CALIFORNIA DREAMING

Joe Colannino and Roberto Ruiz, ClearSign Combustion, USA, introduce an innovative piece of technology that was able to help a Californian refinery reduce its NO_X emissions.

Refinery fuels present manifold challenges to achieving ultra-low emissions. Most refinery heaters are natural draft rather than forced draft (as was the case with a refiner in California, US, which is discussed later in this article). Natural draft offers minimal airside momentum for flame shaping. Additionally, many ultra-low nitrogen oxide (NO_X) solutions rely on flue gas recirculation (FGR) – an inconvenience for natural draft units. If FGR is used, a costly conversion to forced draft is often required.

Moreover, refinery fuel is notoriously variable. Most hydrocarbons require approximately 100 ft^3 of air per Btu of heating value (ft^3/Btu), but hydrogen requires about 20% less air on that basis. It is not atypical for hydrogen content in a refinery fuel to swing threefold in concentration, with occasional excursions to much higher concentrations. Hydrogen has a higher flame temperature than hydrocarbons. Since NO_X is thermally driven, rising hydrogen content typically leads to higher NO_X.

NO_X formation

Except from upset conditions or maloperation, refinery fuels typically contain no fuel-bound nitrogen.[*] Without fuel-bound nitrogen, the major pathway to NO_X formation is actual fusion of the nitrogen (N_2) and oxygen (O_2) from the combustion air. This occurs primarily in the thermal (Zeldovich) NO_X-formation mechanism. Thermal NO_X formation may be understood as a function of the integral of time (linear), temperature (exponential), and oxygen concentration (square root). This is given in the following equation where C_{NO}, C_{N2}, and C_{O2} are the concentration of

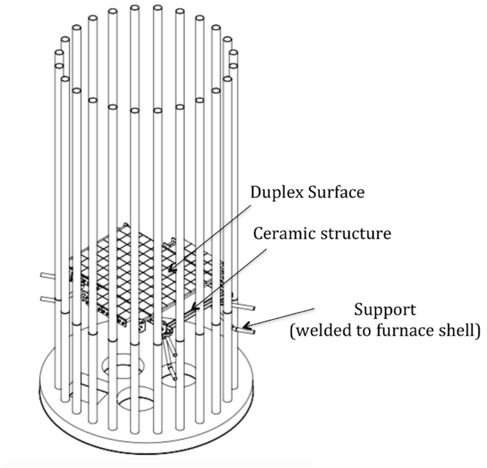

Figure 1. The surface is anchored at a predetermined distance above the burner floor (note the three burner cutouts there) to provide for rapid and complete combustion without appreciable NO_X or CO.

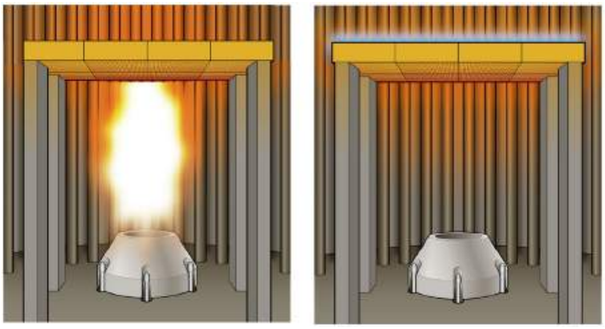

Figure 2. The technology operates in two steps. First, a burner is used to warm the DUPLEX surface (left); second, the flame is transferred to the DUPLEX surface (right) generating 5 ppm NO_X without appreciable CO.

nitric oxide, N_2, and O_2, respectively; *A* and *b* are constants; *t* is time; and *T* is temperature:

$$C_{NO} = AC_{N2}\int_0^t e^{-\frac{b}{T}}\sqrt{C_{O2}}\,d\theta$$

How ULNBs work

Ultra-low NO_X burners (ULNBs), which produce less than 10 ppm NO_X, typically reduce NO_X by attempting to reduce flame temperature, and to a lesser extent, local O_2 concentration. One way to reduce the flame temperature is through the use of FGR. The flue gas adds inert mass to cool the flame, as well as homogenising it. Since NO_X is exponentially weighted with temperature, small regions of peak flame temperature can dominate NO_X production. Adding additional mass and momentum in the form of recirculating flue gas can help to homogenise the flame and reduce peak flame temperatures, thereby lowering NO_X.

Another common ULNB technique is to stage combustion in discrete zones to decrease local available O_2 concentration. If local O_2 can be minimised, then less O_2 is available to fuse with N_2 and form NO_X.

