

Minimizing NOx-Emissions of Heavy Oil fired Boilers combining Fuel Additives and SNCR



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Introduction

All operators of crude and heavy fuel oil fired boilers have the same objectives. They have to maximize the efficiency of their plants and minimize the operating costs as much as possible. This leads to an increasing combustion of lower fuel oil qualities which contain high quantities of Sulfur, Vanadium, Nitrogen and Asphaltene.

The low quality oils are more difficult to burn and cause corrosions and deposits on the boiler tubes and the components installed downstream the boiler. The increasing requirements to control emissions of NOx, SO2, and Particulats from utility and industrial boilers have created a need for technologies capable of achieving high levels of emission controls at low costs.

This paper describes a modern Low NOx Burner, additional improvements of the combustion with special treatments of the fuel oil, and the combination with the SNCR technology in order to achieve the required low NOx emissions in a cost effective manner.

Major NOx control technologies

NOx control technologies can be classified into two categories:

Primary measures	=	combustion control technologies
Secondary measures	=	post-combustion control technologies

The objective of all combustion control technologies is to avoid or to minimize the formation of NOx during the combustion. This can be achieved by reducing the oxygen and decreasing the temperature in the primary combustion zone, so that non completely reacted (burned) carbon compounds (CnHm radicals, CO, residual coke) are available in enriched form and have a reducing effect on already formed NO.

In the secondary combustion zone, the combustion will be completed by addition of air. In order to get optimum results, i.e. low NO and maximum burn-out, a long residence time in the reducing atmosphere of the primary combustion zone, and a

good mixture with the combustion air in the secondary combustion zone are essential.

In order to comply with the requirements of low - NO_x combustion, the following primary measure are being taken alone or in combination with each other :

- adjustment and optimisation of burners and combustion air
- reduction of excess air
- air staging in the combustion zone and/or in the burners
- fuel staging
- flue gas recirculation
- water & steam injection (minor influence)

The effectiveness of such primary measures depends very much on the boiler design and the characteristics of the fuel; each individual case has to be studied carefully with regard to :

- stability of the flame
- corrosion in the furnace
- burn-out of the fuel
- fuel range
- NO_x reduction
- efficiency of the boiler
- cost

In practical applications compromises have to be found between the technical possibilities and the affects on cost and operation.

Burner Design

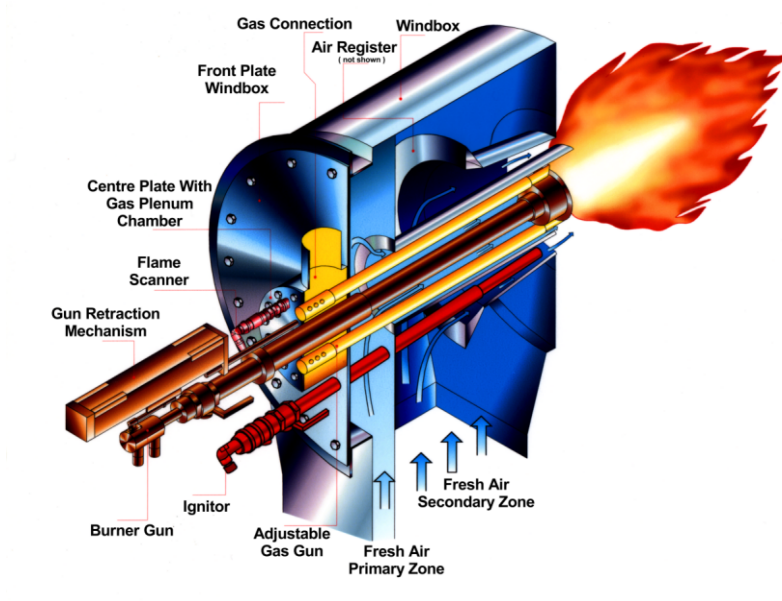


Figure 1: M&S Low NO_x - Burner Generation / NAB (ST)

The design of the burner is very important for oil and gas fired boilers. **Figure 1** shows the modern M&S Low NOx Burner (NAB / ST) with internal flue gas recirculation in the combustion zone of the furnace. With this modern design emission values are achievable which previously were only possible with the external recirculation of the flue gas.

