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How to reduce emission of nitrogen oxides [NOx] from marine diesel engines in relation to Annex VI of MARPOL 73/78

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HOW TO REDUCE EMISSION OF NITROGEN OXIDES FROM MARINE DIESEL ENGINES

In relation to the Annex VI of MARPOL 73/78

By

NAM, DONG
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A dissertation submitted to the World Maritime University in partial fulfilment of the requirements for the award to the degree of

MASTER OF SCIENCE

in

MARITIME SAFETY & ENVIRONMENTAL PROTECTION
(Engineering Stream)

2000

DECLARATION

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

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

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ABSTRACT

Title of Dissertation: **How to reduce emission of Nitrogen Oxides (NOx) from marine diesel engines: in relation to the Annex VI of MARPOL 73/78.**

Degree: **MSc**

In September 1997, the Protocol of 1997 to MARPOL 73/78 was adopted to introduce the new Annex VI - Air pollution from ships. When the Protocol enters into force, the requirements of the NOx will be applied to each diesel engine with a power output of more than 130 kW which is installed on a ship, or which undergoes major conversion, on or after 1 January 2000. Annex VI deals with a wide range of air pollution control matters including regulations on halons, Hydro-chlorofluorocarbons (HCFCs) and other ozone depleting substances, Nitrogen oxides (NOx), Sulphur oxides (SOx), Volatile organic compounds (VOCs), shipboard incinerators and fuel oil quality. However, the main focus has so far been on reducing the NOx.

The NOx Technical Code introduces a new concept of engine family, engine group, parent engine and the technical file to be determined before issuing the Engine International Air Pollution Prevention Certificate (EIAPP Certificate) and the International Air pollution Certificate (IAPP Certificate). Because the new Annex VI has not yet come into force, guidelines have been introduced to issue a Statement of Compliance (SOC Certificate).

NOx formation builds up by reaction between nitrogen and oxygen in the combustion air (thermal NOx), by reaction between exhaust gas hydrocarbon and combustion air oxygen (prompt NOx) and by reaction between nitrogen bindings in fuel (fuel NOx).

Thermal NOx is decisive for total emission and all the reducing methods are targeted to reduce that component. NOx emission can be reduced by primary methods such as retard injection, fuel nozzle modification, change of compression ratio, water direct injection, water emulsification, exhaust gas recirculation (EGR) and secondary method such as selective catalytic reduction (SCR).

Key words: Air Pollution, Nitrogen Oxides (NOx), Emission, Diesel engine. Certification,

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LIST OF ABBREVIATIONS

ABS	American Bureau of Shipping
CFCs	Chlorofluorocarbons
Circ.	Circular
CO	Carbon monoxide
CO_2	Carbon dioxide
DWI	Direct Water Injection
EGR	Exhaust Gas Recirculation
EIAPP	Engine International Air Pollution Prevention
EPA	Environmental Protection Agency
H_2O	Water
HC	Hydrocarbon
HCFCs	Hydro-chlorofluorocarbons
HFO	Heavy Fuel Oil
IAPP	International Air Pollution Prevention
IMO	International Maritime Organization
ISO	International Organization for Standardization
kg	kilogram
KR	Korean Register of Shipping
kW	kilowatt
kWh	kilowatt hour
m/m	mass per mass
MARPOL 73/78	International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 relating thereto
MBD	MAN B&W Diesel

MDO	Marine Diesel Oil
MEPC	Marine Environment Protection Committee
MER	Marine Engineers Review
MHI	Mitsubishi Heavy Industries
N_2	Nitrogen gas
N_2O	nitrous oxide
NH_3	Ammonia
$(NH_2)_2 CO$	Urea
NO	Nitric oxide
NO_2	Nitrogen dioxide
NOx	Nitrogen oxides
ODS	Ozone Depleting Substances
PCBs	Polychlorinated biphenyls
PM	Particular matter
PVCs	Polyvinyl chlorides
rpm	revolutions per minute
S	Sulphur
SCR	Selective Catalytic Reduction
SFOC	Specific Fuel Oil Consumption
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
SOC	Statement of compliance
SOLAS	International Convention for the Safety of Life at Sea, 1974, and its Protocol of 1978
SOx	Sulphur oxides
TDC	Top Dead Center
VOCs	Volatile organic compounds
WNSD	Wartsila NSD

Chapter 1
INTRODUCTION

1.1 Background of the study

Environmental issues have been more topical than ever. Recently, the emission control legislation, focused on reducing air pollution from the shipping industry is now contemplated by many regulatory agencies and authorities around world. The shipping industry has been excepted from legislation. Also the relatively moderate amounts of air pollution generated by ship, on a global scale, compared to many other sources of air pollution has been considered.

As for marine diesel engines, they have been developed under two major technologies of thermal efficiency and reliability for the past 20 years. At the present time, with the various legislation of air pollution, the marine diesel engine is facing another major theme, the environment problem, and most of the technological efforts concentrate on this matter.

In September 1997, the Protocol of 1997 to MARPOL 73/78 was adopted to introduce new Annex VI. This Annex requires that survey of engines and equipment shall be conducted in accordance the NOx Technical Code. When the Protocol of 1997 enters into force, the requirements of the NOx emission restriction apply to each diesel engine with a power output of more than 130 kW which is installed on a ship on or after 1 January 2000, or which undergoes major conversion on or after 1 January 2000 except for lifeboat engine and emergency generator.

Annex VI of MARPOL 73/78 deals with a wide range of air pollution control matters including ozone depleting substances, acid deposition materials, volatile organic compounds, incineration and fuel oil quality. However, the main focus has so far been on reducing the NOx emissions because NOx regulation will be retrospectively applied to each engine installed on board a ship, or which undergoes major conversion on or after 1 January 2000, upon the date of entry into force.

1.2 Scope, objectives methodology of the study

The aim of this diddertation is to provide information on NOx problems to those who are concerned, such as ship owners and operators as well as surveyors, designers and manufacturers of marine diesel engines and equipment. There will naturally be some questions. Why is the air pollution from a ship so important? What is the content of the new Annex VI and NOx Code? When will this regulation enter into force?; What is NOx and How is NOx formed?; Then, how to reduce NOx emission? In this study those questions will be examined systemically from chapter 2 through chapter 5.

The objectives of this dissertation are:

1. To introduce the background of the legislation of the International Convention for the Prevention of Air Pollution from Ships and the major contents of the Convention.
2. To provide rationale behind the Technical Code on Control of Emission of Nitrogen Oxides from Marine Diesel Engines (NOx Code) by summarizing and analyzing it.
3. To research and review various possible NOx reduction methods for marine diesel engines.

4. To make proper proposals and recommendations to meet IMO goals concerning the prevention of air pollution from ships efficiently.

In chapter 2, the background of Annex VI is introduced which includes the process of adoption of 1997 Protocol to MARPOL 73/78. The content of Annex VI is reviewed carefully in relation to the NOx Technical Code such as the entry into force versus application date. The purpose of this chapter is to identify those regulations in the new Annex which require to be addressed immediately as well as those which should be considered in the medium to long term.

In chapter 3, the NOx Technical Code is summarized and also some new concepts in the NOx Technical Code such as engine family, engine group, parent engine and the technical file are introduced. Furthermore, the procedure of survey and certification for the Engine International Air Pollution Prevention Certification (EIAPP Certificate) and the International Air pollution Certificate (IAPP Certificate) is examined in relation to the Statement of Compliance Certificate (SOC Certificate).

However, chapters 2 and 3 do not cover all the contents of Annex VI and the NOx Technical Code in detail. Therefore, those would be regarded as a sort of reference book and should be read in conjunction with the IMO publication "Annex VI of MARPOL 73/78, Regulations for the Prevention of Air Pollution from Ships and NOx Technical Code."

In chapter 4, the evaluation and contribution of air pollution from the marine diesel engine is introduced. This includes the different kinds of pollutants such as carbon monoxide (CO), sulphur oxides (SOx), nitrogen oxides (NOx), hydrocarbons and particulate material from marine diesel engines. In the last part of this chapter, the formation of NOx i.e. thermal NOx, prompt NOx and fuel NOx are studied in light of Zeldovich's mechanism for thermal NOx formation.

In chapter 5, the development of engineering technology and various methods for controlling NOx formation are discussed. Practical methods for marine NOx reduction can be divided into post-combustion (secondary method) such as Selective Catalytic Reduction (SCR) and combustion methods (primary method) of which more than several options exist. Some of them are: retard ignition, fuel modification, Exhaust Gas Recirculation (EGR), fuel emulsification and water direct injection. The concentration is put on the discussion of advantages and disadvantages regarding the cost, maintenance, efficiency and practical application of different options.

This study reviews and analyzes the current design concept of the marine diesel engine concerning NOx reduction as well as the new Annex VI and the NOx Technical Code. Research papers submitted by various national and international institutions to the MEPC committee of IMO are widely used and cited in this study. Many other valuable books and periodical articles were searched through the WMU library system and Internet. Interviews with knowledgeable people such as professors, experts on engine manufacturers and colleagues were made.

Chapter 2
REVIEW OF ANNEX VI OF MARPOL

2.1 Background of MARPOL 73/78 Annex VI

2.1.1 Background

Environmental issues have been more topical than ever and concern for our global environment is extending through all sections of society in the world. In the past the development of international regulations for marine pollution prevention was concentrated on the pollution of the sea water and the coastal regions. Recently, the emission control legislation, focused on reducing air pollution from the shipping industry is now contemplated by many regulatory agencies and authorities around world.

The shipping industry has so far been exempted from legislation, partly because there has been no practical way of emission control technology at hand which is suitable for a ship borne installation. Also, the relatively moderate amounts of air pollution generated by ships, on a global scale, compared to many other sources of air pollution has been considered.

While conservation of the global environment has been a major outstanding issue for quite a time, interests concerning the environmental effect of emission from ships has greatly increased. Likewise, the International Maritime Organization (IMO) has recognized the importance of prevention of air pollution from ships. The emission regulations proposed by IMO were the first global maritime exhaust emission regulations. After long disscussions these regulations were adopted at the conference of Parties to MARPOL 73/78 in September 1997 as Annex VI of MARPOL 73/78 – Regulations for the Prevention of Air Pollution from Ships.

Annex VI of MARPOL 73/78 deals with a wide range of air pollution control matters including regulations on halons, Hydrochlorofluorocarbons (HCFCs) and other ozone depleting substances such as Nitrogen oxides (NOx), Sulphur oxides (SOx), volatile organic compounds (VOCs), shipboard incinerators and fuel oil quality. However, Annex VI does not cover a number of issues such as carbon dioxide (CO_2), hydrocarbons (HC) and particulate matter (PM). Recently, at the 44th session of MEPC on December 1999, the USA submitted a document calling for limits for hydrocarbons (HC) and particulate matter (PM). As for CO_2, the conference adopted a Resolution, which invites organizations to undertake a study of CO_2 emissions for the purpose of establishing the amount and relative percentage of CO_2 emissions from ships, as part of the global inventory of CO_2 emission. Indeed, like the other existing Annexes to MARPOL, the development of air pollution Annex will have to continue after its implementation process.

Annex VI differs from the other Annexes to MARPOL in some ways. The effects of air pollution may be felt hundreds of miles away from its source and the evidence of pollution is not so clear. It also introduces a new term ‘emission’ instead of using ‘pollution’ as in the other Annexes. Moreover, Annex VI follows the explicit amendment process while all other Annexes are tacit amendment process.

2.1.2 Progress

Annex VI had been under development at the IMO for a period of nine years before finally being adopted in the Protocol of 1997 to amend the Convention. However, the subject of ship generated air pollution has been a topic of discussion for much longer.

At IMO, in the mid 19980s the Marine Environment Protection Committee (MEPC) was reviewing the quality of fuel oils in relation to discharge requirements in Annex I and the issue of air pollution was discussed. In September 1988, at the twenty-sixth session of the MEPC, the committee agreed to include the issue of air pollution in its work program, following a proposal from Norway. In addition, the Second International Conference on the Protection of the North Sea, held in November 1987, had issued a declaration in which the ministers of North sea states agreed to initiate actions within appropriate bodies, such as IMO, "leading to improved quality standards of heavy fuels and to actively support this work aimed at reducing marine and atmospheric pollution." (Pardo, 2000)

In March 1989, at the twenty-seventh session of the MEPC, the committee agreed to take the prevention of air pollution from ships as part of the committee's long term work program.

In November 1990, at the thirtieth session of the MEPC, a draft of Annex VI to MARPOL 73/78 was prepared, which included target limits of HCFCs, Halon, NOx, SOx and VOCs. This led to the adoption of an IMO Resolution A.719(17) in November 1991.

In September 1991, at the twenty-first session of the Sub-Committee on Bulk Chemicals, the basic clauses to be included in the new annex were developed, which later was used as a working model for the new annex.

In October/November, the IMO assembly at the seventeenth session, adopted resolution A.719(17) on the prevention of air pollution from ships. This resolution was adopted unanimously and regarded as a major step forward for the prevention of air pollution from ships.

In November 1992, at the twenty-second session of the Sub-Committee on Bulk Chemicals, a draft Annex VI to MARPOL 73/78 was prepared. The new draft Annex VI had been developed over the six years at the Sub-Committee on Bulk Chemicals and its Working Group on Air Pollution.

In September 1997, in accordance with the decision of the IMO Assembly, the International Conference of Parties to MARPOL 73/78 finally adopted the Protocol of 1997 to amend the Convention, which sets out the new Annex VI, Regulations of the Prevention of Air Pollution from the ships. This enabled specific entry force conditions to be set out in the protocol and included also the Technical Code on Control of Emission of Nitrogen Oxides from Marine Diesel Engines (NOx Technical Code).

2.2 Review of MARPOL 73/78 Annex VI

2.2.1 Entry into force

The Protocol shall enter into force twelve months after the date on which not less than fifteen states, the combined merchant fleets of which constitute not less than 50 percent of the gross tonnage of the world's merchant shipping.

In the same way, paragraph 2 of Resolution 2 states that the provisions of the NOx Technical Code shall enter into force, as mandatory requirements, for all Parties to the 1997 Protocol on the same date as the entry into force of that Protocol.

In comparison, Regulation 13 (Nitrogen oxides (NOx)) states that the regulation shall apply to each diesel engine which will be installed on a ship constructed on or after 1 January 2000. However, the new Annex VI has not come into force yet. Therefore, in terms of legal point of view, it is clear that the requirements of this regulation could not be enforced before the entry into force of the Protocol 1997 to MARPOL 73/78.

As can be seen in table 2.1, the compliance of each diesel engine which is installed on a ship constructed on or after 1 January 2000, but before the date of entry into force, is not unenforceable until the time when Annex VI enters into force. Furthermore, the issuance of EIAPP Certificate and the initial survey to such engines may be delayed by up to 3 years. Whilst exiting engines, those not subject to major conversion, will not be subject to any such inspections.

There are some doubts about the date of entry into force. The protocol is still some way from reaching the required level of ratification to enter into force. So far only two nations, Sweden and Norway, have ratified the 1997 protocol of MARPOL 73/78. Concerning this problem, IMO issued the MEPC Circ. 344. "Interim guidelines for the application of the NOx Technical Code." This circular states:

"While the requirements of this regulation could not be enforced before the entry into force of the Protocol, it should be clearly understood that engine installed on ships constructed on or after 1 January 2000, or engines which undergo a major conversion on or after 1 January 2000 will have to meet these requirements once the Protocol enters into force."

