We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Chapter 8

Sea Transport Air Pollution

Ivan Komar and Branko Lalić

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/59720

1. Introduction

The aim of this chapter is to provide an overview of the air pollution generated by diesel engines of the ocean-going ships and the technologies as well as methodologies available to reduce these emissions. This chapter begins with general significant information of the air pollutant emission from ships followed by a summary of the International Maritime Organization (IMO) regulatory MARPOL Annex VI being developed to control marine shipping emissions as well as information on the various types of the ocean-going ships and their prime movers with particular emphasis on marine diesel engines as sources of air pollution from ships. For better understanding of the formation of air pollutants from marine diesel engines, authors gave a brief overview of the working principles of marine diesel engines as well as their combustion process and chemistry of the pollutant formation during that process. Finally, the chapter concludes with an analysis of several control methods that can effectively reduce harmful pollutant emissions from marine diesel engines.

Climate change on Earth is one of the largest civilised problems at the beginning of the twenty-first century. Anthropogenic impact on the Earth's climate became one of the crucial environmental issues of modern civilisation in the late twentieth century. Therefore, nowadays the ecology and preservation of human environment have become two of the very important human activities all over the world. Besides primary pollution from the land, nowadays attention is being paid to the pollution from the ships. In recent decades, shipping industry and maritime traffic have rapidly developed. From the economic point of view, this trend, which continues today, has a very positive impact on economic development but on the other hand, a very negative impact on the environment in terms of air pollution. Exhaust gases from marine diesel engines are the primary source of emissions from ships and contribute significantly to environmental pollution. Ocean-going ships are the major contributors to global emissions of several hazardous air pollutants such as nitrogen oxides (NOx), sulphur oxide

INTECH
open science | open minds

© 2015 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

(SOx), fine particulate matter (PM), hydrocarbons (HCs), carbon monoxide (CO) and greenhouse gas carbon dioxide (CO_2).

The presence of these pollutants has local and global impact. Impacts on local (or regional) air quality are mainly linked to pollutants such as PM, NOx and sulphur, while CO_2 has a global impact on climate [1]. The amount of gases emitted from marine engines into the atmosphere is directly related to the total fuel oil consumption. While pollutant emissions from land-based sources are gradually decreasing, those from shipping show a continuous increase. It is estimated that by 2020, the emissions NOx and SOx from international shipping around Europe are expected to equal or even surpass the total emissions from all land-based mobile, stationary and other sources in the 25 EU member states combined (see Figure 1). It should be noted that these figures refer only to ships in the international trade and do not include emissions generated from shipping in countries' internal waterways or from ships plying harbours in the same country, which are given in the domestic statistics of each country [2].

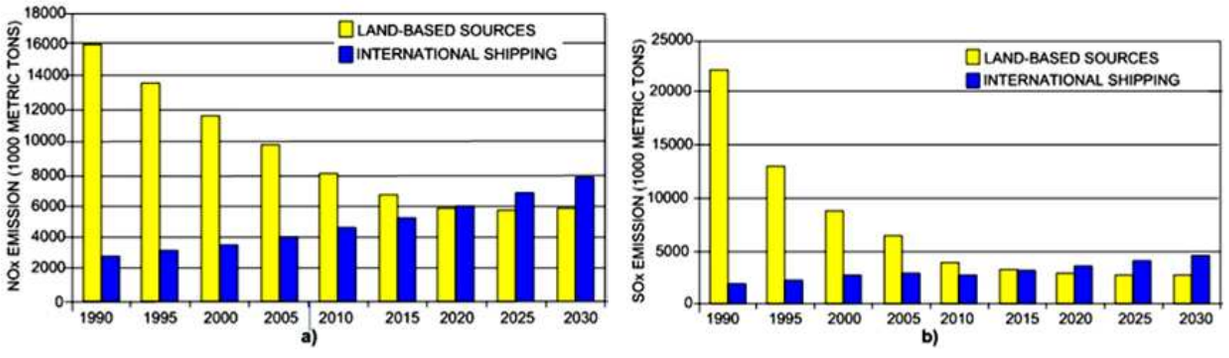

Figure 1. Emissions NOx (a) and SOx (b) 1990–2030 from land-based sources and international shipping

It has been estimated that about 90 % of the total sulphur dioxide (SO_2) and NOx emissions from ships in the North Sea, including the English Channel, originate from a zone of approximately 50 nautical miles from the coast line. International shipping was estimated to be a source of 97 % of the total SO_2 and NOx emissions in the North Sea within a distance of 100 nautical miles from the seaboard, as in [3]. The emissions of sulphur dioxide (SO_2), particulate matter (PM) and greenhouse gases (GHGs) from global shipping were increased from 585 to 1096 million tons between 1990 and 2007. The CO_2 emissions from international shipping are estimated at 943.5 million tons for the year 2007 and CO_2 emissions from global shipping are about 1 billion tons for the year 2006. International shipping is responsible for 3 % of global CO_2 emissions as in [4].

2. International regulation concerning air pollution from merchant shipping

Regulations concerning air pollution from merchant shipping are developed at the global level. Because shipping is inherently international, it is vital that shipping is subjected to uniform

http://dx.doi.org/10.5772/59720

regulations on issues such as air emissions from ships. The shipping industry is principally regulated by the International Maritime Organization (IMO), which is a UN agency based in London and responsible for the safety of life at sea and the protection of the marine environment. IMO ship pollution rules are contained in the 'International Convention on the Prevention of Pollution from Ships' known as MARPOL 73/78, which represents the first set of regulations on marine exhaust emissions. The original MARPOL Convention was signed on 17 February 1973, but did not come into force. The current Convention is a combination of the 1973 Convention and the 1978 Protocol. MARPOL73/78 contains 6 annexes concerned with preventing different forms of marine pollution from ships:

- Annex I deals with regulations for the prevention of pollution by oil.
- Annex II details the discharge criteria and measures for the control of pollution by noxious liquid substances carried in bulk.
- Annex III contains general requirements for issuing standards on packing, marking and labelling.
- Annex IV contains requirements to control pollution of the sea by sewage.
- Annex V deals with different types of garbage, including plastics, and specifies the distances.
- Annex VI deals with gaseous emissions of ship engines and installations: the Convention regulates sulphur oxide, nitrogen oxide and particulate matter emissions from ship exhausts and prohibits deliberate emissions of ozone-depleting substances. It also contains provisions allowing for the creation of special Emission Control Areas (ECA) with even more stringent controls on air pollutant emissions. Annex VI also forbids any (deliberate) emission of an ozone-depleting substance, such as halons and chlorofluorocarbons (CFCs) as well as any new installation of equipment using these gases. Annex VI entered into force on 19 May 2005 and sets limits on nitrogen oxides, sulphur oxides and volatile organic compound (VOC) emissions from ship exhausts and prohibits deliberate emissions of ozone-depleting substances [5]. Annex VI regulation 13, nitrogen oxides (NOx), applies to diesel engines over 130 kW installed on ships built on or after 1 January 2000, excluding engines for emergency purposes such as emergency generator engine, lifeboat engine, etc.

Three different levels (tiers) of NOx control apply based on the ship construction date as follows:

- *Tier 1* entered into force in 2005 and applies to marine diesel engines installed in ships constructed on or after 1 January 2000 and prior to 1 January 2011.
- *Tier 2* entered into force in 1 January 2011 and replaced the Tier 1 NOx emission standard globally. It applies globally for new marine diesel engines installed in ships constructed on 1 January 2011 or later. Tier 2 NOx emission levels correspond to about 20 % reduction from the Tier 1 NOx emission standard. Tier 2 is applicable outside the Tier 3 designated Emission Control Areas (ECA).[1]
- *Tier 3* will enter into force in the year 2016 and it will by then apply for new marine diesel engines > 130 kW installed in ships constructed on 1 January 2016 or later when operating

inside the ECA. The Tier 3 NOx emission level corresponds to an 80 % reduction from the Tier 1 standard. The NOx emission limits are expressed as dependent on engine speed (n) in revolution per minute (RPM). These are shown in Table 1 and Figure 2 [6,7].

Tier	Effective date	NOx limit (g/kWh)		
		n < 130	130 < n < 2000	n > 2000
Tier I	2000	17	45 $n^{-0,2}$	9,8
Tier II	2011	14,4	44 $n^{-0,2}$	7.7
Tier III	2016	3,4	9 $n^{-0,2}$	1,96

Table 1. NO_X limits according to MARPOL Annex VI

For engines with an engine speed lower than 130 RPM, the Tier III level is 3.4 g/kWh. When operating outside an ECA, the engine must meet the Tier II limit of 14.4 g/kWh. Engines with an engine speed higher than 130 RPM must meet even lower limits (see Table 1 and Figure 2). Any abatement technology reducing the NOx emission to the required level can be accepted.

Furthermore, MARPOL Annex VI has set a maximum global fuel sulphur limit of currently 3,5 % in weight (from 1 January 2012) for any fuel used on board a ship. Annex VI also contains provisions allowing for special SOx Emission Control Areas (ECA) to be established with more stringent controls on sulphur emissions. In an ECA, the sulphur content of fuel oil used on board a ship must currently not exceed 1 % in weight. The MARPOL Annex VI has undertaken a review with the intention to further reduce emissions from ships. The current and upcoming limits for future fuel oil sulphur contents are presented in Table 2 and Figure 2 [6,7].

Fuel sulphur cap	Area	Date of implementation
Max. 1 % S in fuel	ECA	1 July 2010
Max. 3,5 % S in fuel	Globally outside ECA	1 January 2012
Max. 0,1 % S in fuel	ECA	1 January 2015
Max. 0,5 % S in fuel	Globally outside ECA	1 January 2020

Table 2. Sulphur limits in fuel according to MARPOL Annex VI

The rules of SOx apply to all ships, no matter the date of ship construction. Although the SOx requirements can be met by using a low-sulphur fuel, the regulation allows alternative methods to reduce the emissions of SOx to an equivalent level.

1 Designated Emission Control Areas (ECA) that are defined by the IMO currently comprise the Baltic Sea, the North Sea, the English Channel, the US Caribbean Sea and the area outside North America (200 nautical miles – see Figure 3) The first sulphur Emission Control Area (ECA) was established in the Baltic and came into force internationally on 19 May 2005, and all ships were required to either use the 1.5 % low-sulphur fuel or fit an exhaust gas cleaning system as required by regulation 14 of Annex VI 12 months from this date which was 19 May 2006.

