Chapter 4

NOx Control by Reducing Temperature

Editor's Note:

Chapter 4 is written by Dr. Brian Doyle and is drawn primarily from material developed for the NOx Emissions course offered by the Rutgers Air Compliance Center from 2000 to 2008.

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4 NOx Control - Reduced Flame Temperature

NOx is formed during combustion because the high temperatures break apart a few N_2 molecules making N atoms available to react with oxygen. N_2 is very stable and only decomposes at very high temperatures, so NOx is formed primarily in the hottest regions of the flame - at temperatures above 3000˚F. Any change in combustion that reduces peak flame temperature will reduce the formation of thermal NOx. It should be noted that NO is quite stable and once formed in the combustion zone, it does not decompose as the flue gases cool off. But, if NOx formation can be suppressed in the flame zone, it will not be formed by secondary reactions downstream. So the primary methods of suppressing NOx formation are:

(1) reducing peak flame temperature and
(2) reducing the amount of oxygen present in the peak temperature zones.

In this chapter we explore the common approaches to reducing flame temperature. Note that reducing flame temperature will only reduce the thermal NOx. It has no effect on fuel NOx. Therefor flame temperature reduction techniques are most effective on sources where there is little fuel NOx present - those fired on natural gas or distillate oil. That being said, thermal NOx is always present, so flame temperature reduction is almost always part of any NOx reduction effort - including coal fired boilers where most of the NOx comes from fuel nitrogen.

NOx vs Temperature

Our atmosphere is very stable - there is no tendency for oxygen and nitrogen molecules to react or combine - at ambient temperature. However, at combustion temperatures above 3000˚F the N_2 molecule can break apart so nitrogen atoms can react with oxygen atoms to form NOx in the flame. In simple terms, the hotter the flame, the more NOx is created and the faster it does so. Figure 4.1 shows the results of an early chemical modeling of NOx formation in a typical diffusion burner.

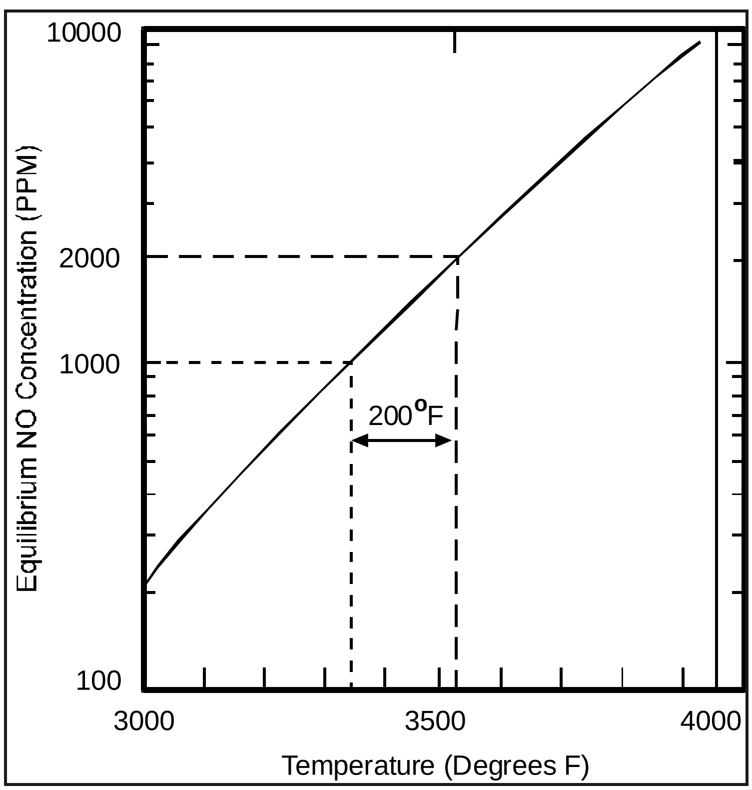


Figure 4.1 NOx Dependence on Temperature

Note that the ordinate (vertical axis) is logarithmic. There are two observations to take away from this example.