"Each engine which will become, retrospectively, subject to the provisions of regulation 13 of Annex VI of MARPOL 73/78 upon its entry into force, should be certified in accordance with the requirements of the NOx Technical Code."

<table>
<tr><th></th><th></th><th></th><th>1.1.2000</th><th>Entry into force date</th><th>+ 3years</th></tr>
<tr><td rowspan="2">Reg.5&6 Survey & Cert.</td><td>Existing ship prior entry into force</td><td colspan="3">SOC with Annex VI (not mandatory)</td><td>IAPP Cert. required</td></tr>
<tr><td>New ship post entry into force</td><td colspan="2"></td><td colspan="2">IAPP Cert. required prior to ship’s entry into service</td></tr>
<tr><td rowspan="3">Reg.13 NOx</td><td>Existing engine prior 1.1.2000</td><td rowspan="2"></td><td colspan="2">(Engines subject to Major conversion need SOC with NOx code)</td><td>(Affected engines need EIAPP Cert. & Initial survey)</td></tr>
<tr><td>New engine post 1.1.2000</td><td colspan="2">Engines need SOC with NOx code</td><td>EIAPP Cert. & Initial survey required</td></tr>
<tr><td>New engine post entry into force</td><td colspan="2"></td><td colspan="2">EIAPP Cert. & Initial survey required prior to ship’s entry into service</td></tr>
</table>

Table 2.1 Survey, Certificate and entry into force date

Furthermore, if the conditions for entry into force of the Protocol have not been met by 31 December 2002, the conference adopted resolution 1 in order to avoid unacceptably long delays in the entry into force. It has been agreed that the Marine Environment Protection Committee (MEPC) will identify the impediments to entry into force of the Protocol and initiate any necessary measures to alleviate those impediments, as a matter of urgency, at it's first meeting thereafter.

2.2.2 Survey, Inspection and Certification (Reg. 5&6&13)

After the date of Annex VI entry into force, every ship of 400 gross tonnage or above engaged in voyages to ports under the jurisdiction of other Parties, shall be subject to initial survey, intermediate survey and periodical survey to ensure a ship's compliance with this Annex.

Ships constructed before the date of entry into force shall comply with Annex VI not later than the first scheduled drydocking, but in no cases later than three years after the date of enter into force.

Paragraph (4) of regulation 5 provides mandatory guidelines of the Technical Code on Control of Emission of Nitrogen Oxides from Marine Diesel Engines (NOx Technical Code), stating how the survey of engines and equipment for compliance with regulation 13 (Nitrogen oxides) shall be conducted.

After a successful survey in accordance with the regulations of this Annex, the International Air Pollution Prevention Certificate (IAPP Certificate) shall be issued for a period not exceeding five years from the date of issue.

According to the NOx Technical Code, all engines within Reg.13 requirements need an Engine International Air Pollution Prevention Certification (EIAPP Certificate). This certificate will be one of the key requirements in the issuing of the International Air pollution Certificate (IAPP Certificate) for a ship.

However, the new Annex VI has not come into force for the time being, so guidelines have been introduced to solve this problem by issuing a sort of interim certificate. The authorized organization (e.g. Classification Societies), by the flag state, can issue a Statement of Compliance (SOC Certificate). The SOC Certificate will be transformed into the EIAPP Certificate when the new Annex VI enters into force.

After entry into force of Annex VI and upon satisfactory compliance with the code requirements, 'Statement of Compliance' with the NOx Technical Code should be issued by the flag state administration or an organization acting on behalf of the administration. The Statement of Compliance is intended as an interim measure pending issuance of the Engine International Air Pollution Prevention Certification (EIAPP Certificate) and/or the International Air pollution Certificate (IAPP Certificate) upon entry into force of Annex VI. (MEPC/cir.344, 1998)

2.2.3 Nitrogen oxides (Reg. 13)

2.2.3.1 NOx emission limit

The emissions of NOx (calculated as the total weighted emission of NO_2) from each diesel engines with a power output of more than 130 kW, which installed on a ship constructed after 1 January 2000 or which undergoes major conversion on or after 1 January 2000, will have to be under the following limits:

- 17.0 g/kWh (grams/kilo watt hour), when ***n*** is less than 130 rpm
- 45.0 $\boldsymbol{n}^{(-0.2)}$ g/kWh, when ***n*** is 130 or more but less than 2000 rpm
- 9.8 g/kWh, when ***n*** is 2000 rpm or more

where ***n*** = rated engine speed (crank shaft revolutions per minutes).

For those engines within the scope of the Annex VI a major conversion is defined as where the engine is replaced by a new engine built on or after 1 January 2000, where the maximum continuous rating of an engine is increased by more than 10% or where it is subject to a substantial modification. The definition of 'substantial modification' depends on when the ship was built. For those built on or after 1 January 2000 substantial modifications are those which could potentially cause the engine to exceed the NOx limits as set out in the regulation.

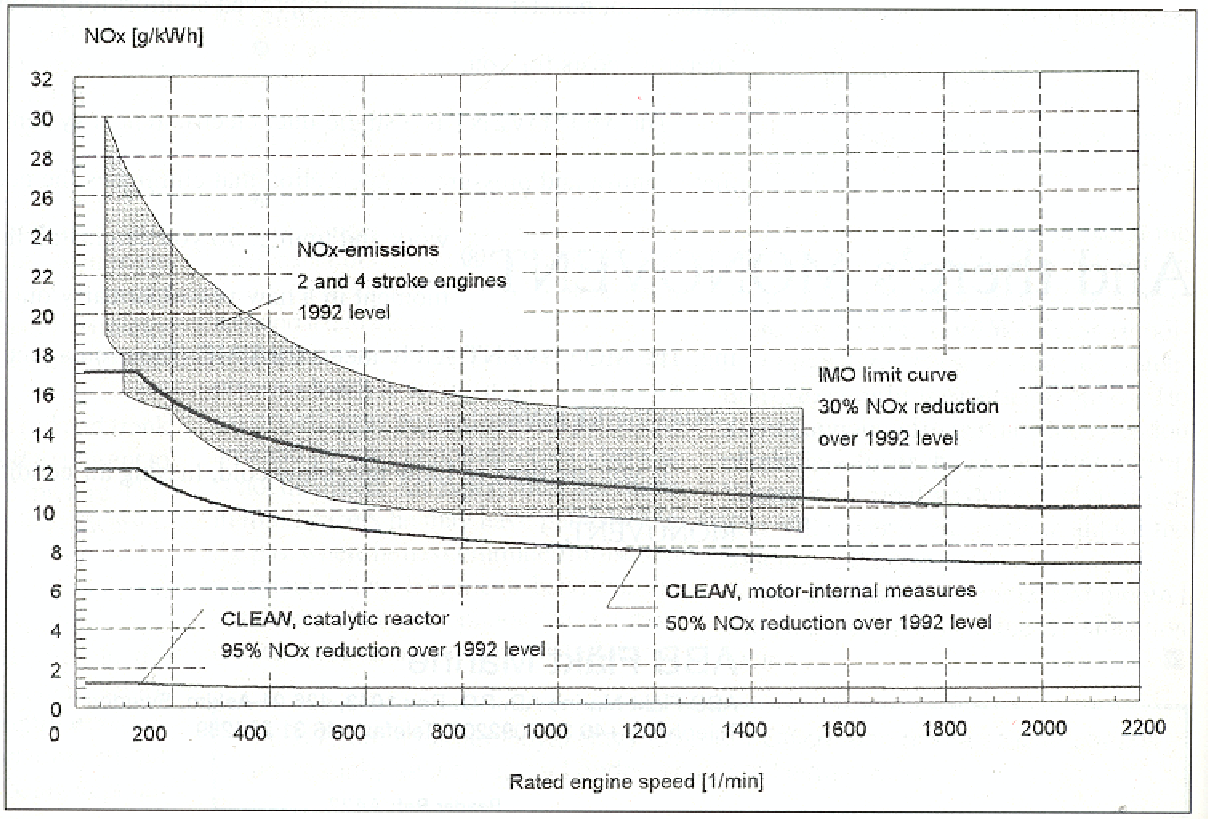

Fig.2.1 NOx emission limits compared with actual emission levels at 1992. Source: MER, 1996, 22.

This regulation does not apply to emergency diesel engines, engines installed in lifeboats and any device or equipment intended to be used solely in case of emergency, and engines installed on ships solely engaged in voyages within waters subject to the sovereignty or jurisdiction of the state the flag of which the ship is entitled to fly, provided such engines are subject to an alternative NOx control measure established by the Administration. Moreover, this regulation does not address NOx emissions from ship's boilers, gas turbines and incinerators.

The maximum allowable NOx emission (Fig.2.1) vary with the rated speed of the engine. Low speed engines are allowed a higher limit than medium and higher speed engines. The limit figures represent a 30% reduction of the usual NOx emission values of year 1992designs. More stringent emission limits are taken into account by IMO. The MEPC, as a matter of urgency, will review the emission limits at a maximum of five year intervals after entry into force.

IMO sees the 30% target only as the first step. For a smooth and technically practicable implementation, the NOx reduction for new engines shall be reviewed and modified as necessary. But any new limitation in the course of the step by step approach will not be applied retrospectively, except in connection with a major conversion of an engine.

2.2.3.2 Further NOx emission limits

More stringent controls are already faced in environmentally sensitive trading regions such as the Baltic Sea. The Swedish government's initiatives offering reduced port charges for low NOx tonnage and Norway's proposed ecology taxes and fees for shipping are likely to be mirrored by Denmark, Finland and Germany. EU-wide measures are also planned. (MER, 1999)

According to Fleischer (1996), in the USA the Environmental Protection Agency (EPA) proposed , in 1994, a federal rule for marine engines operating within the USA and in US territorial waters. The EPA has also proposed an emission fee for voyages to the ports of Los Angeles/Long Beach. The proposed regulation is based on an established USA-EPA practice for on high way and off-highway engine applications.

Average limit values for NOx (limit: 9.2g/kWh), HC, CO and PM are proposed for all engines above 37 kW.

2.2.3.3 Present status of NOx reduction

After the time Regulation 13 concerning NOx emission limits was chosen, the engine manufacturers have continued their research about emission control technologies for marine diesel engines, especially looking at the influence of minor changes in engine design such as adjustments to the compression ratio and injection timing. Already engine manufacturers have been gearing up for such moves, and have reached remarkable results.

According to a recent document submitted to MEPC by Japan and the United states in December 1999, the two countries insist on IMO to take action as appropriate for the purpose of early entry into force of the 1997 Protocol and to begin a dialogue to establish a second tier of emission limits for marine diesel engines, respectively.

Japan carried out research on whether domestic engines comply with the NOx regulations or not, insisting that the share of Japanese made 2-stroke main engines in the world is about 50%, and the share of Japanese made 4-stroke main engines is about 10%. With regard to the Japanese engines, 100% of the2-stroke engine type will comply with the NOx requirements and about 85% of the 4-stroke engine type will comply with the requirements. About 90% of the 4-stroke engine type for generators will comply with the requirements.

Japan carried out this research on domestic engines, however it can be assumed that the situation should be similar in other countries, considering the technology standards in other countries and the fact that most of such engines, especially all types 2-stroke engine, are manufactured based on the same world wide licenses.

Similarly, the document submitted by the United States concerning test data acquired by the US-EPA in connection with the domestic marine diesel engine control program suggests that the use of these technologies will result in significant reductions in NOx emissions. Wartsila NSD has also been experimenting with technology for large ocean-going propulsion engines. They estimate that direct water injection technology can achieve a 50 to 60% reduction of NOx emissions. This technology can be used with all fuel types and is available for retrofit operations. Selective Catalyst Reduction (SCR) techniques can achieve 85 to 95% reduction of the NOx emissions. (MEPC 44, 2000)

2.2.4 Sulphur oxides (SOx)

Regulation 14 on control of SOx emission will apply to every type of combustion equipment regardless of its use including auxiliary and main propulsion, emergency diesel engines and engines installed in lifeboats. Unlike the NOx regulation, there is no mention about capacity limit of power output or any exception.

The sulphur content of fuel oil used on board shall not exceed 4.5% m/m except within a SOx emission control area. It is a relatively high limit compared with 1.5% m/m within SOx emission control areas. Likewise, the international standards organization presently sets at 5.0% for the majority of residual fuel oils.

However, ships which are trading within a SOx emission control area will have to meet the more stringent emission requirement of not exceeding 1.5% m/m, or an exhaust cleaning system such as SOx scrubber which can be used to reduce the SOx emission to a maximum of 6.0 g/kWh. Within SOx emission control areas, using separate fuel systems may be a best option concerning operational and procedural aspects by fully flushing all fuels exceeding 1.5% m/m before entering into such areas.

The SOx emission control areas will be strictly controlled by Annex VI with criteria and procedures for their designation. At the time of adoption of the new Annex only the Baltic Sea was designated as a SOx emission control area. However, the North Sea states are presently preparing for designation of the North Sea.

The sulphur content of fuel oil intended for use on board, both within a SOx emission control area or not, shall be documented by the supplier by means of the bunker delivery note, which must be kept on board for a period of three years after the fuel oil has been delivered on board.

There is a 12 month allowance to meet the limit of SOx emission control areas after entry into force of the 1997 Protocol and, similarly, in the case of designation of new SOx emission control areas. It gives ships relatively sufficient time to comply with this regulation if structural alterations are required, such as separate oil tanks and fuel oil systems.

2.2.5 Fuel oil quality

Regulation 18 - Fuel oil quality is directly related to SOx emission limits and is an operative regulation. When fuel oil is delivered on board a bunker delivery note shall be issued by the bunker suppliers and be retained on board for a period of three years after the fuel oil has been delivered on board.

This regulation also requires that, for each bunker delivery, a representative sample of the fuel delivered shall be sealed and retained under the ship's control until the fuel is substantially consumed but in any case for a period of not less than 12 months from the time of delivery.

2.2.6 Incinerators

Regulation 16 requires that all incinerators installed on board a ship on or after 1 January 2000 shall be approved by Administrations in accordance with requirements contained in IMO resolution MEPC 76(40) on Standards specification for shipboard incinerators. However, exiting incinerators installed on board ships prior to 1 January 2000 may still be used after entry into force of the Annex VI, although the incineration of polyvinyl chlorides (PVCs) in them will be prohibited

As with the NOx regulation, Regulation 16 will be retrospectively applied on the date of entry into force of Annex VI, so until that time this regulation is unenforceable. As a result, although an incinerator may have been type approved in accordance with MEPC 76(40) at the time of its manufacture, some other requirements such as operating manual and operator training may not be required until the initial survey for issuance of the IAPP Certificate is carried out.

2.2.7 Ozone-depleting substances

Regulation 12 will prohibit the deliberate emissions of ozone-depleting substances such as Halons and chlorofluorocarbons (CFCs). Deliberate emissions include emissions occurring in the course of maintaining, servicing, repairing and disposing of systems of equipment, except that deliberate emissions do not include minimal releases associated with the recapture or recycling of an ozone depleting substance.

New installations which contain ozone-depleting substances shall be prohibited on all ships. However, new installations containing hydrochlorofluorocarbons (HCFCs) are permitted until 1 January 2020. This regulation also requires that all of the substances covered by the regulation, and equipment containing such substances, should be delivered to appropriate reception facilities upon removal from ship. The provision for reception facilities is covered by Regulation 17.

