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Technologies for the Reduction of Nitrogen Oxides Emissions

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ABSTRACT: When it comes to gas turbines, their main problem concerning pollutant emissions is represented by nitric oxides. Among other emissions, sulphur oxides being much reduced due to the use of liquid distilled and gas fuels with a low content of sulphur. Using water or steam injection became the favourite method during the '80s and especially the '90s since "dry" methods and catalytic reduction were both at the beginning of the development phase. Catalytic convertors have been used since the '80s and they are still used although the costs of renewing the catalyst are very high. In the last twenty years a gradual decrease has been registered on the limits of nitric oxides from 75 ppm to 25 ppm, and now the target is oriented towards the 9 ppm level. The evolution of burning technologies of combustion makes it possible to control the level of production of nitric oxides even from the source without being necessary to use "humid" methods. This, of course, opened the market for gas turbines because they can function even in areas with limited quality water reserves, such as maritime platforms and in the desert. In this paper, we are going to show that, although water injection is still used, "dry" control technologies of burning became favourite methods for the majority of users on the industrial power generators market. The great dependency between the creation of nitric oxides and the temperature reveals the effect of direct water or steam injection on reducing nitric oxides. Recent research showed that a reduction up to 85% of nitric oxides may be obtained by using the water or steam injection all together with the improvement of aerodynamic character of the burning room.

1 INTRODUCTION

Among different solutions for reducing nitrogen oxides emission we can therefore mention the following: introduction, through different methods, of water or steam, in combustion rooms, recirculation of combustion gases, selective or non-selective catalytic reduction, use of monitoring systems and electronic control of functional processes of energetic installation providing fuel combustion in optimal conditions for obtaining as low emissions' values as possible.

The International Maritime Organization (I.M.O.), in Annex VI MARPOL 73/78 draws attention both on sulphur oxides and especially on nitrogen oxides, for which methods of determination on board ships, calculus methods, as well as reduction solutions are emphasized. I.M.O. is at the same time the main regulating organism in the marine environment pollution domain. (Uzunov, 1997)

Regarding gas turbines installations, as well as other naval energetic installations, in the matter of emissions reduction, the most used ones are water or steam injection systems, combustion gases recirculation or re-combustion, as well as selective catalytic reduction. (Woodyard, 2006)

2 REDUCING NOX EMISSION

Regarding gas turbines, the main problem concerning pollutant emission is represented by NO_x. Among other emissions, SO_x being much reduced due to the usage of liquid distillate or gas fuels with a reduced content of sulphur.

The next figure presents the method of reducing NO_x emission in the last 40 years, in the case of using gas turbines first by the usage of steam injection in the combustion rooms (the so called wet combustion rooms) and then in the \`90's through the system of dry combustion room with a low level of NO_x (Dry Low NO_x Combustors). The new systems already in use conceive a reduction of emissions of NO_x below 9 ppm.

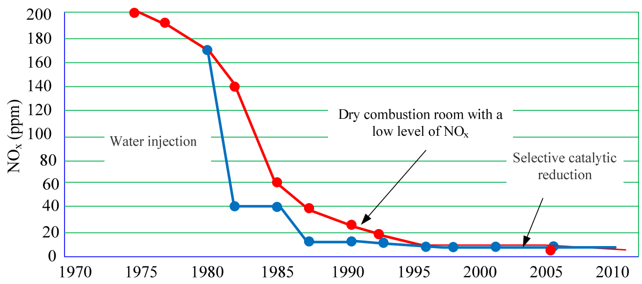

Figure 1. Control of NO_x emissions in time

Starting from 1977 it was admitted that there is a range of methods of control of nitrogen oxides:

- using combustion rooms divided into several burning areas in which production of nitrogen oxides varies in order to decrease them;
- using a primary zone of the combustion room very tight in order to decrease temperature of the peak of the flame by attenuation;
- using water or steam injected together with fuel for cooling the zone in the vicinity of the injection burner;
- using inert gasses of evacuation which are re-circulated in the reaction zone;
- catalytic cleaning of evacuation.

Using water or steam injection became the favourite method in the \`80's and especially the \`90's from the moment when "dry" methods and catalytic reduction were both at the beginning of the development phase. Catalytic converters were used from the \`80's and they are still used; although renewal costs of the accelerator are very high.

In the last twenty years, a gradual decrease of the limits of NO_x was registered from 75 ppm to 25 ppm, and now the target is oriented to the level of 9 ppm.

