

# TECHNOLOGIES USED ON MARITIME BOILERS FOR THE REDUCTION OF NO<sub>x</sub> EMISSIONS

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**Abstract:** *This paper presents the Flue Gas Re-circulation (FGR), Water and Steam Injection (WSI), Air and Fuel Staging (AFS), and Post-Combustion technologies designed to reduce emissions from maritime boilers, usually used on steam power plants. The intent of the paper is to explain the processes, mechanisms, and impacts of the technologies on NO<sub>x</sub> emission reduction and boiler and turbine operation.*

**Keywords:** *pollution, fuels, water, burning, boiler.*

## 1. Introduction

An understanding of the mechanisms and chemical reactions that produce pollutant emissions have enabled engineers and scientists to develop techniques for reducing emissions of these pollutants. Along with carbon-monoxide (CO), sulfur oxides (SO<sub>x</sub>) and particulate matter, NO<sub>x</sub> emissions have been identified as contributors to acid rain and ozone formation, visibility degradation and human health cancers. As a result, CO, SO<sub>x</sub>, NO<sub>x</sub> emissions from most combustion sources are regulated and required some techniques of control. Several studies have investigated the application of these techniques to the maritime boiler equipment.

In maritime boilers, the most common control techniques include: application of combustion control systems capable of maintaining low levels of excess air with safe limits for CO; upgrading of airflow distribution systems for stoker fired boilers; reduction of fuel bound nitrogen in residual fuels by blending distillate oil; use of modified oil gun nozzle tips for residual

oil combustion; application of diluents for gaseous fuel combustion, including air, steam and flue gas; installation of burners designed to combust fuel at low NO<sub>x</sub> generation rates.

## 2. NO<sub>x</sub> Formation

There are a number of different formation mechanisms responsible for NO<sub>x</sub> 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

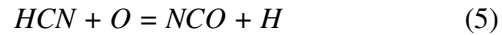
The thermal mechanism, also known as "extended *Zeldovich* mechanism", is responsible for the majority of NO<sub>x</sub> emissions from diesel engines when peak combustion temperatures exceed 2000 K.

Since temperatures of this magnitude are desirable to maximize engine efficiency, this mechanism has been studied extensively and is fairly well understood.

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The three chemical reactions that are important in this mechanism are:

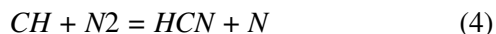


The overall reaction rate for this mechanism is slow and it is very sensitive to the temperature. As a consequence, thermal NO only appears in significant quantities in the post combustion. Also, the actual NO concentration from this mechanism deviates significantly from equilibrium concentrations.

This gives this mechanism a very strong time dependence that is important for low speed engines.

## 2.2. Prompt NO

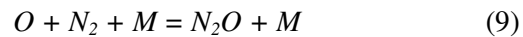
The prompt NO mechanism, also known as the "Fenimore mechanism", is very rapid and results in NO formation in the combustion zone. The most important pathway for prompt NO is initiated by the rapid reaction of hydrocarbon radicals from the fuel with molecular nitrogen, leading to the formation of amines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



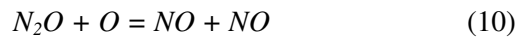
Subsequent rapid conversion to NO is strongly affected by O and OH. Prompt NO is most significant when combustion occurs at fuel concentrations higher than stoichiometry where there is a high concentration of hydrocarbon radicals to form HCN and the concentrations of O and OH are still high enough to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

## 2.3. N<sub>2</sub>O Pathway

Another NO formation mechanism important in combustion is the N<sub>2</sub>O pathway. The initial reaction for this pathway is the three body reaction:



While N<sub>2</sub>O generally reverts back to N<sub>2</sub>, 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:



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<sub>2</sub> reaction in the thermal mechanism.

These are the most important formation mechanisms.

## 3. Combustion Modification Techniques

This section presents the application of low emission combustion modification techniques used in maritime boilers.

