WATER BASED TECHNOLOGIES USED ON DIESEL ENGINES FOR THE REDUCTION OF NOₓ EMISSIONS

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Abstract: There is international effort focused on the reduction of gaseous emissions that contribute to global warming and atmospheric pollution. Ships are responsible for a portion of this pollution contributing to environmental degradation. Exhaust from marine diesel engines includes air pollution in the form of nitrogen oxides, carbon oxides, unburned hydrocarbons and particulate matter. These have been proven to have a negative impact on health and the environment. Increasingly, these marine sources are being targeted for reduction.

Keywords: pollution, fuels, water, burning.

1. Introduction

NOₓ formation in diesel engines is a very complex process and despite years of experimental research and modeling work it is still not fully understood. The current understanding of this process comes from direct measurements as well as study of flames under simplified conditions. This is then linked to the existing knowledge of diesel combustion.

This paper will present the water based NOₓ emission control technologies used on marine diesel engines. Specifically the following technologies:
- Humid air motor (HAM);
- Combustion Air Saturation System (CASS);
- Direct water injection (DWI);
- Saturation air motor (SAM).

The intent of the paper is to explain the processes, mechanisms, and impacts of water introduced in the diesel engine, on NOₓ emission reduction and engine operation.

2. NOₓ Formation

There are a number of different formation mechanisms responsible for NOₓ in combustion processes. The relative importance of these different mechanisms is strongly affected by the temperature, pressure, flame conditions, residence time and concentrations of key reacting species.

2.1. Thermal NO

The thermal mechanism, also known as "extended Zeldovich mechanism", is responsible for the majority of NOₓ emissions from diesel engines when peak combustion temperatures exceed 2000 K.

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Since temperatures of this magnitude are desirable to maximize engine efficiency, this mechanism has been studied extensively and is fairly well understood. The three chemical reactions that are important in this mechanism are:

\[ O + N_2 = NO + N \]  
\[ N + O_2 = NO + O \]  
\[ N + OH = NO + H \]

The overall reaction rate for this mechanism is slow and it is very sensitive to the temperature. As a consequence, thermal NO only appears in significant quantities in the post combustion. Also, the actual NO concentration from this mechanism deviates significantly from equilibrium concentrations. This gives this mechanism a very strong time dependence that is important for low speed engines.

### 2.2. Prompt NO

The prompt NO mechanism, also known as the "Fenimore mechanism", is very rapid and results in NO formation in the combustion zone. The most important pathway for prompt NO is initiated by the rapid reaction of hydrocarbon radicals from the fuel with molecular nitrogen, leading to the formation of amines or cyano compounds that subsequently react to form NO. The most important initiation reaction for prompt NO is:

\[ CH + N_2 = HCN + N \] (4)

Subsequent rapid conversion to NO is strongly affected by O and OH. Prompt NO is most significant when combustion occurs at fuel concentrations higher than stoichiometry where there is a high concentration of hydrocarbon radicals to form HCN and the concentrations of O and OH are still high enough to cause the HCN to proceed to NO through the following reaction sequence:

\[ HCN + O = NCO + H \] (5)

\[ NCO + H = NH + CO \] (6)

\[ NH + H = N + H_2 \] (7)

\[ N + OH = NO + H \] (8)

### 2.3 N\(_2\)O pathway

Another NO formation mechanism important in combustion is the N\(_2\)O pathway. The initial reaction for this pathway is the three body reaction:

\[ O + N_2 + M = N_2O + M \] (9)

While N\(_2\)O generally reverts back to N\(_2\), this is not always the case. Under conditions where the air/fuel ratio is lean, NO can form through either of the following two reactions:

\[ N_2O + O = NO + NO \] (10)

\[ H + N_2O = NO + NH \] (11)

This NO formation route is fuel and pressure dependent. At higher pressures and lower temperature, the three-body initiation becomes competitive with the \( O + N_2 \) reaction in the thermal mechanism. These are the most important formation mechanisms.

### 3. Regulations

There are a number of national and international regulatory organizations that propose limitations on NO\(_x\) as well as other harmful emissions. The International Maritime Organization (IMO), through the International Convention for the
Prevention of Pollution from Ships (MARPOL, Annex VI) regulates this on a global level. They have developed an approach to reducing green house gas (GHG) emissions, including NO\textsubscript{x}. Member countries of the IMO must therefore adhere to the regulations that they have put forth. However, some organizations have committed to adopting regulations that are more stringent.