http://dx.doi.org/10.5772/59720

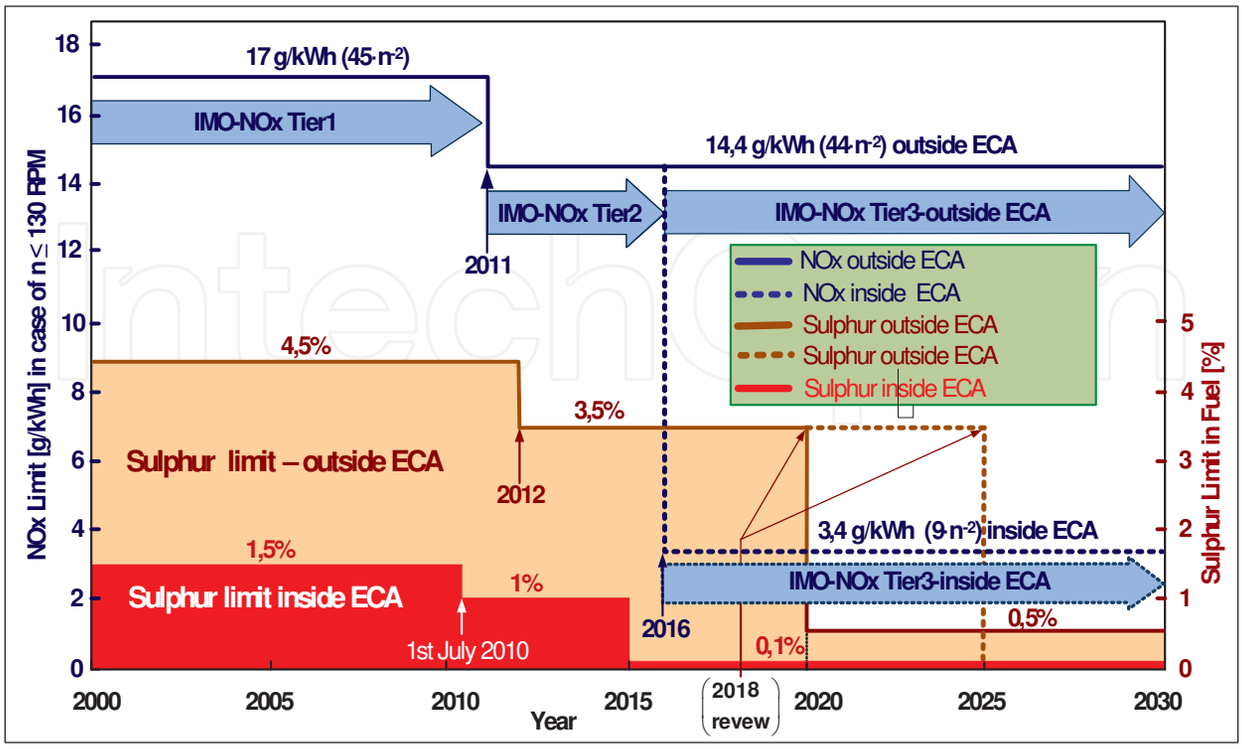

Figure 2. Reduction of NOx and sulphur in fuel on the global and ECA limit

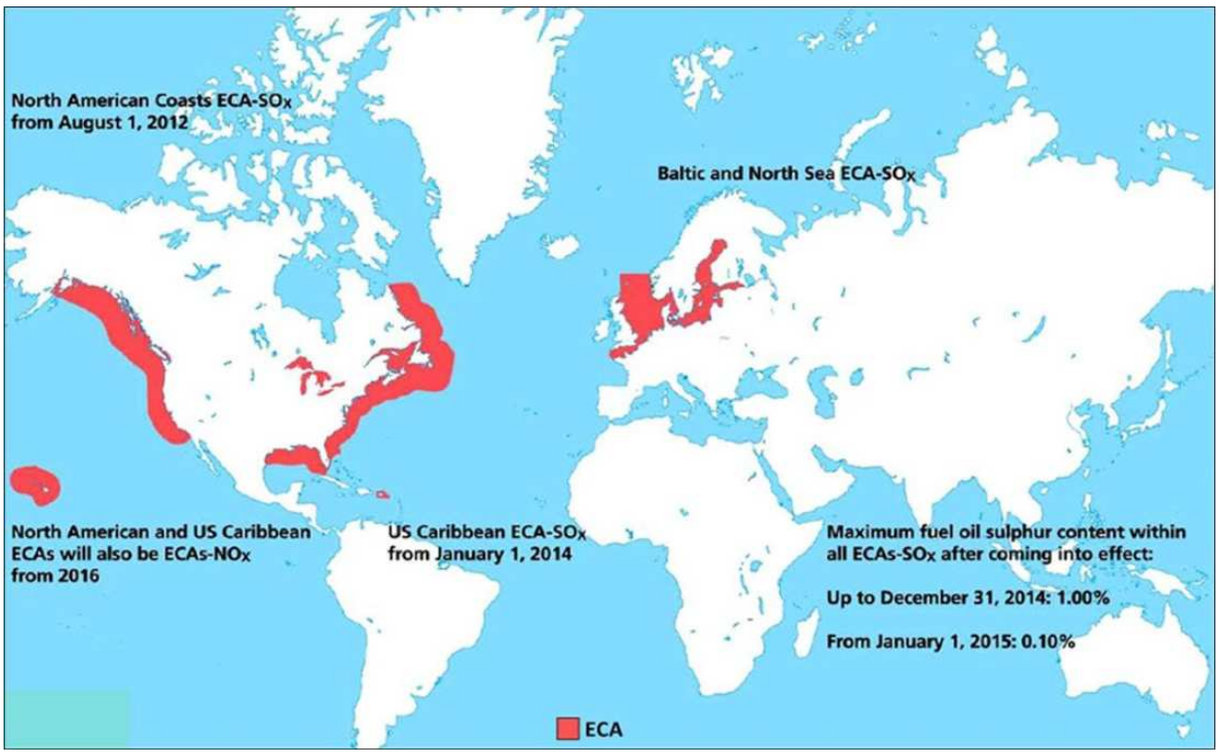

Figure 3. Existing Emission Control Areas as per MARPOL Annex VI (source: www.marlink.com)

The sulphur ECA limit which entered into force in 1 January 2015 can be met using a low-sulphur fuel with sulphur below 0.1 %. The global limit, outside sulphur ECA, can be met using fuel with sulphur content below 0.5 %, which will be required from 2020. The date of the global limit reduction may be changed to 2025 as a result of a feasibility review to be conducted no later than 2018 (see Figure 2).

In order to comply with the requirements of Regulation 14 of MARPOL, the burning of low-sulphur fuel oils (LSFOs) was introduced. There is also an EU regulative about the sulphur content in marine gas oil. Namely, in accordance with EU's marine fuel sulphur directive (1999/32/EG, Article 4 with amendment as per directive 2005/33/EC), the sulphur content in marine gas oil within the territorial waters of an EU member state may not exceed 0.1 % by weight. This applies to all ships regardless of flag. As of 1 January 2010, the sulphur content of any marine fuels may never exceed 0.1 % by weight for ships in port with the exception of short stays in port (up to 2 h).

For ships continuously operating on low-sulphur fuel oil and for those that may be fitted with an exhaust cleaning system, there is no issue. However, for ships which burn heavy fuel oil with 3.5 % sulphur content and are not equipped with scrubbing equipment, the problem of compliance is much greater as large quantities of fuel are being mixed during the oil change-over to low-sulphur fuel oil. MARPOL Annex VI Regulation 14 requires those ships using separate low-sulphur fuel to comply with this regulation and in entering or leaving an Emission Control Area, shall carry a written procedure showing how the fuel oil changeover is to be done, allowing sufficient time for the fuel oil service system to fully flushed out all fuel oils exceeding the applicable sulphur content prior to entry into a sulphur Emission Control Area. The volume of low-sulphur fuel oils in each tank as well as the date, time and position of the ship when any fuel oil changeover operation is completed prior to the entry into an ECA or commenced after exit from such an area shall be recorded in such logbook as prescribed by the Annex VI Regulation.

Furthermore, ships are also an important source of greenhouse gas (GHG) pollutants. According to the Green House Gas study by the IMO consensus, international shipping emitted 843 million metric tonnes of carbon dioxide, 2.7 % of the global CO_2 emissions in 2007. Including domestic shipping and fishing ships larger than 100 gross tonnes (GT),[2] the amount would increase to 1.019 billion tonnes, i.e. 3.3 % of the global CO_2 emissions. At the present trend, this percentage could go two or three times higher from the present by 2050 emissions [8, 9].

In order to control this CO_2 emission from shipping, the first formal CO_2 control regulations were adopted by the IMO at the 62nd session of the Marine Environment Protection Committee (MEPC) in July 2011. The amendments to MARPOL Annex VI included the addition of Chapter 4 on regulations on energy efficiency for ships to make mandatory the Energy Efficiency Design Index (EEDI) for new ships and the Ship Energy Efficiency Management Plan (SEEMP)

2 Gross tonnage (GT) determined under the IMO 1969 Tonnage Convention represent the total volume of of ship's enclosed spaces measured in register tonne (RT) where 1RT=100 f3 or 2,83 m3, conversely. Net tonnage (NT) determined under the IMO 1969 Tonnage Convention represents the volume of cargo spaces (cargo holds and cabins) in register tonne (RT).

http://dx.doi.org/10.5772/59720

for all ships. The regulations apply to all ships of 400 GT and above and are entered into force in 1 January 2013.

The basic formulation of EEDI is based on the ratio of total CO_2 emission per tonne mile. As CO_2 depends upon fuel consumption and fuel consumption depends upon the total power requirements, eventually this EEDI formulation has certain impact on ship design parameters and hydrodynamics. The SEEMP establishes a mechanism for a shipping company and a ship to improve the energy efficiency of ship operations. The SEEMP provides an approach for monitoring ship and fleet efficiency performance over time using. The results from the study that IMO ordered from Lloyd's Register and Det Norske Veritas to estimate the impact of the new requirements show that the EEDI will, as new ships are built, gradually reduce the emissions from the world fleet with 3 % in 2020, 13 % in 2030 and 30 % in 2050. The SEEMP will not directly mandate an emission reduction, but by increased awareness of costs and reduction potentials, the study estimated the reduction to be between 5 and 10 % from 2015 onwards [9,10].

3. Sea ship classification and quantification

As per rules of the Shipping Classification Societies, ship is defined as 'a floating unit intended for sea-going service with length greater than 12 meters and with GT greater than 15, or which carries more than 12 passengers. The present definition does not apply to ships of war and troopships'. Marine ocean-going ships are generally very large ships designed for deepwater navigation. Depending on the nature of their cargo, ships can be divided into different categories, classes and types. A majority of these ships can be classified as one of the following: tanker, bulk carrier, container ship, ro-ro ship, general cargo ship, reefer ship and passenger ship. There are also smaller ship types, which are not included in the largest categories of ship, as fishing ships intended and equipped for fishing or exploiting other living resources of the sea; tugs, a ship specially constructed and equipped for towing and/or rescuing and salvage of ships or other floating units; ships used by authorities which include the following types: pilot boats, rescue ships, police boats, custom boats, etc.; training ships provided for training of marine personnel gaining training and practical marine experience to develop seafaring skills suitable for a professional career at sea and provided with special equipment and arrangements suitable for that purpose (teaching rooms, accommodation spaces for teachers and trainees, etc.); research ship, a ship without cargo spaces, engaged in scientific research, noncommercial expeditions and surveys, carrying scientists, technicians and members of expeditions, and provided with special equipment and arrangements suitable for that purpose (i.e. laboratories, accommodation for research personnel, etc.); supply ship, a ship mainly intended and equipped for the carriage of special personnel, special materials and equipment which are used to provide facilities to offshore units and other marine installations, as well as to provide assistance in performing special activities; and icebreakers and recreational ships such as yachts classified as recreational craft for personal or commercial use, having hull length greater than 12 m, having facilities and accommodation for extended navigation, authorised

to carry not more than 12 passengers, excluding crew. The following is a brief description of the characteristics of the main types of ocean-going ships:

Tanker is a merchant ship designed to transport liquids or gases in bulk. The major types of tanker ship include the oil tanker, the chemical tanker and gas carrier.

Oil tanker is a ship which is constructed primarily to carry oil in bulk and comes in two basic types: the crude carrier, which carries crude oil, and the clean product tanker, which carries the refined products, such as petrol, gasolene, aviation fuel, kerosene and paraffin. Tankers also include ship types such as combination carriers. Combination carrier is a general term applied to ships intended primarily to carry oil or dry cargoes, including ore, in bulk (ore/oil ships, oil/bulk/ore – OBO). These cargoes are not carried simultaneously. Generally they are constructed with a single deck, two longitudinal bulkheads and a double bottom throughout the cargo length area and intended primarily to carry ore cargoes in the centre holds or of oil cargoes in centre holds and wing tanks.

Chemical tankers are ships which are constructed generally with integral tanks and intended primarily to carry chemicals in bulk.

Gas carrier can be divided into two types: the *LNG tanker* carries liquified natural gas and the *LPG tanker* carries liquified petroleum gas. Tankers can range in size of capacity from several hundred deadweight tons (DWT),[3] which include ships for servicing small harbours and coastal settlements, to the real giants of several hundred thousand DWT: the VLCC (very large crude carrier) of between 200,000 and 300,000 DWT and the ULCC (ultra large crude carrier) of over 300,000 DWT.

Bulk carriers are sea-going self-propelled ships which are constructed and intended primarily to carry dry cargoes in bulk such as ore, coal, pulp, rock, cement, scrap metal, grain, flour, rice, fertilisers, sugar or any cargo that travels in bulk. Bulk carriers range from about 25,000 DWT ('handysize') through the medium-size ('Panamax') ships of about 75,000 DWT, to the giant ('capesize') ships of over 200,000 DWT.

Container ships are a type of dry cargo ships specially designed and equipped with the appropriate facilities for carriage of containers. They carry standardising container at 20-feet long (TEU – twenty-foot equivalent unit) or 40-feet long (FEU – forty-foot equivalent unit). Today's container ships are being built to take up to18,000 TEU.

Ro-ro (roll on/roll off) is a cargo ship (ferry) specifically designed for the carriage of vehicles, which embark and disembark on their own wheels, and/or goods on pallets or in containers which can be loaded or unloaded by means of wheeled vehicles. Another type of ro-ro is a passenger ship (ROPAX). The acronym ROPAX (roll-on/roll-off passenger) describes a ro-ro ship built for freight vehicle transport along with passenger accommodation. Ro-ro ships have built-in ramps that allow the cargo to be efficiently rolled on and off the ship when in port. The ramps and doors may be stern-only, bow and stern or side for quick loading.

3 Deadweight tonnage (also known as deadweight abbreviated to DWT) is a measure of how much weight a ship is carrying or can safely carry. It is the sum of the weights in metric tonnes of cargo, fuel, freshwater, ballast water, provisions, passengers and crew.

http://dx.doi.org/10.5772/59720

General cargo ship is a ship intended for the carriage of general cargo which will not be carried in containers.

Refrigerated cargo ship or reefer ship is a ship (excluding liquefied gas carriers and fishing ships) specially intended to carry permanently refrigerated cargoes such as fruits, vegetables, dairy products, fish and meat and has fixed refrigeration installations and insulated holds. Excluding the temperature control, the reefers are similar to other dry cargo ships or containers.

Passenger ship as per rules of the ship's classification society is a self-propelled ship with a permission to carry more than 12 passengers, specially designed and equipped for that purpose, with a single or multi-deck hull and superstructure and with cabin accommodation for passengers.

As of 1 January 2013, there were 48,732 merchant ships (597,709,000 GT) involved in international trade, registered under the flags of over 150 nations (see Figure 4).