The internal flue gas recirculation generated with this type of burner does not require any special measures and installations as flue gas recirculation fans and additional flue gas ducts. Various combustion air streams cause a partial back flow of the flue gases in the furnace. The oil guns and the gas lances are equipped with Low NOx tips. While the oil gun has a pneumatic retraction mechanism the gas lances can be adjusted and removed externally.

The formation of thermal NOx depends very much on the amount of oxygen which is present while the combustion takes place. With a high excess of combustion air (oxygen) the flame is very hot resulting in high NOx levels and lower efficiency. The burn-out of the fuel in this mode of operation is good and the CO- and particulate emissions are relatively low.

The opposite happens when the oxygen supply is low. In an oxygen lean environment the flame is 'cold' and thermal NOx cannot be formed to a large extent. Furthermore, the available oxygen preferably reacts with the Carbon (C) of the fuel instead with the Nitrogen (N). However, since the burn-out of the fuel is not complete the emissions of unburned carbon and CO are higher, while the efficiency of the boiler is better than in cases with a high excess of combustion air.

Fuel Oil Treatment

Especially with heavy fuel oil qualities the required emission levels cannot be reached with low NOx burners alone. In these cases the additional treatment of the fuel oil is very often an effective option. In most cases the emissions of CO, NOx and particulates can be decreased considerably or even kept within the limits simply by feeding some additives into the fuel oil which enhance or expedite the combustion at lower temperatures.

Very efficient for example is PentoMag 4100 an oil soluble, organometallic blend of MgO, Iron and asphaltene dispersants which will

- clean the heavy fuel oil system from the point of injection
- keep the boiler free from deposits and corrosion
- reduce the unburned carbon and thus the solid emissions by ca. 40 %
- increase the pH of the ash to 3

Depending on the boiler design a reduction of the exit gas temperature of at least 10° C is possible. This will lead to higher **efficiency** of the boiler (0.5% per 10°C) and less fuel consumption and operating costs.

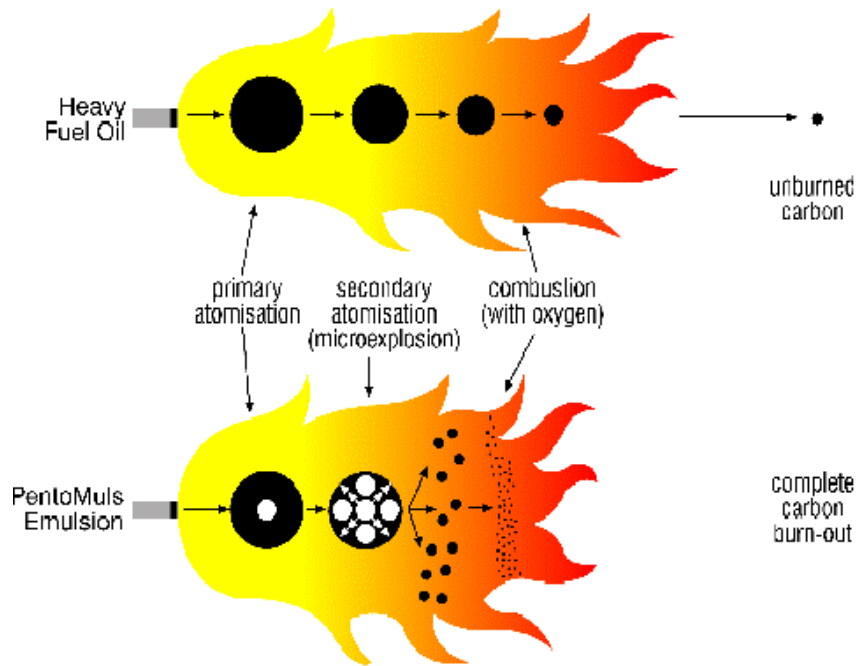


Figure 2: Principle of Water-in-Oil Emulsion

Another efficient method to optimize the combustion and to minimize the technical and environmental impact is to burn a stable water-in-oil emulsion (Figure 2). Generally the heavy oils cannot be burned completely, so that approx. 80% of the ash consists of unburned carbon. With the water-in-oil emulsion, the small water droplets inside the oil explode as soon as the oil ignites. The micro explosions cause the fuel oil droplets to fragment in thousands of micro droplets which now can burn out completely so that almost no unburned carbon remains.