The MARPOL, Annex VI, NO\textsubscript{x} emission limits are:

<table>
<thead>
<tr>
<th>Emissions limits</th>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine Speed (n)</td>
<td>NO\textsubscript{x} [g/kWh]</td>
</tr>
<tr>
<td>$n &lt; 130$ rpm</td>
<td>17.0</td>
</tr>
<tr>
<td>$130$ rpm $\leq n &lt; 2000$ rpm</td>
<td>$45 / n^{0.2}$</td>
</tr>
<tr>
<td>$n \geq 2000$ rpm</td>
<td>9.8</td>
</tr>
</tbody>
</table>

**Fig. 1 Emissions resulted from the diesel engine**

4. NO\textsubscript{x} Reduction

4.1. Intake Air Humidification

Of the different approaches for introducing water into the combustion chamber, humidifying the intake air has the potential to provide the greatest reductions in NO\textsubscript{x}. Water/fuel (W/F) ratios from 1 to 3 are possible (depending on charge air temperature) with this approach if the energy for water evaporation is provided by waste engine heat from either the exhaust or the cooling system.
A number of approaches for intake air humidification have been attempted. While there are some differences in the approaches, the most successful intake air humidification systems take significant steps to ensure that only water vapor enters the cylinder and that liquid water does not carry over into the cylinder and cause cylinder liner corrosion problems. In order to get high NO\textsubscript{x} reductions, this often means that the humidity of the air is near saturation as it enters the engine and that the intake manifold air temperature is as high as the engine can tolerate.

\textit{Munters} has the propriety of the first intake air humidification system, named the Humid Air Motor (HAM).

The basic design and principles of the \textit{Munters} Humid Air Motor is described in one of their patents. Next figure shows a diagrammatic of the HAM. A humidification tower is placed between the intake air compressor and the engine. Water that is pre-heated with waste engine heat is sprayed from nozzles at the top of the column into the air flow entering from the bottom. An amount of water far in excess of that required to saturate the air is supplied. Only 5\% to 10\% of the water sprayed into the tower evaporates. Water that does not evaporate into the air is collected at the bottom and re-circulated. Supplying excess heated water accomplishes two things. It makes the system self-regulating. The amount of humidity added to the intake air, assuming that the tower is sufficiently sized to allow saturation of the air, is governed by the temperature and pressure of the air during the humidification process. The excess heated water also provides heat for the evaporation process. This minimizes the temperature drop of the air in the humidification tower ensuring that the humidity of the air stays as high as possible. Also by supplying excess water that has been pre-heated from waste engine heat, use of steam that would otherwise need to be generated from higher temperature heat sources can be avoided.

The HAM process designed by \textit{Munters} was first bench tested on a MAN B&W 3V40/50 prototype 4 stroke medium speed diesel engine in the research and development facilities of S.E.M.T. Pielstick in-service verification was carried out in co-operation with Viking Line on one engine (12 PC2.6, 5,750 kW) onboard the RoRo ferry "Mariella" operating in the Baltic Sea. The HAM system was installed on main engine No. 1 in the summer of 1999. NO\textsubscript{x} reductions of 60 \% were claimed with a final certification value of 4.4 g/kWh NO\textsubscript{x}. The humidification vessel is 4 m long, 1.4 m in diameter and has 3 humidifier stages which humidify and cool the air from approximately 160 °C at the outlet of the compressor down to approximately 65-70 °C. The air reaches about 98 \% relative humidity which corresponds to an absolute humidity in the range of 60 to 80 g water/kg dry air. Sea water is used and re-circulated until the salt content increases by about 6 \%.

During the year 2000, \textit{Marioff}, a developer of water mist systems for fire suppression, started to develop the Combustion Air Saturation System (CASS). The key to this system development is the spray nozzle and control system. Air and water in varying ratios are supplied to the nozzle providing water droplet sizes around 50 to 200 µm and W/F ratios from 0.5 to 2.5. The air/water ratio supplied to the nozzle is varied so that the water droplet size is a function of engine load with the smallest droplet sizes produced when the engine load is low and good evaporation is more difficult. Early in 2001, a press release was issued that stated that \textit{Marioff} and \textit{Wärtsilä} had formed a partnership. During 2001 and early 2002, full-scale engine tests were carried out at \textit{Wärtsilä} in Finland.
Reduction of NO\textsubscript{x} to less than 3 g/kWh was claimed at the time for starting values of 10-15 g/kWh.

4.2. Direct Water Injection

This method of NO\textsubscript{x} reduction can be carried out with two slightly different variations by injecting water directly into the cylinder head via a separate nozzle, or by alternating fuel and water through a specially designed nozzle. Both of these techniques for adding water are based on the same fundamental concept: injecting water into the system at the combustion cylinder reduces high peak temperatures, which in turn reduces NO\textsubscript{x} formation.