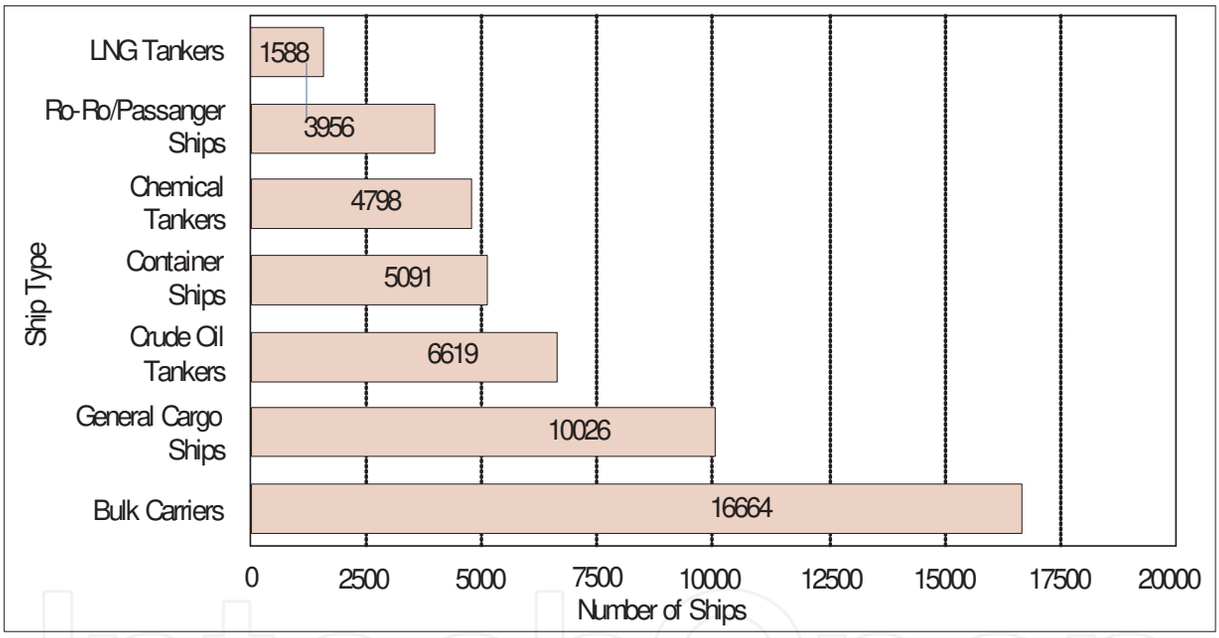

Figure 4. Number of the main types of ocean-going ships in the world merchant fleet as of 1 January 2013 (source: http://www.statista.com)

3.1. Ship engines

The power needed on ships is generated through main and auxiliary engines often called prime mover in the literature and can be sorted as diesel engine, gas turbine, steam turbine and electric motor. The diesel engine is the most common prime mover in the merchant marine, mainly due to its low fuel consumption in comparison with other prime movers. Power ranges between 0.25 MW for the smallest high-speed engines and 100 MW for the for the biggest low-speed marine diesel engines. The main advantages of diesel engines are the following: it is relatively insensitive to fuel quality; it can be operated by light fuel as well as the heaviest

residual fuels; and it has high reliability and high efficiency. In the other hand, the main disadvantages of diesel engines are pollutant emissions, low power-to-weight ratio if compared with gas turbine and vibration and noise.

From the application viewpoint, three main types of diesel engines are available: low-speed diesel engines (rpm<200), medium-speed diesel engines (200<rpm<1000) and high-speed diesel engines rpm>1000).

From the construction viewpoint, two types can be distinguished: two-stroke low-speed engines and four-stroke engines (medium or high speed). Low-speed diesel engines are dominant in the deep sea tanker, bulk carrier and containership sectors. Such types of engines are used as ship's propulsion engine without gearbox, i.e. directly connected to the propeller shaft system. These engines are currently the most efficient in terms of the specific fuel consumption, but NOx emission level from these engines is very high in comparison with medium- or high-speed marine diesel engines (see Figure 5b). The diesel engines have specific fuel consumptions around 160–185 g/kWh, against the 220–240 g/kWh of gas turbines and 300 g/kWh of steam turbines (see Figure 5a).

Medium-speed engines are used for auxiliaries such as alternators and for the main propulsion engine, with a gearbox to provide a propeller speed reduction, for smaller cargo ships, ferries, passenger cruise liners, ro-ro carriers, supply ship, icebreakers, etc., while high-speed engines are used as propulsion and for auxiliaries in smaller ships as fishing ships, tugs, pilot ships, recreational ships, etc.

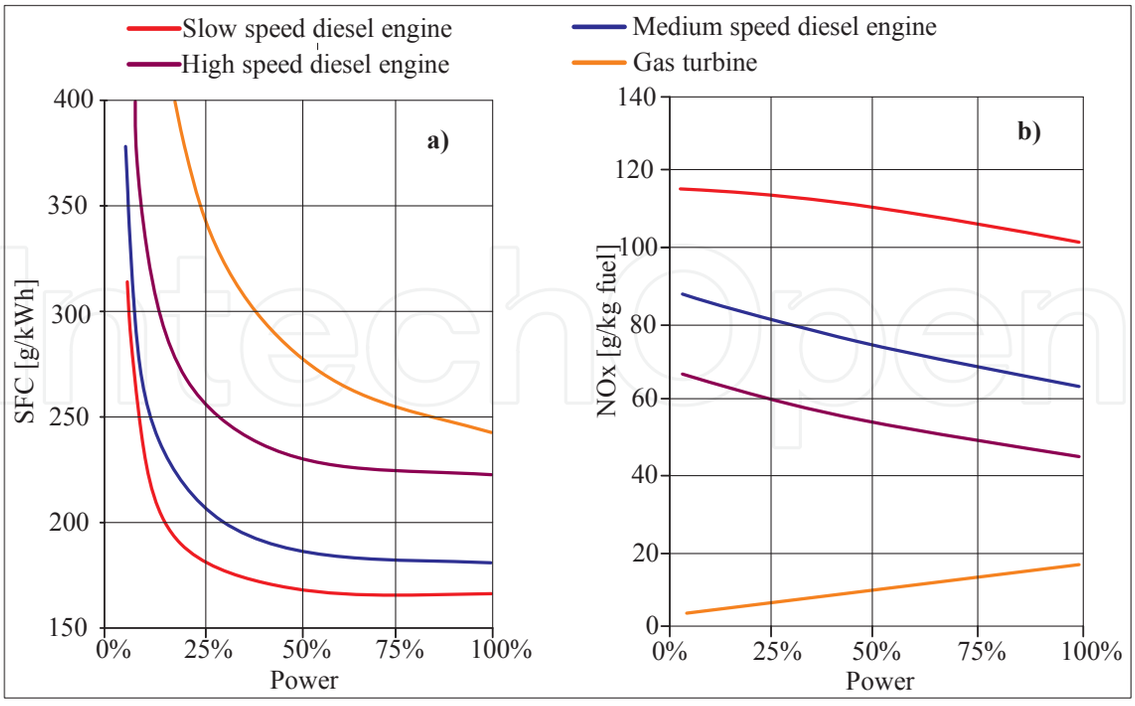

Figure 5. a) Specific fuel consumption of prime movers b) NOx emission ratio for prime movers

http://dx.doi.org/10.5772/59720

3.2. Marine diesel engine: Type and working principles

The diesel engine is reciprocating internal combustion engine where chemical energy of the fuel is converted into thermal energy by means of combustion reactions of the fuel, and then the thermal energy is converted into mechanical work. The actual cycle inside the engine can be done either in four strokes (two crank revolutions) or in two strokes (one crank revolution) [11]. A stroke is defined as the distance travelled by the piston between the top dead centre (TDC) and the bottom dead centre (BDC). Cycles in the four-stroke engine are compression, power, exhaust and intake strokes. During compression stroke, the piston moves upwards from BDC to TDC. Inlet and exhaust valves are closed, and the combustion air is compressed and thus increases air pressure and temperature (110 to 220 bar and 600 °C to 800 °C depending on the type of engine). Fuel is injected several crank degrees before TDC and ignited by the high temperature of the compressed air. Combustion starts at the end of the compression stroke. The combustion is continued over a considerable crank angle after TDC, while the combustion gases expand and perform work on the piston, forcing it down. This is power stroke. Towards the end of the stroke, the exhaust valve opens which releases the combustion gases into the exhaust manifold or exhaust gas receiver. Thereafter during the exhaust stroke, the piston moves from BDC to TDC. The exhaust valve is open and the rest of the combustion gases are forced out of the cylinder by the upward stroke of the piston. The gases that remain in the cylinder are dispelled by a scavenging process; the inlet valve is opened early, whereas the exhaust valve is closed late, so that both are open at the same time (overlap period). Thereafter during the intake stroke, the piston moves downwards from TDC to BDC. The inlet valve is open and the exhaust valve closed, while the cylinder is filled with a charge of fresh air and thereafter is ready for the compression stroke. A complete cycle takes four strokes. However, the power stroke is the only useful one, which suggests that there is a useful stroke every two crank revolutions.

Slow-speed marine diesel engine (65–200 rpm) operates on the two-stroke cycle. This means that this engine has one working or power stroke per every crank revolution. The main difference comparing two-stroke with the four-stroke cycle is that charging and exhaust take place without the piston enforcing the process. During the compression stroke, the inlet ports and exhaust valve are closed and a volume of air is trapped into the cylinder. The piston moves upwards to TDC, thus compressing this combustion air and causing a temperature and pressure rise (110 to 160 bar and 600 °C to 800 °C depending on the type of engine) that is sufficient to ignite the fuel that has been injected few degrees before TDC. At the end of the compression stroke, combustion starts and continues several degrees during power stroke. The combustion gases expand and perform work on the piston, forcing it down from TDC to BDC. At the end of expansion, exhaust valve opens and combustion gases blow down to exhaust receiver pressure. By the time the inlet ports are open, the cylinder pressure will have reached a pressure lower than that of the scavenging air, so scavenging starts. These processes take place in one stroke. Scavenging, which starts while the piston moves downwards, is completed while the piston moves upwards. Both the inlet ports and exhaust valve are opened, and fresh air from scavenging air receiver enters the cylinder, forcing the exhaust gases out. The scavenging and compression processes take place in another stroke. The process described

here is for uniflow scavenging. It is necessary to compress the scavenging air by the turbocharger in order to scavenge the cylinder. The principal scheme of a turbocharged marine diesel engine is shown in Figure 6 as in [12]. Turbocharger (TC) is composed of the compressor (C) driven by the gas turbine (T) that receives its power from the heat energy of the exhaust gases flowing through. The compressor and the turbine are directly coupled and they are built together in a common housing. The gas turbine, usually one-stage axial type, is located after an exhaust gas receiver (EGR) which collects the exhaust gases from all the engine cylinders. The one-stage centrifugal-type compressor feeds compressed air through scavenging air cooler into scavenging air receiver (SAR) that supplies all the engine cylinders.

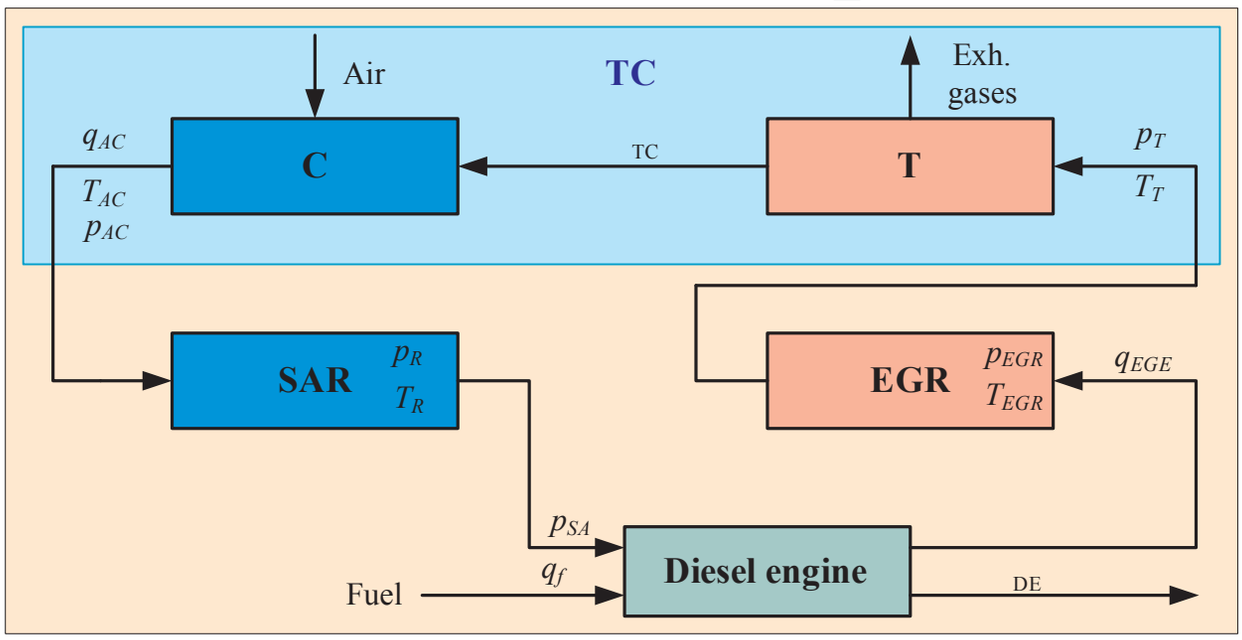

Figure 6. Principal scheme of turbocharging marine diesel engine

3.3. Types of fuel oils for marine diesel engine

Marine diesel engines use three types of liquid fuels standardised by ISO 8217 fuel standard for marine distillate fuels as gas oil (GO) with max. density of 890 kg/m^3 at 15 °C, marine diesel oil (MDO) with max. density from 890 to 900 kg/m^3 at 15 °C and heavy fuel oil (HFO) with max. density from 920 to 1010 kg/m^3 at 15 °C as in [13]. ISO 8217 fuel standard for marine distillate fuels also defines the values of the essential properties of each type of the fuel. The most important properties of marine fuels are as follows:

- Kinematic viscosity, expressed as mm^{2}s^{-1}, is a measure for the fluidity of the fuel at 50 °C. The viscosity of a fuel decreases with increasing temperature. The moment the fuel leaves the injectors, the viscosity must be within the limits prescribed by the engine manufacturer in order to obtain an optimal spray pattern; otherwise, it will lead to poor combustion, deposit formation and energy loss.