### 3.1. Flue Gas Re-circulation (FGR)

Flue gas re-circulation (FGR) is a well-known technique for oxides of nitrogen (NO<sub>x</sub>) control in marine or industrial

applications. This control technique reduces both oxygen partial pressure and flame temperature. This is due to increasing the proportion of inert gas in the combustion zone, and this reduction has its greatest effect on reducing the thermal NO formation. It has been demonstrated in a small-scale boiler and in laminar diffusion flame that introducing the re-circulated flue gas with the fuel results in a much greater reduction in NO<sub>x</sub> per unit mass of recirculated gas, when compared to mixing

the flue gas with air. This technique is referred to as fuel injection recirculation (FIR). For example, NO<sub>x</sub> emissions were reduced from 90 to 30 ppm with 5 % FIR, while 23 % conventional wind-box FGR was required to achieve the same reduction. Large water-tube boilers would require considerable auxiliary power consumption for larger amounts of re-circulation, nevertheless small re-circulation rates (up to 10 %) give useful improvements in overall NO<sub>x</sub> emissions.

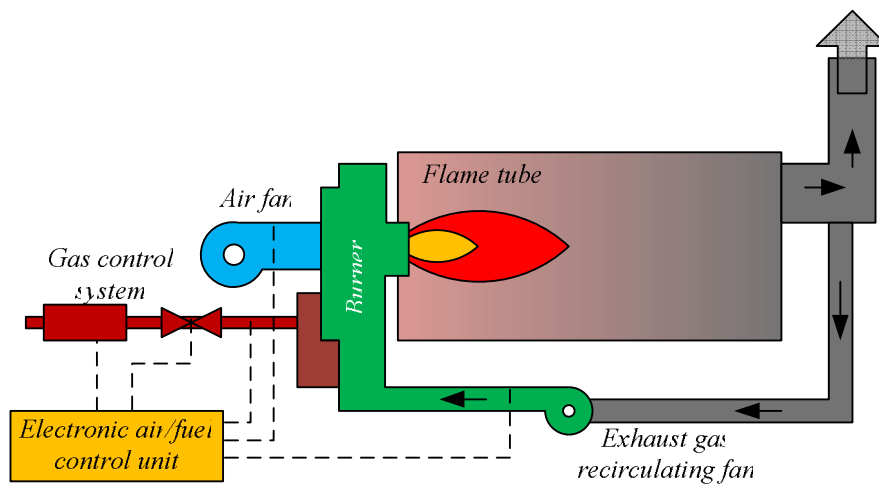


Fig.1. Flue Gas Re-circulation System

Figure 1 shows the practical technique of the external exhaust gas re-circulation using a separate fan, where the principle of this technique is to re-circulate controlled quantities of exhaust gases from the boiler into the combustion air. However, in this case, care is taken to maximize the heterogeneity of the mixing to ensure maximum temperature suppression in the flame. The practical feasibility of the exhaust flue gas recirculation has been

investigated by several scientists who found that significant reduction of NO<sub>x</sub> (50 %) could be achieved if 20 % or less of the total external exhaust gases is re-circulated at base load conditions.

The degree of reduction, which can be achieved, is dependent on the fuel, the concentration of nitrogen oxide at the boiler exit and the degree of re-circulation.

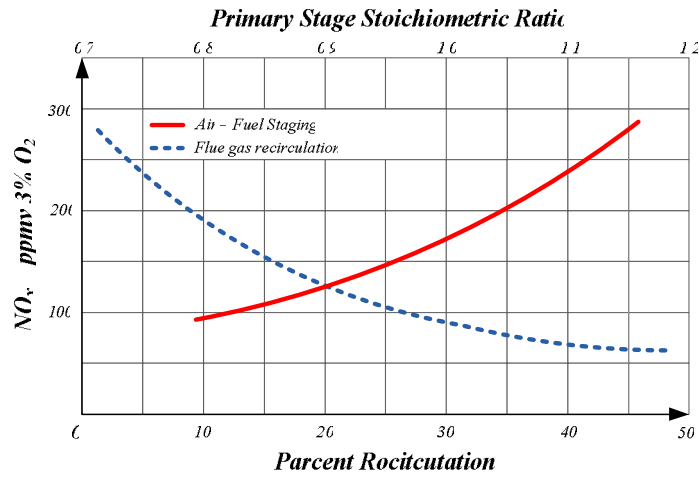


Fig.2. FGR Diagram

Representative reductions in NO<sub>x</sub> emissions that can be achieved in utility boilers burning natural gas using flue gas re-circulation are shown in Figure 2.