The use of Halons in new fixed fire fighting installations has already been banned under SOLAS as of 1 October 1994 (SOLAS Reg.II-2/5.3.1), and IMO is considering similar action for portable halon extinguisher. The use of chlorofluorocarbons (CFCs), mainly used in air conditioning and refrigeration units, will be prohibited in all new installations after entry into force of Annex VI.

Chapter 3
SUMMARY OF NOx TECHNICAL CODE

3.1 General

The NOx Technical Code is a compulsory guideline specifying the requirements for the testing, survey and certification of marine diesel engines so as to ensure their compliance with the NOx emission limits of Reg. 13 of Annex VI to MARPOL 73/78. The regulation will come into force twelve months after the date on which not less than 15 States, the combined merchant fleets of which constitute not less than 50 percent of the gross tonnage of the world's merchant shipping. If the regulation comes into force all diesel engines with a power output of more than 130 kW, which are installed on a ship constructed after 1 January 2000, will have to fulfill these requirements.

Therefore, all engines within the above mentioned regulation need an Engine International Air Pollution Prevention Certification (EIAPP Certificate). This certificate will be one of the most important requirements in the event of issuing the International Air pollution Certificate (IAPP Certificate) for the ship. However, the new Annex VI has not yet come into force for the time being. So, guidelines have been introduced to solve this problem by issuing a sort of interim certificate. The authorized organization (e.g. Classification Societies) by the flag state, can issue a Statement of Compliance (SOC Certificate) and will approve the NOx technical file after confirming a proper certificate procedure at the engine manufacture's site

(MEPC/cir.344). The SOC Certificate will be transformed into the EIAPP Certificate when the new Annex VI comes into force.

The emissions of NOx (calculated as the total weighted emission of NO_2) from diesel engines with a power output of more than 130 kW, which are installed on ships constructed after 1 January 2000 or which undergoes major conversion on or after 1 January 2000, will have to be under the following limits:

- 17.0 g/kWh (grams/kilo watt hour), when ***n*** is less than 130 rpm
- 45.0 $\boldsymbol{n}^{(-0.2)}$ g/kWh, when ***n*** is 130 or more but less than 2000 rpm
- 9.8 g/kWh, when ***n*** is 2000 rpm or more

where ***n*** = rated engine speed (crank shaft revolutions per minutes).

3.2 Survey and Certification

3.2.1 Types of survey and certification

For the purpose of clear understanding the complicated NOx Technical Code, first of all the following definitional terms have to be born in mind. Each marine diesel engine shall be subject to the following surveys:

- **Pre–certificate survey:** done to ensure that the engine, as designed and equipped, complies with the NOx limits at a test bed prior to installation on board. After confirming compliance, the EIAPP Certificate or SOC Certificate will be issued.
- **Initial certification survey:** done to ensure that the engine, including any modifications or adjustments since the pre-certification, complies with the NOx limits after the engine is installed on board the ship. This survey, as part of the ship's initial survey, may lead to the issuance of a ship's initial IAPP Certificate.
- **Periodical and Intermediate survey:** done to ensure that the engine continues to fully comply with the NOx limits as part of a ship's surveys required in regulation 5 of Annex VI.

To comply with the above mentioned surveys and certification requirements, there are five alternative methods which the engine manufacturer, ship builder or shipowner can choose for testing, measuring and calculating the NOx emission from a diesel engine. The five methods are:

1. **test-bed testing** for the pre-certification survey.
2. **on-board testing** (only for engines not pre-certified) for combined pre-certification and initial certification survey in accordance with the full test-bed requirements.
3. **on-board engine parameter check method** for confirmation of compliance at the initial, periodical and intermediate surveys for pre-certified engine or engines that have undergone modification or adjustments.
4. **on-board simplified measurement method** for confirmation of compliance at the periodical and intermediate surveys of confirmation of pre-certified engines for initial certification surveys.
5. **on-board direct measurement and monitoring** for confirmation of compliance at periodical and intermediate surveys only.

3.2.2 Pre-certification of an engine

Prior to installation on board a ship every marine diesel engine shall be adjusted to meet the applicable NOx emission limit and shall be pre-certified by the Administration by issue an EIAPP Certification after the NOx emission measurement on a test-bed.

If an engine cannot be pre-certified on a test-bed due to its size, construction and delivery schedule, the engine may be tested at an on-board test. In such a case, the on-board test has to fully meet all the requirements of a test-bed procedure. Such a survey may be accepted for one engine or for an engine group represented by the parent engine only, but it shall not be accepted as an engine family certification.

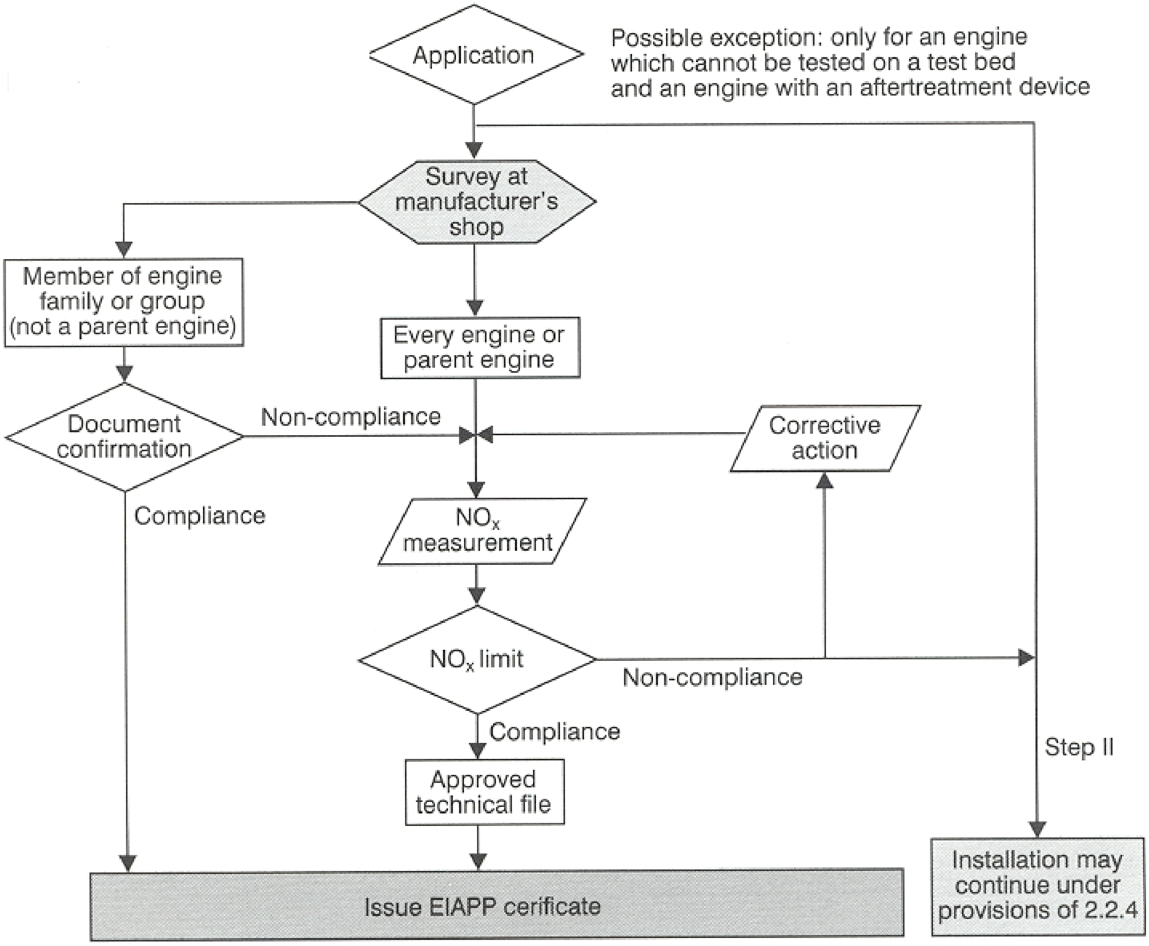

Fig.3.1 Pre-certification survey at the manufacture's shop. Source : NOx Technical Code, pp.101.

For serially manufactured engines the engine family or the engine group concept may be applied. In such a case, test is required only for the parent engine, which is the representative of an engine family or engine group. If the NOx emission values meet the requirements, the NOx relevant engine parameters have to be documented in the technical file. This technical file of the parent engine has to be the same for all member engines. Within an engine family or engine group the EIAPP Certificates will be issued to the parent engine and to every member engine.

If the pre-certification test results fail to meet the NOx emission limits, a NOx-reducing device may be installed additionally. This device must be recognized as an essential component for the engine and will be recorded in the engine's technical file. A typical pre-certification procedure is shown in **Fig.3.1**

3.2.3. Engine group/family concept and parent engine

To avoid certification testing of every engine for serially manufactured engines the engine family or the engine group concept may be applied. In such a case, the testing is required only for the parent engine of an engine family or engine group.

Engine groups or engine families are represented by their parent engines. The certification test is only necessary for these parent engines. Member engines can be certified by checking documents, components, settings etc which have to show correspondence with the parent engine's parameters.

3.2.3.1 The engine family concept

This concept is applied to any mass-produced engines which, through their design, have similar NOx emission characteristics and require no adjustments or modification during installation on board.

Where adjustable features are provided, e.g. for balancing cylinder peak pressures and individual cylinder exhaust gas temperatures, they are to be such that no setting can adversely affect the engine's NOx emission.

The following basic characteristics must be common for all engines within an engine family:

.1 combustion cycle: 2-stroke / 4-stroke
.2 cooling medium: air/ water / oil
.3 individual cylinder displacement: to be within a total spread of 15%
.4 number of cylinders and cylinder configuration
.5 method of air aspiration: naturally aspirated / pressure charged
.6 fuel type: distillate or heavy fuel oil / dual fuel
.7 combustion chamber: open / divided
.8 valve and porting , configuration, size and number: cyl. head / cyl. wall
.9 fuel system type

3.2.3.2 The engine group concept

A engine group is characterized by engines with the same bore and turbo-charging system of one manufacturer. This concept is applied to smaller series of engine produced for similar engine application and which require minor adjustments and modifications during installation. These engines are normally large power engines for main propulsion.

With regard to the allowable adjustments and modifications within an engine group the manufacturer is to provide documentary evidence or historical data to prove that the range of adjustments will permit the engine to operate within the emission limits.

Within an engine group, in addition to the parameters fined above for an engine family, the following parameters and specification must be common to each member engine.

.1 bore stroke dimensions
.2 method and design features of pressure charging and exhaust gas system

- constant pressure
- pulsating system

.3 method of charging air cooling system

- with / without charging air cooler

.4 design features of the combustion chamber

.5 design features of the fuel injection system, plunger and injection cam

.6 maximum rated power at maximum rated speed

3.2.3.3 The parent engine

The parent engine of an engine family or group must be selected, which has the worst NOx emission characteristics of the engine family or group, as documented by the manufacturer and approved by the Administration. This engine will have the highest NOx emission level among all of the engine family or group.

The parent engine for an engine family has to incorporate those features, which will most adversely affect the NOx emission level. During testing of the parent engine of an engine group, the NOx influence of adjustments and modifications has to be demonstrated.

After testing, a technical file should be prepared identifying the components, settings, operation values and ranges of those items which can affect the NOx emissions. This is to give the engine's rated performance, any designation and restrictions. The specification of spare parts is also included. In the case of engine group members the on-board verification procedures must also be given.

The following criteria for selecting the parent engine shall be considered, but the selection process must also take into account the combination of basic characteristics in the engine specification:

.1 main selection criteria

- higher fuel delivery rate

.2 supplementary selection criteria

- higher mean effective pressure
- higher maximum cylinder peak pressure
- higher charge air / ignition pressure ratio
- higher charge air pressure
- higher charge air temperature

In order to support the proposed parent engine selection, adjustment and fit, it may be necessary for the engine manufacturer to have undertaken a number of emission trials to determine the actual effects of the various factors which influence NOx formation during the combustion process.

3.3 Issue of initial IAPP Certificate

When the Annex VI enters into force all ships will need an IAPP Certificate. For the issue of IAPP Certificate every diesel engine shall have on-board verification surveys after installation of a pre-certificated engine on board a ship. During the initial survey, if all of the engines installed on board are verified to remain within the parameters and components and adjustable features recorded in the technical file, the IAPP Certificate will be issued to the ship.

During the initial survey, for the engine family members it will be sufficient to confirm that any maintenance or replacement of NOx sensitive components is in compliance with the technical file specification. For engine group members the engine parameter check method or the simplified measurement method may be used.

If any adjustment or modifications are made which are outside the approved limits documented in the technical file, the IAPP Certificate may be issued only if the overall NOx emission performance is verified to be within the required limits by the engine parameter check method or the simplified measurement method. The flow chart is shown in **Fig. 3. 2**

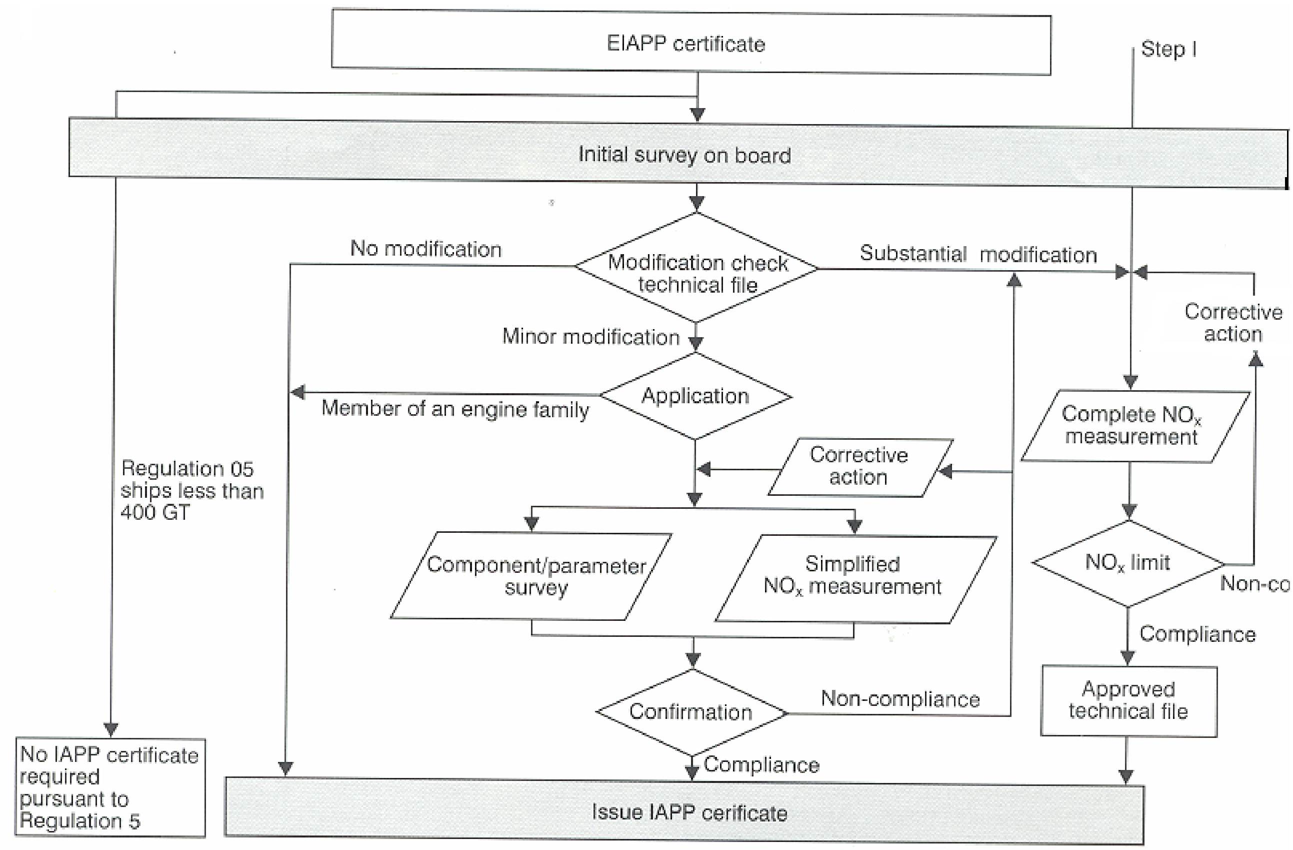

Fig. 3.2 Initial survey on board a ship Source: NOx Technical Code, pp.102.

