

Reduced NO_x Emissions for Natural Gas Fired Water Bath Vaporizer

Natural gas is one of the foremost combustion fuels used throughout the country. It is primarily used to generate industrial and utility electric power, produce industrial process steam and heat, and heat residential and commercial space. Cryoquip has long taken advantage of this cheap and abundant energy source to provide process heat for our Natural Gas Fired Water Bath Vaporizers. Due to the flexibility inherent in the natural gas combustion process, these vaporizers are consistently offered as a reliable and economical option in a wide range of process flow rate capacities.

Fossil Fuel Emission Levels
Pounds per Billion Btu of Energy Input

| Pollutant | Natural Gas | Oil | Coal |
|-----------------|-------------|---------|---------|
| Carbon Dioxide | 117,000 | 164,000 | 208,000 |
| Carbon Monoxide | 40 | 33 | 208 |
| Nitrogen Oxides | 92 | 448 | 457 |
| Sulfur Dioxide | 1 | 1,122 | 2,591 |
| Particulates | 7 | 84 | 2,744 |
| Mercury | 0.000 | 0.007 | 0.016 |

Figure 2: Source Eia - Natural Gas Issues And Trends 1998

Reduction of carbon dioxide emissions is always a chief concern from an environmental stand point, however, 99.9 percent of the carbon dioxide produced during natural gas combustion is a direct result of the combustion process itself. Therefore, aside from the benefit gained from using natural gas as a fuel source, versus using other fossil fuels, there can be only minor improvements to the amount of carbon dioxide produced. These improvements come solely from having a burner system that is properly tuned and efficient. Another lesser-known focus that has become more prevalent in recent years is the reduction of the emissions of nitrogen oxides from natural gas combustion sources.

Nitrogen oxides, or NO_x, is a generic term for the mono-nitrogen oxides NO and NO₂ (nitric oxide and nitrogen dioxide). NO_x gases are formed solely as a byproduct of the natural gas combustion process, and not as a direct product of the combustion reaction. They are produced whenever combustion occurs in the presence of nitrogen, as is the case when air is used as the source of oxygen, and are also produced naturally by lightning in the atmosphere.

NO_x formation occurs by three fundamentally different mechanisms. The principal mechanism of NO_x formation in natural gas combustion is called thermal NO_x. The thermal NO_x mechanism occurs through the thermal dissociation and subsequent oxidation of the diatomic nitrogen molecules found in the combustion air. Most NO_x formed through the thermal NO_x mechanism occurs in the high temperature flame zone near the burners, and are dependent on oxygen concentration, peak temperature and length of time of exposure at peak temperature.

The second mechanism of NO_x formation is called prompt NO_x. The prompt NO_x mechanism takes place in the earliest stage of combustion through reactions of nitrogen molecules in the combustion air and hydrocarbon radicals from the fuel. Prompt NO_x reactions occur within the flame and are generally regarded as negligible when compared to the amount of NO_x formed through the thermal NO_x mechanism. The exception to this is when dealing with ultra-low-NO_x which can successfully achieve thermal NO_x formation values in the realm of single digit ppm concentrations.

The third and final mechanism of NO_x formation, called fuel NO_x, arises from the evolution and reaction of fuel-bound nitrogen molecules with oxygen in the combustion air. This mechanism is easily ignored in natural



Figure 1: Natural Gas Fired Water Bath Vaporizers

As with any winning strategy, continuous improvement and innovation are vital components to success in the future. Cryoquip strives to never let past success give pause to the steady course of progress. As such, we consistently look for potential enhancements that can be made to benefit both the customer and the industry. One particular area of interest that comes to light when discussing natural gas combustion is emissions levels, and the ever-changing landscape of federal and state air quality standards. Although natural gas is already known to be the cleanest burning of all the fossil fuels, as evidenced in the Environmental Protection Agency's data comparisons in Figure 2, it is still clear that the combustion process produces trace amounts of pollutants in the exhaust gases that, in large concentrations, are known to be harmful to humans and the environment.



Photochemical smog over Mexico City, 2010

gas combustion, due to the fact that the characteristically low nitrogen content of natural gas, NO_x formation from fuel NO_x is insignificant.

