



## Emissions from Marine Engines and NO<sub>x</sub> Reduction Methods

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### ABSTRACT

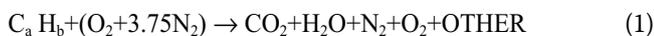
The main theme of this paper is to analyze emissions from marine engines and the process of pollutant formation. As current legislation is more restrictive about nitrogen oxides (NO<sub>x</sub>), special attention was given to these components. In this regard, a state of the art of the most important NO<sub>x</sub> reduction methods is given and the conclusions of the main studies are exposed. It was concluded that the most efficient method in NO<sub>x</sub> reduction is SCR (selective catalytic reduction). Nevertheless, for marine engines there are more appropriate alternatives such as exhaust gas recirculation and water addition because these measures are less expensive, complex and bulky.

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### 1. Introduction

Nowadays, diesel engines power more than 90% of the world's oceangoing ships. Diesel engines have replaced most of the steam turbine systems that were dominant in the 1940s. Most marine fuels are residual heavy fuel oils, which are cheap but contain an important quantity of pollutant substances. Since the 1973 fuel crisis, crude oils have been processed using secondary refining technologies to extract the maximum quantity of refined products (distillates). As a consequence, the concentration of contaminants such as sulfur, ash, asphaltenes, and so on in the residuals has increased.

Diesel engines operate with air excess. Fuel is injected at high pressures into air which has been compressed by the moving pistons. This compression raises the temperature of the air sufficiently to cause the fuel to ignite. Combustion proceeds around the periphery of the fuel spray at temperatures around 2000°C. Combustion products have an important percentage of oxygen (O<sub>2</sub>) and nitrogen (N<sub>2</sub>) from the air, reaction (1).



Other emissions from diesel engines are nitrogen oxides (NO<sub>x</sub>), sulphur oxides (SO<sub>x</sub>), carbon monoxide (CO), unburnt

hydrocarbons (HC), particulates, and so on. Nitrogen oxides are more important in diesel engines than gasoline engines due to the nitrogen and oxygen from the air excess. Typical exhaust emissions from a current diesel engine are shown in Fig. 1, Woodyard (2009).

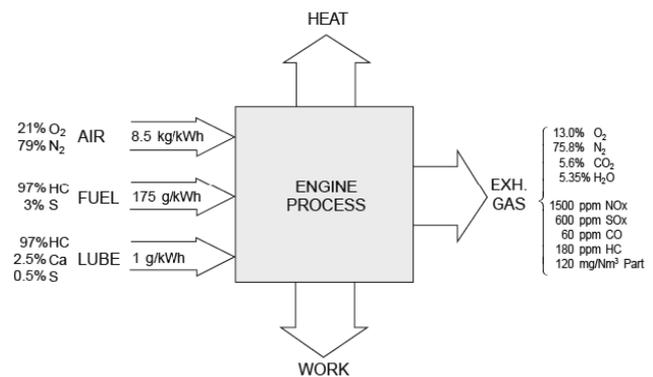


Figure 1. Typical exhaust emissions from a current low speed diesel engine. Woodyard (2009).

Ship emissions may be transported hundreds of kilometers inland. Schwartz (1989) indicated that the median transport velocity of SO<sub>x</sub> and NO<sub>x</sub> is about 400 km per day, and the mean residence times of 1 to 3 days, indicating mean transport distances of 400 to 1200 km. Nevertheless, several posterior studies showed that some 70% or more of emissions by international ships occurs within 400 km of land, Corbett *et al.* (1999); Endresen *et al.* (2003); Eyring *et al.* (2005).

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The purpose of the present paper is to analyze a state of the art of the main pollutants from marine diesel engines. As current legislation focus a special interest in  $\text{NO}_x$ , special attention was given to these components. In this regard, firstly the main pollutants from marine diesel engines are presented. Secondly, current legislation is analyzed and finally the main  $\text{NO}_x$  reduction methods and research studies are analyzed.