3.3.1 Engine parameter check method

The engine parameter check method is for confirmation of compliance at initial, periodical and intermediate surveys for pre-certified engines or engines that have undergone modification or adjustments. Therefore it is necessary to conform that each engine's components, settings and operating values have not deviated from the specifications, which are documented in that engine's technical file.

In practice this method will be the most preferred option for the engine manufacturers and ship owners. This method is likely to consist of a documentation inspection of the engine parameters and an actual inspection of engine components and adjustable features with visual inspection. (American Bureau of Shipping (ABS), 1999)

For engines equipped with after-treatment devices, it will be necessary to check the operation of the after-treatment devices as part of the parameter check. With this method especially for the periodical and intermediate survey, ship owners shall maintain the record book of engine parameters, the list of engine parameters and the technical documentation of engine component modifications.

3.3.2 Simplified measurement method

The simplified measurement method shall be applied for confirmation of compliance at periodical and intermediate survey of confirmation of pre-certified engines for initial certification surveys. This method is a simplified version of the full test bed method and there are certain allowances which may be applied in calculating the final emission figures to take account of possible deviations in instrument accuracy and the presence of nitrogen in the fuel.

All results of measurements, test data and calculations shall be recorded in the engine's test report. Due to the difficulty in carrying out such measurements, this method is likely to be used only for special cases. (ABS,1999)

3.4 Periodical survey on board

To ensure the engine continues to fully comply with the NOx limits, a periodical survey has to be repeated every five years. During the periodical surveys, the surveyor will check whether all of the engines installed on board are verified to remain within the parameters and components and adjustable features recorded in the technical file.

If any substantial modifications are made, a complete NOx emission measurement has to be carried out. In this case, the owner has one more verifying option to choose, the direct measurement and motoring method, in addition to the engine parameter check method and simplified measurement method.

3.5 Technical file

Every diesel engine should be provided with a technical file, prepared by the engine manufacturer and approved by the administration or authorized organization. The technical file should identify those components and settings which influence NOx emissions and confirm the correct specification to ensure compliance with the regulation.

The term of 'technical file' can be seen in many different sections of the NOx Technical Code, requiring specific relevant information at each different condition as follows:

- Engine design which may influence NOx formation
    - components, settings and operating values
    - definition of engine group specification
- Engine performance data
    - test bed engine performance data
    - NOx parameter sensitivity
    - NOx emission for given performance parameters versus load
- On board verification procedure
    - components (I.D number)
    - setting ranges
    - operational parameters (NOx value or parameter range)
    - specification of spare parts
- Report of test-bed testing
    - engine information and set-up (Sample probes and position)
    - test cell specification and calibration of analyzer
    - measured parameters (Calibration data)
    - procedures for actual measurements
    - fuel oil and lube oil specification
    - actual corrections of measured data
- after issuing of the EIAPP, IAPP Certification and in service
    - engine record book (status of engine maintenance, change of components and performance log)
    - emission data
    - fuel oil and lube oil specification

3.6 NOx emission measurement on a test bed

The NOx code includes detailed specifications on measurement procedures on a test bed. The measurement and calculation of exhaust gas emissions is based on the ISO standard 8217. When measuring exhaust gas, to assess NOx emission level, not only NOx but also Carbon monoxide (CO), Hydrocarbons (HC), Oxygen (O_2), Carbon dioxide (CO_2) and Sulphur dioxide (SO_2) have to be measured by using analyzers that comply with the specifications in the NOx code.

In addition to the exhaust gas measurements, engine torque, engine speed, fuel consumption, fuel rack position, charging air temperature and pressure, exhaust gas temperature and ambient temperature/pressure/humidity will be measured. The analyzers comply with the specifications given in the NOx code with regard to measurement method, accuracy and performance sensitivity against other exhaust components. The exhaust gas is taken from the funnel via a common probe and then distributed to the various analyzers. Dependent on the type of analyzer, the calibration uses either nitrogen or a special "zero gas" for zero point adjustment. The valid measuring range is set with a calibration gas "span gas" of suitable concentration corresponding to the exhaust gas component to be measured. (Gatjens H J, 1999)

Chapter 4
FORMATION OF NOx FROM MARINE DIESEL ENGINES

4.1 Exhaust gas of diesel engines

Exhaust emissions from marine diesel engines largely comprise nitrogen, oxygen, carbon dioxides (CO_2) and water vapour, with smaller quantities of carbon monoxide (CO), sulphur oxides (SOx), nitrogen oxides (NOx), hydrocarbons and particulate material. Among exhaust gas from diesel engines, CO_2, SOx, NOx, HC and particulate material are regarded as pollutants. The typical composition of exhaust gas from a diesel engine is shown in **Fig. 4.1**

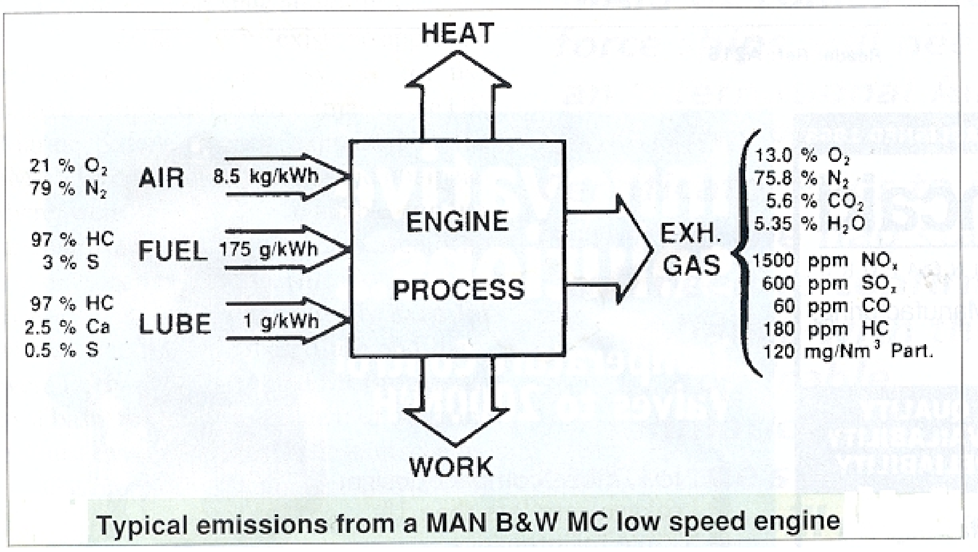

Fig. 4.1 Typical emission from a low-speed diesel engine.

Source: MER, 1997, pp14.

Several emission limitations are on the way globally, but the main focus has so far been on reducing the NOx and SOx emissions because those threat human health, vegetation and the environment. The Annex VI of MARPOL 73/78 consequently regulates only NOx and SOx emissions from diesel engines for the time being.

However, because the use of fossil oil in diesel engines for main propulsion and auxiliary services is a large contributor to atmospheric pollution it is likely to be the focus of further legislation in the future. There is a growing consensus, especially within certain parts of Europe and United States, that other pollutants from diesel engines and other combustion sources in addition to NOx and SOx emission should also be reduced.

4.1.1 Sulphur Oxides (SOx)

The formation of SOx is proportional to the sulphur content in the fuel. All sulphur in fuel will remain in the exhaust gas. e.g. 1 kilogram of sulphur in fuel is oxidized to SO_2 and SO_3 during and after the combustion to 2 kilograms of SO_2 in exhaust gas (the ratio of SO_2 to SO_3 is about 95:5 in diesel exhaust). Therefore reduction of the sulphur content in marine fuel is one feasible method to reduce SOx emission. (Gotmalm O.A.1992). An alternative way of removing SOx from exhaust gas can be effected by water washing the gas in a scrubber, but this leaves another disposal problem of sulphuric acid in the water, which consequently must be neutralized chemically.

The SOx contributes environmentally to the formation of acid rain. SOx in the exhaust gas will eventually be washed from the atmosphere by rain and that will increase the acidity of the soil. Operationally, SOx directly contributes to the low temperature corrosion to exhaust system, cylinder liner and cylinder head. It is therefore an undesirable compound and will be subject to increasing legislation limiting the sulphur content in bunker oil.

As indicated in Chapter 2, Regulation 14 of Annex IV limits sulphur content in marine bunker to 4.5%, and especially 1.5% in the SOx emission control areas. Low sulphur fuel is already available on the market and there are no technical problems regarding pollution prevention through the use of low sulphur, but it requires a lot of energy and investments resulting in a considerable increase in fuel cost. Therefore, the price of fuel oil depends on the sulphur content, a fact that should be considered when evaluating the use of the low sulphur versus the high sulphur and cleaning system.

According to some studies, the total heavy fuel oil and marine diesel consumption in 1980 was estimated to be 110 million tons, and sulphur content was calculated to be 2.91 million tons, based on the assumption that the average weight percentage of sulphur in heavy fuel was 2.82%, and in marine diesel oil 0.94%. It is possible that 2.91 million tons of sulphur could have been emitted, which is equivalent to 5.82 million tons of SO_2. This figure represent 5.3% of the estimated global SO_2 emission. (Okamura B. 1995)

However, there has been no general agreement on the quantity of SOx emission emanating from ships. This issue has been addressed in several submissions to the various meeting within IMO. Calculations vary from around 6million tons each year, or some 5% of the total global emission. Other recent studies have indicated that ship's SOx emissions are approximately 8% of the world wide SOx emissions.

4.1.2 Carbon Dioxide (CO_2)

Carbon Dioxide emission is related to the carbon content of the fuel and is produced wherever fossil fuel undergoes combustion. There is no realistic method yet to control the formation of carbon dioxide in fossil fuel combustion. However, the diesel engine is probably the most effective fossil fuel converter so far and hence produces comparatively less CO_2 compared with other external combustion facilities. (Gotmalm O.A. 1992)

Carbon dioxide is a greenhouse gas contributing to the global warming effect and is thus subject to wide interest, although it does not scare common people so much because carbon dioxide is not poisonous. However, some countries are addressing the carbon dioxide problem quite firmly today and the issue may become more important in the future. IMO has been tasked by the United Nations to take measures to reduce greenhouse gas emissions from merchant ships.

4.1.3 Carbon Monoxide (CO)

Emission of carbon monoxide of diesel engines is a function of the air excess ratio and combustion temperature. The formation is strongly influenced by uniformity of the air/fuel mixture in the combustion chamber.

CO is a highly toxic gas and contributes to smog and ground ozone formation. CO stems from poor combustion at low combustion temperature. Generally, the CO emissions from marine diesel engine are low in comparison with other industrial sources due to the high thermal efficiency of the diesel process.

4.1.4 Hydrocarbons (HC)

During the combustion process a very small part of the hydrocarbon in the fuel is left unburned up to 300ppm depending on the fuel type and the engine design and adjustment. The unburned hydrocarbons are normally stated in terms of equivalent CH_4.

Hydrocarbons are considered carcinogenic, contributing to the greenhouse effect. At the 44th session of MEPC, the US delegation highlighted concerns that NOx and HC emissions from ships may be associated with climate change. Although NOx is not a green house gas, it is an ozone precursor that may react with HC to produce low-level ozone which is a greenhouse gas. The US paper says that in remote ocean areas restricting HC emissions could be the best route to minimize ozone production. (Motor Ship, 2000,April)

4.1.5 Particulates (PM)

Particulates contribute to formation of smog but have also a detrimental effect on turbo-charger and exhaust gas boiler performance. Particulates in a diesel engine is defined in the ISO 8178 standard as 'any material collected on a specified filter medium after diluting the exhaust gases with clean filtered air to a temperature of less than or equal to 325k (52 °C) as measured at a point immediately upstream of the primary filter.'

Particulate emissions originate from partly burned fuel, partly burned lube oil, ash content of fuel oil and cylinder oil. Even if the fuel is atomized in the combustion chamber the combustion process involves small droplets of fuel, which evaporate, ignite and are subsequently burned. During the process a minute part of the oil will be left as a nucleus mainly comprising carbon. Particulate emissions thus vary with the fuel oil composition and with the lube oil type and dosage.

Particulates in the form of carbon soot, metal oxides, sulphates and unburned HC are a result of insufficient combustion and fuel and lubricating oil impurities impossible to combust in a diesel engine. A higher combustion temperature is very effective in reducing PM in diesel engines if low sulphur fuel is used, especially if the engine is well tuned. (Gotmalm O.A. 1992)

4.2 NOx formation

4.2.1 Overview of the NOx problem

According to Nevers N.D. (1995), although nitrogen forms eight different oxides, our principal air pollution interest is in the two most common oxides: nitric oxide (NO) and nitrogen dioxide (NO_2). In addition, we are beginning to be concerned with nitrous oxide (N_2O). Ordinary air contains almost 80% nitrogen (N_2) and some of this nitrogen is oxidized to NOx (NO, NO_2 and N_2O) during the combustion process.

NO is a colorless gas that has some harmful effects on health, but these effects are substantially less than those of an equivalent amount of NO_2. In the atmosphere and in industrial devices NO reacts with O_2 to form NO_2, a brown colored gas that is a seriously respiratory irritant. NO and NO_2 are often treated together as one problem of as a quasi species, and written NOx. Most regulations for NOx emissions base all numerical values on the assumption that all of the NO is converted to NO_2. The conversion of NO to NO_2 will continue in the atmosphere. NO_2 will be washed out by rain and eventually increase the acidity of the soil by acid rain. NOx are released to the atmosphere chiefly by large combustion sources such as fossil fuel fired power plants and oil fired diesel engines.

NOx is also known as one of the reasons for ozone depletion which has an adverse effect on health in addition to acid rains. According to the report submitted by the United States at the 44th session of MEPC, NOx emissions from marine diesel engines are of concern to the international community due to their contribution to ground level ozone. Ground level ozone is formed when hydrocarbons and oxides of nitrogen react in the presence of sunlight. Over the past few decades, many researchers have investigated the health effects associated with both sort-term and prolonged acute exposures to ozone.

Emission values for various components of air pollution from marine diesel engines are influenced by fuel oil quality and engine condition, and it is difficult to define representative emission factors. A report submitted by Norway at MEPC concluded that the international shipping contributes with about 7 % of the world total discharge of NOx. Whilst, according to the document submitted by United States at 44th session of MEPC (1999), some studies estimate the total contribution of marine diesel engines to NOx inventories at 4 % or higher. A recent study by Corbett and Fischbeck estimates that these engines may contribute as much as 14 % of the world-wide nitrogen emissions from fossil fuels annually.

