)) for simultaneous removal of nitrogen oxides (NOx), sulfur dioxide (SO2), and mercury (Hg0). *Journal of the Air & Waste Management Association*, *69*(7), 857-866.

Catalytic Converter. (2021, September 10). In *Wikipedia.* https://en.wikipedia.org/wiki/Catalytic_converter

Ding, J., Zhong, Q., & Zhang, S. (2014). Catalytic efficiency of iron oxides in decomposition of H2O2 for simultaneous NOX and SO2 removal: Effect of calcination temperature. *Journal of Molecular Catalysis A: Chemical*, *393*, 222-231.

EGCSA, (2012). A practical guide to exhaust gas cleaning systems for the maritime industry. *EGCSA Handbook 2012*. https://www.egcsa.com/wp-content/uploads/EGCSA-Handbook-2012-A5-size-.pdf

Endres, S., Maes, F., Hopkins, F., Houghton, K., Mårtensson, E. M., Oeffner, J., ... & Turner, D. (2018). A new perspective at the ship-air-sea-interface: The environmental impacts of exhaust gas scrubber discharge. *Frontiers in Marine Science*, *5*, 139.

Helfritch, D. J., & Feldman, P. L. (1984). Flue gas SO2/NOX control by combination of dry scrubber and electron beam. *Radiation Physics and Chemistry (1977)*, *24*(1), 129-143.

Huang, X., Ding, J., & Zhong, Q. (2015). Catalytic decomposition of H2O2 over Fe-based catalysts for simultaneous removal of NOX and SO2. *Applied Surface Science*, *326*, 66-72.

Ibrahim, S. E. R. W. A. H. (2016). *Process evaluation of a SOx and NOx exhaust gas cleaning concept for marine application* (Master's thesis).

James J. Corbett (2003). Updated emissions from ocean shipping. *Marine Policy, College of Marine Studies, University of Delaware, Newark, Delaware, USA.*

Javed, M. T., Ahmed, Z., Ibrahim, M. A., & Irfan, N. (2008). A comparative kinetic study of SNCR process using ammonia. *Brazilian Journal of Chemical Engineering*, *25*(1), 109-117.

Jiang, L., Kronbak, J., & Christensen, L. P. (2014). The costs and benefits of sulfur reduction measures: sulfur scrubbers versus marine gas oil. *Transportation Research Part D: Transport and Environment*, *28*, 19-27.

Kaiser, S., Weigl, K., Spiess-Knafl, K., Aichernig, C., & Friedl, A. (2000). Modeling a dry-scrubbing flue gas cleaning process. *Chemical Engineering and Processing: Process Intensification*, *39*(5), 425-432.

Khan, N. E., & Adewuyi, Y. G. (2010). Absorption and oxidation of nitric oxide (NO) by aqueous solutions of sodium persulfate in a bubble column reactor. *Industrial & engineering chemistry research*, *49*(18), 8749-8760.

Krishna P. Shrestha, Lars Seidel, Thomas Zeuch, and Fabian Mauss. *Energy & Fuels* **2018** *32* (10), 10202-10217. DOI:10.1021/acs.energyfuels.8b01056

Kukkonen, L. (2019). Determining the effect of wash water parameters on the polycyclica aromatic hydrocarbons mass balance in open loop exhaust gas cleaning systems.

Lahtinen, J. M. (2016). Closed-loop exhaust gas scrubber onboard a merchant ship: technical, economical, environmental and operational viewpoints.

Le Fevre, C. N. (2018). A review of demand prospects for LNG as a marine fuel.

Lebedevas, S., Norkevičius, L., & Zhou, P. (2021). Investigation of effect on environmental performance of using LNG as fuel for engines in seaport tugboats. *Journal of Marine Science and Engineering*, *9*(2), 123.

Lighthouse, (2020). Aftertreatment of methane slip from marine gas engines. An overview of the issue in a context of emission levels, engine trends and sustainability matters, including a case study involving installation of a catalyst on a tanker. *Swedish Maritime competence center.* *https://www.lighthouse.nu/sites/www.lighthouse.nu/files/fs12_2020_aftertreatment_of_methane_slip_from_marine_gas_engines.pdf*

Liu, Y., Zhang, J., & Wang, Z. (2012). A study on kinetics of NO absorption from flue gas by using UV/Fenton wet scrubbing. *Chemical engineering journal*, *197*, 468-474.