1. High flame temperatures create large amounts of NOx and, although it's not shown, the formation rate at high temperature is much faster. So high temperature combustors create a lot of thermal NOx - provided there is some oxygen present.

2. A flame temperature drop of less than 200˚F results in a 50% NOx reduction. A 500˚F drop reduces NOx by an order of magnitude. So NOx reduction concepts that reduce flame temperature are very effective at reducing thermal NOx.

There are many ways to reduce peak flame temperatures. We will look at the three most common methods: water injection, flue gas recirculation and lean premixed combustion. Note at the outset that cooling the flame makes it less stable. As the temperature drops into the range of 2500˚F to 3000˚F, maintaining stable combustion becomes a challenge.

Reducing NO_x with Water Injection

There are a number of methods of cooling the flame, but three methods are most commonly used - **water injection, flue gas recirculation** and **lean premix combustion**. The cooling effect of spraying water in with the fuel is obvious. Water injection was the most common method to reduce emissions from combustion turbines from 1970 until the 1990's. Figure 3.2 is an example of the effect of water or steam injection on turbine emissions. Water injection is not commonly used in other types of combustion sources.

Water injection in a turbine requires very clean water, but there is only a small penalty to engine efficiency. Water provides cooling that would otherwise have to be provided with air - because the maximum allowable turbine inlet temperature is far below the peak flame temperature in the primary zone. Any reduction in the amount of air pumped through the engine improves

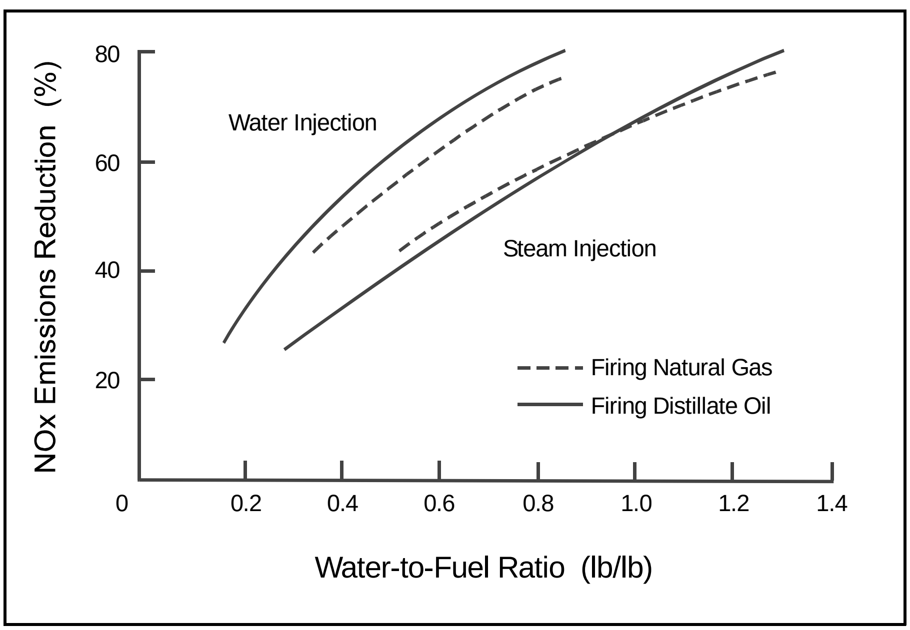


Figure 4.2 Effect of Water/Steam Injection on Turbine NOx

efficiency. Injected water turns to steam which provides added mass flow through the turbine, thus adding power that partially compensates for the energy lost to evaporating water. Water flow rate can be almost as high as the fuel flow rate and NO_x emissions can be reduced by 70-80%.

Water quality is critical, because any contaminants in the water will tend to plate out on the turbine blades, degrading turbine performance. Thus a substantial water purification system is part of injection system for any turbine. The cost of installing and maintaining this system is a drawback to the use of water injection to reduce turbine NOx.

Water injection is not commonly used on boilers because it is hard to make it work well and there are usually other less expensive alternatives for reducing NOx. Water injection has been tried on reciprocating engines, but it reduces engine efficiency and tends to cause operating problems.