Nitrogen oxide emissions reductions up to 70 %, corresponding to NO<sub>x</sub> emissions in the range 50 - 100 ppmv (at 3 % O<sub>2</sub>) have been achieved in large-scale utility boilers.

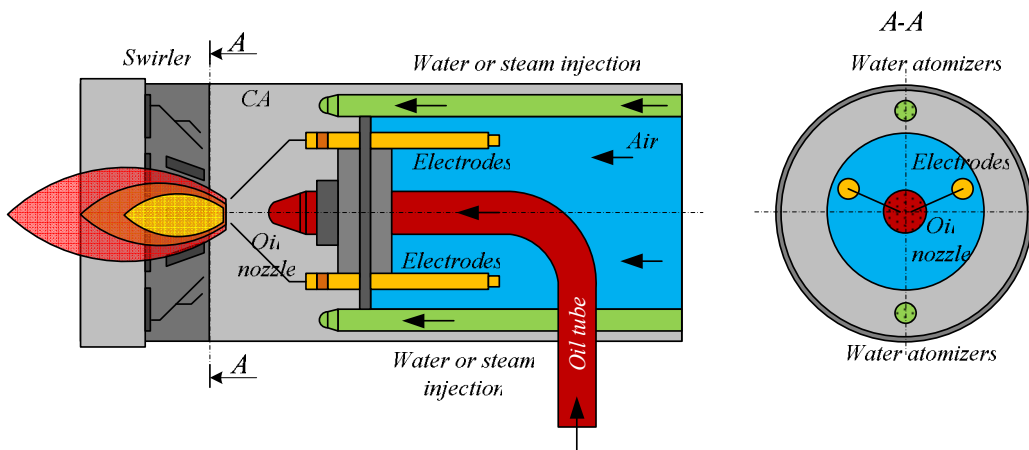


Fig. 3. Burner head with water and steam injection

**3.2. Water and Steam Injection (WSI)**

Addition of water or steam as a diluents through burnt-gas recirculation can be beneficial method for reducing NO<sub>x</sub> in maritime boilers. However, injection of

water or steam into the combustion zone has a similar physical effect to that of combustion gas re-circulation. In some cases the water or steam is injected directly into the flame, either through a number of separate nozzles located at the head end of

the combustor or through holes that are integrated into the fuel nozzle. In conventional combustors, and by using water injection system shown in Figure 3, a reduction of NO<sub>x</sub> (25 %) has been achieved by with a mass ratio of water/fuel injection of 0.95 (as you can see in Figure 4), and this was associated with the increase of CO concentration. When steam is used to reduce NO, emissions, it may also be injected directly into the combustion zone or into air, which subsequently flows into the combustion

zone. In some installations the steam is injected into the compressor discharge air.

This method is simple but inherently wasteful, because only about 40 % of the steam actually flow into the combustion zone. By introducing steam through the atomizing circuit of the oil gun, NO<sub>x</sub> reductions of up to 25 % can be achieved.

Also, a reduction up to 50 % of NO<sub>x</sub> has been observed in two-stage methane-air flames when 5 % water by mass was added to the air stream.