So, why worry about reducing NO_x emissions when most are concerned with eliminating greenhouse gases, in the form of CO₂ emissions? There are several answers to that question. The first is an issue we are all too familiar with, being located in Southern California. Smog. Specifically, photochemical smog, a major component of which is NO₂. The majority of NO_x produced during combustion (approximately 95 percent) is in the form of NO. Once emitted into the atmosphere, however, NO is rapidly and continuously oxidized to form NO₂. Where high concentrations of

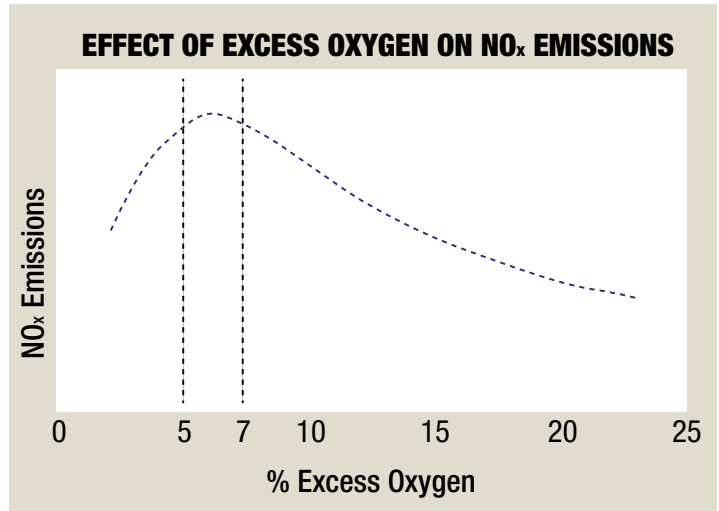


Ozone formation

this compound and certain other volatile organic compounds (VOCs) accumulate and react in the presence of sunlight, photochemical smog is formed. NO₂ molecules themselves, in high concentrations, have been found to cause damage to sensitive lung tissue in senior citizens, children, and those with preexisting heart and lung conditions.

Another major component of photochemical smog is tropospheric ozone, which is also produced as a byproduct of NO_x emissions. Tropospheric ozone is ozone (O₃) which is formed and concentrated near ground level, when sunlight causes an NO₂ molecule to react with a VOC molecule to produce NO and ozone. The NO molecule then reacts with free radicals in the atmosphere to produce a new NO₂ molecule. In this way, each molecule of NO can produce ozone multiple times. This process repeats until the VOC molecules are reduced to short chains of carbon compounds that cease to be photo reactive. A VOC molecule can usually support this

process about 5 times. Ozone is exceedingly dangerous, because it reacts strongly to destroy or alter many biological molecules, and can reduce forest growth and crop yields in high concentrations. In humans, ozone can reduce lung capacity and worsen pre-existing heart and lung conditions. The negative effects of tropospheric, ground level ozone contrast sharply with the protection from harmful UV-B radiation provided by the layer of stratospheric, or upper atmospheric, ozone, known as the ozone layer.



Effect Of Excess Oxygen On Nox Emissions

A third effect caused by excessive NO_x emissions is acid rain. NO₂ can dissolve in atmospheric moisture to form nitric acid, a component of acid rain. Although nitric acid is not particularly harmful to humans, except in concentrations much higher than could be achieved by this process, it can be harmful to plant life and structures. By the same process that creates nitric acid in the atmosphere, NO₂ has been found to contribute the eutrophication of coastal and stagnant waters. Eutrophication occurs when a body of water suffers an increase in nutrients that leads to a reduction in the amount of oxygen in the water. This produces an environment that is destructive to fish and other wildlife.

Factoring in all of the effects that NO_x gases contribute to, it quickly becomes clear that there are a number of benefits to reducing the population and environmental exposure to these gases. This is why in 1971, the Environmental Protection Agency (EPA) set ambient pollutant standards for NO₂ as part of the National Ambient Air Quality Standard (NAAQS). NO₂ is used as the indicator, because it forms quickly from combustion emissions, and it is not only itself a harmful air pollutant, but the contributing reactant to the formation of ground level ozone and acid rain. Since then, it has been found that over 90 percent of NO_x emissions are anthropogenic (generated by human activity), 49 percent of which is formed from transportation sources, and 46 percent of which is from fuel combustion sources. As a result of state and federal efforts to meet and exceed the NO₂ concentrations standards, the average annual ambient NO₂ concentrations have decreased by more than 40 percent since 1980. With the increased use of low NO_x-emitting burners, these numbers will continue their decreasing trend.

NO_x emissions can be reduced for natural gas combustion in a number of ways. The most common and economical ways focus on reducing the flame temperature during combustion. This can be accomplished using a few different techniques.