Flue Gas Recirculation

Flue gas recirculation (FGR), also called exhaust gas recirculatoin (EGR), works by mixing some flue gas with the incoming combustion air. This increases the mass flow through the combustion zone and decreases the concentration of O_2 available for combustion. Increasing the gas flow in the combustion zone decreases the temperature, because the same amount of energy is distributed to a larger thermal mass.

Two versions of the concept of drawing gas from the exhaust ducts and mixing it with combustion air are shown in Figure 4-3. The upper path, sometimes called "induced FGR" uses the ID fan inlet suction to draw gas from the stack. This increases the flow through

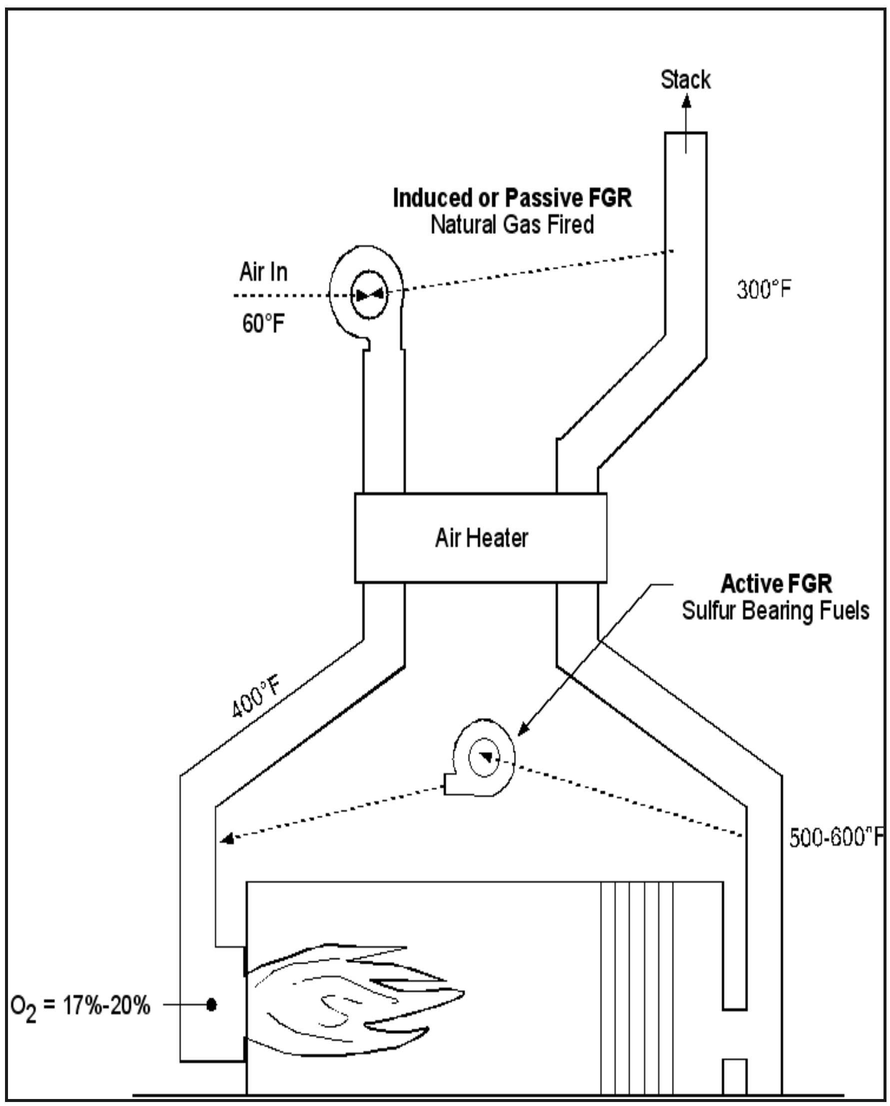
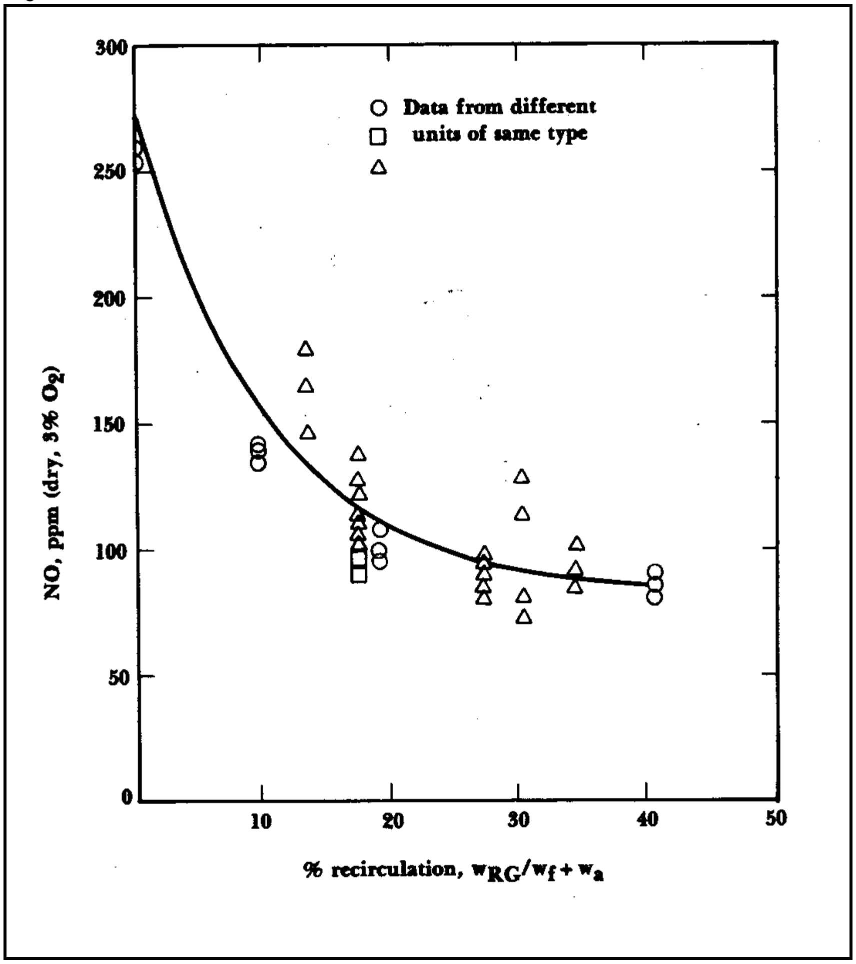