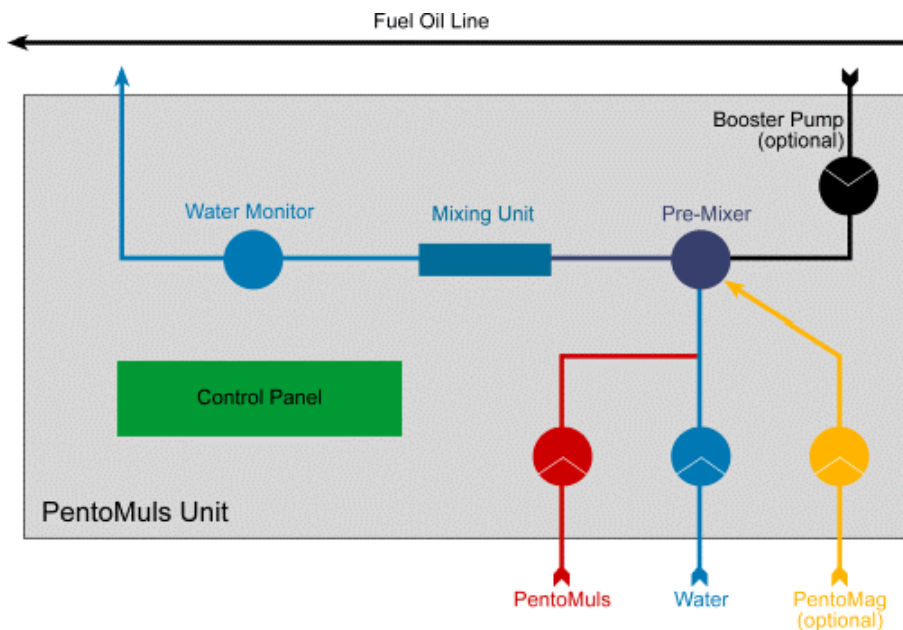


Figure 3: Functional Diagram of Water-in-Oil Emulsion

In order to produce the required stable water-in-oil emulsion special chemicals have been developed. **Figure 3** shows a simplified functional diagram of the equipment which can be easily installed without changes to the existing fuel system. For controlling the deposits on the boiler tubes and SO₃ emissions other PentoMag products can be blended into the fuel oil simultaneously.

The major benefits of the emulsion technology are summarized as follows:

Environmental

- Reduction of NO_x-Emissions up to 30 %
- Reduction of solid Emissions up to 80 %
- Reduction of CO-Emissions 10 ppm
- Reduction of SO₃ conversion up to 90 %
- Elimination of acid smut fallout

Economical

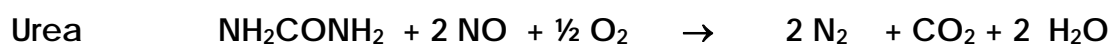
- Clean fuel system
- No high and low temperature deposits
- No high and low temperature corrosions
- Higher efficiency due to better heat transfer
- Higher boiler availability due to less outages for repairs
- Efficiency increase by reducing exit flue gas temperature

Post Combustion

The objective of the secondary measures is to reduce the content of NO_x in the flue gas after the combustion. Post combustion NO_x control technologies which are widely used are the Selective Catalytic Reduction (SCR) process and the Selective Non Catalytic Reduction (SNCR) process.