Lloyd`s register, (2015). Your options for emissions compliance. Retrieved from Lloyd`s register. *Guidance for shipowners and operators on the Annex VI SOx and NOx regulations*. https://indico.cern.ch/event/659434/attachments/1528660/2391372/229-77064_Your_options_for_emissions_compliance.pdf

Macagnano, A., Zampetti, E., Bearzotti, A., & De Cesare, F. (2015). 10 Electrospinning for Air Pollution Control. *Electrospinning for advanced energy and environmental applications*, 243.

MAN B&W. (2016, July). *MAN B&W G50ME-C9.5-TII, Project Guide, Electronically Controlled, Two-stroke Engines*. https://www.academia.edu/33566549/G50ME_C?email_work_card=view-paper

MAN Diesel & turbo, (2011). *Costs and Benefits of LNG as Ship Fuel for Container Vessels.* Retrieved from MAN diesel & turbo: https://www.mandieselturbo.com/docs/default-source/shopwaredocuments/costs-and-benefits-of-lng3739431d863f4f5695c4c81f03ac752c.pdf?sfvrsn=3

Miller, Bruce G. (2017). 10-Formation and control of Nitrogen Oxides. *Selective Non-Catalytic Reduction.* https://www.sciencedirect.com/topics/engineering/selective-non-catalytic-reduction.

Miola, A., Ciuffo, B., Giovine, E., & Marra, M. (2010). Regulating air emissions from ships. *The state of the art on methodologies, technologies and policy options. Joint Research Centre Reference Report, Luxembourg, EUR24602EN, ISBN*, 978-992.

Mukherjee, A., Bruijnincx, P., & Junginger, M. (2020). A perspective on biofuels use and CCS for GHG mitigation in the marine sector. *Iscience*, *23*(11), 101758.

Otheitis, N., & Kunc, M. (2015). Performance measurement adoption and business performance. *Management decision*.

R.Quiceno, J.Perez-Ramirz, J. Warnatz, O. Deutschmann. (2006). Applied Catalysis A: General, 303 (2006) 166-176]

Rehmatulla, N., Calleya, J., & Smith, T. (2017). The implementation of technical energy efficiency and CO2 emission reduction measures in shipping. *Ocean Engineering*, *139*, 184-197.

Rolls-Royce, (2016, February). *Project Guide – Bergen engine type B35:40 Gas*. https://www.rolls-royce.com/~/media/Files/R/Rolls-Royce/documents/marine-product-finder/Projeg%20Guide%20B3_540%20Gas.pdf

Ryu, Y., Kim, T., Kim, J., & Nam, J. (2020). Investigation on the Emission Characteristics with a Wet-Type Exhaust Gas Cleaning System for Marine Diesel Engine Application. *Journal of Marine Science and Engineering*, *8*(11), 850.

Samuelsen, A., Daewel, U., & Wettre, C. (2019). Risk of oil contamination of fish eggs and larvae under different oceanic and weather conditions. *ICES Journal of Marine Science*, *76*(6), 1902-1916.

Schneiter, D. (2019). Greenhouse Gas (GHG) Emissions from LNG Engines. Review of the Two-Stroke Engine Emission Footprint.

Sharif, H. M. A., Mahmood, N., Wang, S., Hussain, I., Hou, Y. N., Yang, L. H., ... & Yang, B. (2021). Recent advances in hybrid wet scrubbing techniques for NOx and SO2 removal: State of the art and future research. *Chemosphere*, 129695.

Singh, A. P., Singh, S. P., Singh, A., Gupta, S., Raj, V., Kumar, S., ... & Kumar, B. (2020, February). Application of Air Purifier Drone to Control Air Pollutants in Domestic and Industrial Areas. In *2020 International Conference on Electrical and Electronics Engineering (ICE3)* (pp. 676-679). IEEE.

Sofiev, M., Winebrake, J. J., Johansson, L., Carr, E. W., Prank, M., Soares, J., ... & Corbett, J. J. (2018). Cleaner fuels for ships provide public health benefits with climate tradeoffs. *Nature communications*, *9*(1), 1-12.