Fuel combustion technologies evolution makes it possible for the control of the level of production of NO_x right to the source without necessitating "wet" methods. This, of course, opened the market for gas turbines as they can function even in the zones with limited quality water reserves, for example maritime platforms and in the desert. (U.S. Navy, 2008)

Although water injection is still used, "dry" technologies of controlling combustion became the favourite methods for the majority of users on the market of the power industrial generators.

DLN (Dry Low NO_x) was the first acronym used, still along with the apparition of requirements of control of NO_x without implicating an increase in the level of carbon monoxide and hydrocarbons which are not burnt, led to DLE (Dry Low Emissions).

The largest part of NO_x produced in the combustion room is called „thermal NO_x". This is produced by a series of chemical reactions between nitrogen (N_2) and oxygen (O_2) in the air which is found at high temperatures and pressures inside the combustion room of the gas turbine.

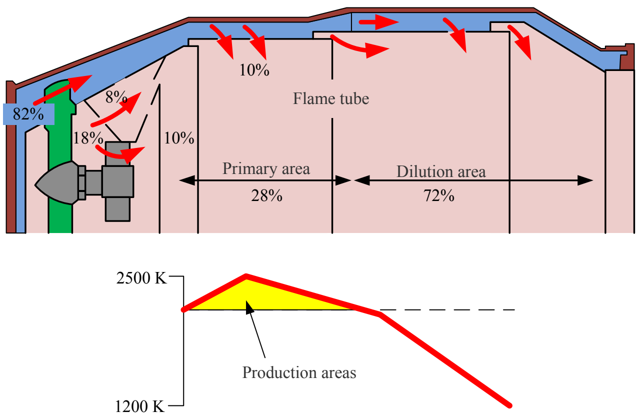

Figure 2. Production of NO_x in a classic combustion room

The rate of development of reactions is dependent on the high temperatures, and the rate of production of NO_x becomes important at the temperature of the flame of approximately 2088 K (1815 ^oC). Figure 2 presents schematic the temperatures of the flame and areas of production of NO_x from the interior of a combustion room. The design of the combustion room determines combustion of the whole quantity of fuel in a series of areas passing from the state of rich in fuel to that of poor in fuel, on the entire power interval.

The great dependence between formation of NO_x and temperature reveals the direct effect of the water or steam injection on the reduction of NO_x. Recent researches showed that a reduction of up to 85% of NO_x may be obtained through water or steam injection together with optimizing the aerodynamic of the combustion room.

Inside a regular combustion room, such as the one in figure 2, the air debit which enters in the first area is limited to almost 10 %. The rest of the debit is used for the mixture of combustion and for cooling the combustion room. The maximum temperature is reached in the first area, and it is almost 2503 K (2230 ^oC) and after mixing the combustion fluid with the cooling air, the temperature decreases to the value of 1643 K (1370 ^oC).

There are three main technologies of reduction of emissions of NO_x which are used for gas turbines. These are:

- Adding water/steam in the combustion room (wet combustion room);

– Dry combustion rooms with low NOx (DLN);
– Selective catalytic reduction.

There are also other technological solutions for reducing NO_x emissions such as recirculation of burnt gases or humidifying the alimentation air, but these are not so much used.

Along with the apparition of international regulations regarding environment pollution a vast process of research and observation began concerning the method of formation of pollutant emission and the influence of some parameters over those as well as looking for technological solutions for their reduction.

Presently, researches lead especially in the direction of conceiving reduction systems of emissions, especially those of NO_x and SO_x. Another research direction is that of determination or prediction of formation processes of emissions.

Several works present as a solution in the problem of pollution the use of alternative fuels, such as bio-diesel. The most important researches in this field were performed at N.R.E.L. (National Renewable Energy Laboratory), prevailing in the field or auto transport. Results show that decreased values of sulphur oxides and mechanical particles are obtained, and for nitrogen oxides the reduction is possible only by using some additives for improving the cetane ratio.

3 SOLUTIONS FOR REDUCING NITROGEN OXIDES EMISSIONS

According to international regulations in the field of marine environment pollution, along the time a series of control and reduction of pollutant emissions measures were developed resulting from fuel combustion.

The study of these measures made it easier to understand the chemical processes of formation and reduction of pollutant agents. Generally, the purpose which is targeted in the study of pollution is to respect standards of quality of air and water in the marine environment. (Moldoveanu, 2005) International programmes of reduction of pollution of the marine environment may be divided into long term and short term programmes of control of pollution.