- Density expressed as kg/m^3 at 15 °C is an indicator of the ignition quality particularly for the low-viscosity HFOs.
- The sulphur content which depends on the crude oil origin and the refining process. When a fuel burns, sulphur is converted into sulphur oxides which has environmental implications. Maximum permitted sulphur content in the marine fuels is 3,5 %.
- Flash point is the temperature at which the vapours of a fuel ignite. The minimum flash point for marine fuels is 60 °C as per the IMO SOLAS Convention.
- Carbon residue is determined by a laboratory test performed under specified reduced air supply. It gives an indication of the amount of hydrocarbons in the fuel which have difficult combustion characteristics.
- Water in fuel is a contaminant and does not yield any energy. The percentage of water in the fuel can be translated into a corresponding energy loss for the customer. Water is removed on board the ship by centrifugal purification.
- Ash content is a measure of the metals present in the fuel (for GO and MDO max. 0,01 mass % and for HFO from 0,04 to 0,15 mass %), either as inherent to the fuel or as contamination.
- Vanadium and nickel are elements found in some heavy fuel oil molecules. Upon combustion, vanadium oxides are formed, and some have critical melting temperatures. The most critical are the double oxides/sulphates with sodium. The maximum permitted quantity is 50 to 450 mg/kg.
- Cetane index is a measure for the ignition quality of the fuel in a diesel engine. The higher the speed of the engine required, the higher the cetane index.
- Heating value (calorific value) is defined as the amount of heat that is released during combustion of 1 kg of fuel. Assumed that after combustion the water content in the fuel is present as vapour, the condensation heat is not included in the heating value and it is referred to as the net calorific value or lower heating value. Standard net calorific value for GO is 44,000 kJ/kg, for MDO 42,000 kJ/kg and for HFO 40,500 kJ/kg.

4. Combustion process in the marine diesel engines and formation of the air pollutants

4.1. Combustion stoichiometry

The aim of the combustion stoichiometry is to determine the required amount of air and fuel in order to achieve complete combustion. A stoichiometric mixture contains the exact amount of fuel and oxidiser, so that after combustion is completed, all the fuel and oxidiser are consumed to form combustion products. This ideal stoichiometric mixture approximately yields the maximum flame temperature, as all the energy released from combustion is used to heat the products. As in references [14], combustion stoichiometry for a general hydrocarbon

fuel (CαHβOy) can be expressed by equation (1) and it can be applied only for single-component hydrocarbons (HC):

$$C_\alpha H_\beta O_y + \underbrace{\left(\alpha + \frac{\beta}{4} - \frac{y}{2}\right)\cdot\left(O_2 + 3{,}76N_2\right)}_{\text{stoichiometric air amount}} \rightarrow \alpha CO_2 + \frac{\beta}{2}H_2O + 3{,}76\cdot\left(\alpha + \frac{\beta}{4} - \frac{y}{2}\right) \quad (1)$$

Typical approaches for multiple-component hydrocarbon fuels develop the stoichiometric combustion using the general principle of atomic balance, making sure that the total number of C, H, N and O atoms is the same in the products and the reactants (e.g. multiple-component mixture of a 95 % methane (CH_4) and 5 % hydrogen (H_2)):

$$0{,}95CH_4 + 0{,}05H_2 + 1{,}925\left(O_2 + 3{,}76N_2\right) \rightarrow 0{,}95CO_2 + 1{,}95H_2O + 7{,}238N_2 \quad (2)$$

If less air than the stoichiometric amount is used, the mixture is described as rich fuel or rich mixture, and if excess air is used, the mixture is described as lean fuel or lean mixture. For this reason, it is appropriate to determine the amount of the combustible mixture using one of the following methods: a)Fuel-air ratio (FAR), b) equivalence ratio (Φ) and c) percent excess air (% AE).

a. *Fuel-air ratio (FAR)* or f is the actual ratio of fuel mass m_f and air mass m_a and it is expressed as

$$f = \frac{m_f}{m_a} \quad (3)$$

and it is usually bounded by 0 and ∞. For a stoichiometric mixture, equation (3) becomes

$$f_s = \left.\frac{m_f}{m_a}\right|_{ST} = \frac{M_f}{\left(\alpha + \frac{\beta}{4} - \frac{y}{2}\right)\cdot 4{,}76\cdot M_a} \quad (4)$$

where M_f is the molar mass of fuel and M_a molar mass of air which is approximately 28.96 kg/kmol. The stoichiometric mixture fuel-air ratio of the most hydrocarbon fuels is bounded by 0.05 and 0.07. Air-fuel ratio (AFR) is reciprocal of FAR and it is expressed as AFR=f^{-1}.

b. *Equivalence ratio (Φ)* is the actual ratio of fuel-air ratio f to the stoichiometric fuel-air ratio f_s:

$$\Phi = \frac{f}{f_s} = \frac{m_{as}}{m_a}, \quad (5)$$

http://dx.doi.org/10.5772/59720

and its value is bounded by 0 and ∞. $\Phi < 1$ is a lean mixture; $\Phi = 1$ is a stoichiometric mixture; and $\Phi > 1$ is a rich mixture. The fuel in the combustion process must be mixed with a greater amount of air than in stoichiometric mixture because it is not possible to bring the ideal amount of air to each fuel molecule in order to mix them perfectly so that complete combustion is achieved. In the combustion analysis, an alternative variable lambda (λ) is often used by engineers. Lambda is the ratio of the actual air-fuel ratio to the stoichiometric air-fuel ratio defined as

$$\lambda = \frac{AFR}{AFR_s} = \frac{1}{f / f_s} = \frac{m_a}{m_{as}} = \frac{1}{\Phi} \tag{6}$$

c. *Percent excess air* (% AE) is the amount of air in excess of the stoichiometric amount and it is defined as

$$\%EA = 100 \cdot \frac{m_a - m_{as}}{m_{as}} = 100 \cdot \left(\frac{m_a}{m_{as}} - 1 \right) \ \% \tag{7}$$

4.2. Combustion process in marine diesel engine

Process of fuel combustion is comprised of the following steps: entry of fuel jet into the combustion chamber, disintegration of the jet into droplets, decomposition of larger droplets into smaller, droplet heating, droplet evaporation, mixing of fuel vapour with the surrounding air, simultaneous auto-ignition of fuel mixture in several places, continued evaporation of the droplets and burning around (diffusion combustion), formation of soot during combustion in an area near droplets, temperature drop and slowing reaction due to expansion in the cylinder.

While the combustion temperature is still high, it is necessary that the soot particulate finds their reactants (oxygen) to complete combustion reaction. The phases until the simultaneous ignition of fuel mixture represent a delayed auto-ignition in several places which can be defined as the time or engine crank angle that elapses from the beginning of fuel ignition to the auto-ignition of the mixture.

A good spatial distribution of fuel affects the proper and economical operation of the engine. To achieve a good spatial distribution of fuel, it must be injected at a rate of about 150–400 ms^{-1}, which requires a pressure of over 80 MPa.

Dispersion quality is determined by the injection speed, fuel surface tension, fuel viscosity, density of air in the cylinder, turbulence and cavitation in the nozzle. Better turbulence, mixing with air and combustion can be achieved by better penetration and propagation of jet fuel.

In marine diesel engine, injection is performed by injectors with the nozzles that direct the fuel into the cylinder space. Under the influence of aerodynamic forces of compressed air, fuel jet expands and breaks down into small droplets. The quality of fuel atomisation is defined by a mean diameter of the droplets and their uniformity. Better fuel dispersion is achieved with the

smaller diameters of the nozzle holes, greater injection pressure and higher compression pressure inside the cylinder. The combustion process in a diesel engine can be divided into four phases (see Figure7).

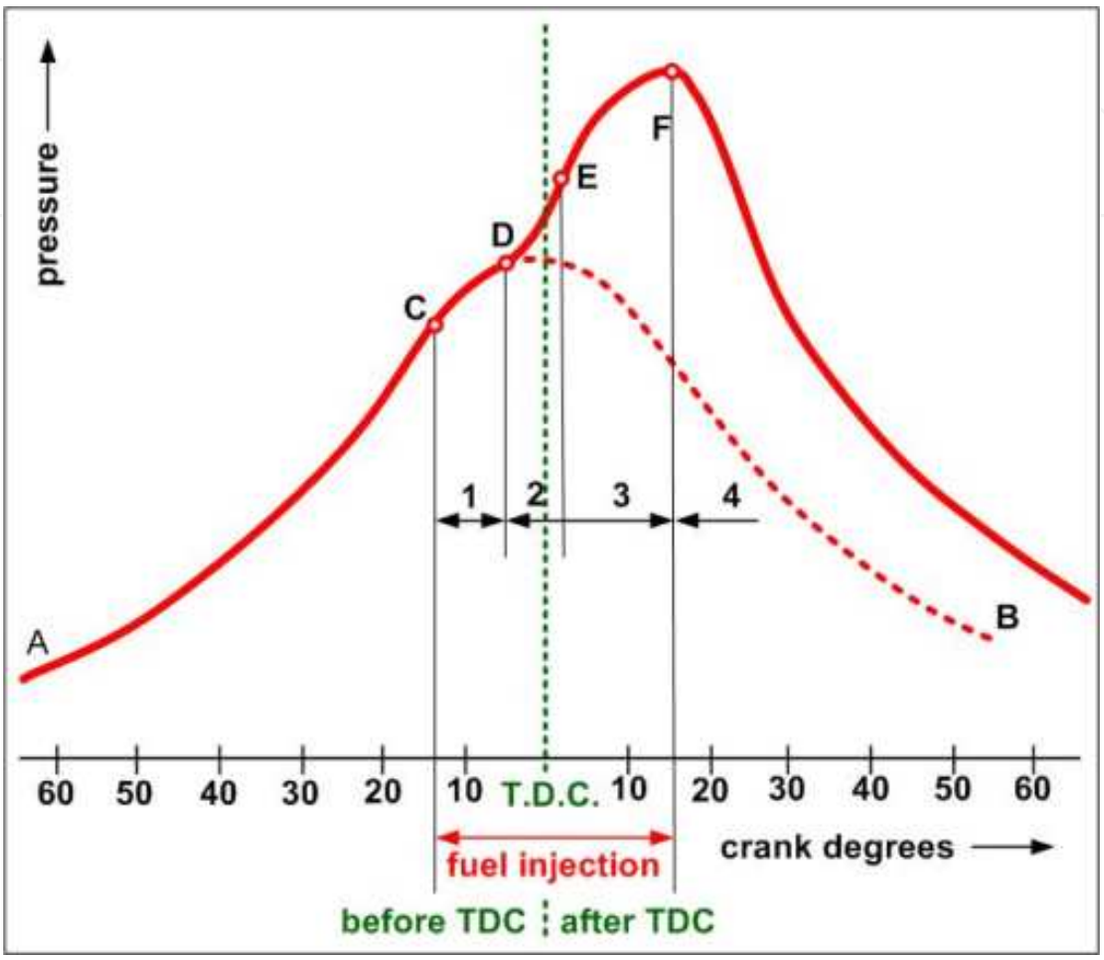

Figure 7. Phases of the combustion process

The first phase, 'ignition delay, curve C-D', defines the period from the beginning of injection until the ignition starts and has an impact on the pollutant formation. This period defines fuel atomisation, evaporation, mixing and the reaction beginning. At sufficiently low turbulence, local flame fronts are created and produce high temperature without soot.

The second phase, 'uncontrolled combustion, curve D-E', is a homogeneous phase of combustion. At this stage, there are sudden ignition and combustion of the already prepared fuel mixture during the delayed ignition phase. Combustion begins simultaneously in several places and conducts intensively, and there is a sudden increase in the pressure and the temperature.

The third phase, 'partially controlled combustion, curve E-F', is diffusion combustion when the fuel droplets vaporise from the surface. Evaporated fuel is mixed with air, and combustion speed is limited by the rate of fuel evaporation and the speed of creating fuel mixture.

http://dx.doi.org/10.5772/59720

The fourth phase, 'after burning, curve F till the end', is the final part of the combustion and it takes about half of the total combustion time duration. During that phase, reaction slows due to expansion and decrease amounts of reactants, and a part of soot that is created during combustion leaves the cylinder as portion of emissions.

4.3. Adiabatic flame temperature

One of the most important features of a combustion process is the highest temperature of the combustion products that can be achieved. The temperature of the combustion products will be the highest when there are no heat losses to the surrounding environment and when all energy released from combustion is used to heat the products. Constant pressure adiabatic temperature calculation, using a mean specific heat capacity method, can be performed for the lean and the rich combustion mixture as in [14]:

a. *For a lean mixture (Φ < 1):*

$$T_{\mathrm{AFT}} = T_{\mathrm{R}} + \frac{\Phi \cdot f_{\mathrm{s}} \cdot LHV}{\left(1 + \Phi \cdot f_{\mathrm{s}}\right) \cdot \overline{c}_{p,\mathrm{P}}} \tag{8}$$

where T_R represents the temperature of the reactants, i.e. fuel which has the compression temperature (T_2) after injection and ignition delay, and $\bar{c}_p$ is an average specific heat capacity of the mixture.

b. *For a rich mixture (Φ > 1):*

$$T_{ATP} = T_R + \frac{f_s \cdot LHV}{\left(1 + \Phi \cdot f_s\right) \cdot \overline{c}_{p,\mathrm{P}}} \tag{9}$$

5. Formation of the air pollutants during combustion process in marine diesel engine

The major pollutants in diesel exhaust emissions are a direct result of the diesel combustion process itself. Typical concentrations of exhaust gas emissions from marine diesel engine largely comprise nitrogen approximately 76 %, oxygen abt. 13 %, carbon dioxide (CO_2) abt. 5 % and water vapour abt. 5 %, with smaller quantities of pollutants: nitrogen oxide (NO_X) abt. 1200 ppm, sulphur oxide (SO_X) abt. 640 ppm, carbon monoxide (CO) abt. 60 ppm, partially reacted and non-combusted hydrocarbons (HC) abt. 180 ppm and particulate matter (PM) abt. 120 mg/Nm^3 [15]. The composition of this gas mixture, liquids and solids that are actually emitted into the air will vary depending on engine type, engine power, operating conditions as well as fuel and lubricating oil type and also depends on whether the emission control system is present. Pollutant formation in marine diesel engine is discussed below.