4.2.2 Thermal, Prompt and Fuel NOx

NOx formation occurs by reaction between nitrogen and oxygen in the combustion air (thermal NOx), by reaction between exhaust gas hydrocarbons and combustion air oxygen (prompt NOx) and by the reaction between nitrogen bindings in fuel (fuel NOx). Thermal NOx is decisive for total emission and all the abatement methods are targeted to reduce that component. The formation of NOx in the combustion chamber is mainly influenced by the temperature and oxygen concentration: the higher the temperature and the longer the residence time at temperature is, the more thermal NOx will be created. (Schiff & Hafen, 1998)

According to Nevers N.D. (1995), NOx are found in combustion gases as thermal, prompt and fuel nitrogen oxides. Fig. 4.2 shows estimates of the contribution from the thermal, prompt and fuel mechanisms to NOx emissions from coal combustion. Below about 1,300 °C the thermal NOx mechanism is negligible compared with the other two, while at the highest temperature it is the most important. If, based on the thermal NOx curve alone, we would predict approximately zero NOx would be produced at temperatures below 1300˚C. At temperatures above 1500˚C, NOx emission rises very sharply. Therefore, lowering the peak combustion temperature is a very effective means of reducing the amount of NOx formed. Therefore, in diesel engines, methods like retarded fuel injection or water in burning are aiming to reduce those peak temperatures and thus also lower the NOx emission.

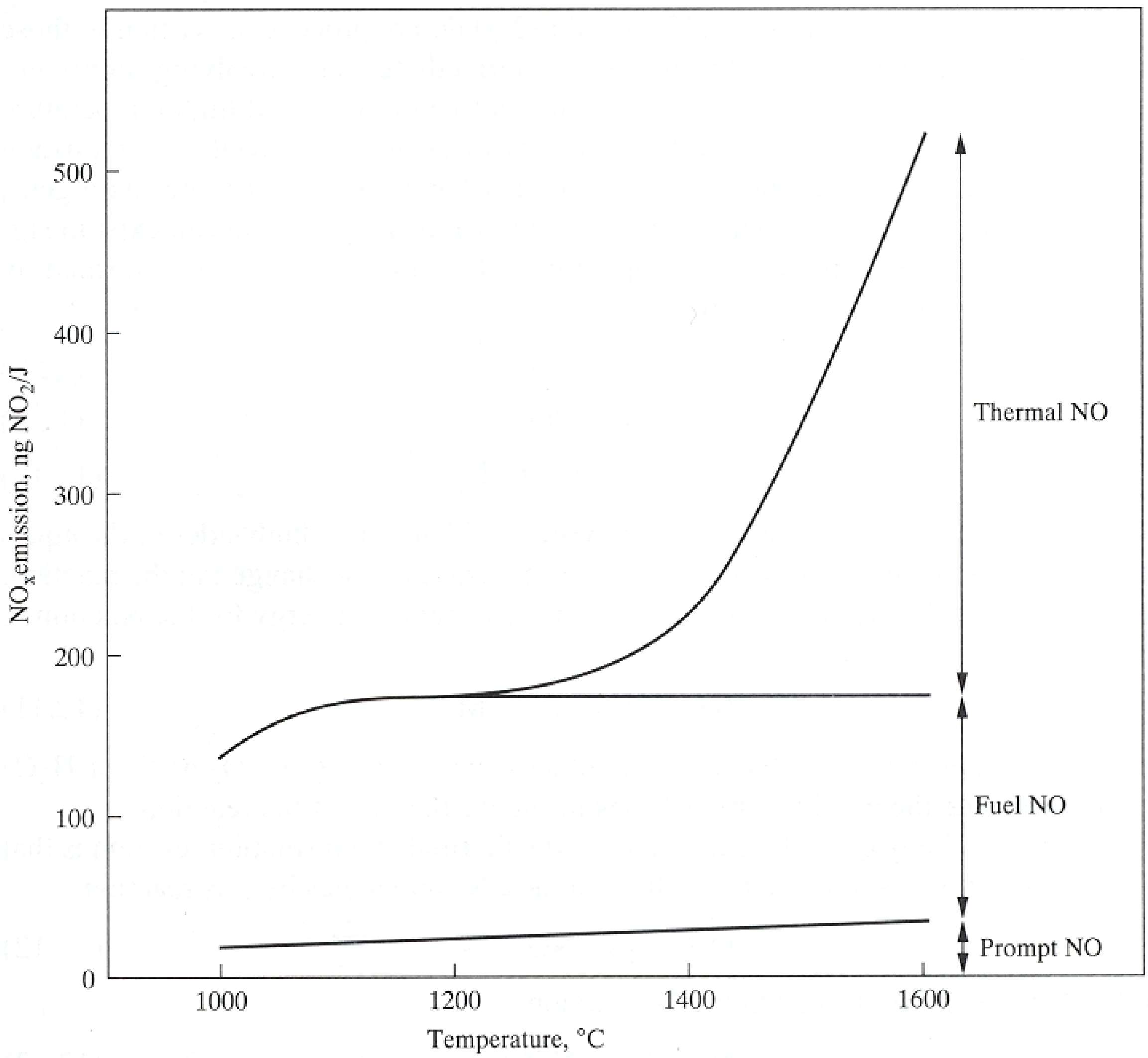

Fig. 4.2 Estimated contribution of three NOx. Source: Nevers N.D. 1995, pp378.

4.2.3 Thermal NOx

According to Nevers N.D. (1995), the thermal NOx builds up by the reaction of atmospheric nitrogen with oxygen by the simple heating of nitrogen and oxygen, ether in a flame or by some other external heating such as a lighting bolt. Thermal NOx are formed very quickly by simple heating of oxygen and nitrogen. The gas is a result of the interaction between nitrogen and oxygen with some of the active carbon species derived from the fuel in the flames. NOx are not observed in flames of fuels with no carbon, e.g. H_2. They cannot be formed only by heating oxygen and nitrogen, the participation of some active carbon species from fuel is also required. In diesel engines the thermal NOx, being mainly a function of the peak combustion temperature, is decisive for the total NOx emission and most of the reduction methods are targeted to reduce the thermal NOx.

First of all, based on the Zeldovich kinetics of thermal NOx formation, the most important reactions for producing NO and NO2 in flames are:

$$NO + 0.5O_2 \leftrightarrow NO_2 \tag{4.1}$$

$$N_2 + O_2 \leftrightarrow 2NO \tag{4.2}$$

Both of these equations are reversible reactions that do not go to completion. However, the reactions shown in Eqs. (4.1) and (4.2) do not exactly proceed as written in those equations. Rather, they proceed by means of intermediate steps involving highly energetic particles called free radicals. The free radicals most often involved in combustion reaction are O, N, OH, H and hydrocarbons that have lost on more hydrogen, e.g., CH_3 or CH_2. These materials are very active and energetic and exist in significant concentrations only at high temperatures. In principle they can be formed by equilibrium reactions like the following equations:

$$N2 \leftrightarrow 2N \tag{4.3}$$

$$O_2 \leftrightarrow 2O \tag{4.4}$$

$$H_2O \leftrightarrow H + OH \tag{4.5}$$

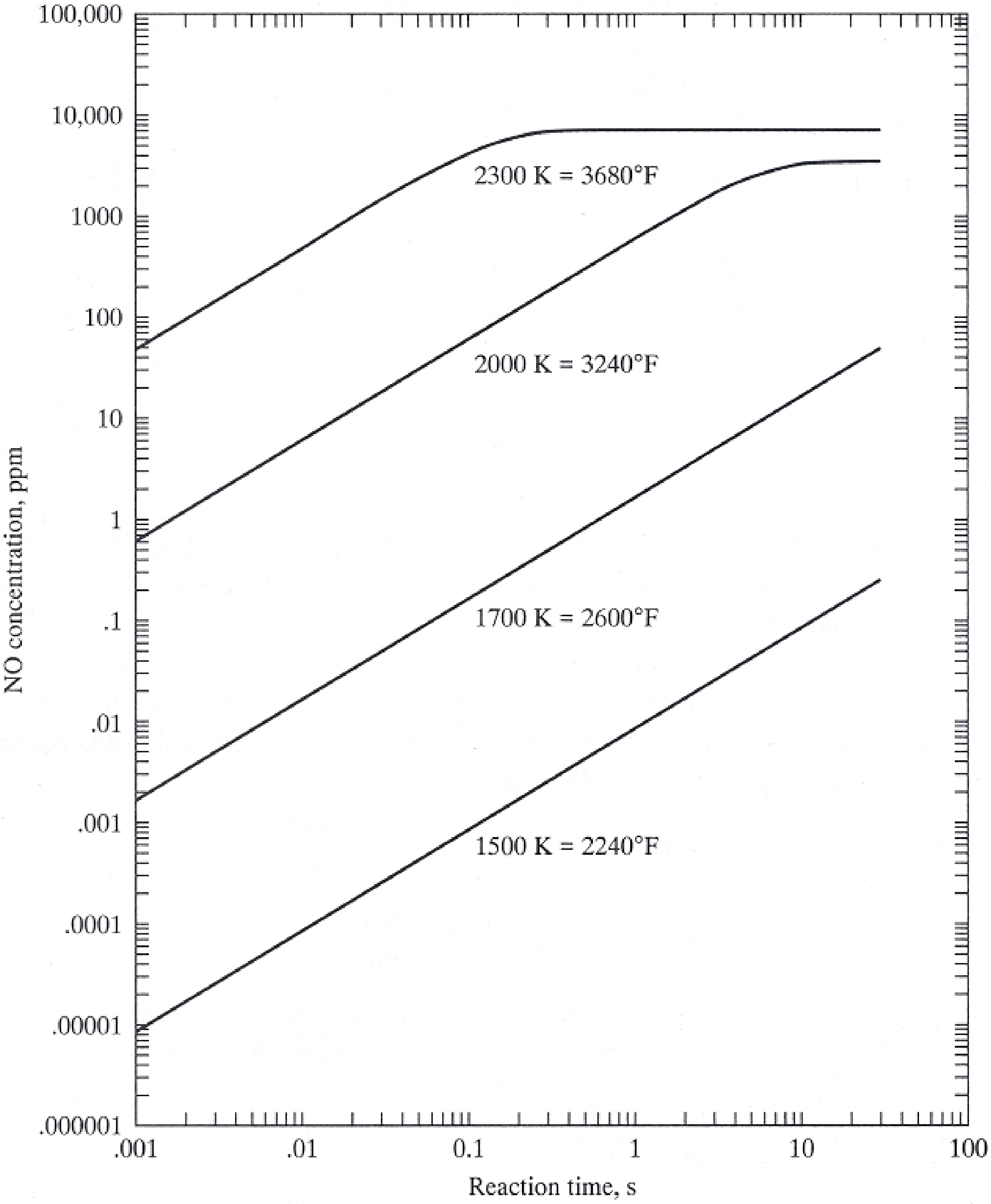

Fig. 4.3 Concentrations of thermal NOx as a function of time and temperature. Source: Nevers N.D. 1995, pp382.

The most widely quoted mechanism for thermal NOx formation reaction is that of Zelovich. It assumes that O radicals attack N molecules by this reaction,

$$O + N_2 \leftrightarrow NO + N \qquad (4.6)$$

and that N radicals can form NO by the reaction

$$N + O_2 \leftrightarrow NO + O \qquad (4.7)$$

A more complex version of the Zelovich mechanism is shown in the following equation

$$N + OH \leftrightarrow NO + H \qquad (4.8)$$

From the above equations various degrees of simplification of those mechanisms can be made. According to the Zeldovich simplification of the kinetics of thermal NOx formation, Fig 4.3 clearly shows the expected time-temperature relation for one specific starting gas composition. The formation of NOx in flames can be greatly reduced by manipulating the time, temperature and oxygen content of the flame. Low speed diesel engines with slow burning processes and high air / fuel ratios have the highest emissions due to the long time the oxygen is allowed to react with nitrogen.

4.2.4 Prompt NOx

Also, NOx builds up by reaction between exhaust gas hydrocarbon and combustion air oxygen (prompt NOx). According to Noel de Nevers (1995), the prompt NOx refers to the nitrogen oxide that forms very quickly as a result of the reaction of nitrogen and oxygen with some of the active carbon species derived from the fuel in flames. They are not observed in flames of fuels with no carbon, e.g., H_2. They cannot be formed by simply heating oxygen and nitrogen, but the participation of some active carbon species from the fuel is required.

During the first part of combustion, the carbon-bearing radicals from the fuel react with nitrogen by the following equation;

$$CH + N_2 \leftrightarrow HCN + N \qquad (4.9)$$

and several similar reactions involving the CH and C radicals. The N thus produced attacks O by the following equation to increase the amount of NO formed;

$$N + O_2 \leftrightarrow NO + O \qquad (4.10)$$

Then the HCN partly reacts with O_2 producing NO by the following equations;

$$HCN + OH \leftrightarrow CN + H_2O \quad (4.11)$$

$$NH + OH \leftrightarrow N + H_2O \quad (4.12)$$

$$CN + O_2 \leftrightarrow CO + NO \quad (4.13)$$

4.2.5 Fuel NOx

Fuel NOx are formed by the conversion of nitrogen, which is originally present in the fuel, to NOx. According to Noel de Nevers (1995), most of the fuel nitrogen is converted in flame to HCN, which then converts to NH or NH_2. The NH and NH_2 can react with oxygen to produce NO + H_2O, or they can react with NO to produce N_2 + H_2O. Thus the fraction of the fuel nitrogen that leaves the flames as NO is dependent on the NO/O_2 ratio in the flame zone. Keeping the oxygen content of the gases in the high temperature part of the flame low, significantly lowers the fraction of the fuel nitrogen converted to NO.

Some of the nitrogen oxides emitted to the atmosphere are due to nitrogen contaminants in fuels, but the contribution of that nitrogen to the total NOx in the combustion products is minimal. Typically, fuel NOx accounts for only about 10 to 20 percent of the total NOx emissions. Thermal NOx is the main contributor to total NOx emissions.

In comparison, sulphur oxides are formed from the sulphur contaminants in fuel. Thus removing all sulphur from the fuels would completely eliminate sulphur emission from fuel combustion. Furthermore, most of fuels used in diesel engine contain little nitrogen.

Chapter 5
REDUCTION METHODS OF NOx

5.1 General concept of NOx reduction

The diesel engine has so far been developed under the two major technologies of thermal efficiency and reliability. At present the diesel engine development is also facing another major theme, the environment problem, and most of the technological efforts concentrate now on this matter. Engine builders have to look in this direction and must make efforts to solve the environmental problems that combined with good engine performance and high reliability were previously developed.

As for marine diesel engines, since and long before the legislation of MARPOL Annex VI, all concerns are on the reduction of NOx emissions. Practical methods for marine diesel engine NOx reduction can be divided into Primary methods and Secondary methods. It has been known there are no difference between slow, medium and high-speed engines because they all have diesel cycle with air compression and combustion process in high temperature and high pressure condition.

5.1.1 Primary methods

Primary methods are aimed at reducing the amount of NOx formed during combustion. The basic aim of most of these measures are to lower the maximum temperature in the cylinder, since this result inherently in a lower NOx emission.

The low NOx combustion system is based on a combination of compression ratio, injection timing and injection rate. Therefore, when considering NOx reduction method it should be taken into account that all different NOx reduction methods can affect each other.