Figure 4-3. Glue Gas Recirculation (FGR) System

the fan, but otherwise there is no energy penalty. The lower path, "active FGR" requires a dedicated fan and pumps relatively hot gas across is significant pressure differential into preheated combustion air - which means that the FGR fan is fairly large. Active FGR systems use a significant amount of power.

Passive FGR is simple, but it cannot be used if there is sulfur in the fuel because acid in the flue gas will condense and corrode the metal in the air supply system. Active FGR systems avoid condensation by keeping the acid above the condensation temperature of about 280˚F. So passive FGR can be used on a natural gas fired boiler because there is no sulfur, but most other fuels require an active FGR in conjunction with an air heater.

Figure 4-4 Effect of FGR on Gas Fired Boiler Emissions



Flue gas recirculation has been used both on boilers and on reciprocating engines. The penalty on boiler efficiency and performance is almost negligible with recirculation rates up to 20-25%. When there is no fuel nitrogen present, NO_x can be reduced by 75% or more as indicated in Figure 4-4. The NOx reduction varies from on system to another depending on how the exhaust gas is introduced to the flame. FGR is typically a part of any effort to substantially reduce NOx emissions from a boiler. Exhaust gas recirculation on RICE requires considerable development and tuning to avoid significant degradation of performance and efficiency. On stationary engines the NOx reduction is frequently not substantial.