3.1 *Recirculation of burnt gases*

Recirculation of burnt gases, FGR (Flue Gas Re-circulation) is one of the most well-known techniques in the field of the steam generators, used with the purpose of reducing the content of the nitrogen oxides (NO_x). This technique uses both the reduction of pressure of alimentation air of the burning point of flame tube and the reduction of the temperature of the flame. This is due to an increase of the content of inert gas in the burning area which leads to a limitation of the thermal formation process of NO_x.

Analysing the diverse applications of reduction techniques of emissions from steam generators, it was notices that much better results are obtained in reducing NO_x, if burnt gases are introduced along with the fuel, unless air would be introduced along with the fuel.

This technique (combined introduction of fuel mixed with burnt gases) is called re-circulated fuel injection, FIR (Fuel Injection Re-circulation). For example, emissions of NO_x have been reduced from the value of 90 ppm to the value of 30 ppm using a system type 5 % FIR, while it was necessary the use of 23 % of a classical FGR system „Windbox”, for obtaining the same reduction of NO_x. Steam generators used in the naval field would necessitate considerable quantities of auxiliary power for conceiving recirculation.

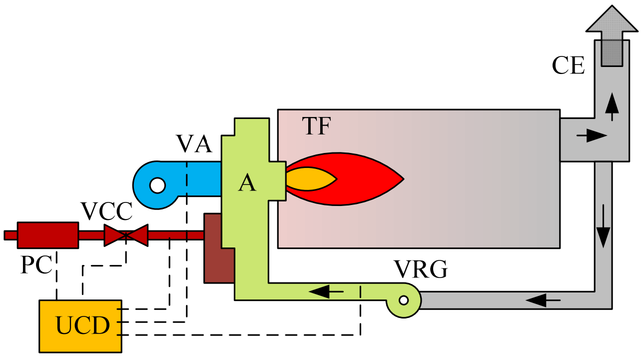

Figure 3. Recirculation system of burnt gases

In the next figure, an application of the recirculation of burnt gases technology is presented with a separated ventilator. Quantities of re-circulated gas are controlled with precision by the control unit of dosage (UCD). Researches performed on this system showed that a reduction of over 50 % of emissions of NO_x is obtained if evacuation gasses are re-circulated in a percent of 20 % from their total quantity.

Signification of notations in figure 3 is: TF – flame tube (combustion room); A – burner; CE – evacuation funnel; VRG – ventilator for recirculation of burnt gases; VA – air ventilator; VCC – fuel control valve; PC – fuel pump; UCD – dosage control unit.

The reduction degree which may be obtained is a function of the fuel nature, concentration of NO_x which may be obtained and the recirculation degree. In the diagram in figure 8.2, dependence on these parameters is presented.

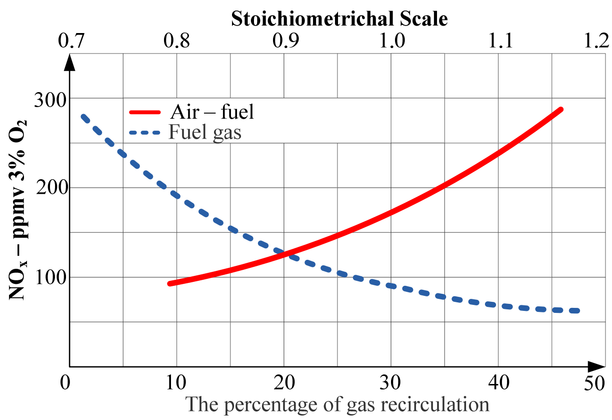

Figure 4. The effect of the mixture air – fuel and burnt gases – fuel over the production of NO_x

3.2 *Water or steam injection*

WSI (Water or Steam Injection) as an agent of dilution in burnt gases re-circulated lead to a significant decrease of the content of nitrogen oxides. Otherwise, water or steam injection in the area of combustion has a similar effect with that of recirculation technology of burnt gases. In some cases, water or steam are injected directly in the flame, either by separate nozzles disposed on the burner or by integrated orifices in the fuel pulveriser. (Moran, 2006) For conventional burners, using the water injection system presented in the figure, a reduction of 25% of NO_x could be obtained with a report water-fuel (WFR) equal to:

$$WFR = \frac{95\ g\ water}{100\ g\ fuel} = 0.95$$

which led to an increase in the content of CO.