Primary methods can be categorized as follows:

- Altered fuel injection
  - Fuel nozzle modification (5.2.1)
  - Retarded fuel injection (5.2.2)
  - High pressure fuel injection (5.2.3)
- Water addition
  - Direct water injection (5.3.1)
  - Water emulsified fuel (5.3.2)
  - Stratified water injection (5.3.3)
  - Intake air Humidification (5.3.4)
- Combustion air treatment
  - Exhaust gas recirculation (5.4)
  - Adjustment of inlet /exhaust valve (5.2.5)
- Change of engine process
  - Compression ratio (5.2.4)

5.1.2 Secondary methods

Secondary methods, aimed at removing NOx from the exhaust gas by downstream treatment. The Selective Catalytic Reduction (SCR) is the most well known method of so called exhaust gas after treatment.

5.1.3 Manufacturer's application

Table 5.1 Manufacturers' NOx method application. Source: Kim J. H. (2000)

NOx reduction Method		MBD	WNSD	MHI
Internal treatment	Fuel nozzle modification	●	●	●
	Retarded fuel injection	x	●	●
	Emulsified fuel	■	■	O
	Water direct injection	x	■	O
	Stratified water injection	x	■	x
	Exhaust gas recirculation	O	O	O
	Compression ratio	O	●	●
	Intake air Humidification	O	x	x
	Modification of Turbocharger	●	●	●
	Adjustment of exhaust valve	x	●	●
Secondary	Selective Catalytic Reduction	■	■	■

● : Application method to deal with IMO regulation

O : Not considering as an application method to deal with IMO regulation, but has been developing/researching

x : Not considering

■ : Application method to deal with further stringent NOx regulation

Some of the manufacturers', who are widely involved in Korean shipbuilding industries, NOx method applications are shown in the table 4.1. This source is from an interview with Dr. Kim Jong-Huon who has been dealing with NOx matters for many years and is working for Korean Register of Shipping as a manager in the statutory department. The abbreviations of the manufacturer are as follows:

MBD : MAN B&W Diesel
WNSD : Wartsila NSD
MHI : Mitsubishi Heavy Industries

5.2 Combustion treatment methods

In recent years diesel engines have been modified for low NOx formation by optimization of the injection timing, rate and spray configuration, the valve timing, the supercharging, the compression ratio and the mixing in combustion space. All these methods are targeting to lowering the peak combustion temperature, which is a very effective means of reducing the amount of NOx formed.

With these measures, unfortunately, the amount of PM and HC will increase instead, and there is a substantial fuel penalty as efficiency drop due to poor combustion. Therefore, this side-effect matter will be discussed with low NOx formation in the following paragraphs.

5.2.1 Fuel nozzle modification (Slide type/Multi-hole)

Different fuel nozzle types and models have significant impact on NOx formation, and the intensity of the fuel injection has also an influence. The NOx formation is influenced by the formation and combustion of the fuel/air mixture, the local temperature level and the oxygen concentration in the fuel spray area.

According to MAN B&W (1996), they have developed a fuel valve incorporating a conventional conical spindle seat as well as a slide valve inside the fuel nozzle, minimizing the sack volume and thus the risk of after-dripping. The configuration substantially reduces NOx emissions as well as smoke and CO emission but the expense of a slightly higher fuel consumption. **Fig. 5.1** shows the design of the mini-sac and slide fuel valve.

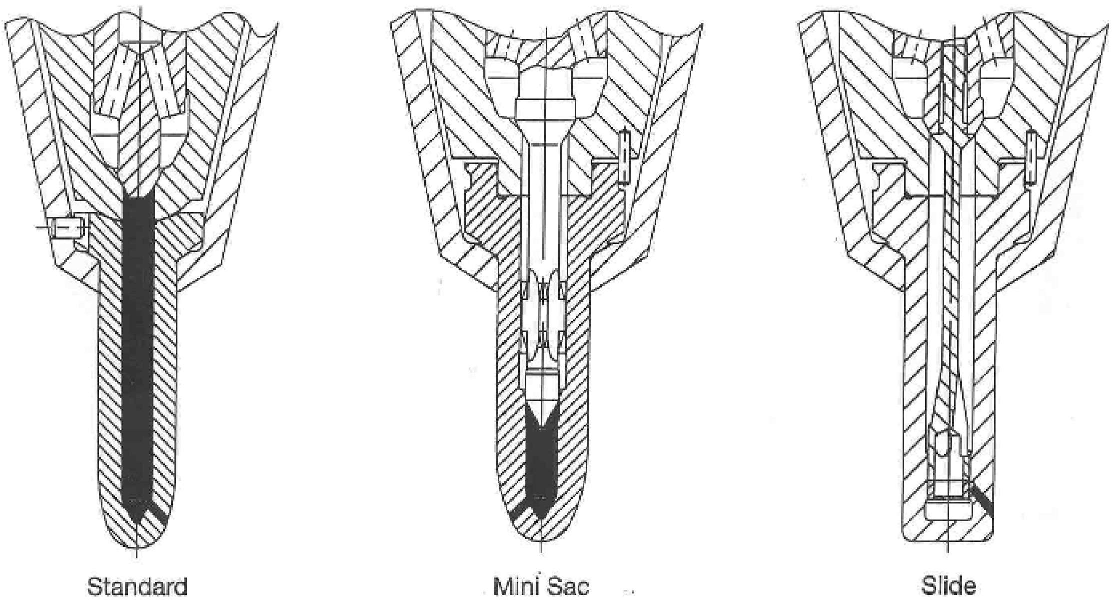

Fig. 5.1 Design of the mini-sac and slide fuel valve. Source: Kim J.H. 1999.

NOx formation from the diesel engine is estimated to be attributable to the generation of the local combustion field caused by the non-uniformity of the fuel distribution in the combustion chamber. Reduction of the NOx formation ratio has been obtained by increasing the number of injection holes of the fuel nozzle so that the non-uniform fuel distribution is changed to as uniform a combustion field as possible, and the combustion is free from the locally high temperatures.

As MER (1997, February) reported, “MAN B&W cites tests with a K90MC engine at 90% load which yielded the following results (NOx ppm/15% oxygen)”:

Standard fuel valve/nozzle: 1594ppm

Six-hole fuel nozzle: 1494ppm

Slide-type fuel nozzle: 1232ppm

As for multi-hole nozzle, a test was carried out with a standard fuel atomizer having 10 injection holes, and with a fuel atomizer having 14 injection holes while the injection angle and total area of the injection holes are the same, and a fuel atomizer with the changed nozzle sac capacity. When the number of injection holes is the same, little difference was shown in NOx value by size of the nozzle sac. In the standard condition, NOx is reduced by 14% if the number of the injection holes is changed from 10 to 14 while the fuel consumption was degraded by 0.9%. NOx was reduced by 16% while the fuel consumption is increased by 1%. The exhaust gas temperature was little changed. (Tonabe, Honda & Otani, 1999)

5.2.2 Retarded fuel injection

As can be seen in chapter 3, NOx formation is a function of the temperatures and of the partial pressure of oxygen and nitrogen at the location in the combustion zone with the highest temperature, and of the time span in which this happens. Retarding the start of injection, to reduce the firing pressure, is a well known and fairly simple way of reducing NOx emissions, which can be used on most engine types.

Primary NOx control methods aim at reducing the local peak temperatures in the combustion chamber. Reducing the firing pressure via injection retardation will readily both lower the peak temperature and the NOx emissions. However, it also reduces the maximum temperature and leads to a higher fuel consumption. For a long time, however, we thought we were doomed to accept the trade-off in fuel consumption caused by low-NOx adjustments. The big challenge has consequently been to combine low-NOx emissions with low fuel consumption.

Ignition Retardation can result in a 30% reduction of NOx emissions by reducing Tmax, as combustion is delayed from TDC. Residence time at high temperatures is also reduced, thereby contributing to NOx reduction. However, in addition to the increase in specific fuel consumption, this method can also increase particulates. Increased particulates can result in higher rates of turbocharger fouling as well as insulating deposits in the exhaust gas boiler. In spite of these disadvantages, the injection retardation do not require extra system elements, and therefore this measure is commonly used to optimize the emission behavior for on-road engines.(Leva, 1995)

Electronically controlled fuel injection and engine management systems will be further developed and will provide the ability to retain optimum combustion characteristics with regard to high energy efficiency and low emissions at all power levels and for varying fuel qualities. The electronic-hydraulic system on the engine can perform a pre-injection before the main injection. (Hadler, 1995)

5.2.3 High-pressure of fuel injection

An increased fuel injection rate leads to a short and distinct injection period. Injection valve opening pressure is raised to improve atomization at the start and stop of injection, and to maintain the higher pressure needed for a shorter injection period and reduced ignition delay. Consequently, this method lowers the maximum temperature in the cylinder, thus resulting in low NOx emission

According to Murayama (1994), a study shows that the injection pressure of 150-160MP with extremely retarded injection timing will result in smoke free combustion. To achieve smoke-free combustion without increased in specific fuel consumption, noise and vibration smaller injection nozzle diameters are necessary.

With smaller nozzle diameters, specific fuel consumption does not deteriorate despite the longer injection duration because atomization and turbulence improve mixing and so shorten the combustion duration. Pilot injection is introduced for the control of injection rate in the early stages of high-pressure injection. Even though direct NOx reduction by pilot injection is only a small amount, a simultaneous reduction of NOx and particulate can be obtained. 35% reduction of NOx and 39% reduction of particulate are possible without an adverse effect on fuel consumption.

5.2.4 The increased compression ratio

The low NOx combustion system is based on an optimized combination of compression ratio, injection timing and injection rate. The parameters affecting the combustion process are manipulated to secure a higher cylinder pressure by increasing the compression ratio.

According to Vogt (1995), the increased compression ratio is one of the most efficient measures which can easily be implemented both technically and in terms of costs. This is also beneficial to an improved ignition of heavy fuels of ever declining quality. However, the increase in compression ratio in connection with a reasonable design of the combustion chamber is subject to certain limits set by the stroke/bore ratio.

According to Wartsila Diesel, the compression ratio of the standard Vasa 32 engine was increased from 12 to 14:1 to secure a sufficiently high compression temperature. The smaller combustion space dictated reshaping of the piston crown and cylinder cover flame plate to allow for the fuel jets and good air/fuel mixing. A new piston was developed for the higher maximum firing pressure raised by 10 bar to 165 bar. (MER, 1997, June)

5.2.5 Reduction of the Overlap Period of Inlet/Exhaust Valve

When the inlet/exhaust valve overlap period is reduced by some degrees compared with an ordinary setting, the scavenging process will be strongly disturbed and instead of fresh air a relatively high amount of burnt gas will be trapped in the cylinder. This trapped gas acts as an inert gas for the following combustion and thus reduces the NOx formation. This method will have similar effects as exhaust gas recirculation method.

Unfortunately, there is not only the positive effect on NOx reduction by this measure, but also some other negative effects. Depending on the valve overlap, the exhaust gas temperature and the temperature of the exhaust valve will increase and perhaps exceed the limit for HFO-operation. Also the soot formation will increase and can exceed the visibility limit. A careful design of the combustion chamber and the injection components, such as injection pressure, injection shape and nozzle configuration, can diminish these negative effects.(Vogt, 1995)

Another similar alternative method is to retard the inlet valve closing timing. When the inlet valve closing timing is delayed and the actual compression ratio is reduced in a condition where the charged air temperature is kept constant, and the charged air pressure is increased, the compression temperature is dropped, and the combustion temperature is also dropped correspondingly, and NOx can be reduced. (Tonabe, Honda & Otani, 1999)

5.3 Water based method

Introducing water into the combustion chamber can reduce peak combustion temperature, thus reducing the amount of nitrogen oxides formed. This can be done by direct injection of water, by introduction of water by use of an emulsified fuel or by humidifying the scavenge air.

As The Motor Ship (2000, April) reported, "Both Wartsila NSD and MAN B&W have recently announced 'smokeless' medium- speed engines which use of water to reduce NOx levels and the amount of particulate. Wartsila NSD uses direct water injection through a single valve with two needles, while MAN B&W prefers fuel water emulsion. Mitsubish has three year's in-service experience of a medium speed engine with stratified fuel injection."

5.3.1 Direct water injection

Water injection into the combustion process reduces NOx formation. The combustion temperature peaks will decrease, thus reduce NOx. Water has a relatively high molar heat capacity and the introduction of water reduces the partial pressure of oxygen. The heat load is also reduced by the evaporation process, which consumes energy.

The NOx reduction potential for water direct injection method is typically 50-60%. With the direct water injection, fuel consumption will slightly increase. The water consumption is high up to 50% of the fuel consumption, and the operational cost is relatively low than the water emulsified fuel method. Investment costs for the special nozzles and control devices must be taken into consideration. Especially, the fresh water generation must be capable enough for the large amount of water consumption.

As the Marine Propulsion International (1999, July) reported, Wartsila NSD has developed and applied direct water injection (DWI), i.e. injection of water directly into the combustion chamber via a separate nozzle. Large amounts of water can be used, enabling a substantially higher NOx reduction level, 50-60%, than can be achieved with the alternative methods of water introduction. The key element of the design concept is the combined injection valve through which both fuel and water are injected. The same valve is used for operation in water injection and fuel injection. One needle in the combined nozzle is used for water injection, and the other for fuel injection. Water injection starts before fuel injection, in order to cool down the combustion space to ensure low NOx formation.

With this method, a high-pressure pump pressurizes the water to 200-400 bar. After filtration and dampening of the pressure pulses the water is fed, at the correct pressure, to the injectors via a regulating valve. For safety reasons the water supply into each cylinder incorporates a sensitive mechanical flow fuse which quickly shuts off the water in case of excessive water flow. Water injection and timing is electronically controlled and can be adjusted by programming the control unit from a keyboard. (MER, June, 1999)

5.3.2 Water emulsified fuel

It has been verified that water emulsification of the fuel oil can result in a significant reduction of NOx emissions. The influence of water emulsification varies with the engine type, but generally 1% of water reduces NOx by 1%. Emulsification is performed before the circulating loop of the fuel oil system, in a position in the fuel flow to the engine from which there is no return flow (Fig 5.2). Thus it is the fuel flow that controls the water flow. The flow can also be controlled by measuring the NOx in the exhaust gas. (MAN B&W, 1996)

According to Leva (1995), the test engines demonstrated that NOx reductions of up to 35% are possible with a fuel water emulsion of 50/50. The implementation of this technique requires a high capacity fuel handling system on the engine to maintain unaffected power output. Water rates in the 10% range have resulted in NOx reductions of between 6-12%.

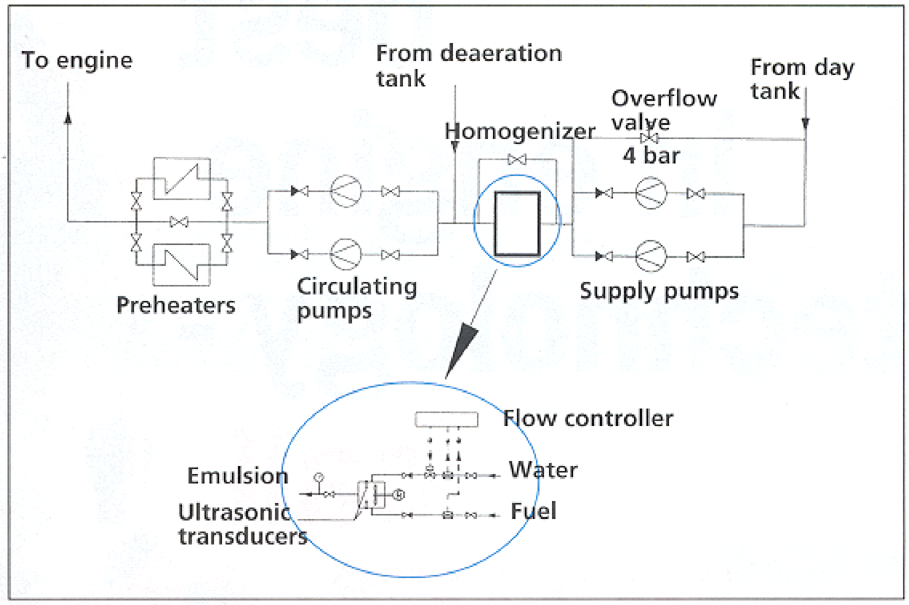

Fig.5.2 Water emulsification system on a low speed engine. Source: MER, 1997, May. pp.22

If a water based method is selected the fresh water capacity must be enlarged in most cases. A 14 MW engine installation may need 30 tons fresh water/day just for NOx reduction. This is well over normal demand e.g. on a cargo ship and must be considered as an additional cost. Also, the method of emulsification and subsequent stability of the emulsion are important to the efficiency of this method. (Schiff & Hafen,1998)

According to the MAN B&W (1996), it was verified years ago that water emulsification leads to a significant reduction of NOx with no effect whatsoever on the maintenance costs. A standard engine design permits the addition of some 20% of water at full load, thanks to the volumetric capacity of the fuel injection pumps, but this does not represent a limit from the combustion point of view.