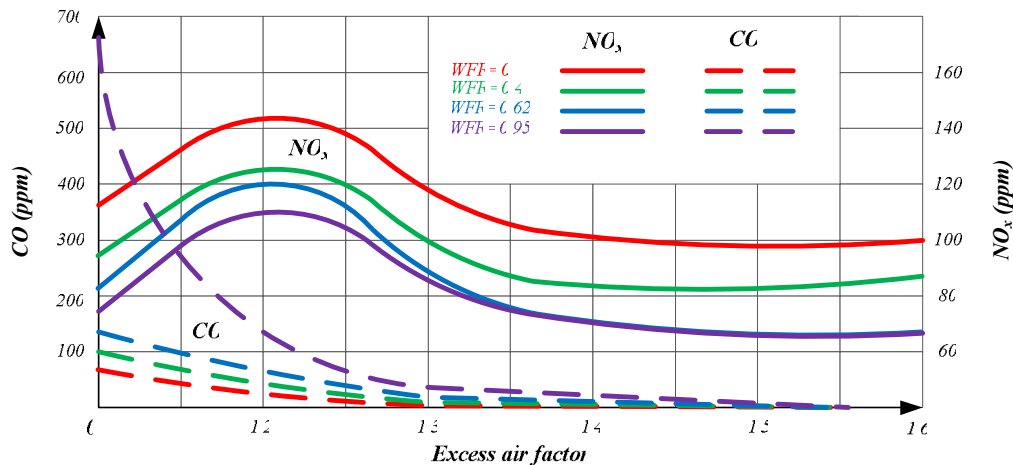


Fig.4 WSI Diagram

### 3.3. Air and Fuel Staging (AFS)

Air and fuel staging means the division of combustion zones into areas of sub-stoichiometric and over-stoichiometric combustion. The purpose of this measure is to effect combustion under conditions of insufficient air, which has the results of a low nitrogen oxide concentration, and then to transfer the products of this incomplete combustion to a subsequent over-

stoichiometric stage. The principles of air and fuel staging are applied to heavy fuel oil combustion systems, but are most applicable to water-tube boilers which have a lower furnace heat release rate and the resultant greater volume in which to achieve complete combustion. Different burner geometries to achieve staging in boilers and furnaces, termed low- NO<sub>x</sub> burners, have been developed.

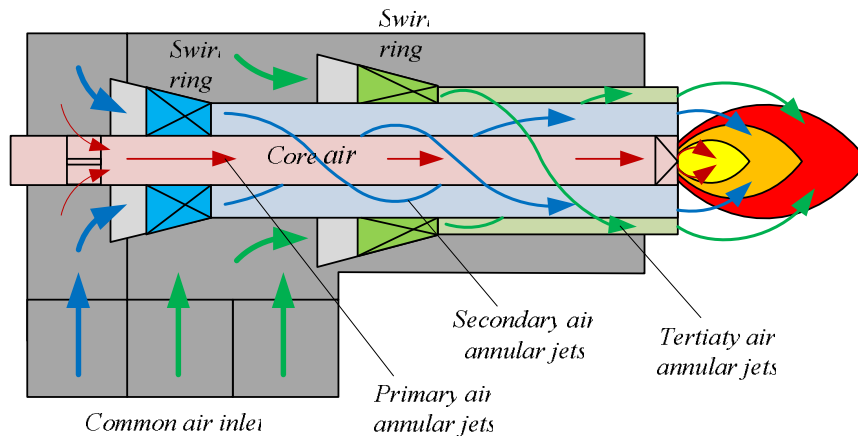


Fig.5. AFS System

A common characteristic of most low- $\text{NO}_x$  burners is that the primary combustion zone is fuel-rich, with staged introduction of additional air (see Figure 5). Reduction of  $\text{NO}_x$  emissions by staging in the range of 50 - 70 % has been achieved in practice.

#### 4. Exhaust Modification Techniques

##### 4.1. Re-Burning

Natural gas re-burning for  $\text{NO}_x$  control is currently a mature technology, which has been successfully, demonstrated at full-scale boilers. In re-burning (NO recycling) approach, a lean primary combustion stage is followed by a fuel-rich re-burning zone, where additional fuel is injected, with the remaining combustion air being introduced downstream of the re-burning zone. The chemical mechanism of re-burning involves the recycling of NO formed in the primary stage by reactions with hydrocarbon radical species (cyano compounds which mainly CN and HCN) in the fuel-rich re-burning stage. Under fuel-rich conditions, these cyano compounds may react preferentially to form  $\text{N}_2$  and consequently reduce NO.

Natural gas re-burning is a practical technique for controlling emissions of nitrogen oxides ( $\text{NO}_x$ ) from existing utility and large industrial boilers fired by any fossil fuel or waste material. In most boilers, this highly effective and flexible process can reduce  $\text{NO}_x$  emissions by 60-70 % using natural gas (total heat input).

The gas re-burning process reduces emissions without replacing or modifying existing burner equipment and required no chemical reagents or catalysts. In coal-fired boilers,  $\text{SO}_2$ , particulate, and  $\text{CO}_2$  are also reduced.