## 2. Emissions from marine engines

As shown above, the main emissions from marine engines are nitrogen ( $\text{N}_2$ ), oxygen ( $\text{O}_2$ ), water ( $\text{H}_2\text{O}$ ) and carbon dioxide ( $\text{CO}_2$ ).

Oxygen, nitrogen and water vapor are not toxic. Carbon dioxide is not toxic either, but it contributes to the greenhouse effect (global warming). Nevertheless, it is an inevitable product of combustion of all fossil fuels, see reaction (1). Recent studies have estimated that 2.7% of global  $\text{CO}_2$  emissions are attributable to ships, Eyring *et al.* (2005), estimating  $\text{CO}_2$  emissions from shipping of the same order as  $\text{CO}_2$  emissions from aviation. Speed reduction is an operational measure which offers significant  $\text{CO}_2$  reductions. A 10% speed reduction gives 20% reduction in fuel consumption over the same distance, Kuiken (2008).

Other emissions from ships are described in what follows.

### 2.1. Nitrogen oxides ( $\text{NO}_x$ )

Nitrogen oxides are generated from nitrogen and oxygen at high combustion temperatures. As mentioned above, diesel engines operate at lean mixtures. The burnt gas is depleted of unconsumed oxygen, which has a significant effect on the rate of  $\text{NO}_x$  formation.  $\text{NO}_x$  formation increases with the combustion temperature, the residence time of the burnt gas at high temperature and the amount of oxygen present. For this reason, slow speed engines produce more  $\text{NO}_x$  than medium speed engines because the combustion process spans a longer time period so there is more time available for  $\text{NO}_x$  formation.

$\text{NO}_x$  are carcinogenic and contribute to the ozone layer depletion and acid rain. Recent studies have estimated around 15% of global  $\text{NO}_x$  emissions are attributable to ships, Eyring *et al.* (2005).

### 2.2. Sulphur oxides ( $\text{SO}_x$ )

Sulphur oxides are produced by oxidation of the sulphur in the fuel. Compared with land-based power installations, fuel burnt by much of shipping has a considerable sulphur content, up to 4.5% and more, and contributes significantly to the overall amount of global sulphur oxide emissions at sea and in port areas.

$\text{SO}_x$  are the mayor source of acid rain. Besides, they can be carried over hundreds of miles in the atmosphere before being deposited in lakes and streams, reducing their alkalinity. Recent studies have estimated around 5-8% of global  $\text{SO}_x$  emissions are attributable to oceangoing ships, Eyring *et al.* (2005).

Corbett *et al.* (2007) estimates that  $\text{SO}_x$  constitute 16% of sulfur emissions from all petroleum sources, and 5% of sulfur from all fossil fuels including coal.

### 2.3. Particulate matter (PM)

Particulate matter is a complex mixture of inorganic and organic compounds. Its formation depends on numerous factors, such as incomplete combustion, partly unburned lube oil, thermal splitting of hydrocarbons from the fuel and lube oil, ash in the fuel and lube oil, sulphates and water, and so on. Two mechanisms are the main responsible for particulate matter formation:

- Nuclei mode particles consist mainly of condensed hydrocarbons and sulphates. The gaseous precursors condense as temperature decreases in the exhaust system and after mixing with cold air in the atmosphere. The sulphates arise from combination of  $\text{SO}_x$  and water in the exhaust. The high sulphur content of marine fuels leads to relatively high levels of sulphate particulates.
- Accumulation mode particulates are formed during combustion by agglomeration of primary carbonaceous particles and other solid materials. The majority of the accumulation mode particulates form in the core of the burning fuel spray. They are known as 'black carbon' or 'soot', and its visible evidence is smoke.

Some particulates are carcinogens. There are studies which estimate shipping-related particulate emissions as approximately 60000 cardiopulmonary and lung cancer deaths annually, with most deaths occurring near coastlines in Europe, East Asia and South Asia, Corbett *et al.* (2007).