5.1. Nitrogen oxides (NOx)

Nitrogen oxides (NOx) generate thermally from atmospheric nitrogen oxygen in the intake or scavenging air. The oxidation of atmospheric nitrogen is influenced by local conditions in the combustion chamber, such as the maximum cylinder pressure, local peak temperatures and local air- fuel ratio. The primary reaction product is nitric oxide (NO) by approximately 90 % of the volume, but about 5 % of it is converted into nitrogen dioxide (NO_2) later in the combustion cycle, during expansion and during the flow through the exhaust system. At the same time, a very limited proportion of nitrous oxide N_2O is also formed. Further oxidation of NO to NO_2 subsequently continues at ambient temperatures after the exhaust gases have passed out to the atmosphere. Nitrogen oxide is of particular concern because of its detrimental effects on respiration and plant life, as well as its significant contribution to acid rain. In addition, NOx, together with volatile organic compounds (VOC), is also involved in a series of photochemical reactions that lead to an increase in troposphere ozone which, in turn, adversely affects human health and natural vegetation. These problems are only pronounced on land and especially in urban areas.

Analysis of the combustion process in the cylinder and the reactions which are involved in formation of NO has identified three main sources of NO formation of which, as mentioned above, some is converted to NO_2 to give the NOx mixture. These sources are thermal NO formation, prompt NO formation and fuel source. A majority of the NO emission is generated by internal combustion engines through the thermal process.

a. *Thermal nitric oxide (NO) formation*

During the combustion process in diesel engine, high temperatures are reached. Around 1700 K, and above up to 2500 K, sufficient thermal energy is available to dissociate oxygen, nitrogen and also other molecules formed during the combustion process itself. The recombination of the elements leads to the formation of NO. The reaction processes are quite slow so that most nitrogen oxides are formed during the mixing of the stoichiometric combustion gases with excess air in the cylinder. In low- and medium-speed diesel engines, by far the most important part of NOx is generated in the thermal NO process.

Formation of nitric oxide can be represented with three chemical reactions based on Zeldovich mechanism as in [16]:

$$N_2 + O \rightarrow NO + N \tag{10}$$

$$N + O_2 \rightarrow NO + O \tag{11}$$

$$N + OH \rightarrow NO + H \tag{12}$$

The first two reactions show the formation of nitric oxide for the lean mixture and the third for the rich mixture. The first reaction is the rate-limiting step due to its very high temperature

http://dx.doi.org/10.5772/59720

activation. The high activation energy is required to break the triple bond in the nitrogen molecule (:N≡N:), which occurs at high combustion temperature; this is named thermal nitrogen monoxide (NO). The formation rate of thermal NO is practically insignificant if the temperature is below 1700 K. On the other hand, if the temperature rises, especially over 2000 K, the formation of thermal NO is strongly accelerated. The formation of thermal NO may be reduced by lowering and controlling the temperature peaks and minimising flue gas residence at high temperatures. As in [17], the equation for the total formation rate of thermal nitrogen oxides (NOx) is

$$\frac{d\left[NO_x\right]}{dt} = \frac{6 \cdot 10^{16}}{T^{0,5}} \cdot e^{\left(\frac{-69090}{T}\right)} \cdot \left[N_2\right] \cdot \left[O_2\right]^{0,5}, \tag{13}$$

where T is absolute flame temperature (K), N_2 nitrogen molecule concentration (molcm^{-3}), O_2 oxygen molecule concentration (molcm^{-}) and dNOx/dt nitrogen oxide speed formation (molcm^{-3}).

b. *Prompt nitric oxide (NO) formation*

Prompt nitric oxide can be formed promptly at the flame front by the presence of hydrocarbon radicals produced only at the flame front at relatively low temperature. Nitric oxide generated via this route is named 'prompt nitric oxide (NO)'. Hydrocarbon (HC) radicals react with nitrogen molecules with the following sequence of reaction steps:

$$CH + N_2 \rightarrow HCN + N \tag{14}$$

$$HCN + N \rightarrow \cdots \rightarrow NO \tag{15}$$

Nitrogen reacts with an HC radical to produce hydrogen cyanide HCN, and further, HCN reacts with nitrogen to produce nitric oxide via a series of intermediate steps. In contrast to thermal NO mechanisms that have activation temperature above 1700 K from (160), prompt NO can be formed starting at low temperature, around 1000 K as in [17].

c. *Fuel sources of NO formation*

NO formation from fuel becomes important when using heavy fuel oil because such fuels contain more organic nitrogen than marine diesel oil and other distillate fuels. Heavy fuel oil can contain up to 0.5 % nitrogen which increases the total NOx emission by as much as 10 %.

5.2. Sulphur oxides (SOx)

Formation of sulphur oxides (SOx) in the exhaust gases is caused by the oxidation of the elemental sulphur in the fuel into sulphur monoxide (SO), sulphur dioxide (SO_2) and sulphur trioxide (SO_3) during the combustion process. SOx emissions in diesel engine exhaust gas

mostly comprise of sulphur dioxide and a small amount of sulphur trioxide. The stable products such as sulphur dioxide (SO_2), hydrogen sulphide (H_2S), carbon disulfide (CS_2) and disulfide (S_2) are created during the combustion of the rich mixtures. The radical sulphur monoxide (SO) reacts with oxygen (O_2) to produce sulphur dioxide (SO_2) at high temperatures. The amount of sulphur dioxide emissions depends on the sulphur content of the fuel used and cannot be controlled by the combustion process. Furthermore, sulphur trioxide (SO_3) cannot be created in the combustion under fuel-rich conditions, even when the combustion is near the stoichiometric point. However, if there is even a 1 % air excess, sulphur trioxide rapidly increases in its quantity. Typically, the amount of SO_3 is 5 % of the amount of sulphur oxides (SO_2 and SO_3). For example, if the fuel contains 3 % sulphur, the volume of SOx generated is around 64 kg per tonne of fuel burned; if fuel with 1 % sulphur content is used, SOx emission amount is about 21 kg per tonne of fuel burned as in [18]. SOx formed from diesel exhaust is corrosive and is partly neutralised by an engine's lubricating oil which is used as a typical base. Moreover, sulphur oxides (SOx) combine with moisture to form sulphuric acid (H_2SO_4), which is then excreted in the form of acid rain. It has a harmful effect on plants and human health and can damage many objects including buildings. Sulphur dioxide emissions also negatively impact human health; sulphate particles particularly can induce asthma, bronchitis and heart disease.

5.3. Carbon monoxide (CO)

The formation of carbon monoxide (CO) is a result of incomplete combustion of organic material, which is due to a lack of oxygen or low temperature at some points in the combustion chamber. Also the same reasons lead to the formation of hydrocarbons (HC). Hydrocarbons can also be formed from evaporation of the lubrication oil towards the end of the firing period. In diesel engines, the formation of carbon monoxide is determined by the air/fuel mixture in the combustion chamber, and since diesel fuel has a consistently high fuel-air ratio and the efficient combustion process, formation of this toxic gas is minimal. Nevertheless, insufficient combustion can occur if the fuel droplets in a diesel engine are too large or the level of turbulence is insufficient or swirl is created in the combustion chamber. When burning heavy fuel oil, the hydrocarbon emissions are lower than from the light fuel oil combustion due to lower evaporating level.

5.4. Hydrocarbon (HC)

Hydrocarbon (HC) emissions as fraction of the exhaust gases from diesel engines predominantly consist of unburned or partially burned fuel and lubricating oils as a result of insufficient temperature. This often occurs near the cylinder wall where the temperature of the air/fuel mixture is significantly less than in the centre of the cylinder. In the atmosphere, the hydrocarbons are subjected to photochemical reactions with nitrogen oxides forming the ground-level ozone and smog. Hydrocarbon (HC) emissions are represented as total hydrocarbons (THC) or as non-methane hydrocarbons (NMHC), as in [19].

http://dx.doi.org/10.5772/59720

5.5. Particulate matter (PM)

Particulate matter is a mixture of organic and inorganic substances largely comprising elemental carbon, ash minerals, heavy metals, condensed sulphur oxides, water and a variety of unburned or partially burned hydrocarbon components of the fuel and lubricating oils. More than half of the total particulate mass is soot (inorganic carbonaceous particles), of which the visible evidence is smoke. Some of the fuel particles do not burn completely, and they are emitted as droplets of heavy liquid or carbonaceous material. The incomplete burning is a result of locally low quantities of excess air. A mistimed or otherwise poorly operating fuel injection and poor mixing of fuel within the cylinder also result in incomplete combustion and increased the particulate matter emissions. Soot particles (unburned – elemental carbon) are not themselves toxic, but they can cause the build-up of aqueous hydrocarbons (HC), and some of them are believed to be carcinogens. Particulates constitute no more than around 0.003 % of the engine exhaust gases. Almost the entire diesel particle mass is in the fine particle range of 10 microns or less in diameter (PM_{10}). Approximately 94 % of the mass of these particles are less than 2.5 microns ($PM_{2.5}$) in diameter. Diesel PM is of specific concern because it poses as a lung cancer hazard for humans as well as a hazard from noncancer respiratory effects such as pulmonary inflammation. Because of their small size, the particles are readily respirable and can effectively reach the lowest airways of the lung along with the adsorbed compounds, many of which are known or suspected mutagens and carcinogens. Secondary reactions of NOx and SOx can also produce PM.

The most effective method of reducing particulate emissions is to use lighter distillate fuels; however, this leads to added expense. Additional reductions in particulate emissions can be achieved by increasing the fuel injection pressure to ensure that optimum air/fuel mixing is achieved. The third method of reducing particulate emissions is to use cyclone separators, which are effective for particle sizes greater than 0.5 μm.

5.6. Carbon dioxide (CO_2)

Carbon dioxide is one of the basic products of combustion and is not toxic; however, it has been linked to the 'greenhouse effect' and global warming. Diesel engine exhaust gases containing CO_2 as a result of carbon and oxygen O_2 combustion. The maximum concentration of carbon dioxide will be generated during stoichiometric combustion, i.e. when complete amount of fuel reacts with oxygen from the air during combustion. The actual concentration of CO_2 depends on the relative contents of carbon (C), hydrogen (H) and other combustible elements in the fuel. The maximum values of carbon dioxide for common types of marine fuel are shown in Table 3 [20], assuming that the exhaust is dry.

The maximum value of carbon dioxide (CO_2 max) can be calculated according to the following expressions:

$$CO_2 \max = \frac{\text{No. of } CO_2 \text{ molecules produced by complete combustion of fuel}}{\text{Total no. of molecules of combustion products}} \tag{16}$$

Fuel	CO_2 max (%)
Natural gas	11.9
Light fuel oil	15.5
Heavy fuel oil	15.8

Table 3. CO_2 max values for marine fuel, assuming the gases are dry

For 'wet' exhaust gases

$$CO_2 \max = \frac{c}{c + \frac{h}{2} + \frac{79,1}{20,9} \cdot \left(c + \frac{h}{4} \right)} \ \%, \tag{17}$$

For 'dry' exhaust gases

$$CO_2 \max = \frac{c}{c + \frac{79,1}{20,9} \cdot \left(c + \frac{h}{4} \right)} \ \% \tag{18}$$

Carbon dioxide (CO2) concentration can be calculated in the exhaust gas emissions according to equation (19), provided that oxygen concentration (O_2), maximum concentration of carbon dioxide (CO_2) max and fuel type are known, as in [20]:

$$\left[CO_2 \right] = \frac{CO_2 \max \cdot \left(20,9 - \left[O_2 \right] \right)}{20,9}. \tag{19}$$

Emission	Source
NOx	Function of peak combustion temperature, oxygen content and residence time (function of engine speed in rpm)
SOx	Function of fuel oil sulphur content
CO	Function of the air excess ratio, combustion temperature and air/fuel mixture
HC	Function of the amount of fuel and lubricating oil left unburned during combustion process
PM	Originates from unburned fuel as well as ash content in fuel and lubricating oil
CO_2	Function of combustion

Table 4. Summary of pollutants

Reduction of carbon dioxide emissions can be achieved by reducing specific fuel oil consumption (SFOC) since the amount of CO_2 produced is directly proportional to the volume of fuel used and therefore to the engine efficiency. An alternative is to use fuel with a low carbon ratio relative to hydrogen, which greatly increases the price of marine fuel oils. Table 4 provides a summary for the pollutants discussed above.

6. Methods for reducing harmful pollutant emissions from marine diesel engines

Different methods of reducing the pollutant emission from ship's diesel engines are briefly described in the following text. The focus is more on NOx and SOx than on other emissions, but some attention will be given to them as well.

6.1. NOx emission reduction technologies

Nitrogen oxides (NOx) are an important air pollutant created as a by-product of combustion. Air contains primarily nitrogen (N_2) and oxygen (O_2). The heat generated during combustion causes nitrogen (N_2) and oxygen (O_2) to react to form NO_X which is in direct proportion to peak combustion temperature and pressure. Therefore, NO_X emissions can be mitigated by engine controls that decrease combustion temperature and/or aftertreatment of the exhaust gas. NOx reduction methods are generally categorised as primary methods or internal measure and secondary methods or aftertreatment. The primary methods include changes to the combustion process within the engine and can be divided into three main categories: combustion optimisation, water-based controls and exhaust gas recirculation. Many of the mentioned methods aim to reduce NOx emissions by reducing peak temperatures and pressures of the combustion process in the engine cylinder. Secondary methods or aftertreatment implies post-combustion abatement in which the exhaust gas is treated in order to remove NO_X, either passing it through a catalyst or plasma system. Each of these methods is discussed below.