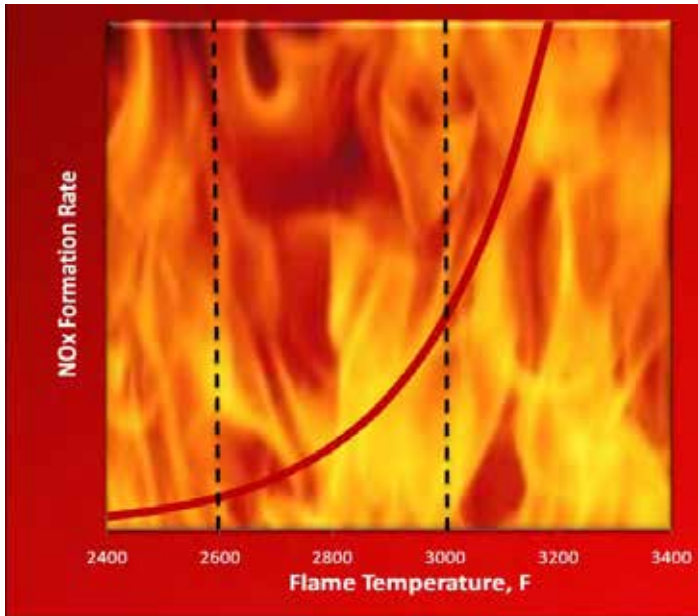


Figure X: Flame Temperature vs. NOx Formation Rates

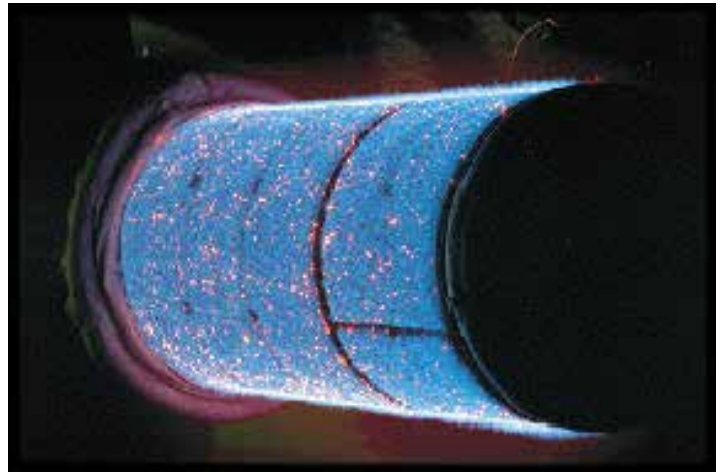
The first technique is to use a flue gas recirculation (FGR) system. In a FGR system, a portion of the exhaust gas (flue gas) is recycled from the exhaust stack to the burner air intake, mixed with the incoming combustion air, and fed into the burner. The recycled flue gas consists of combustion products which act as inerts during the combustion of the fuel/air mixture. This serves to reduce the formation of NOx, by two mechanisms. Primarily, the recirculated gas acts as a diluent to reduce the combustion temperatures, thus suppressing the thermal NOx mechanism. As a secondary mechanism, FGR also reduces NOx formation by limiting the amount of oxygen available for the dissociated nitrogen atoms to react with, because the majority of the oxygen in the flue gas has already been consumed by the initial combustion process. With this process, we are able to reduce NOx emissions by over 60 percent



Figure 6: FGR Piping

Another technique that has been implemented by burner manufacturers, which we have found to be a very robust solution to reducing NOx emissions, has been the use of pre-mixed surface stabilized combustion burner designs. This method reduces the flame temperature through the use of excess air in the combustion gas. Typically, the implementation

of high excess air (fuel lean) mixtures results in flame instability at high capacities. By pre-mixing the fuel and air in a primary chamber, distributing the mixture through a mesh of metal or ceramic fiber, and maintaining combustion uniformly across the surface of this mesh, combustion stability is preserved, and NOx formation is greatly reduced. This technique eliminates the need for external piping required for the FGR system, and achieves a lower flame temperature by operating leaner, while at the same time creating a homogenous mixture of fuel and air to prevent the existence of fuel rich combustion zones. In certain applications, this system is capable of reducing the formation of NOx by as much as 90 percent.



Surface Stabilized Combustion

A third method that may soon become an option to further reduce NOx emissions, employs the process of fuel staging. In this method, the fuel is divided into primary and secondary streams and injected into separate combustion zones. In the primary zone, fuel lean combustion reduces flame temperature. In the secondary zone, the oxygen depleted air from the primary zone prevents further NOx formation. This is typically a less economical solution, but with the combustion of fuel staging and external FGR, NOx levels can be reduced to meet and exceed even the most exacting local emissions standards.

Employing any one of these techniques also requires the use more sensitive control systems in order to ensure that the burner system is always running at the optimal efficiency. To achieve the most efficient combustion throughout the entire capacity range of a given burner system, we have employed several strategies which allow for a more fine tuned combustion curve under various conditions. By adding a variable speed drive to the blower motor, a system is able to achieve the desired air flow within a much smaller range to maintain the proper fuel/air ratio needed for optimal combustion. In addition, exhaust gas monitoring systems, such as an O₂ trim system, monitors the amount of excess O₂ present in the exhaust gas and automatically adjusts the variable frequency drive (VFD) setting to compensate for high or low readings caused by varying ambient conditions. A burner system operating with these components in place can provide the highest level of emissions control yet possible for a natural gas fired vaporizer.

For further information, go to www.cryoquip.com.