### 2.4. Carbon monoxide

As mentioned above, emissions of carbon monoxide are typically low for diesel engines and more important for gasoline engines. In marine diesel engines, the formation is strongly influenced by the uniformity of the air/fuel mixture in the combustion chamber, and CO results from incomplete combustion due to a local shortage of air and the dissociation of carbon dioxide. It is toxic to animals and plants.

### 2.5. Unburnt hydrocarbons

Emissions of hydrocarbons are also typically low for diesel engines and more important for gasoline engines. In marine diesel engines, hydrocarbons are created by the incomplete combustion of fuel and lube oil, and the evaporation of fuel. They are also emitted directly from cargo such as oil and petroleum products by evaporation. Hydrocarbons are carcinogenic and contribute to the greenhouse effect.

## 3. Legislation

The global and regional impact of air pollution from ship engines has not been addressed until recently, by agencies as En-

Environmental Protection Agency, European Commission and International Maritime Organization.

The U.S. Environmental Protection Agency (EPA or sometimes USEPA) is an agency of the United States federal government created for the purpose of protecting human health and the environment by writing and enforcing regulations.

The European Commission is the executive body of the European Union responsible for proposing legislation, implementing decisions, upholding the Union's treaties and day-to-day running of the EU. In 2002, the European Commission adopted a European Union strategy to reduce atmospheric emissions from ships.

At the international level, the International Maritime Organization (IMO) is an agency which develops and maintains a develop and maintain a comprehensive regulatory framework for shipping and its remit today includes safety, environmental concerns, legal matters, technical co-operation, maritime security and the efficiency of shipping. In 1973, IMO adopted MARPOL 73/78, the International Convention for the Prevention of Pollution From Ships. Marpol 73/78 is one of the most important international marine environmental conventions. It was designed to minimize pollution of the seas. Annex VI of the MARPOL convention regulations for the prevention of air pollution by ships, setting limits on sulphur oxide and nitrogen oxides. Concerning  $\text{SO}_x$ , it limits the sulfur content in fuels. Concerning  $\text{NO}_x$ , it establishes a curve which indicates the maximum allowable  $\text{NO}_x$  emission levels related to engine speed, applicable to marine diesel engines built after 2000, 2011 and 2016.

Due to IMO regulations, the most important gas component that has to be reduced in diesel exhaust emissions is  $\text{NO}_x$ . For this reason, the following section describes  $\text{NO}_x$  reduction methods and investigations about them.

#### 4. $\text{NO}_x$ reduction methods

Briefly, there are two procedures to reduce  $\text{NO}_x$ , primary and secondary measures. Primary measures aim at reducing the amount of  $\text{NO}_x$  formed during combustion by optimizing engine parameters with respect to emissions. As shown above, the main factors influencing  $\text{NO}_x$  formation are the concentrations of oxygen and nitrogen and the local temperatures in the combustion process. Therefore, primary measures focus on lowering the concentrations, peak temperature and the amount of time in which the combustion gases remain at high temperatures.

On the other hand secondary measures remove  $\text{NO}_x$  from the exhaust gases by downstream cleaning techniques. The mostly used primary and secondary measures are analyzed in what follows.

##### 4.1. Primary measures

###### *Decrease of injection duration, delay of start of injection and pre-injection*

A delayed injection leads to lower peak pressures and therefore temperatures. Retarding injection timing also decreases

the amount of fuel burnt before peak pressure, thus reducing the residence time and degree of after-compression of the first burnt gas.

Okada *et al.* (2001) applied an injection timing retard of  $7^\circ$  to the MAN B&W 4T50MX research engine and they obtained a reduction of  $\text{NO}_x$  by about 30% and an increased in consumption by about 7%. Li *et al.* (2010) also analyzed the influence of the fuel injection advance angle on nitrogen oxide emissions.

Moreno Gutiérrez *et al.* (2006) studied the consumption and  $\text{NO}_x$  emissions in several marine engines with different injection timings.