6.1.1. Primary methods or internal measure

The primary methods include changes to the combustion process within the engine and can be divided into three main categories. The first category is combustion optimisation; the second one is water-based control which consists of water injection, water/fuel emulsion and humidification; and the third category is exhaust gas recirculation. These methods have generally low impact on fuel consumption. Another drawback is to retrofit the system of existing engines. Tier II limits under MARPOL Annex VI, Regulation 13, can be achieved using primary controls.

a. *Combustion optimisation*

There are a number of ways to modify the combustion process, each aimed to reduce NOx emissions. Optimisation of the engine combustion process includes modifying the spray pattern by modification of the fuel valve design, injection timing, intensity of injection and

injection rate profile (injection rate shaping), compression ratio, scavenge air pressure and scavenge air cooling. Delayed injection timing is very effective in reducing NOx but increases fuel consumption and smoke. It is usually combined with increased compression pressure and decreased injection duration to minimise or avoid increase in fuel consumption. Other operational modifications that could be made to reduce emissions are combustion chamber optimisation, variable valve timing, increasing the turbo efficiency, the use of a fuel injection system that can be easily adjusted (e.g. electronically controlled injection system) and decrease in the engine air intake temperature using Miller supercharging.[4] Modification of the fuel valve design means replacing the conventional injectors with fuel efficient valves (e.g. slide valves) that optimise the fuel injected into the cylinder. These valves differ from conventional valves in their spray patterns, and they are designed to reduce the dripping of fuel from the injector into the postinjection combustion zone. This fuel entering late the combustion zone is subjected to lower temperatures and therefore results in the emission of unburnt fuel (PM) and VOCs. Changing the conventional fuel valves with slide valves has a significant impact on NOx reduction and PM emissions since PM is a product of incomplete combustion and unburnt fuel. Currently, the slide fuel valves are only applicable for slow-speed two-stroke diesel engines. However, all new engines of this type are supposed to have these valves fitted as the standard. The fuel nozzle was optimised for NOx simultaneously with the development of the slide valve. Tests on a 12K90MC engine (55MW at 94 rpm) at 90 % load showed a 23 % reduction in NOx emissions for a slide-type valve compared with a standard valve and nozzle and with a 1 % fuel consumption increase. Furthermore, increasing the number of injectors per cylinder enables the combustion process to be better controlled and therefore more efficient combustion. However, additional injectors, piping and associated equipment are associated with a cost penalty. Nowadays, modern slow-speed engines use three fuel injectors located near the outer edge of the combustion chamber. With sequential injection, each of the three nozzles in a cylinder is actuated with different timings. Pulsed injection gives about 20 % NOx reduction with about 7 % increase in fuel consumption. Sequential and pre-injection gave less NOx reduction and less fuel consumption increase. The effects are the result of changes in the overall pressure development and interaction between fuel sprays. Pre-injection can be used to shorten the delay period in medium-speed engines and thus decreases temperature and pressure during the early stages of combustion, resulting in reduced NOx. Pre-injection can reduce particulates which are increased by other NOx control measures, thus allowing greater flexibility in NOx control. Delayed injection combined with increased compression ratio have effect on reducing the maximum combustion pressure and hence temperature. By using this simple technique, a reduction of up to 30 % can be achieved. However, delayed injection increases fuel consumption up to 5 % in specific fuel oil consumption due to later burning, as less of the combustion energy release is subjected to the full expansion process and gas temperatures remain high later into the expansion stroke, resulting in more heat losses on the

4 Reduced scavenge air temperature reduces combustion temperatures and thus NOx. For every 3 OC reduction, NOx may decrease by about 1 %. On four-stroke engines, the Miller concept can be applied to achieve low scavenge air temperature. Using a higher-than-normal pressure turbocharger, the inlet valve is closed before the piston reaches bottom dead centre on the intake stroke. The charge air then expands inside the engine cylinder as the piston moves towards bottom dead centre, resulting in a reduced temperature. Miller supercharging can reduce NOx by 20 % without increasing fuel consumption.

http://dx.doi.org/10.5772/59720

walls. In some engines, the timing adjustment can be made while in service. Smoke and emission of PM also increase due to reduced combustion temperatures and thus less oxidation of the soot produced earlier in the combustion, as in [21]. Furthermore, increasing injection pressure leads to better atomisation of the fuel and therefore to reduction in particulates and CO. Since combustion is cleaner, this technique tends to increase NOx reduction. There is also the new generation of the electronically controlled camshaftless engines that allow great flexibility for optimisation of the combustion process over the full range of operating conditions. These computer-controlled engines have allowed greater operational flexibility. As far as NOx is concerned, the main features are computer control of variable injection timing (VIT), injection rate shaping, variable injection pressure and variable exhaust valve closing (VEC). Variable exhaust closing gives the ability to change the effective compression ratio. With variable injection timing and variable exhaust valve closing, it is possible to optimise the injection timing delay and increased compression ratio over the whole load range to maintain peak pressures at low load while avoiding excessive peak pressures at high load. Computer-controlled camshaftless engines are equipped with common rail injection techniques which give high injection pressures and thus good spray characteristics even at low loads granting of NOx reduction emissions.

b. Water-based control

The second category is water-based controls consisting of water injection, water/fuel emulsion and humidification. Water-based controls reduce emissions of the NOx from diesel engines by introducing freshwater at different stages of the combustion process. Introduction of water into the combustion chamber reduces maximum combustion temperature due to the absorption of energy for evaporation and the increase in the specific heat capacity of the cylinder gases and thus reduce emissions of the NOx [23]. The in-cylinder evaporation of the water also improves the atomisation of the fuel and causes it to burn more completely. Freshwater can be introduced in the charge air (humidification), through direct injection into the cylinder or through water/fuel emulsion. Water/fuel emulsion is the process of introducing water into the fuel prior to injection into the combustion cylinder and can reduce smoke, while humidification can increase smoke. Direct water injection is the process of introducing water directly into the combustion cylinder at pressures of 200–400 bar. The water is injected into the cylinder by a combined injection valve and nozzle that allow injection of water and fuel oil. The process is electronically controlled. Direct injection of water and water/fuel emulsions place the water more directly in the combustion region, where it has maximum effect on NOx production. Generally, direct water injection or water/fuel emulsions will yield about 1 % reduction in NOx for every 1 % of water-to-fuel ratio. This one-to-one ratio is consistent up to about 30 % water content, at which point the combustion temperature decreases too much, resulting in an increase in PM emissions. Alternative to water injection and water/fuel emulsion is the scavenge air humidification as a second category of the primary methods for NOx emission reduction that implies injection of very fine water mist in scavenge airstream after the turbocharger using special nozzles (Scavenge Air Saturation System). The fine water droplets evaporate fast, and further heat is introduced in the scavenge air. Humidification requires about twice as much water for the same NOx reduction compared with direct injection of water

and water/fuel emulsions. Humidification can reduce NOx levels down to 2 to 3 g/kWh without fuel consumption penalty. Similar technique that is used for humidification of the engine scavenge air is the so-called humid air motor (HAM). In this system, hot compressed air from the turbocharger is led to a humidification tower and exposed to a large surface area and flushed with hot water. The water can be heated by a heat exchanger connected to the jacket cooling system or using an exhaust gas boiler. One manufacturer claims considerable success in service in reducing NOx emissions with the added claim of increasing the indicated power of the engine at certain loads, therefore reducing fuel consumption hence proportionally reducing CO_2 emissions. The actual degree of NOx reduction varies from 10 % to over 60 %, depending on the engine type and which of the above reduction methods are adopted. For example, the experiment carried out on the Viking Line's MS Mariella has shown a NOx emission reduction from 17 to between 2.2 and 2.6 g/kWh and a decrease in fuel consumption of 2–3% using the HAM system [24].

c. *Exhaust gas recirculation (EGR)*

The exhaust gas recirculation (EGR) system is based on lowering of the combustion temperature and oxygen concentration thus lowering NOx. EGR reduces combustion temperatures by increasing the specific heat capacity of the cylinder gases and by reducing the overall oxygen concentration, taking away a part of the exhaust gases and mixing it into the engine intake air. Some of the exhaust gas is cooled and cleaned before recirculation to the scavenge air side. The usage of the exhaust gas as intake air reduces the oxygen content in intake air from 21 % to 13 % which limits the NOx that can be formed and reduces the amount of combustion products that can take place. In engines operating on poor-quality fuel, external EGR can lead to fouling and corrosion problems. The residue from cooling and cleaning the exhaust gas on ships using heavy fuel oil contains sulphur in a form which is difficult to dispose of. The relative changes in measured emission parameters as a function of the recirculation amount at 75 % engine load show that at increased recirculation amounts, the HC and PM emissions are reduced corresponding to the reduction of the exhaust gas flow from the engine. Increased recirculation amount leads to increase in CO emissions due to lower cylinder excess air ratios and thus lack of oxygen in the combustion chamber. Furthermore, EGR tends to increase smoke by reducing the O_2 concentration, increasing the combustion duration and decreasing the combustion temperature. All of that may be controlled using additional techniques such as water in fuel to achieve an optimum balance between NO_X, CO and PM. Test engine work by MAN Diesel & Turbo has shown that, with 40 % recirculation, EGR has the potential to reduce NO_X down to Tier III levels on a two-stroke low-speed marine engine and that increased fuel consumption, carbon monoxide emissions and PM emissions resulting from reduced combustion efficiency are manageable with engine adjustments. It is also reported that specific fuel consumption is greatly improved when using EGR to reduce NO_X down to Tier II limits, when compared with using engine adjustments to achieve the same level of emissions, particularly at part load as in [25]. There are many different components to an EGR system such as high pressure exhaust gas scrubber fitted before the engine turbocharger, cooler to further reduce the temperature of the recirculated gas, water mist catcher to

remove entrained water droplets, high-pressure blower to increase recirculated gas pressure before reintroduction to the engine scavenge air and automated valves for isolation of the system. The scrubber in the EGR system is used to remove sulphur oxides and particulate matter from the recirculated exhaust, to prevent corrosion and reduce fouling of the EGR system and engine components. The system requires the use of an electrostatic precipitator and catalysts to remove the particulates from the exhaust gas before injecting it as intake air. There is also a need for wet-scrubbing technology to remove the sulphur components of the exhaust stream prior to reintroduction into the engine. A cooling unit is also needed to reduce the temperature of the exhaust gas before it returns to the engine.

6.1.2. Secondary methods or aftertreatment

Secondary methods, or aftertreatment, are based on treating the engine exhaust gas itself by passing it through a catalyst or plasma system. There has been much development in selective catalytic reduction (SCR) and nonthermal plasma (NTP) reduction systems over the last few years. Using these methods, NOx emission reductions of over 95 % can be achieved [26].

Selective catalytic reduction (SCR) is an exhaust gas treatment method by which the NOx generated in a marine diesel engine exhaust gas can be reduced to a level in compliance with the NOx Tier III requirements. The method involves mixing of ammonia as a reducing agent with the exhaust gas which is passed over a catalyst where more than 90 % of the NOx can be removed to below 2 g/kWh. The SCR system converts nitrogen oxides into harmless nitrogen and water, by means of a reducing agent injected into the engine exhaust stream before a catalyst. Hydrocarbons are also reduced. Exhaust emission abatement systems using SCR technologies usually use an ammonia (NH_3) reductant introduced as a urea/water solution ($(NH_2)_2CO$) into the exhaust stream, prior to the catalyst blocks. For marine systems, a 40 % solution of urea in de-ionised water is typically used for safe handling and toxic risk reasons [27, 28]. The use of urea in the system breaks down the NOx emissions to N_2 and H_2O. The degree of NOx removal depends on the amount of ammonia added. A NOx reduction efficiency of 90 % can be achieved using a urea injection rate of 15 g/ kWh. NOx is reduced according to the following overall reaction scheme [26,27,29]:

Urea decomposition before entering the reactor:

$$(NH_2)_2CO\ (\text{urea}) \rightarrow NH_3(\text{ammonia}) + HNCO\ (\text{isocyanic acid}) \tag{20}$$

$$HNCO\ +\ H_2O \rightarrow NH_3 +\ CO_2 \tag{21}$$

The resulting quantity of CO_2 is minor when compared with that resulting from fuel combustion.

NO_X reduction at the catalyst:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (22)$$

$$2NO + 2NO_2 + 4\ NH_3 \rightarrow 4N_2 + 6H_2O \quad (23)$$

$$6NO_2 + 8NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \quad (24)$$

Equation 22 shows the main SCR reaction as nitric oxide dominates in the exhaust. The reaction shown at equation 23 occurs at the fastest rate up to an NO_2:NO ratio of 1:1. However, at higher ratios, the excess NO_2 reacts slowly as per equation 24. The rate of urea injection must be sufficient to reduce NO_X emissions to the required level but not so great to avoid ammonia slip. Control is based on the load and speed of the engine with active feedback provided on some systems by NO_X and ammonia emission monitoring. At engine start-up, urea injection is initiated once the catalyst reaches operating temperature, which is key for effective NO_X reduction performance, deposit prevention and avoidance of ammonia slip. Catalysts have considerable heat capacity so the time taken to reach the injection trigger temperature is dependent on a number of factors including the minimum catalyst operating temperature recommended for the fuel type, the period of cooldown since the engine was last operated, the size of the catalyst and the engine load pattern at start-up. Injection can begin up to 30 min after a fully cold start, whereas it may begin within 10–15 min if the catalyst is still warm from running in the previous 6–10 h. SCR units are typically installed in the exhaust system of a diesel engine, if applicable, before the exhaust gas economiser and as close as possible to the engine because of the relatively high exhaust gas temperatures required by the catalysts for effective NOx reduction reactions. The SCR catalysts may also be integrated with the engine by close coupling to the engine, typically applicable to small high-speed diesel engines. For slow-speed diesel engines with inherently low relative exhaust gas temperatures, this may necessitate the integration of the SCR reaction chamber and catalysts before the turbocharger exhaust turbine. Depending on the engine load, the exhaust gas temperature on this side is 50–175 °C higher than on the low pressure side. Even though the reactor is placed before the turbine, the exhaust gas temperature will normally still be too low at low loads. To increase the temperature, a cylinder bypass from the scavenge air receiver to the turbine inlet is installed. The bypass is controlled by the cylinder bypass valve.

