

Emissions Control, NO_x, CO, CO₂,

In order to make an effective emission technology selection, the fundamentals of the combustion process and the underlying hardware changes must be understood. This section provides an overview of the combustion process and finishes with a description of the hardware needed, based on the technology selected.

Virtually all combustion processes commercially available for Boiler systems produce some levels of NO_x, and CO emissions. Depending on the fuel type, SO₂, and particulate are also formed. Typically, the contributions of NO_x formations originate as NO. This NO is further oxidized in the exhaust system or later in the atmosphere to form the more stable NO₂ molecule. There are three (3) mechanisms by which NO_x is formed in the burner combustion process, namely; Thermal NO_x, NO_x, which is formed at high temperatures inside the combustion zone, Prompt NO_x, which is quickly formed upon combustion of a fuel, and Fuel NO_x, which is formed from the bound up Nitrogen in the fuel.

These mechanisms are discussed in greater detail in the following paragraphs.

Thermal NO_x is formed by a series of chemical reactions in which oxygen and nitrogen present in the combustion air dissociate and subsequently react to form oxides of nitrogen. The major contributing chemical reactions are known as the Zeldovich mechanism, and take place in the high temperature area of the boiler combustion zone. Simply stated, the Zeldovich mechanism postulates that thermal NO_x formation increases exponentially with increases in temperature and linearly with increases in residence time. Flame temperature is dependent on the air/fuel ratio. The Fuel/Air stoichiometric ratio is the point at which a flame burns at its highest theoretical temperature. Prompt NO_x, a form of thermal NO_x, is formed in the proximity of the flame front as intermediate combustion products such as HCN, N, and NO are oxidized to form NO_x.

Prompt NO_x is formed in both fuel rich flame zones and dry low NO_x (DLN) combustion zones. The contribution of prompt NO_x to overall NO_x emissions is relatively small in conventional near stoichiometric combustors, however, this contribution is an increasingly significant percentage of overall thermal NO_x emissions in Low NO_x and Ultra Low NO_x combustion.

Fuel NO_x is formed when fuels containing nitrogen are burned. Molecular nitrogen, present as fuel bound nitrogen, N₂, in some natural gas, does not contribute significantly to fuel NO_x formation. Some low Btu synthetic fuels contain nitrogen in the form of ammonia (NH₃), and other low Btu fuels such as sewage and process waste stream gases also contain nitrogen. When these fuels are burned, the nitrogen bonds break and some of the resulting free nitrogen oxidizes to form NO_x. With excess air, the degree of fuel NO_x formation is primarily a function of the nitrogen content in the fuel. The fraction of fuel bound nitrogen (FBN) converted to fuel NO_x decreases with increasing nitrogen content, although the absolute magnitude of fuel NO_x increases. For example, a fuel with 0.01 percent nitrogen may have 100 percent of its FBN converted to fuel NO_x, whereas a fuel with a 1.0 percent FBN may have only a 40 percent conversion rate. Natural gas typically contains little or no FBN. As a result, when compared to thermal NO_x, fuel NO_x is not currently a major contributor to overall NO_x emissions from boilers firing natural gas.

The emission of SO₂ in the boiler exhaust is more highly dependant on the type of fuel burned. Essentially, 100% of the sulfur in the fuel will be converted to SO₂ during combustion. Heavy fuels generally have a much higher Sulfur and Nitrogen component, burn much hotter, and thus produce larger SO₂ and NO_x emissions. The level of NO_x formation in a boiler, and hence the NO_x emissions, is unique (by design factors) to each boiler and burner design and operating mode. The primary factors that determine the amount of NO_x generated are the burner design, boiler configuration, the types of fuel being burned, ambient conditions, and operating cycles. These factors are discussed below.

Burner Design The design of the burner is the most important factor influencing the formation of NO_x. Design parameters controlling air/fuel ratio and the introduction of excess air (EA) or flue gas recirculation (FGR) into the combustor strongly influence thermal NO_x formation. Thermal NO_x formation is primarily a function of flame temperature and residence time. The extent of fuel/air mixing prior to combustion also affects NO_x formation. Simultaneous mixing and combustion results in localized fuel rich zones that yield high flame temperatures in which substantial thermal NO_x production takes place.

The recirculation of flue gas (FGR) into a conventional combustor provides a heat sink, adds mass that effectively reduces peak flame temperature, thereby reducing thermal NO_x formation. Premixing air and fuel at a fuel lean ratio approaching the lean flammability limit significantly reduces peak flame temperature, resulting in minimum NO_x formation during combustion. This is known as simulated premix combustion.

Simulated Premix Burners. Conventional burner combustors are diffusion controlled. The fuel and air are injected in separate zones. Combustion occurs locally at stoichiometric interfaces resulting in hot spots that produce high levels of NO_x. In contrast, premix combustors generally operate in a premixed mode, where air and fuel are mixed before entering the combustor. In premixed flames, the underlying principle is to supply the combustion zone with a completely homogenous, lean mixture of fuel and air. This homogenous mixing, generally results in a much lower production NO_x

compounds during combustion. Additionally, a useful byproduct of this combustion technique is it is essentially free of carbon formation, especially when gaseous fuels are used. This is an important factor as it means that more air is available for lowering the temperature of the combustion zone and improving the combustor pattern factor.