Al-Sened and Karini (2001) found that pre-injection can be used to shorten the delay period and thus decrease temperature and pressure during the early stages of combustion, resulting in reduced  $\text{NO}_x$ . Besides, they found a decrease in particulates emission.

Fankhauser and Heim (2001) also found that pre-injection reduces  $\text{NO}_x$  with a slightly increase in fuel consumption. They studied a Sulzer RT-Flex common rail engine. With triple injection, the fuel charge is injected in separate, short sprays in succession. With sequential injection, each of the three nozzles in a cylinder is actuated with different timing. The results showed about 30%  $\text{NO}_x$  reduction with about 8% increase in fuel consumption.

Kontoulis *et al.* (2008) studied numerically the effect of multiple injection strategies in the Sulzer RTA58T marine engine. They demonstrated that, by adding a pilot injection, appropriately timed, it is possible to reduce  $\text{NO}_x$  emissions and save fuel at the same time, particularly 1.7% of fuel reduction. Panagiotis *et al.* (2009) also studied numerically the multiple injection in a marine engine, the Sulzer RT-flex58T-B and they also got a decrease in  $\text{NO}_x$  and consumption.

###### *Modification of fuel injectors*

Al-Sened *et al.* (2001) studied a medium speed engine, the MAN B&W RK215, and found that, reducing spray cone angle from 140 deg to 130 deg, reduced  $\text{NO}_x$  by 32% and increased fuel consumption by 6%. The reason is that the smaller spray angle reduced the air entrainment into the spray resulting in less prepared mixture for the premixed combustion phase. Al-Sened *et al.* also found that increasing nozzle tip protrusion from 2 mm to 6 mm gave 6% less  $\text{NO}_x$  and slightly increased fuel consumption, because the spray was closer to the piston bowl wall giving lower cylinder pressure and temperature.

MAN B&W (MAN B&W, 1997) studied the slide-type fuel valve, which is a zero sac volume so the entry of fuel into the combustion chamber after injection ceases is minimized. Tests on a 12K90MC engine showed a 23% reduction in  $\text{NO}_x$  emissions with a 1% fuel consumption increase. Bludszuweit *et al.* (1998) also studied a slide-type fuel valve. They analyzed the MAN B&W 5S70MC engine and found a slight decrease in fuel consumption. The same conclusion was obtained by Egeberg and Ostergaard (2001) after studying a MAN B&W K98MC engine. Holtbecker (1999) also studied a slide-type fuel valve. They analyzed the Sulzer 4RTX54 research engine, obtaining a decrease in  $\text{NO}_x$  and besides HC and particulate emissions. He argued that the main source of smoke and soot

deposits is the fuel remaining in the injector sac hole. Sowman (1998) studied a low NO<sub>x</sub> fuel injection valve in a Mitsubishi UEC52LSE slow speed engine, obtaining a 19% reduction of NO<sub>x</sub> with only a 2% increment in fuel consumption.

Concerning the number of holes, shape and size, Freitag *et al.* (2001) optimized the injection in a MTU Serie 8000 to improve mixing and reduce soot generation by optimizing the number of nozzle holes, hole shape and spray angle. Schlemmer-Kelling and Rautenstrauch (2001) studied the nozzle hole diameter and the number of injection holes in a MAN B&W RK125 medium speed engine. They concluded that reducing nozzle hole diameter and increasing the number of nozzle holes reduces the NO<sub>x</sub> emissions.

#### *Modification of the combustion pressure*

Okada (2001) showed that where maximum cylinder pressure is limited, constant pressure combustion gives the greatest thermal efficiency. Combustion constant pressure is achieved by high compression pressure followed by delayed fuel injection and short combustion duration.