The emulsification is done before the circulating loop of the fuel oil system, i.e. at a point in the fuel flow to the engine from which there is no return flow that controls the water flow. The addition could also be controlled by actually measuring the NOx in the exhaust. This would be the case if continuous monitoring of NOx was required. For vessels using emulsified fuel, a specifically designed safety system is built into the external fuel oil system so that an electrical black out on board will not influence the fuel /water emulsification stability, and the engine can be started up without changing to fuel without water.

According to the Motor Ship (2000, April), the fuel emulsification system favored by MAN B&W's IS (Invisible Smoke) engines use a homogeniser to mix fuel and water on the low-pressure side of the module. The increased volumes require larger diameter fuel pipes, and they must be able to withstand the higher pressure needed to ensure the water will not vaporize. Higher capacity fuel pumps are also required, and these impose greater loads on the camshaft. This makes retrofitting difficult, although the standard fuel pumps have some spare capacity that may be utilized. On the low-speed side MAN B&W has used ultra-sonic homogenisers to mix the fuel and water for some land-based engines.

With fuel water emulsion one or two very small water droplets are contained inside each fuel droplet. It take the peak off the heat release but leave the combustion duration unaltered. This provides the maximum NOx reduction for a given volume of water with least fuel penalty. As the Motor Ship (2000, April) reported, "A recent test on a 48/60IS engine showed NOx levels of around half the IMO limit by adding only 15% water. The usual rule is 1% water equals 1% NOx reduction. MAN B&W

says fuel consumption is 176 g/kWh and smoke emission only approaches the visibility limit when load is reduced to 25%. Previous tests with direct water injection showed a fuel consumption penalty of 4-5 g/kWh when 40-50% NOx reduction is required."

5.3.3 Stratified fuel-water injection

Water can be added to the combustion chamber through separate nozzles,by means of the stratified injection of water and fuel from the same fuel nozzle. Mitsubishi favors stratified fuel/water injection which uses a single injector with two inputs. A pilot injection of fuel is followed by water, fuel and water again, and ends with fuel. An electronically controlled hydraulic circuit is used to create and time the water 'insertions' to the fuel stream. The company says this system can be retrofitted without machining of the cylinder cover and can give up to 50% reduction in NOx without increasing the wear rates. A year-long trial onboard a 5,000 dwt training vessel fitted with a 6UEC52 engine showed the system to be reliable. (The Motor Ship, 2000, April)

5.3.4 Humidification

Humidifying the scavenging air is another way of introducing water into the combustion zone by means of water or steam. The NOx reduction potential in this case is about 20%, because the amount of water into the cylinders is restricted by the water dewpoint in the air manifold. However, too much water in the scavenge air may be harmful to the cylinder condition. (MER, 1997, February)

5.4 Exhaust Gas Recirculation (EGR)

Exhaust gas recirculation method means that exhaust gas, with a low oxygen content, is introduced into the combustion chamber by an independent blower. Some of the exhaust gas is cooled and cleaned before recirculation to the scavenge air side. When the combustion charge air contains less oxygen and the CO_2 has a higher heat capacity than nitrogen and oxygen, lower peak temperatures can be expected using this method.

Its effect on NOx formation is partly due to a reduction of oxygen concentration in the combustion chamber, and partly due to the content of water and carbon dioxide in the exhaust gas. The high molar heat capacities lower the peak combustion temperature which curbs the formation of NOx. (MER, 1999, May)

In principle, exhaust gas can be recirculated both before and after the turbocharger, as shown in Fig.5.3, but in both cases the gas has to be cooled and cleaned. EGR can be a severe drawback, especially on board a ship, as influent from the exhaust gas which contains sulphur in a non-disposable form as well as unburned hydrocarbons, soot and ash. EGR could be the right solution in process, in refineries etc, and the concept is still being studied for shipboard use. (MAN B&W, 1996)

According to MAN B&W (1996), the partial pressure of the reagents of oxygen and nitrogen can only be influenced by changing the specific amount of air allowed into the engine per kWh, or by changing the ratio between the two. Changing the specific amount of air for a normally-controlled engine does not reduce the pressure, as the firing pressure control system will adjust to the specified level, so the only effect will be a higher heat load on the combustion chamber when the air amount is reduced. NOx will hardly be influenced at all. The ratio between oxygen and nitrogen can be changed by exhaust gas recirculation (EGR). If we recirculate 15% of the exhaust gas the resulting oxygen concentration in the intake air will be reduced from 18-21%, and the impact on NOx formation will be significant.

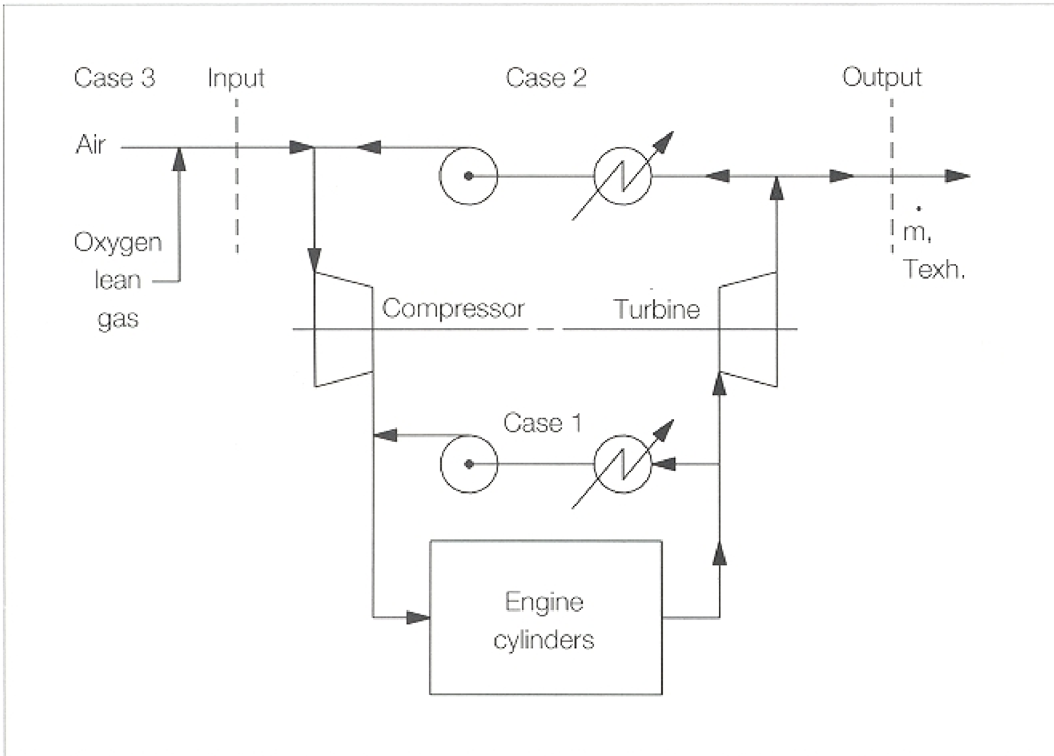

Fig.5.3 Layout of EGR system. Source: MER, 1999, May, pp.21.

The disadvantages of this method are increased smoke and particulate quantities and a potential for increased turbocharger and exhaust gas boiler deposition. Fouling of these components will result in reduced thermal efficiency. Moreover there are good possibilities of low temperature corrosion in the gas cooler and its downstream components. Due to poor fuel quality, especially in the marine diesel engine, the EGR system can be problematic because it increases soot emission and can cause increased engine wear. This system, however, is not currently commercially available for HFO burning, it is widely used in automotive applications. (Leva, 1995)

5.5 Selective catalytic reduction

Selective Catalytic Reduction (SCR) is the most well known method of exhaust gas after treatment so far. Typically, very high NOx reduction levels, i.e 90-95%, are achievable. Therefore, it can be applied if further stringent NOx reduction is regulated. The reduction of the nitrogen oxides takes place by injecting ammonia or urea into the exhaust gas at a temperature of 320-420 ˚C. When the ammonia/exhaust gas mixture is passing through a catalyst the nitrogen oxides, which primarily consist of NO and NO_2, are converted according to the following reaction schemes:

$$4NO + 4NH_3 + O_2 \leftrightarrow 4N_2 + 6H_2O$$

$$6NO_2 + 8NH_3 \leftrightarrow 7N_2 + 12H_2O$$

As can be seen from the above schemes, this method involves no disposal problem because the conversion of the nitrogen oxides does not create any secondary pollution, as the products formed are only nitrogen and water vapour.

The degree of NOx removal depends on the amount of ammonia or urea added (expressed by the NH_3/NOx ratio). At high NH_3/NOx ratio, high degree of NOx removal can be obtained, but at the same time the amount of unused ammonia (called the NH_3 slip) in the cleaned flue gas will increase. It is desirable that the concentration of unused ammonia in the cleaned gas is as low as possible, because of cooling of the flue gas in the downstream boiler or heat exchanger, the ammonia may react with SO_3 in the exhaust gas and lead to fouling of the heating surface by ammonium sulphates. (Sondergaard, 1995)

To solve the above mentioned problem MAN B&W introduced following technique: the amount of NH_3 injected into the exhaust gas duct is controlled by a process computer, dosing the NH_3 in proportion to the NOx produced by the engine as a function of engine load. The relationship between the NOx produced and the engine load is measured during test runs on the engine test bed. The relationship obtained is programmed into the process computer and used for the feed-forward control for the NH_3 dosage. The ammonia dosage is subsequently adjusted for bias by a feed-back system on the basis of the measured NOx outlet signal. A schematic layout of the system design is shown in Fig. 5.4. (MAN B&W, 1996)

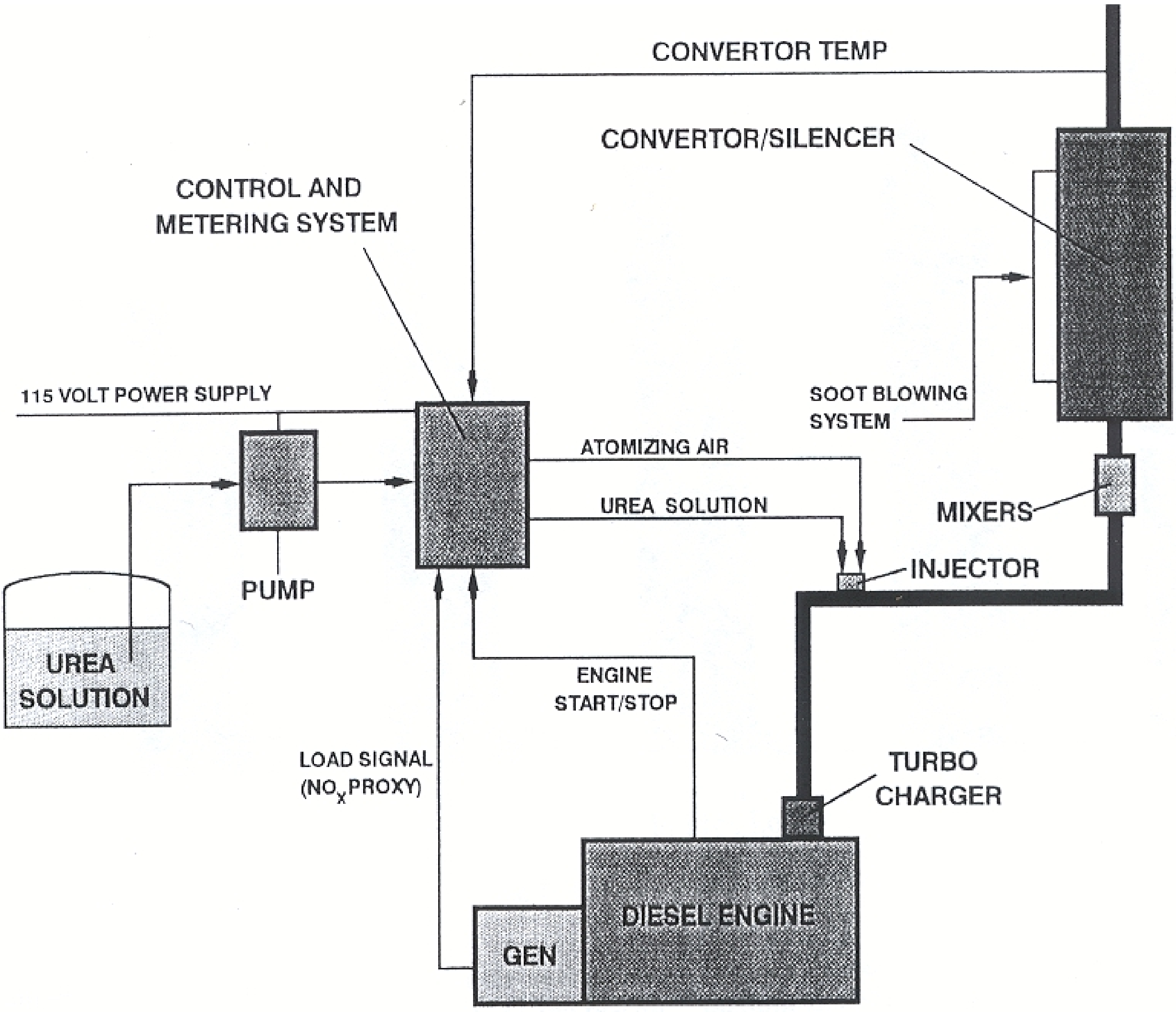

Fig. 5.4 Schematic layout of SCR system. Source: Wright & Burlingham, 1996, pp.48.

The SCR reactor contains several layers of catalyst. The catalyst volume and the size of the reactor depend on the activity of the catalyst, the desired degree of NOx reduction, the NOx concentration, the flue gas pressure and the acceptable NH3 slip. The amount of catalyst can be expressed by the term velocity (abbreviated NHSV), which is defined as the number of cubic meters of exhaust gas per hour which are treated per treated per cubic meter of catalyst. Fig. 5.5 shows an example of how the NOx reduction and the NH3 slip vary with the NH_3/NOx ratio for two different catalyst volumes (NHSV).