SNCR and SCR processes have in common that both reduce NO_x to N₂ and H₂O with ammonia or ammonia based reagents like urea. The major difference of the two systems is that the reaction without catalyst takes place at temperatures which only can be found within the boiler, while with a catalyst the reaction typically takes place outside the boiler at temperatures between 300 °C to approx. 400 °C.

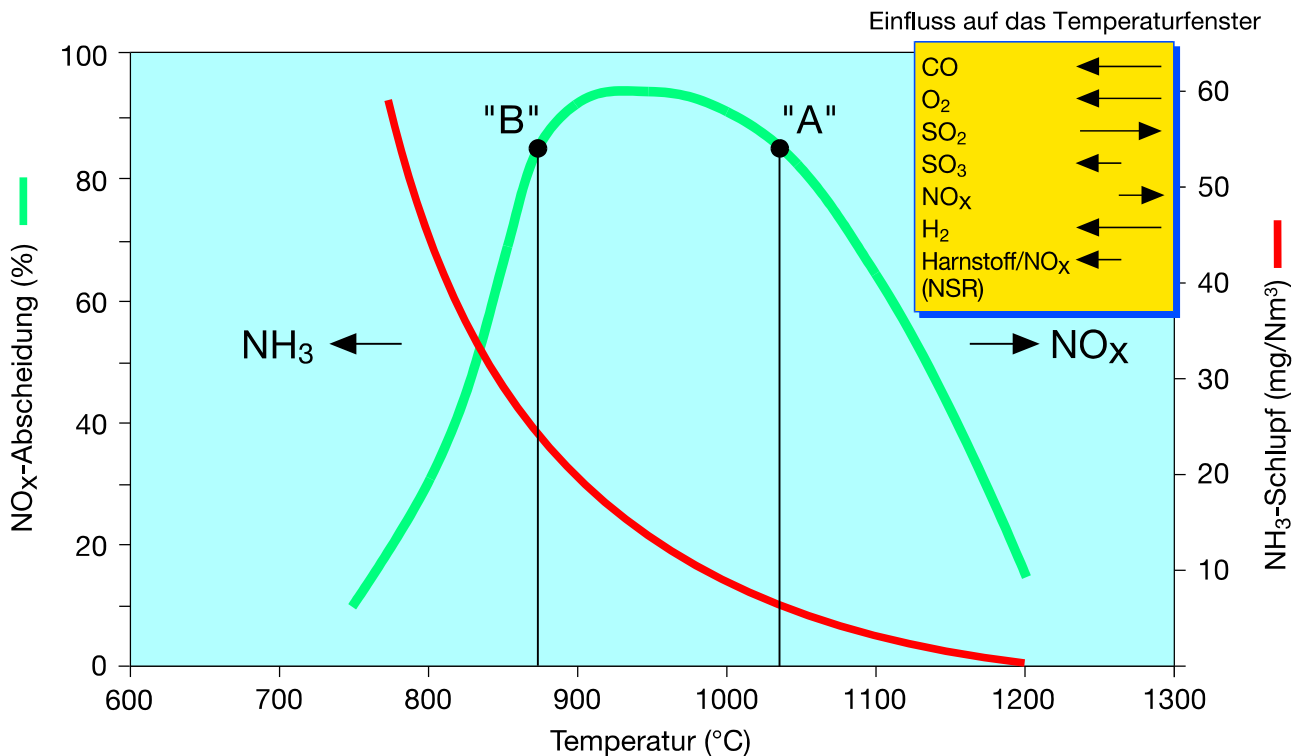
In both cases molecular nitrogen, water and carbon dioxide are formed according to the overall reactions for



or for



For the SNCR process the optimum temperature range in which a significant NOx reduction is achieved is between approximately 900 °C and 1100 °C depending on the flue gas composition (**Figure 4**). A major impact have CO and O2 who shift the temperature window to the left side and SO2 which shifts the temperature window to the right side.



"A"- Optimale Temperatur für SNCR alleine (niedriger Ammoniak Schlupf)
 "B"- Optimale Temperatur für SNCR + SCR (hoher Ammoniak Schlupf)

Figure 4: NOx Reduction as a Function of Temperature

At temperatures above this range, ammonia is increasingly oxidized, i.e. nitrogen oxides are formed.