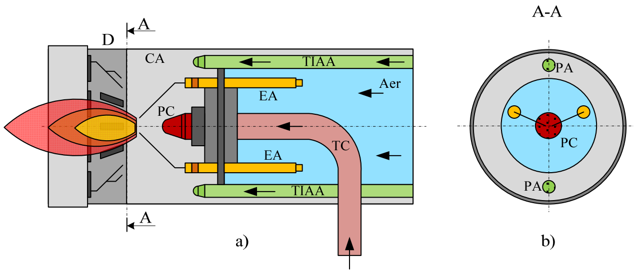

Figure 5. Water or steam injection burner

Significance of notations in figure 5 is: D – flame diffuser; CA- burner body; TC – fuel tube; PC – fuel pulveriser; EA – combustion electrodes; TIAA – water or steam injection tubes; PA – water or steam pulveriser.

When steam is used for reducing NO_x, this may be injected directly in the combustion room of in the alimentation air, which by moving reaches also the combustion room. For some systems, steam is injected in the discharge air of the ventilator for introducing fresh air in the combustion room.

This method is much simpler from a constructive point of view but less efficient because only 40% of the steam reaches precisely the combustion area.

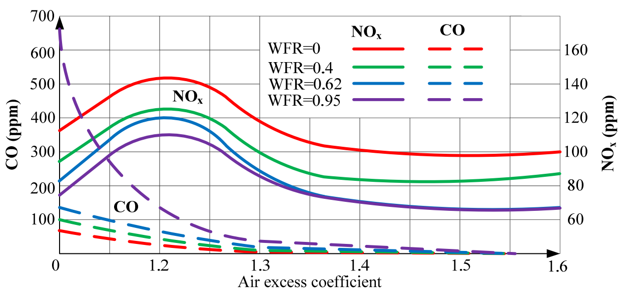

Figure 6. Influence of the air excess coefficient and water or steam injection over the production of carbon monoxide and nitrogen oxides

The system is used for gas turbines also. Here WSI (Water or Steam injection) action still by lowering the temperature of the flame, by ensuring a dilution agent having effect over the thermal mechanism of formation of NO_x. Water may be injected directly in the combustion room of the turbine, or it may be turned into steam, using heat recuperated from evacuation gases and then injected in the combustion room.

In order to realize the level of reduction of NO_x obtained by using water, a larger quantity of steam needs to be used.

3.3 *Separation of the air from the fuel*

The technology for separation of air from the fuel, AFS (Air and Fuel Staging), is represented by the division of the combustion areas in areas with sub-stoichiometric combustion and areas with supra-stoichiometric combustion. The purpose of this procedure is to determine that combustion should be performed in conditions of insufficiency of air, which has as a result a lower rate of formation of nitrogen oxides.

Further on, incomplete combustion products are transferred and oxidised in the supra-stoichiometric combustion area. This technology of separation of air from fuel is most often used in case of steam generators which are using heavy marine fuel, especially for aqua-tubes generators having lower values of the transmission coefficient of heat resulting therefore in a larger volume in which complete combustion may be performed. Over time, several types of burners were built with different geometries with the purpose of obtaining a good stratification of the poor or rich in air areas, these burners bearing the name of low NO_x burners. A common trait for the majority of burners with low NO_x is that the primary combustion area is reach in fuel by reducing the quantity of air introduced.

Significance of the notation in Figure 7 is the following: ACA – common air alimentation; JAP – primary air jet; JAS – secondary air jet; JAT – tertiary air jet.