When opening the bypass, the mass of air through the cylinders will be reduced without losing the scavenge air pressure, and, accordingly, the exhaust gas temperature will increase. This system makes it possible to keep the temperatures above the required level. However, the cylinder bypass will increase the SFOC depending on the required temperature increase. Selective catalytic reduction is the only technology currently available to achieve compliance with the Tier III NOx standards for all applicable engines. Another option is selective non-catalytic reduction (SNCR), which works in a similar way with selective catalytic reduction but without the use of a catalyst. A reducing agent (ammonia or urea) injected during the combustion process converts the nitrogen oxides into nitrogen and water, reducing NOx

emissions by 50 % [30]. The drawback of this system is that it is less efficient than the SCR method, because only 10–12 % of ammonia reacts with NOx. Since the cost of ammonia is relatively high and since the system requires extensive modification to the engine, the SNCR option does not appear to be competitive. Plasma reduction systems are based on the use of plasma. This is a partially ionised gas composed of a charge of a neutral mixture of atoms, molecules, free radicals, ions and electrons. Electrical power is converted into electron energy, and the electrons create free radicals, which destroy pollutants in exhaust emissions. Experiments have shown that plasma reduction systems can reduce NOx by up to 97 % [30]. It seems to be flexible in terms of size and shape and should be at relatively low cost. However, for marine use, it is still in the development phase.

6.2. SOx reduction technologies

The emission of sulphur dioxide is directly proportional to the content of sulphur in fuel. To meet the restrictions on emissions of sulphur oxides (SOx) and PM (particulate matter) that are determined by the MARPOL convention Annex VI which specifies a global and a local (ECA) limit on the sulphur content in marine fuel, there are only two possibilities for reducing SOx emissions: either use fuels with low sulphur content (there will be no restrictions in the use of heavy fuel oil) or apply an exhaust gas cleaning system to reduce the total emission of SOx. Although the SOx requirements can be met by using a low-sulphur fuel, the regulation allows alternative methods to reduce the emissions of SOx to an equivalent level. The process of exhaust gas cleaning is performed in a scrubber unit. There are two main types of SO_X scrubber: wet scrubbers that use water (seawater or fresh) as the scrubbing medium and dry scrubbers that use a dry chemical. The wet scrubbing technology is based on the fact that sulphur oxides dissolve in water. This means that when the exhaust gas is sprayed with the alkaline water in the scrubber, the SOx will dissolve in the scrubbing water and be cleaned from the exhaust gas. The water is injected into the exhaust gas stream and is discharged from the bottom of the scrubber. The alkalinity in the scrubbing water will neutralise the SOx emissions. The scrubbing water must be cleaned of particulate matter and other contaminants before being discharged out into sea. Wet scrubbing systems which are normally fitted on marine engines may be categorised as open-loop system, closed-loop system or hybrid system.

Open-loop systems – In an open-loop technology, the water comes from the sea and goes directly to the scrubbers. After the scrubbing process, the water goes through water treatment and to the sea again. This system takes advantage of the natural alkalinity of seawater to buffer the acidity of SO_X gases. The seawater flow rate in open-loop systems is approximately 45 m^3/MWh. Sulphur oxide removal rate is close to 98 % with full alkalinity of the seawater, meaning emissions from a 3.5 % sulphur fuel will be the equivalent of those from a 0.10 % sulphur fuel after scrubbing [29]. The sulphur oxides generated in the combustion process are dissolved and removed by the scrubber water. Sulphur dioxide (SO_2) is dissolved and ionised to bisulphite and sulphite, which is then readily oxidised to sulphate in seawater containing oxygen. As in reference [29], similarly sulphuric acid, formed from SO_3, and hydrogen sulphate dissociate completely to sulphate according to chemical reactions:

For SO_2:

$$SO_2 + H_2O \rightarrow H_2SO_3\left(sulphurous\ acid\right) \rightarrow H^+ + HSO_3\left(bisulphite\right) \tag{25}$$

$$HSO_3^-\left(bisulphite\right) \rightarrow H^+ + SO_3^{2-}\left(sulphite\right) \tag{26}$$

$$SO_3^{2-}\left(sulphite\right) + 1/2\,O_2 \rightarrow SO_4^{2-}\left(sulphate\right) \tag{27}$$

For SO_3:

$$SO_3 + H_2O \rightarrow H_2SO_4\left(sulphuric\ acid\right) \tag{28}$$

$$H_2SO_4 + H_2O \rightarrow HSO_4^-\left(hidrogen\ sulphate\right) + H_3O^+ \tag{29}$$

$$HSO_4^-\left(hidrogen\ sulphate\right) + H_2O \rightarrow SO_4^{2-}\left(sulphate\right) + H_3O^+ \tag{30}$$

Closed-loop systems use freshwater treated with sodium hydroxide (NaOH) as the scrubbing media for the neutralisation of SO_X. This results in the removal of SO_X from the exhaust gas stream as sodium sulphate according to the following chemical reactions as in [29]:

For SO_2:

$$NA^+ + OH^- + SO_2 \rightarrow NaHSO_3\left(aq\ sodium\ bisulphite\right) \tag{31}$$

$$2NA^+ + 2OH^- + SO_2 \rightarrow Na_2SO_3\left(aq\ sodium\ sulphite\right) + H_2O \tag{32}$$

$$2NA^+ + 2OH^- + SO_2 + 1/2\,O_2 \rightarrow Na_2SO_4\left(aq\ sodium\ sulphate\right) + H_2O \tag{33}$$

For SO_3:

$$SO_3 + H_2O \rightarrow H_2SO_4\left(sulphuric\ acid\right) \tag{34}$$

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4\left(aq\ sodium\ sulphate\right) + 2H_2O \tag{35}$$

http://dx.doi.org/10.5772/59720

In a closed-loop technology, absolutely no water comes from the sea. The freshwater comes from a buffer tank and is cooled by the seawater. The freshwater is composed of NaOH and leaves the buffer tank to go to the scrubber. After the scrubbing process, the water comes back to the buffer tank, cleaned by a filter. The black water goes to a sludge tank and the clean water goes back to the scrubbing cycle. A big storage tank fills up the buffer tank. Closed-loop systems can also be operated when the ship is operating in enclosed waters where the alkalinity would be too low for open-loop operation. Closed-loop systems typically consume sodium hydroxide in a 50 % aqueous solution. The dosage rate is approximately 15 l/MWh of scrubbed engine power of a 2.70 % sulphur fuel is scrubbed to equivalent to 0.10 %. Using a closed-loop technology can have some advantages. First, there is a possibility to increase the pH level in order to reduce more SOx. Also there is no corrosion of the parts and less discharge water to clean. The running costs of the closed-loop technology are relatively high because it uses NaOH which is 0.2 €/kg and its required monitoring units. Also the sludge tanks have to be discharged at the harbour which costs a lot of money. The closed-loop reduces about 98 % SOx in the exhaust gas.

Hybrid system – A hybrid system is a mixture of both open loop and closed loop. In harbours and ECA, the system can operate with freshwater without generating any significant amount of sludge to be handed at port calls. At open sea, the system switches to the seawater open loop. Using a hybrid technology can have some advantages. First, if the ship is running at open sea, after switching to open loop, the accumulated water of the buffer tank can slowly be removed back to the sea. Also, the tank is slowly filled up again to prepare for the arrival at sensitive areas.

Dry SO_Xscrubber known as an 'absorber' brings the exhaust gas from diesel engine in the multistage absorber where contact with calcium hydroxide ($Ca(OH)_2$) granules reacts with sulphur dioxide (SO_2), forming calcium sulphite as in reference [29]:

$$SO_2 + Ca(OH)_2 \rightarrow CaSO_3(calcium\ sulphite) + H_2O \tag{36}$$

The sulphite is then oxidised and hydrated in the exhaust stream to form calcium sulphate dihydrate, or gypsum:

$$2CaSO_3 + O_2 \rightarrow 2CaSO_4(calcium\ sulphate) \tag{37}$$

$$CaSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(calcium\ sulphate\ dihydrate - gypsum) \tag{38}$$

Similarly, chemical reactions take place for SO_3:

$$SO_3 + Ca(OH)_2 + H_2O \rightarrow CaSO_4 \cdot 2H_2O(calcium\ sulphate\ dihydrate - gypsum) \tag{39}$$

Using a dry scrubber can have some advantages. First, the good point of this technology is that the desulphurisation unit requires, aside from electrical energy, only $Ca(OH)_2$ in the shape of spherical granulates. Also the dry scrubber further operates as a silencer. Dry scrubbers typically operate at exhaust temperatures between 240 °C and 450 °C. Calcium hydroxide granules are between 2 and 8 mm in diameter with a very high surface area to maximise contact with the exhaust gas. Within the absorber, the calcium hydroxide granules ($Ca(OH)_2$) react with sulphur oxides to form gypsum ($CaSO_4$ $2H_2O$). To reduce SO_X emissions to those equivalent to fuel with a 0.1 % sulphur content, a typical marine engine using residual fuel with a 2.70 % sulphur content would consume calcium hydroxide granules at a rate of 40 kg/MWh (i.e. a 20 MW engine would require approximately 19 tonnes of granulate per day) [29, 30]. The dry scrubber reduces up to 99 % SOx in the exhaust gas. It will be absolutely no problem to fulfil all the IMO 3 requirements for 2016. The dry scrubber compared to the wet scrubber has lower investment costs and higher running costs and requires a lot of space which reduces the benefits. The efficiency of the SOx scrubber systems depends on the sulphur content in the fuel and generally ranges up to 97 %. Anyhow, the efficiency system must be sufficient to achieve a SOx emission level that is equal to or lower than the required limit.

On the other hand, it should be noted that the reduction of both NOx and SOx emissions from marine diesel engines be achieved by replacing conventional fuels with alternative fuels, e.g. liquefied natural gas (LNG). In case of using LNG, NOx emission can be reduced by 60 % and SOx emission by 90–100 %.

There is also another option to use onshore power supply at ports which is especially beneficial for local air quality. In this case, NOx and SOx emissions can be reduced by 90 %, while CO_2 reduction depends on the source of electricity. The total CO_2 emission reduction depends on how the used electricity is produced. In the European Union, the use of shore-side electricity rather than electricity generated by a ship using low-sulphur fuel will cut CO_2 emissions by an average of 50 %.

One of the main benefits of shore connection systems stems from the fact that electricity generated on land by power plants has a smaller adverse impact on the ecosystem than that produced by ship engines. Namely, the main cause of air pollution from ships in ports is the use of auxiliary diesel engines to generate electricity on ships. Furthermore, experiments with wind and solar power, biofuels and fuel cells are ongoing and could be useful in the future to reduce air pollution from ships.

In Table 5, overview of different technologies and their potential for reduction of emissions from marine diesel engines are summarised as in [31].

Category	Technology aimed to reduce	NOx	SOx	PM	CO_2
Engine modification	NOx				
	Optimise combustion	20–40%	0%	25–50%	0%
Water-based control	Direct water injection	50%	0%	0%	0%

Category	Technology aimed to reduce	NOx	SOx	PM	CO_2
	Water in fuel (30 % emulsion)	30%	0%	0%	0%
	Scavenge air humidification	30–60%	0%	0%	0%
	Humid air motor	10–70%	0%	40–60%	0%
Exhaust gas recirculation	ERG	20–85%	0%	0%	0%
Aftertreatment	Selective catalytic reduction	90–95%	0%	0%	0%
	SOx	0%	0%	0%	0%
	Scrubber	0%	90–97%	80–85%	0%
(Alternative) fuels	Low-sulphur fuel 2,7 %S to 0,1 %S	0%	97%	20%	0%
	Both NOx and SOx	0%	0%	0%	0%
	LNG	60%	90–100%	72%	0–25%
	Onshore power supply (in harbour only)	97%	96%	89%	Depending on energy source, average 50%