If the temperature is too low, a slower reaction rate allows ammonia slip to occur, which can cause the formation of ammonia salts further along the flue gas pathway and lead to secondary problems like plugging of the air preheater. Ammonia slip should, therefore, be kept to a minimum, and the key is to ensure even distribution of the reduction agents into the flue gas within the optimum temperature range.

Figure 5 shows the major difference between the reagents urea and ammonia water. With urea the decomposition to NH₂-species and thereafter the reaction with NO_x can only start after the dilution water is evaporated. With ammonia water the ammonia evaporates immediately when the dilution water is being

heated up respectively entering the furnace. This leads to a reaction close to the furnace walls while the water droplet penetrates much further into the flue gas stream without reagent.

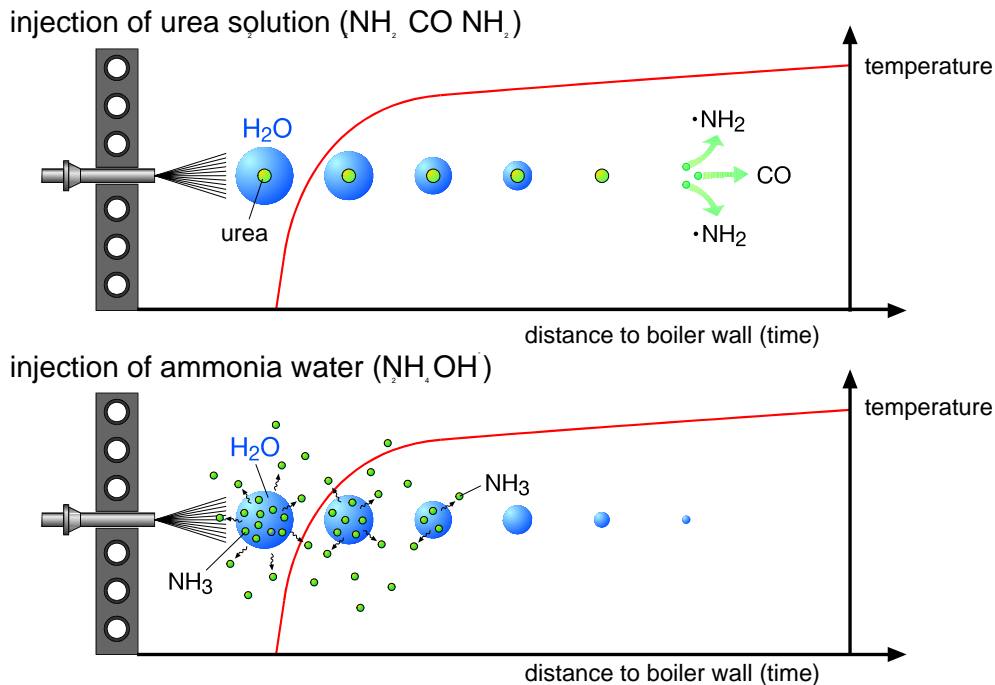


Figure 5: NO_x-Reduction of Urea versus Ammonia Water

The differences in the reagent distribution have a considerable impact on the performance of the respective system. With urea the point where reagent is released can be defined in advance by adjusting the spray characteristics. In a number of cases urea has been injected into the furnace at higher temperatures. This cannot be done for ammonia. If the injection is at the right side of the temperature window, the ammonia system should work adequately for achieving reasonable NO_x-reductions, while the probability of ammonia slip is reduced, but still higher than with urea. If the injection is at the lower side of the temperature window the release of reagent near the walls would result in significant levels of ammonia slip.

In order to overcome this problem and assure an even mixing of the ammonia with the flue gas more energy is needed for generating the momentum for the vaporized ammonia to penetrate into the center of the furnace.