#### *Scavenging air cooling*

Scavenge air cooling aims to reduce the maximum temperature in the cylinder by lowering the temperature before compression. Holtbecker and Geist (1998) showed that for every 3% reduction, NO<sub>x</sub> may decrease by about 1% in the Sulzer RTA84C. Sencic (2010) developed a CFD (Computational Fluid Dynamics) model to simulate the reduction in NO<sub>x</sub> emissions with reducing the scavenging air temperature. Besides, he studied the exhaust gas recirculation and several injection patterns. He studied the MAN 6S50Mc and Wärtsilä RT-flex50 marine engines.

#### *Miller cycle*

In four-stroke engines, the Miller cycle uses a higher than normal pressure turbocharge. The inlet valve is closed before the piston reaches bottom dead center on the intake stroke. The charge air then expands inside the engine cylinder as the piston moves towards bottom dead center resulting in a reduced temperature.

Schlemmer-Kelling and Rautenstrauch (2001) applied Miller cycle to a Caterpillar engine by earlier closing of inlet valves and slightly increased charge pressure and found that NO<sub>x</sub> is reduced but smoke is increased.

#### *Water injection*

There are three possibilities: fuel-water emulsion, direct water injection or humidification. Introduction of water into the combustion chamber reduces NO<sub>x</sub> formation due to the increase in the specific heat capacity of the cylinder gases (water has higher specific heat capacity than air) and reduced overall oxygen concentration. The influence of water varies with engine type, but generally 1% percent of water reduces NO<sub>x</sub> by 1%, Woodyard (2009).

#### *Exhaust gas recirculation (EGR)*

Exhaust gas recirculation lowers the combustion temperature, and consequently NO<sub>x</sub>, by reticulating exhaust gases to the

charge air. This reduces NO<sub>x</sub> formation due to the increase in the specific heat capacity of the cylinder gases (water has higher specific heat capacity than air) and reduced overall oxygen concentration.

Holtbecker and Geist (1998) found 22% NO<sub>x</sub> reduction with 6% EGR in the 4RTX54 research engine. However, they postulated that EGR increases smoke, hydrocarbons and CO. Millo *et al.* (2011) analyzed EGR combined with a Miller cycle in a Wärtsilä W20 marine engine. They obtained NO<sub>x</sub> reductions up to 90%.

#### *4.2. Secondary measures*

The most employed secondary measure in marine engines is SCR (Selective Catalytic Reduction). SCR involves mixing of ammonia with the exhaust gas passing over a catalyst. The ammonia is usually supplied as a solution of urea in water. In order to avoid premature damage of the catalyst system, it is necessary to employ low sulphur fuels.

According to MAN B&W (1997) and Wärtsilä (2002), SCR can remove more of 90% of NO<sub>x</sub>. Jayaran *et al.* (2011) studied SCR in the MAN B&W 7L32/40 marine engine. NO<sub>x</sub> emissions for this engine vary from 15 to 21.1 g/kW-h for heavy fuel oil and 8.9 to 19.6 g/kW-h for marine distillate oil. Applying SCR, they reduced the NO<sub>x</sub> emission factor to less than 2.4 g/kW-h, but it increased the PM emissions by a factor of 1.5–3.8.

## **5. Conclusions**

Due to the lean combustion in diesel engines, these have relatively low emissions of carbon monoxide and hydrocarbons. However, nitric oxides and particulate are more important. Due to the efforts to reduce NO<sub>x</sub> and other pollutants from ships, this paper offers a state of art of the NO<sub>x</sub> reduction methods. It was shown that there are primary and secondary measures. The well-known drawbacks in employing catalytic converters in ships, mainly the necessity of a reducing agent together with the additional space required for the catalytic reactor, make them barely acceptable to marine diesel engine users. Consequently, primary reduction measures are the first choice for to reduce the formation of pollutants on board ships. EGR and water addition are the most employed primary measures. Both can strongly reduce NO<sub>x</sub>, but they increment hydrocarbons and CO emissions.

Concerning SO<sub>x</sub>, chemical and washing/scrubbing desulphurization process are complex, bulky and expensive for shipboard applications. The most economical and simplest approach to reduce SO<sub>x</sub> is thus to use low sulphur fuels.

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