Table 5. Different technologies and their reduction potential

7. Conclusion

Owing to rapidly developed shipping industry and maritime traffic in recent decades, air pollution emissions from ocean-going ships are continuously growing. Exhaust gases from marine diesel engines are the primary source of emission harmful pollutants such as nitrogen oxides (NOx), sulphur dioxide (SO_2), carbon monoxide (CO) and particulate matter (PM) which contribute significantly to environmental pollution, especially in port areas that are often located in or near urban areas, and a significant number of people are exposed to these emissions. The increased air pollutant concentrations and deposition have several negative effects. Nitrogen oxide and particulate matter can contribute to many serious health problems and increased morbidity and mortality (especially from cardiovascular and cardiopulmonary diseases). Nitrogen oxides also contribute to the formation of ground-level ozone, which has a harmful effect on plants and human health. Furthermore, sulphur dioxide and nitrogen oxide emissions increase acidification of sensitive forest ecosystems along the coastal areas and have a harmful effect on plants, aquatic animals and infrastructure by accelerating the deterioration process of various materials. Finally, ships are also a source of greenhouse gas, a pollutant

which contributes to global warming. Recent studies indicate that the emission of CO_2 by ship corresponds to about 3 % of the global anthropogenic emissions. If things remain the same, by 2020, shipping will have been the biggest single emitter of air pollution especially in areas of the dense maritime traffic such as Europe, North America and East Asia which surprisingly surpasses the emissions from all land-based sources together. Since harmful pollutant emissions from ships have great impact on the human health and the environment, it is required to tighten uniform regulations at the global level, bearing in mind that shipping is inherently international. The International Maritime Organization (IMO) responsible for the safety of life at sea and the protection of the marine environment reacts on NOx, SOx, PM and CO_2 emissions from a ship by adoption of Annex VI of the MARPOL 73/78 Convention, titled 'Regulations for the Prevention of Air Pollution from Ships'. MARPOL Annex VI sets limits on NOx and SOx emissions from ship exhausts and prohibits deliberate emissions of ozone-depleting substances. Furthermore, the IMO marks out Emission Control Areas (ECAs) in cooperation with national governments with more stringent controls on sulphur emissions. These areas currently comprise the Baltic Sea, the North Sea, the English Channel, the US Caribbean Sea and the area outside North America (200 nautical miles). Ships are currently being permitted to burn fuel oils with sulphur content of less than 3.5 % while operating outside an ECA but must ensure that they burn fuel with a sulphur content of less than 1 % while within the sulphur Emission Control Areas. In accordance with EU's marine fuel sulphur directive, the sulphur content in marine gas oil within the territorial waters of an EU member state may not exceed 0.1 % by weight. This applies to all ships regardless of flag. Regarding reductions in nitrogen oxide emissions from marine engines, Annex VI introduced Tier I, II and III NOx emission standards for new engines. NOx emission limits are set for diesel engines depending on the engine's maximum operating speed. Tier I and II limits are global, while the Tier III standards apply only in NOx Emission Control Areas. Tier II NOx standards are currently being in force. In order to control CO_2 emission from shipping, the first formal CO_2 control regulations were adopted by the IMO, introducing a new chapter, Chapter 4, to Annex VI. Chapter 4 introduces two mandatory mechanisms intended to ensure an energy efficiency standard for ships: the first is the Energy Efficiency Design Index (EEDI), for new ships, and the second the Ship Energy Efficiency Management Plan (SEEMP) for all ships. The regulations apply to all ships of 400 gross tonnage and above and are entered into force on 1 January 2013. Energy Efficiency Design Index (EEDI) is the first globally binding climate change standard. It is anticipated that global CO_2 reductions of 10 to 20 % could be obtained by implementation of EEDI and SEEMP. Detailed descriptions of the emission restrictions prescribed by Annex VI of the MARPOL 73/78 Convention are listed in section 2 entitled 'International regulation concerning air pollution from merchant shipping'. To meet these restrictions on emissions of harmful pollutants from marine diesel engines, different methods and technical solutions can be implemented. Nitrogen oxide reduction methods are generally categorised as primary methods or internal measure and secondary methods or aftertreatment. Primary methods include changes to the combustion process within the engine and can be divided into three main categories: combustion optimisation, water-based control and exhaust gas recirculation, while secondary methods, or aftertreatment, is based on treating the engine exhaust gas itself by passing it through a catalyst system. MARPOL Annex VI will reduce global ship sourced

NOx emissions at a small rate because it only applies to new installations or major conversions. For NOx levels below MARPOL Annex VI, or for retrofitting, the main measures available now are water/fuel emulsions, direct water injection, inlet air humidification and catalyst system. Technical measures to reduce the sulphur oxide emission from ship's diesel engines include the adoption of low-sulphur fuels, the easiest way of reducing sulphur oxides emission. Usage of an exhaust gas cleaning system, i.e. scrubbers, is a possible alternative to low-sulphur fuels to reduce the total emission of SOx and considerably reduces emissions of other polluting particles. A detailed description of these methods is given in section 5 entitled 'Methods of reducing harmful pollutant emissions from marine diesel engines' As the air pollution emissions from ships are continuously growing, it is necessary to constantly improve and implement the efficient technologies and methods in order to reduce pollutant emissions from marine diesel engines and maintain them within the limits prescribed by MARPOL Annex VI as well as by other national and regional regulations. Some of these technologies and methods include the use of shore connection systems of which the main benefits stem from the fact that electricity generated on land by power plants has a smaller adverse impact on the ecosystem than that produced by ship engines, owing to that of particular concern is the pollution generated by ships at berth. Ships equipped with a green technology receive a higher grade. Furthermore, other technical measures for reducing air pollution from ships include the adoption of liquefied natural gas (LNG) as alternative fuel for marine engines. Wind, solar power, biofuels and fuel cells, the world of alternative energy is ongoing and could be useful for reducing air pollution from ships in the future. Finally, harmful pollutant emissions from ships require a stringent international standard due to their impact on the human health and the environment. It includes extending the SOx Emission Control Areas in the EU (e.g. in the Mediterranean, in the Black Sea, in the Irish Sea and in the North East Atlantic) and designating NOx Emission Control Areas as soon as possible.

Author details

Ivan Komar* and Branko Lalić

*Address all correspondence to: ivan.komar@pfst.hr

University of Split - Faculty of Maritime Studies - Marine Engineering Department, Split, Croatia

References

[1] Wahlström J, Karvosenoja N, Porvari P. Ship emissions and technical emission reduction potential in the Northern Baltic Sea, Finnish Environment Institute, Helsinki 2006 http://cleantech.cnss.no/wp-content/uploads/2011/06/2006-Wahlstrom-ships-

emissions-technical-emission-reduction-potential-in-northern-Baltic-Sea.pdf (accessed 17 July 2014)

[2] Friedrich A et al. Air pollution and greenhouse gas emissions from ocean-going ships, The International Council on Clean Transportation (ICCT), 2007 https://www.georgiastrait.org/files/share/PDF/MarineReport_Final_Web.pdf (accessed 17 July 2014)

[3] Air pollution from ships, The European Environmental Bureau, The European Federation for Transport and Environment, Seas At Risk, The Swedish NGO Secretariat on Acid Rain, Updated November 2004 http://www.airclim.org/sites/default/files/documents/shipbriefing_nov04.pdf (accessed 22 July 2014)

[4] Saracoglu H, Deniz C, Kılıç A. An Investigation on the Effects of Ship Sourced Emissions in Izmir Port, Turkey, The Scientific World Journal, Vol. 2013 (2013), Article ID 218324, http://dx.doi.org/10.1155/2013/218324 (accessed 5 August 2014)

[5] Komar I, Lalić B, Dobrota Đ. Air Pollution Prevention from Croude Oil Tankers with Volatile Organic Compound Emission, International Journal of Maritime Science & Technology "Our Sea", Vol. 57, No. 3-4, 138–145, Dubrovnik, 2010. (ISSN: 0469-6255)

[6] Lalić B, Komar I, Nikolić D. Optimization of Ship Propulsion Diesel Engine to Fulfill the New Requirements for Exhaust Emissions, Transactions on Maritime Science (ToMS), April 2014, Vol. 3, No. 1.3 (2014), 1 Split, 2014, 20–31, DOI:10.7225/toms.v03.n01.003

[7] Herdzik J. Emissions from Marine Engines Versus IMO Certification and Requirements of Tier 3, Journal of KONES Powertrain and Transport, Vol. 18, No. 2 (2011), 161–167

[8] Rashidul SMH. Impact of EEDI on ship design and hydrodynamics master of science thesis, Department of Shipping and Marine Technology Division of Sustainable Ship Propulsion, Chalmers University of Technology, Gothenburg, Sweden, 2011, http://publications.lib.chalmers.se/records/fulltext/151284.pdf (accessed 5 August 2014)

[9] Bazari Z, Longva T. Assessment of IMO mandated energy efficiency measures for international shipping, project final report, Lloyd's Register, London, UK, DNV, Oslo, Norway, IMO, 2011, http://www.imo.org/MediaCentre/HotTopics/GHG/Documents/REPORT%20ASSESSMENT%20OF%20IMO%20MANDATED%20ENERGY%20EFFICIENCY%20MEASURES%20FOR%20INTERNATIONAL%20SHIPPING.pdf (accessed 6 August 2014)

[10] Marty P. Ship energy efficiency study: development and application of an analysis method, PhD Thesis, Universités, École Navale, Nantes, 2014.

[11] Woodyard D. Pounder's Marine Diesel Engines and Gas Turbines, Elsevier, 2004

[12] Komar I, Antonić R, Kulenović Z. Experimental Tuning of Marine Diesel Engine Speed Controller Parameters on Engine Test Bed, Transactions of FAMENA, 33 (2009) 2, ISSN: 1333–1124, Zagreb, 2009, 51–70

[13] ISO 8217:2010/2012 Fuel Standard, Fourth Edition, https://www.bimco.org/News/2010/07/19_ISO_8217.aspx (accessed 20 August 2014)

[14] McAllister S, Chen JY, Fernandez-Pello AC. Fundamentals of Combustion Processes, Springer Science+Business Media, 2011

[15] Emission Control Two Stroke Low Speed Diesel Engines, MAN B&W Diesel A/S, 1996 http://www.google.hr/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&ved=0CBoQFjAA&url=http%3A%2F%2Fwww.flamemarine.com%2Ffiles%2FMANBW.pdf&ei=7nQZVLyUDsXaPPmwgeAI&usg=AFQjCNFBv8IBVUn1vTNfggYmTaJpBLbbjw&bvm=bv.75558745,d.ZWU (accessed 20 July 2014)

[16] Lavoie JB, Heywood JB, Keck JC. Experimental and Theoretical Investigation of Nitric Oxide Formation in Internal Combustion Engines, Combustion Science Technology Vol. 1 (1975), 313–326

[17] Bowman CT. Kinetics of Pollutant Formation and Destruction on Combustion, Progress in Energy and Combustion Science, Vol. 1, No. 1 (1975), 33–45

[18] Kuiken K. Diesel Engines, Part I, Target Global Energy Training; Onnen, 2012

[19] Rakopoulos CD, Giakoumis EG. Diesel Engine Transient Operation - Principles of Operation and Simulation Analysis, Springer-Verlag Ltd., London, UK, 2009.

[20] Technical Bulletin - Combustion Calculations, Normalisations and Conversions, Q Instrument Services Limited, Bishopstown, Cork, Ireland. http://www.qlimited.com/pdf/Land-Combustion-Calculations-Normalisations-&-Conversions-Q.pdf (accessed 5 June 2014)

[21] Fournier A. Controlling Air Emissions from Marine Vessels: Problems and Opportunities, University of California Santa Barbara, February 2006, http://fiesta.bren.ucsb.edu/~kolstad/temporary/Marine_Emissions__2-11-06_.pdf (accessed 5 June 2014)

[22] Lalić B, Komar I, Antonić R. Water-in fuel emulsion as primary method to reduce NOx from diesel engine exhaust gas, Trends in the Development of Machinery and Associated Technology TMT 2009 Conference Proceedings, 2009, Zenica, Barcelona, Catalunya, Istanbul, 457–460.

[23] Miola A et al. Regulating Air Emissions from Ships, European Commission Joint Research Centre Institute for Environment and Sustainability, Luxembourg, 2010, http://ec.europa.eu/dgs/jrc/downloads/jrc_reference_report_2010_11_ships_emissions.pdf (accessed 5 July 2014)

[24] MAN Diesel and Turbo: Tier III Two-Stroke Technology, https://www.google.hr/?gws_rd=ssl#q=MAN±Diesel±and±Turbo%3A±Tier±III±TwoStroke±Technology (accessed 5 August 2014)

[25] Komar I, Antonić R, Matić P. Selective catalytic reduction as a secondary method to remove NOx from exhaust gas of the ship's propulsion diesel engine, Proceedings of the IFAC Conference on Control Applications in Marine Systems Vukić, Zoran; Sauro, Longhi (ed.), Zagreb: CEPOST, 2007.

[26] Emission Project Guide MAN B&W Two-Stroke Marine Engines, MAN Diesel & Turbo, December 2013 http://www.mandieselturbo.com/download/project_guides_tier2/printed/7020-0145-001web.pdf (accessed 5 August 2014)

[27] Ship power four - stroke, Wärtsilä Environmental Product Guide, Vaasa, June 2014, http://www.wartsila.com/file/Wartsila/en/1278528485383a1267106724867-wartsila-o-env-product-guide.pdf (accessed 5 August 2014)

[28]]Lloyd's Register: Understanding Exhaust Gas Treatment Systems - Guidance for Shipowners and Operators, London, June 2012, http://www.google.hr/url?sa=t&rct=j&q=&esrc=s&source=web&cd=2&ved=0CCQQFjAB&url=http%3A%2F%2Fwww.lr.org%2Fen%2F_images%2F213-35826_ECGS-guide1212_web_tcm155-240772.pdf&ei=tlMVVNj9F8PXaubw-gYAF&usg=AFQjCNGz4a8vCcjsE4e1rsDHx1Rj8Rk0rQ&bvm=bv.75097201,d.bGQ (accessed 30 August 2014)

[29] Rr32 Guide to Exhaust Emission Control Options, MS3026, Land & Sea Systems, Bristol September 99, http://wenku.baidu.com/view/f634f9b81a37f111f1855b5f. (accessed 10 August 2014)

[30] CNSS: A Review of Present Technological Solution for Clean Shipping, http://www.google.hr/url?sa=t&rct=j&q=&esrc=s&source=web&cd=2&ved=0CCIQFjAB&url=http%3A%2F%2Fcnss.no%2Fwp-content%2Fuploads%2F2011%2F10%2FSummary-brochure10.pdf&ei=YVkaVPj2KMTfOajQgYAP&usg=AFQjCNGjfvIe8i4zF_nosPD4Ra1XnSyqqg&bvm=bv.75097201,d.ZWU (accessed 5 August 2014)