Figure 6 is a functional diagram showing the main components of a typical SNCR system and the equipment for feeding additives into the fuel oil. The system is installed at two heavy oil fired boilers with two fire tubes in Glückstadt, Germany. The steam capacities of the boilers are 40 t/h each. The emissions of NO_x are limited to 450 mg/Nm³ and particulates to 80 mg/Nm³ at boiler loads ranging from 30 to 100%.

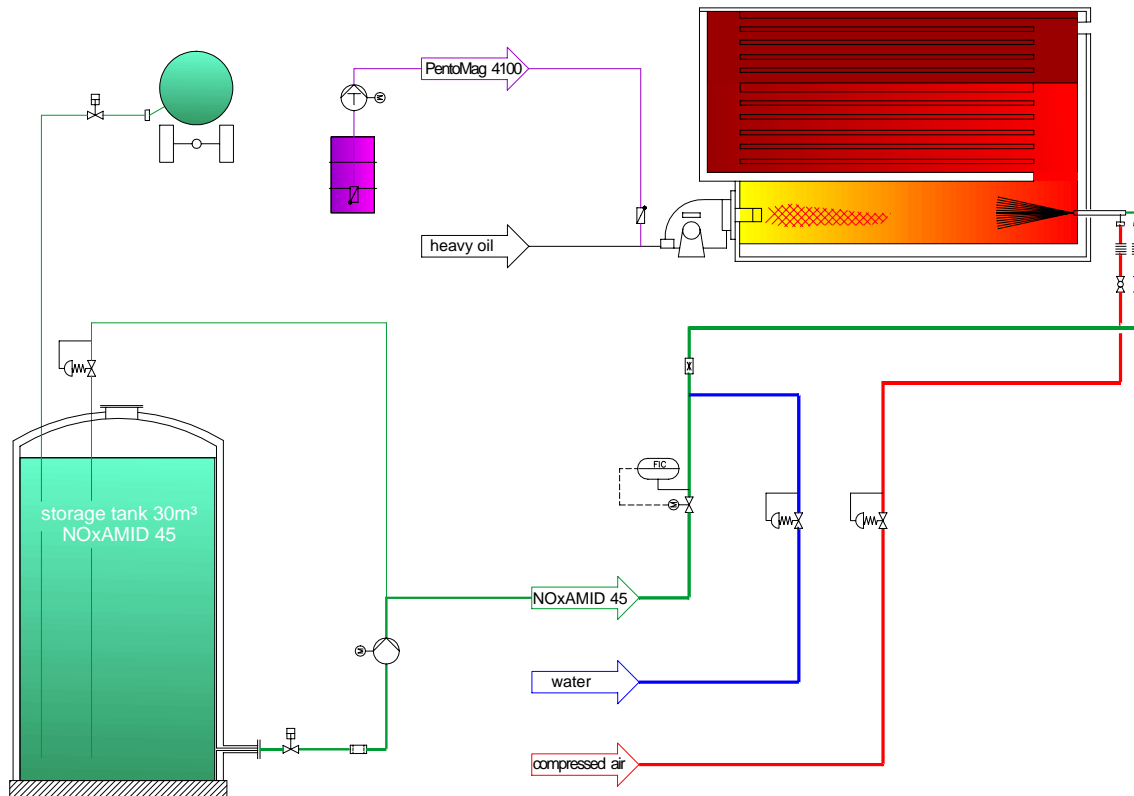


Figure 6: Functional Diagram of Emission Control System for a Fire Tube Boiler

The system for controlling the emissions of particulates and NOx comprises mainly the unit for feeding the combustion improver PentoMag 4100 into the fuel oil, the low NOx-burners, and the SNCR system with the storage tank for the reagent NOxAMID 45, the reagent pumps, the measuring and distribution modules, the process control system and the injectors.

With the fuel additiv PentoMag 4100 the burn out can be improved in such a way that the emissions of particulates can be kept below the limits with considerably less excess air so that the formation of thermal NOx is minimized. With the achieved low NOx baseline the positiv effect for the SNCR system is that less NOx has to be reduced, resulting in less consumption of reagent.

The total plant was commissioned in January 2001 and the guaranteed emission values can be kept.

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