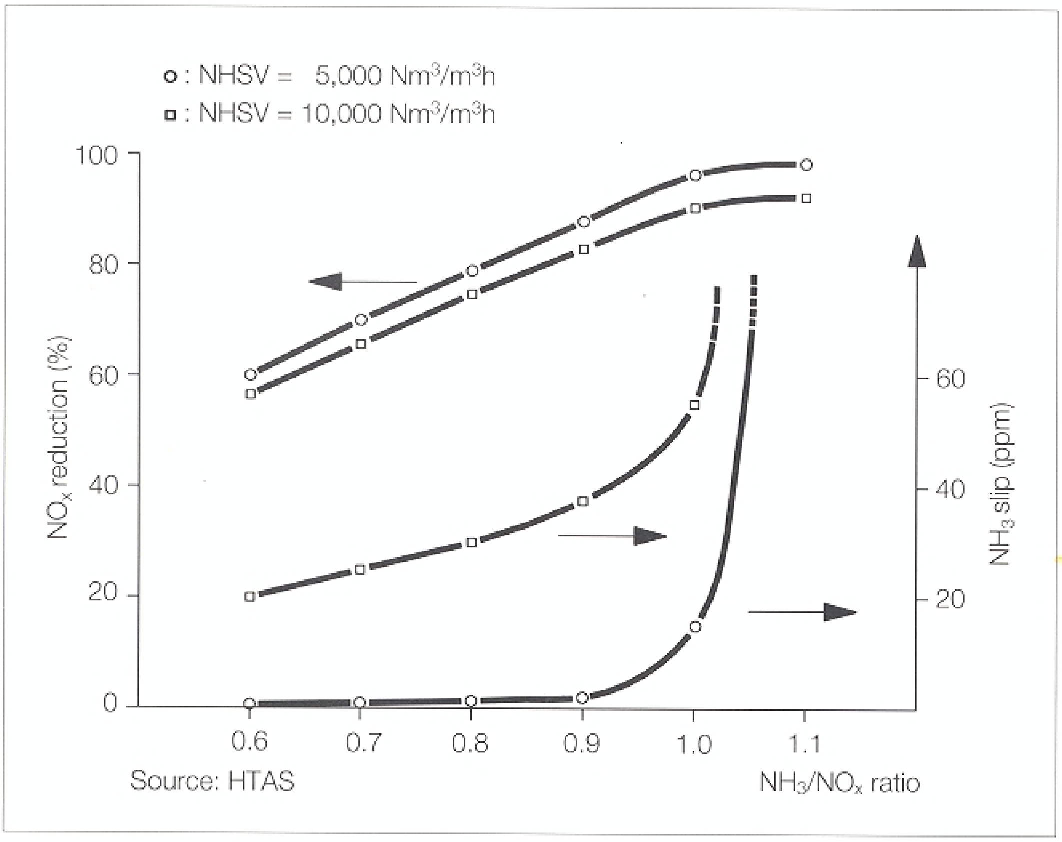

Fig. 5.5 Calculated NH_3 slip and NOx reduction as function of NH_3/NOx ratio. Source: MAM B&W, 1996, pp.11.

As can be seen, both the NOx reduction and the NH_3 slip increase with an increasing NH_3/NOx ratio. It can also be seen that the same NOx reduction can be obtained by using only half the catalyst volume just by increasing the NH_3/NOx ratio a few percent. At the same time the ammonia slip increases considerably. Therefore, the maximum acceptable ammonia slip has a strong influence on the amount of catalyst required. Normally, the SCR units are designed for a steady state ammonia slip of 5-10 ppm. (MAN B&W, 1996)

SCR also needs a certain minimum temperature to operate correctly. The SCR principle is based on a reduction of NOx by catalytic reactions with ammonia or urea in a temperature range of 320-450 ˚C. This temperature is dependent on the sulphur content of fuel according to table 5.2. Too low temperature and high sulphur content wll inrease the risk of the catalyst blocking by ammoniumsulphate. The temperature issue must be considered especially on the engine choice for diesel-electric ships as constant speed engines have decreasing exhaust temperature at decreasing load. This may, in some cases, lead to a too-low temperature for effective SCR operation and later modifications for the turbo-charging system. (Schiff & Hafen,1998)

Table 5.2 Example of recommended minimum exhaust gas temperature in catalyst Inlet depending on fuel contents. Source: Schiff & Hafen, 1998, pp.148.

Sulphur content in fuel	0.5%	1%	1.5-2%	2.5-3%
Minimum catalyst inlet temperature	320 degC	325 degC	330 degC	335 degC

With the lower exhaust temperatures seen in low-speed engines, any catalyst has to be fitted upstream of the turbocharger. The temperature of the catalyst becomes more important if fouling is to be avoided, as the sulphur content rises in the fuel.

In principle, the SCR reactor can be introduced either before or after the turbocharger of both 2-stroke and 4-stroke diesel engines. The SCR reactor must be placed before the turbocharger for 2-stroke diesel engines because the exhaust gas temperature is too low after the turbocharger. In 4-stroke diesel engines the SCR reactor has to be placed after the turbocharger because the exhaust gas temperature is too high before the turbocharger. (Sondergaard, 1995)

As the Motor Ship (2000, April) reported: "Recently, however, evidence is growing that SCR manufacturer' are right in their assertions that sulphur in HFO need not damage or block the catalyst. For instance on the vessel "Finn Eagle" burnt HFO with 2.6% sulphur during the delivery voyage but this did not cause a problem. Also the auxiliary engines aboard "Silja Sympohony" and "Silja Serenade" (run on low-sulphur 0.5% HFO) have had catalysts fitted for five years and recent checks show they are performing as well as they did when new."

SCR is not always the best solution in marine applications because it can be bulky and expensive. The SCR causes high investment costs and high operating costs due to these high costs involved in external measures or complicated handling such as the tank for water injection, and for reasons of reliable effectiveness and safety of operation. SCR has an average volume of 1 m^3/MW and weight of 1kg/kW for medium speed engine. Additionally dedicated urea storage tanks, pumps and injection and control systems must be also provided. Urea consumption is about 20g/kWh for a medium speed engine and 30g/kWh for a low speed engine when the target NOx value is 2g/kWh. (Schiff & Hafen,1998)

In terms of size, modern low-NOx engines have made it possible to introduce a compact combined silencer SCR unit, no larger in size than a conventional silencer. There are several diesel engine power plants equipped with the SCR technique in operation. The catalyst volume and the reactor will be smaller when placed before the turbocharger due to the higher pressure, but introduction of the SCR reactor in this position may be more difficult.

When applying the SCR process for marine diesel engines, the catalyst and the reactor will be exposed to vibrations of a higher degree than on land based power plants. The catalyst and catalyst cassettes therefore have to be specially designed to avoid damage to the catalyst by engine vibrations.

Marine diesel engines are subject to relatively fast load changes. This type of operation puts a higher demand on the speed of controlling the ammonia addition, because fast load changes may otherwise lead to peaks either in the NOx emission or in the NH_3 slip. (Sondergaard, 1995)

Chapter 6
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

In past time, the maritime industry paid little attention to air pollution. That attitude was changed when IMO adopted Annex VI to MARPOL 73/78. Annex VI is concerned with the prevention of air pollution from ships. Because of the transboundary effect of air pollution, and the compelling need for many countries to tackle the growing problems of its effects on human health and global environment, IMO agreed to recommend the early implementation to reduce the emission of NOx from new marine diesel engines. It has also been agreed that, in order to avoid unacceptably long delays in the entry into force of Annex VI, the MEPC will review the impediments to entry into force of the Protocol and any initiate necessary measures to alleviate those impediments, as a matter of urgency, if it has not entered into force by 31 December 2002. Therefore, there is no doubt that Annex VI will enter into force in the future.

Annex VI of MARPOL 73/78 deals with a wide range of air pollution control matters including regulations on halons, Hydrochlorofluorocarbons (HCFCs) and other ozone depleting substances, Nitrogen oxides (NOx), Sulphur oxides (SOx), volatile organic compounds (VOCs), shipboard incinerators and fuel oil quality. However, the main focus has so far been on reducing the NOx and SOx emissions, because the IMO regulations call for a 30% reduction in NOx emissions and a 50% reduction in SOx emissions compared with current levels.

Annex VI to MARPOL 73/78 requires the survey of engines and equipment to be conducted in accordance with the NOx Technical Code. When the Protocol of 1997 enters into force, the requirements of the NOx emission restriction will be retrospectively applied to each diesel engine with a power output of more than 130 kW, which is installed on a ship or which undergoes major conversion on or after 1 January 2000.

According to the NOx Technical Code, all engines within Reg.13 need the Engine International Air Pollution Prevention Certification (EIAPP Certificate). This certificate will be one of the key requirements of issuing the International Air Pollution Certificate (IAPP Certificate) for the ship. However, the new Annex VI has not come into force yet, so guidelines have been introduced to solve this problem by issuing a sort of interim certificate. The authorized organization (e.g. Classification Societies) by the flag state can issue the Statement of Compliance (SOC Certificate). The SOC Certificate will be transformed into the EIAPP Certificate when the new Annex VI enters into force.

To avoid certification testing of every engine for serially manufactured engines, the engine family or the engine group concept may be applied. In such a case, the testing is required only for the parent engine, which is the representative of an engine family or engine group. If the NOx emission values meet the requirements, the NOx relevant engine parameters have to be documented in the technical file. This technical file of the parent engine has to be the same for all member engines. Within an engine family or engine group the SOC Certificates or EIAPP Certificate will be issued to the parent engine and to every member engine.

NOx formation occurs by reaction between nitrogen and oxygen in the combustion air (thermal NOx), by reaction between exhaust gas hydrocarbon and combustion air oxygen (prompt NOx) and by reaction between nitrogen bindings in fuel (fuel NOx). Thermal NOx is decisive for the total emission and all the abatement methods are targeted to reduce that component. The formation of NOx in the combustion chamber is mainly influenced by temperature and oxygen concentration: the higher the temperature and the longer the residence time at temperature, the more the thermal NOx will be created. Therefore, low speed engines with slow burning processes have the highest emission due to the long time the oxygen is allowed to react with nitrogen.

Since or even long before the time the Regulation 13 concerning emission limits of Annex VI to MARPOL 73/78 NOx were chosen, the marine industry has continuously researched emission control technologies for marine diesel engines. Engine manufactures are exploring various ways to develop practical NOx reduction technologies. There are the primary methods such as retard injection, fuel nozzle modification, compression ratio, water direct injection, water emulsification, electronic controls and exhaust gas recirculation (EGR) and secondary methods such as selective catalytic reduction (SCR).

Primary methods are aimed at reducing the amount of NOx formed during combustion. The basic aim of most of these measures is to lower the maximum temperature in the cylinder, since this results inherently in a lower NOx emission. The low NOx combustion process is based on a combination of compression ratio, injection timing and injection rate. Therefore, when considering the NOx reduction method, it should be taken into account that all the different NOx reduction methods may affect each other.

6.2 Recommendations

When choosing a NOx reduction system, concerns over engine emissions and, ultimately, legislation in its various forms, will inevitably require all operators to accept some compromise between minimum environmental impact and optimum machinery cost, performance economy, thermal efficiency of the engine, simplicity and maintainability. Therefore, the choice of NOx reduction system must be initiated from the requested NOx limit level as indicated in Chapter 3. Thus no additional cost penalty will be expected. With current NOx limits, the engine fine tuning method, e.g. fuel valve modification, retard injection and compression ratio, is sufficient and have already been feasible to meet NOx limits. Then, if there will be more stringent NOx limits in the future, the next best solution will be some of the water-based systems. If the strictest proposals should be the regulation, then the only possible choice is based on the exhaust gas after-treatment method such as the compact SCR

Retarding the injection is a relatively simple and cheap way while it involves an inevitable fuel penalty as is the case with other primary methods. However, in addition to the increase in specific fuel consumption, this method can also increase particulates. In spite of these disadvantages, the injection retardation does not require extra system elements. Another similar option is fuel nozzle modification which is one of currently widely used methods. This method reduces NOx emissions as well as smoke and CO emission, but may result in some increase of specific fuel consumption. Modifications to an engine could also be made to cut NOx, e.g. changes of the combustion chamber form, compression ratio and inlet/exhaust valve timing.

Introducing water into the combustion chamber can reduce peak combustion temperature, thus reducing the amount of nitrogen oxides formed. This can be done by direct injection of water or by introduction of water by the use of an emulsified fuel. If a water based method is selected, the fresh water capacity must be enlarged in most cases. The NOx reduction potential for the direct water injection method is typically 50-60%. With the direct water injection method, fuel consumption will slightly increase, and the water consumption is high, but the operational costs are relatively low. Investment costs for the special nozzles and control devices must be taken into the consideration. Especially, the fresh water generator must have capacity enough for the large water consumption. With fuel water emulsion, one or two very small water droplets are contained inside each fuel droplet, which takes the peak off the heat release. This provides the maximum NOx reduction for a given volume of water with least fuel penalty. However this method needs an additional special system to mix fuel and water on the low-pressure side of the module. The increased volumes require larger diameter fuel pipes and they must be able to withstand the higher pressure needed to ensure the water will not vaporize. Investment costs for that special system also must be taken into consideration.

Considering the wider legislative possibilities and taking a longer term view, the SCR represents a potentially viable option. Typically, very high NOx reduction levels, i.e. 90-95%, are achievable. However, the SCR causes high initial investment costs. In addition, the SCR system has a relatively high operating cost, mainly due to the urea or ammonia consumption and catalyst replacement. In terms of size, SCR has been considered as being bulky, but recently modern low-NOx engines have made it possible to introduce a compact combined silencer SCR unit, no larger in size than a conventional silencer.

Furthermore, in certain applications the adoption of such measures may have additional benefits to that of emission reductions. Ship owners may also wish to take into consideration financial incentives which are available to ships visiting certain parts of the world, e.g. Sweden and United States, where reductions in port and fare way fees is offered in return for ships complying with more stringent engine emission limits. For commercial operators, assessing the balance between paying high port dues and fitting emission controlled engines may be relatively simple, especially where standard ship operating patterns are maintained.

In most cases, NOx emission reduction will inevitably result in additional costs to ship owners. As mentioned above, there are several choices which could be selected to meet the NOx limits. However, it will be left to the ship owners to calculate, analyze and select their best possible option with regard to initial investment cost, operation cost, simplicity and maintainability, according to a ship's particular mode of operation. Also, it is ultimately the ship owner's responsibility to ensure that his vessel complies with the NOx regulation.

As indicated in Chapter 3, the compliance of each diesel engine which is installed in a ship constructed on or after 1 January 2000 is not unenforceable until such time as the Annex VI enters into force. Furthermore, the issuance of IAPP Certificate and the initial survey of such engines may be delayed by up to 3 years. However, earlier compliance with the regulation is recommended to ship owners. It is much easier and more cost-effective to order equipment to be supplied in accordance with coming regulations than attempt to upgrade existing equipment to meet standards for which it was not originally designed. In addition, if an engine cannot be pre-certified on a test-bed, the on-board test has to fully meet all the requirements of a test-bed procedure; this means that, in such cases, the on-board test may cause huge problematic matters due to practical difficulties to meet the full test bed procedure on board a ship.

Similarly, although an engine has been certified the Statement of Compliance (SOC) in accordance with the NOx Technical Code at the time of its manufacture, evidence of continuing compliance may not be required until such time as the initial survey for issuance of the IAPP is carried out. However, in order to avoid the retrospective regulatory compliance problems associated with NOx emission, the owner should ensure that the ship will be maintained in continuing compliance with the relevant NOx emission limits, with documentary evidence such as "record book of engine parameters" and "technical documentation of an engine component modification"

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