The primary benefit of injecting water directly into the cylinder through a separate nozzle is that both the amount of water and the timing that the water is injected are variable and can be controlled separately from the fuel. Similarly, the amount of water injected in sequence with fuel from a single nozzle can be varied although the timing of injection is dependent on the W/F ratio. In general, these methods allow for substantial amounts of water to be added to the system, which can, in turn, lead to large reductions in NO\textsubscript{x} emissions. Another attribute of direct water injection into the cylinder is that liquid water can usually be directed towards the flame more efficiently.

Fig. 2. Humid Air Motor System

Fig. 3. Combined Nozzle Used by Wärtsilä
Current DWI systems by Wärtsilä boast NO$_x$ emission reduction of 50-60% (without adversely effecting power output), which translates to 4-6 g/kWh of NO$_x$ (for Marine Diesel Oil) and 5-7 g/kWh (for Heavy Fuel Oil). The system typically operates at a W/F ratio of 0.40 to 0.70.

The Wärtsilä technique for DWI also allows for water shut-off, as the water system is controlled separately from the fuel, so that the engine can be operated with or without water injection. Wärtsilä claims that both investment and operational costs are low and that space requirements for the system is minimal, allowing for easy installation.

4.3. Saturation Air Motor

The SAM system for saturation and cooling of the compressed air from the compressor side of the turbocharger has been tested from an engine performance point of view on the 4T50ME-X research engine. The tests gave promising results with regard to the ability of reducing NO$_x$ emissions. However, long-term influence of the SAM system on engine components as well as operation with a salt content of up to 3.5% could not yet be investigated.

The SAM system has a sea water injection stage, where a surplus of sea water is injected for saturation and cooling of the hot air from the compressor. The sea water stage will provide a near 100% humidification of the scavenge air and supply all of the water for humidification.

The freshwater stages 1 and 2 will be near temperature neutral to the scavenge air and create a small freshwater production depending on the operation parameters chosen. The freshwater stages only act as cleaning stages for removal of any salt which may pass with the air from the sea water stage. A continuous accumulation of salt in the freshwater stages would eventually cause the salt content to reach an unacceptably high level. This is counteracted by cooling the saturated air with the air cooler and generating some extra freshwater for stage 2. The extra freshwater is then sent upstream on the tank side of the SAM system, as illustrated in the figure. Thereby the content of salt in the freshwater stages can be controlled.

A vital aspect in ensuring that no or a minimum of salt gets into the engine is a good efficiency of the water drainage. All the water drainage systems are, subsequently, based on the slug principle followed by mechanical water separation in metal foam. Measurements on a small pilot plant has indicated an efficiency as high as 99.6% with this solution. The efficiency of the water drainage for the sea water and fresh water stages is 99%.

5. Conclusions

The precursors to the formation of nitrogen oxides during the combustion process are nitrogen and oxygen. Together these compounds comprise 99% of the engine intake air. Oxygen will be consumed during the combustion process, with the amount of excess oxygen
available being a function of air/fuel ratio
which the engine is operating under. The nitrogen remains largely unreacted in the combustion process; however a small percentage will be oxidized to form various oxides of nitrogen. The nitrogen oxides \((NO_x)\) which can be formed include \(NO\) and \(NO_2\), while the amounts are primarily a function of flame or combustion temperature and, if present, the amount of organic nitrogen available from the fuel.

![Fig.5. S.A.M. System](image)

It is also a function of the time the nitrogen and the excess oxygen are exposed to the high temperatures associated with the diesel engine’s combustion process. In other words, the higher the combustion temperature (e.g., high peak pressure, high compression ratio, high rate of fuel delivery, etc.), the greater the amount of \(NO_x\) formation. A low-speed diesel engine, in general, tends to have more \(NO_x\) formation than a high-speed engine. \(NO_x\) has an adverse effect on the environment, causing acidification, formation of ozone, nutrient enrichment, and contributes to adverse health effects globally.

Depending on the specific design of the particular engine, different \(NO_x\) modifications and adjustments are possible and usual. These include the engine parameters as follows: injection timing, injection nozzle, injection pump, fuel cam, injection pressure for common-rail systems, architecture of the combustion chamber, compression ratio, turbocharger type and build, charge air cooler, charge air pre-heater, valve timing, \(NO_x\) abatement equipment (water injection), \(NO_x\) abatement equipment (emulsified fuel, fuel/water emulsion), \(NO_x\) abatement equipment (exhaust gas recirculation), \(NO_x\) abatement equipment (selective catalytic reduction).
References

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7. Wärtsilä: *Technical Documentation*;