Lean Premixed Combustion

One of the most significant developments in low NOx combustion is the development of burners that reduce peak combustion temperature by premixing the fuel and operating sufficiently lean (excess air) that flame temperatures don't reach NOx formation temperatures. Figure 4-5 is a

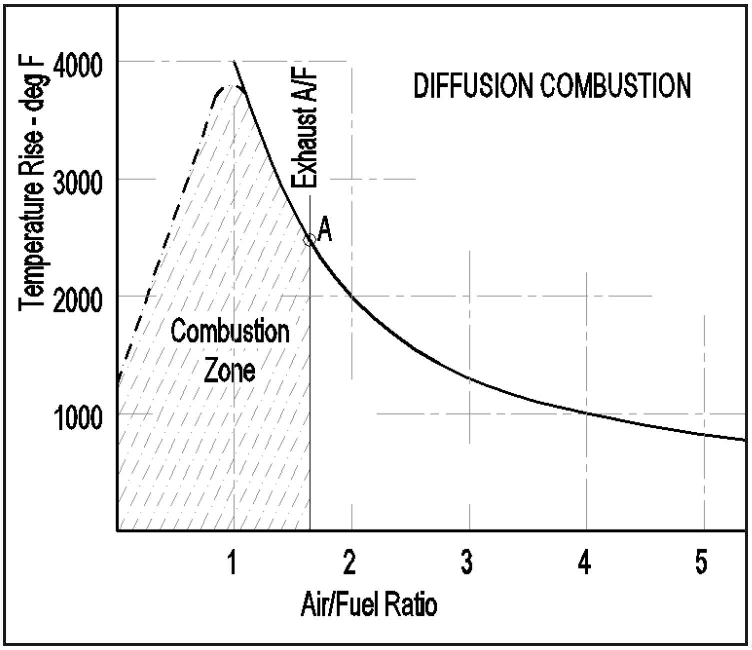


Figure 4-5 - Diffusion & Premixed Temperatures

repeated of Figure 3-1 with a combustion zone shaded to show the range of diffusion combustion temperatures. Diffusion temperatures span the shaded range because mixing occurs during combustion and at some point the fuel passes through the stoichiometric point (equivalence ratio = 1) where very high temperature is possible. Premixed combustion occurs at a single air/fuel ratio equal to the exhaust air/fuel ratio. So premixed combustion temperatures can never exceed a level shown as point “A” on the graph. If you can achieve stable combustion and control the A/F ratio to relatively lean value, perhaps a level near 1.5, then the maximum possible flame temperature can be held to moderate levels - 3000˚F or less.

The problems with premixed lean combustion are:

1. A lean mixture is hard to ignite - it takes a high energy ignition source, and

2. A small deviation to the right - leaner operation - is likely to extinguish the flame. Any flame cooler than about 2500˚F tends to be very tenuous.

So most of the premixed lean combustors are new on the scene (1990+) in response to NOx requirements. The main exception is the gasoline engine. It’s been around a long time, but even here, the advent of low NOx engines with very precise air/fuel ratio control is quite recent. Suffice it to say, most of the traditional burner designs used diffusion combustion because they are relatively easy to design and operate. Until there were low NOx emission requirements, there was no need for the complexity of a very lean premix design. We will look at these in more detail in Chapters 6&7.

Catalytic Combustion

Catalytic combustion is a branch of premixed combustion - it requires a gas fuel that can be premixed with air. As discussed in Chapter 3 catalysts allow combustion to occur at very low temperature with the result that thermal NOx is virtually eliminated. Low temperature combustion is achieved by operating at very lean air/fuel ratios where normal combustion isn’t practical, or even possible. Air pollution engineers are familiar with catalytic combustion when it is used in thermal oxidizers to destroy low concentrations of volatile organic compounds (VOC). In those applications the temperature rise in the catalyst is a few hundred degrees, at most, because not much VOC (fuel) is being burned. But when the catalyst is the main burner, the fuel concentration is much higher and the potential temperature rise can be more than a thousand degrees. If the exhaust temperature from the catalyst is higher than the catalyst destruction temperature, the combustion device will have a short life. Hence two of the challenges in designing catalytic burners are (1) make sure the inlet temperature is maintained high enough to activate the catalyst, but (2) keep the outlet temperature below the destruction point. So the combustion system must be designed with sufficient preheat or initial small burner before the catalyst. And if the desired operating temperature is over about 1800˚F, there must be secondary combustion after the catalyst. So catalytic combustors are potentially more complex than standard burners and can require large expenditures for design and development.