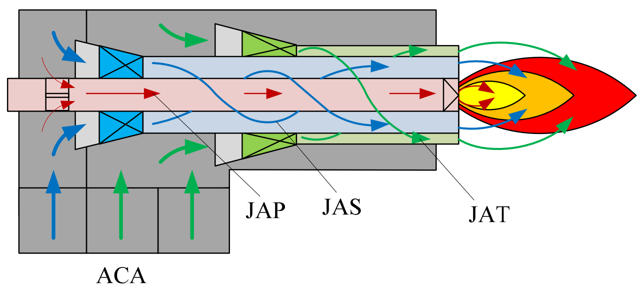

Figure 7. Air stratification burner

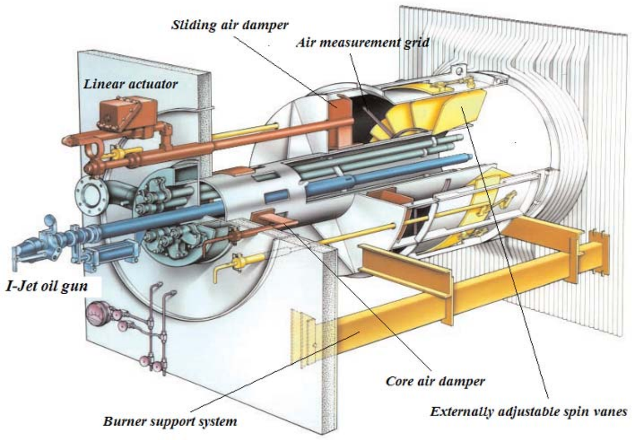

Figure 8. Air stratification system produced by Babcock & Wilcox (XCL-S Burner)

3.4 *Re-burning with natural gases*

Re-burning with natural gases for the emissions' control of NO_x is a method which proved its efficiency in the applications for naval steam generators. In the re-burning technology (recycling of NO) a poor in fuel combustion is first performed, followed by a rich in fuel combustion. Chemical mechanism of re-burning implies recycling of nitrogen oxides, formed in the first stage of poor combustion and eliminating those by the reaction of hydro-carbonated radicals (composed by the cyanic type, CN or HCN) which appears in the rich in fuel area. In the condition of the rich in fuel combustion, these compounds shall react in order to form N_2 leading to a substantial reduction of NO.

Re-burning with natural gases is a useful technology for the reduction of nitrogen oxides emissions. This process may reduce nitrogen oxides emissions with up to 60 – 70%. Generally the process and reactions produced necessitate the separation of the steam generator in three distinct areas, presented in figure 9. These areas are:

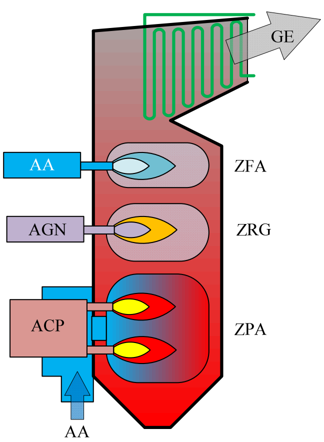

Figure 9: Steam generator with re-burning

Primary combustion zone (ZPA). In this zone combustion may be realised with an excess coefficient of air reduced to a minimum value, in order to decrease formation of NO_x and in order to provide optimal conditions for performing re-burning. In this area, liquid fuel is burnt, still with 10-20% less than in normal conditions of functioning (without re-burning);

Gases re-burning zone (ZRG). In this area there is a natural gas injected (10-20%) over the first combustion area. This leads to a rich in fuel area, in which hydro carbonated radicals which reacts with NO_x leading to the formation of N_2;

Final combustion zone (ZFA). In this area an air excess is added in order to oxide particles of liquid fuel or gas left un-burnt.

Signification of notations in figure 9 is the following: ZPA – primary combustion zone; ZRG – gas re-burning zone; ZFA – burning final zone; AA – air alimentation; ACP – primary fuel alimentation; AGN – natural gas alimentation; GE – evacuation gases.

4 CONCLUSION

In related papers, especially those of foreign authors, attention is aimed first to nitrogen oxides and then to sulphur and carbon oxides. The great majority of authors present solutions available from the production companies of naval energetic installations, solutions which were already presented in this paper, yet at the same time they emphasize the manner in which pollutant emissions are produced, as well as their effect on the marine environment and the costs for different constructive solutions that they impose.

Along with the arise of international regulations regarding environment pollution, a vast research and observation process of the manner of production of pollutant emissions began, and also of the influence of some parameters on them as well as looking for some technological solutions in each case.

Presently, researches are especially directed towards conceiving some systems of reduction of such emissions, especially those of NO_x and SO_x. Another research direction is that of determination or prediction of emissions' formation processes.

According to international regulations regarding the marine environment pollution, a series of emissions of control and reduction of pollutant emissions resulted from fuel combustion was developed in time.

The study of these measures made it easier to understand the chemical processes of formation and reduction of pollutant agents. Generally, the purpose of the study of pollution is to obey quality standards of air and water in the marine environment. International programmes of reduction of pollution in the marine environment may be therefore divided into long and short term pollution control programmes.

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