Sorrels, J. L., Randall, Carrie Richardson Fry, and Karen S. Schaffner. (2019, April). Selective Noncatalytic Reduction. *EPA Air Pollution Control Cost Manual*. https://www.epa.gov/sites/default/files/2017-12/documents/sncrcostmanualchapter7thedition20162017revisions.pdf

Stein, J., Kind, M., & Schlünder, E. U. (2002). The influence of HCl on SO2 absorption in the spray dry scrubbing process. *Chemical engineering journal*, *86*(1-2), 17-23.

STX-MAN, (2013). *Vol-1 Operation_MC,MC-C,MC-9_Edition 2013_R3-pdf*.

Thor, P., Granberg, M. E., Winnes, H., & Magnusson, K. (2021). Severe Toxic Effects on Pelagic Copepods from Maritime Exhaust Gas Scrubber Effluents. *Environmental science & technology*, *55*(9), 5826-5835.

Tran, T. A. (2017). NA. *Journal of Marine Science: Research & Development*, *7*(6), 243.

US EPA, (2011, November). Exhaust Gas Scrubber Washwater Effluent. *United States Environmental Protection Agency Office of Wastewater Management Washington, DC 20460.* *https://www3.epa.gov/npdes/pubs/vgp_exhaust_gas_scrubber.pdf*

Viatte, C., Clerbaux, C., Maes, C., Daniel, P., Garello, R., Safieddine, S., & Ardhuin, F. (2020). Air pollution and sea pollution seen from space. *Surveys in Geophysics*, *41*(6), 1583-1609.

Wartsila, (2013, April). *Wärtsilä 20 PRODUCT GUIDE*. https://d1wqtxts1xzle7.cloudfront.net/53862259/wartsila-o-e-w-20-pg.pdf?

Wartsila, (2015, September). *Wärtsilä 32 - PRODUCT GUIDE.* https://www.wartsila.com/docs/default-source/product-files/engines/ms-engine/product-guide-o-e-w32.pdf?

Wartsila, (2019, July). *Wärtsilä 50DF PRODUCT GUIDE*. https://cdn.wartsila.com/docs/default-source/product-files/engines/df-engine/product-guide-o-e-w50df.pdf?

Wartsila, (2019, November). *Wärtsilä 46DF PRODUCT GUIDE*. https://www.wartsila.com/docs/default-source/product-files/engines/df-engine/product-guide-o-e-w46df.pdf?

Woodyard, D. (2009). *Pounder's marine diesel engines and gas turbines*. Butterworth-Heinemann.

Yang, Z. L., Zhang, D., Caglayan, O., Jenkinson, I. D., Bonsall, S., Wang, J., ... & Yan, X. P. (2012). Selection of techniques for reducing shipping NOx and SOx emissions. *Transportation Research Part D: Transport and Environment*, *17*(6), 478-486.

Zhang, L. L., Wang, J. X., Sun, Q., Zeng, X. F., & Chen, J. F. (2012). Removal of nitric oxide in rotating packed bed by ferrous chelate solution. *Chemical Engineering Journal*, *181*, 624-629.

Zhang, T. (2019). Comparative analysis of SOx emission control technologies for container ships.

Zhao, R., Xu, L., Su, X., Feng, S., Li, C., Tan, Q., & Wang, Z. (2020). A numerical and experimental study of marine hydrogen–natural gas–diesel tri–fuel engines. *Polish Maritime Research*.

Zhao, Y., Hao, R., Yuan, B., & Jiang, J. (2016). Simultaneous removal of SO2, NO and Hg0 through an integrative process utilizing a cost-effective complex oxidant. *Journal of hazardous materials*, *301*, 74-83.

Zheng, C., Xu, C., Zhang, Y., Zhang, J., Gao, X., Luo, Z., & Cen, K. (2014). Nitrogen oxide absorption and nitrite/nitrate formation in limestone slurry for WFGD system. *Applied energy*, *129*, 187-194.

Zhou, J., & Wang, H. (2020). Study on efficient removal of SOx and NOx from marine exhaust gas by wet scrubbing method using urea peroxide solution. *Chemical Engineering Journal*, *390*, 124567.