Catalytica developed the XONON gas turbine combustor based on catalytic combustion with NOx emissions of only 1-2 ppm (corrected to 15%) O_2.
The company developed a combustor for one of the smaller GE engines and it's been running successfully for several years. Given this success, the question is why isn't the technology more widely applied? The answer lies is the cost of development and market demand. Turbine engine combustor development is very expensive and the cost would be incurred for each engine line. The engine manufacturers know that once the demonstrated a catalytic combustor for one of their larger engines, then they would be pressured into developing the technology for all their engines. Meanwhile, engine emissions using lean premixed (dry low NOx) combustors and SCR are approaching the level that can be achieved with catalytic combustion.

Alzeta has produced burners under a cleaver concept that addresses both the preheat and peak catalyst temperature rise by passing the premixed fuel and air through a porous ceramic can or thimble.
Combustion is initiated as the mixture passes through the wall of the can, but it's complete outside of the can. The cool air fuel mixture flowing into the inside surface prevents the walls from overheating, but combustion heat, in and beyond the catalyst is sufficient to maintain the reaction. Since the catalyst has significant thermal mass, the Alzeta "flame" won't blow out if there is a momentary loss of fuel flow. This gives it more stability than straight premixed combustion. A turbine application has been demonstrated, but adoption by the gas turbine industry is likely to be limited for reasons noted above. Application in boiler burners is possible, but there is a thermal efficiency penalty whenever a boiler is operated fuel lean - more than a few percent excess air.

Other Temperature Approaches

One other approach to reducing flame temperature has been tried but is much less common. If the combustion air temperature is cooled, the flame temperature will be cooler. Flame temperature is (approximately) the sum of initial temperature plus flame temperature rise. The fuel provides the same energy input regardless of air temperature, so a cooler input gives a slightly cooler flame. In boilers, cooler combustion air is achieved by bypassing the air heater, which raises the stack temperature meaning the boiler loses more heat - it's less efficient. FGR has a relatively small efficiency penalty and it's more effective at reducing NOx, so an air heater bypass is not attractive.

Cooler air fed to a combustion turbine generally doesn't reduce NOx emissions because the combustion temperature is maintained by increasing the fuel flow. Cooler inlet air does allow the turbine to produce more power - the larger the air mass flow through a turbine, the higher the power output. This is the reason for installing a chiller or evaporative cooler (fogging system) on the turbine inlet. NOx is modestly reduced by the presence of water vapor during combustion.

In most combustion systems, there are NOx reduction technologies that are cheaper and more effective than cooling the combustion air, so cooling the combustion air hasn't seen many applications.

Review Exercises

1. Name two fundamental approaches to reducing combustion NOx formation.

2. How does flame temperature affect the conversion of fuel nitrogen to NOx?

3. Water injection is primarily used on what type of combustion systems?

4. Passive flue gas recirculation can be used on boilers firing what type of fuel?

5. In a premixed flame is NOx reduced by increasing or decreasing the excess air level?

6. Are catalytic combustors used with oil fuel?

7. List a technical problem associated with catalytic combustor design/operation.

Review Question Answers

1. a) Reduce peak flame temperatures, b) Reduce flame zone oxygen level.

2. Flame temperature does not affect fuel NOx formation.

3. Combustion turbines.

4. Passive FGR is only used on gas fired boilers. If there is any sulfur in the fuel (oil or coal) condensed acid will damage the combustion air system.

5. In a premixed combustor NOx is reduced by increasing the excess air (air/fuel ratio) - that reduces flame temperature, see Figure 4-5.

6. No. Oil cannot be premixed, so a catalyst cannot be used.

7. Catalytic combustor issues:

Only applicable to gas fired systems.
Preheating is required to activate the catalytic reaction.
Overheating can occur if there is too much fuel - excessive exhaust temperature.

References