Type of Fuel The level of NO_x, SO₂, and particulate emissions varies for different fuels. To a lesser extent CO, as this is primarily a result of the efficiency of combustion. In the case of thermal NO_x, this level increases with flame temperature. For gaseous fuels, the constituents in the gas can significantly affect NO_x emissions levels. Gaseous fuel mixtures containing hydrocarbons with molecular weights higher than that of methane (such as ethane, propane and butane) burn at higher flame temperatures, and as a result can increase NO_x emissions greater than 50 percent over NO_x levels for methane gas fuel. Refinery gases and some unprocessed field gases contain significant levels of these higher molecular weight hydrocarbons. Conversely, gas fuels that contain significant inert gases, such CO₂, generally produce lower NO_x emissions. These inert gases serve to absorb heat during combustion, thereby lowering flame temperatures and reducing NO_x emissions. This is the resultant effect of adding flue gas recirculation to a combustion process. Other examples of this type of gas fuel are air blown gasifier fuels and some field gases. Combustion of hydrogen also results in high flame temperatures, and gases with significant hydrogen content produce relatively high NO_x emissions.

Distillate oil burns at a flame temperature that is approximately 150 °F higher than that of natural gas. As a result, NO_x emissions are higher when distillate oil is burned instead of natural gas. Low Btu fuels such as coal gas burn with lower flame temperatures, which result in substantially lower thermal NO_x emissions than those produced by natural gas or distillate oil. Fuels such as # 6 and # 2 fuel oils generally produce more NO_x compounds than natural gas. However, SO₂ and particulate levels can be greatly reduced with a lighter, and lower sulfur containing fuels such as # 2 diesel, with a sulfur content less than 0.5% by weight.

NO_x Control: SCR, and SNCR Selective Catalytic Reduction (SCR). The SCR process consists of injecting ammonia upstream of a catalyst bed. It is critical to the design of the SCR to produce efficient and complete mixing prior to the ammonia making contact with the catalyst surface. NO_x combines with the ammonia embedded on the catalyst surface, and is reduced to molecular nitrogen through the activation energy of the catalyst. SCR is capable of over 95 percent NO_x reduction (reference Peerless Mfg. Co. Dallas, Tx.) Titanium Oxide in a homogenous extruded substrate is the SCR catalyst material most commonly used, though vanadium pentoxide, noble metals, or zeolites are also used, depending on the type of fuel and operating temperature of the exhaust gas. The ideal operating temperature for a conventional SCR catalyst is 400 to 750 °F. New catalyst formulations have been developed which extend these temperature ranges. However, with these new catalyst formulations are associated deeper catalyst beds which increase pressure drop, shorter catalyst life, and higher capital cost, etc.

Typically, the catalyst reactor is mounted on a spool piece, located within the exhaust stack or in the discharge duct before the stack section, at a location where the gas temperature of a boiler is typically in the ideal range of 450 to 750 °F. High temperature zeolite SCR catalysts for applications have been developed that permit continuous SCR operation at temperatures as high as 1050 F. High temperature SCR catalysts must be used with applications where exhaust temperature ranges from 850 to 1000 F range.

A certain amount of ammonia slip occurs when using SCR. Ammonia slip is usually limited by permit conditions to 5 or 20 ppm, corrected to 3 percent O₂. Ammonia is classified as an air toxic compound in California. Ammonia passing through the SCR and emitted to atmosphere can combine with nitrate (NO_x) or sulfate (SO₄) in the ambient air to form a secondary particulate, either ammonium nitrate or ammonium sulfate. Based on 1995 District data, ambient NO_x and SO₄ concentrations are greater than ambient ammonia concentrations.

SO₂ Control SO₂ control is briefly discussed for completeness, however not considered applicable in a natural gas only environment.

The wet venturi scrubbing technique is a wet system capable of removing both SO₂ and particulate in flue gas from oil fired and coal-fired boilers burning medium- to high-sulfur fuels. In the basic process, the centrifugal scrubber imparts a spinning motion on the gas passing through, resulting from a tangential entry of the gas stream. The particulate are impacted into the wet scrubbing droplets injected before the venturi. The flue gas passes through a venturi scrubber located downstream of the boiler exhaust; the particulate emissions are embedded and grown in size through the collision mechanism. The cyclonic action then serves to remove the particulate from the gas stream. SO₂ is then reacted with the caustic solution (NaOH), which is injected into the spray mechanisms. Cleaned flue gas then passes into the atmosphere through the stack. The process is expected to achieve SO₂ reductions of 90%.

The basic process chemistry associated with the SO₂ removal, consist of injecting potassium, ammonium, or sodium salt solution into the gas stream. As described above, this application uses Sodium Hydroxide (NaOH) solution. The pH of the entrainment fluid is then controlled, and the resulting salt formations are removed through a blowdown mechanism. The solution is considered wastewater, is not available for further SO₂ removal, and is therefore not considered a regenerative process.