In gas re-burning, natural gas is injected into an upper region of the boiler to convert  $\text{NO}_x$  in combustion gases to  $\text{N}_2$ . The overall process design and reactions involve three zones of the boiler as shown in Figure 6:

##### Primary combustion zone

In the primary combustion zone, existing burners fired by coal, oil, or gas are turned down by 10 to 20 %. The burners or cyclones may be operated at the lowest excess air consistent with normal commercial operation to minimize  $\text{NO}_x$  formation and to provide appropriate conditions for re-burning.

### Gas re-burning zone

Natural gas (between 10 to 20 % of boiler heat input) is injected above the primary combustion zone. This creates a fuel-rich region where hydrocarbon radicals react with NO<sub>x</sub> to form N<sub>2</sub>. Gas re-burning injectors require new boiler-wall penetration on most boilers units.

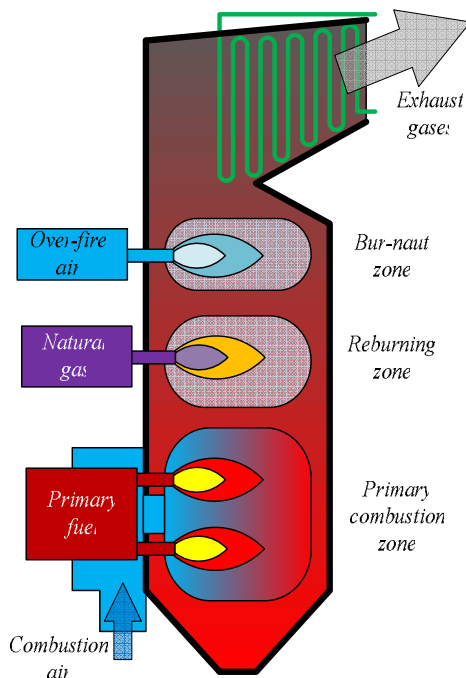


Fig.6. *Re-Burning System*

### Burnout zone

A separate over-fire air system redirects air from the primary combustion zone to a location downstream of the gas re-burning reaction zone to ensure complete combustion of un-reacted fuel and combustible gases. This separate over-fire air system requires boiler penetrations and ducting.

### 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 boiler intake air. Oxygen will be consumed during the combustion process, with the amount of excess oxygen available being a function of air/fuel ratio with the boiler is operating under. The nitrogen remains largely un-reacted in the combustion process; however a small percentage will be oxidized to form various oxides of nitrogen. The nitrogen oxides (NO<sub>x</sub>) which can be formed include NO and NO<sub>2</sub>, while the amounts are primarily a function of flame or combustion temperature and, if present, the amount of organic nitrogen available from the fuel.

It is also a function of the time the nitrogen and the excess oxygen are exposed to the high temperatures associated with the maritime boiler combustion process. In other words, the higher the combustion temperature the greater the amount of NO<sub>x</sub> formation.

Depending on the specific design of the particular boiler, different NO<sub>x</sub> modifications and adjustments are possible and usual. These include the boiler parameters as follows: injection nozzle, architecture of the combustion chamber, NO<sub>x</sub> abatement equipment (water injection), NO<sub>x</sub> abatement equipment (emulsified fuel, fuel/water emulsion), NO<sub>x</sub> abatement equipment (exhaust gas recirculation), NO<sub>x</sub> abatement equipment (selective catalytic reduction).

### References

1. Bocănete, P.: *Turbine cu abur. Construcție și exploatare*. Constanța. Editura Dobrogea, 1996.
2. Boubel, Richard W.: *Fundamentals of air Pollution*. Academic Press, 1994;

3. Creţa, G.: *Turbine cu abur şi gaze*. Bucureşti. Editura Didactică şi pedagogică, 1981.
4. El-Mahallawy, Fawzy, El-Din Habik, Saad: *Fundamentals and Technology of Combustion*. Elsevier Science, 2002.
5. IMO, *MARPOL 73/78, Anexa VI*. Londra, 1998.
6. Karlsson, B., Quintiere, J.G.: *Enclosure Fire Dynamics*. CRC Press, Florida, 2000.
7. Melinte, S.: *Generatoare de abur navale*. Constanţa. Editura Academiei navale “Mircea cel Bătrân”, 1979.
8. Woodyard, D.: *Pounder’s Marine Diesel Engines and Gas Turbines*. Woburn. Elsevier-Butterworth Heinemann, 2004.