Staging fuel and air also stretch the flame. A longer flame has more radiating surface and can exchange heat with the surrounding process to lower its temperature and thermal NO_X.

Common problems with ULNBs

Common problems with ULNBs in refinery service are the requirement for FGR, potential for plugging of fuel nozzles, decreased stability, and flame impingement. First, FGR is difficult to come by in a refinery because most heaters are natural draft and do not have enough excess draft pressure to induce sufficient FGR to reduce NO_X. This can be overcome by converting the heater to forced draft operation, but this is often not economically practical. Moreover, FGR contains significant moisture, which can condense or corrode moving parts such as air dampers and registers. Second, UNLBs generating less than 9 ppm require copious quantities of FGR – approximately 30% of the total flue gas must be returned to the burner inlet. Even greater amounts of FGR are required to achieve sub-5 ppm NO_X. For all these reasons, FGR is generally impractical as a sub-5 ppm NO_X solution in a refinery. This limits UNLBs in refinery service to approximately 10 ppm NO_X, except under exceptional circumstances.

Staging fuel requires a multiplicity of orifices. Since the heat release for a given unit is fixed, dividing the fuel circuit into a greater number of fuel orifices reduces individual orifice size. Refinery fuels are typically not as clean as natural gas and small holes in the fuel circuit may plug, leading to safety, stability, and operational problems. Moreover, ULNBs tend to have much longer flames due to air and fuel staging, and such flames can impinge on process tubes and downstream structures, again creating safety and operational problems. For example, continual flame impingement can lead to fouling inside the process tube. The fouling acts as an insulator and interferes with the ability of the process fluid to cool the tube, resulting in local overheating and the possibility of rupture or explosion. Intermittent flame impingement can lead to cyclical reduction and oxidation of superalloy tubes in refinery heaters. The superalloys in refinery heaters rely on a protective oxide coating to maintain their high temperature resistance to oxidation. Flame impingement can reduce this oxide coating, so when the metal is re-exposed to oxygen it re-oxidises. As this cycle re-occurs, the metal is slowly consumed, resulting in reduced wall thickness and ultimately rupture.

In short, ULNBs are generally impractical for sub-5 ppm NO_X in refinery service.

SCRs

In some cases, selective catalytic reduction (SCR) provides a solution for NO_X reduction that can achieve sub-5 ppm NO_X. With SCR, ammonia (NH_3) is reacted with NO_X over a catalyst in a downstream reactor to produce elemental nitrogen and water, according to the global reaction:

$$NH_3 + NO + ½\ O_2 = N_2 + 3/2\ H_2O$$

Often, it makes more economic sense to control process units with a central SCR, rather than individual SCR reactors for each process unit. However, SCR requires a

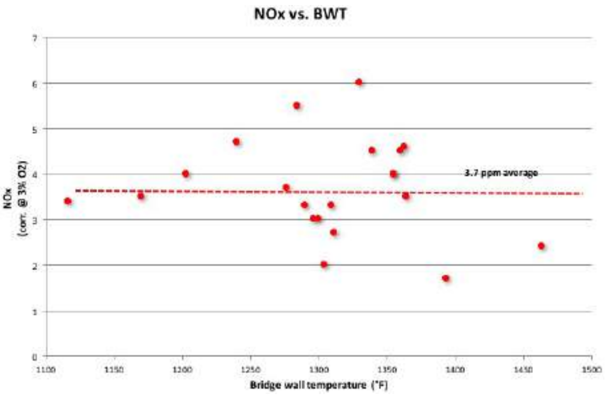

Figure 3. NO_X vs bridge wall temperature: NO_X from DUPLEX operation is a weak function of bridgewall temperature, with average NO_X emissions below 4 ppm.

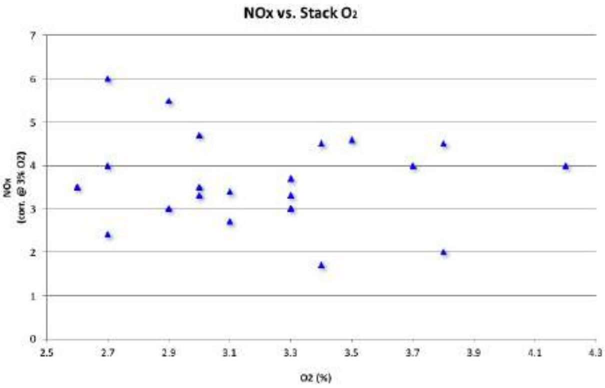

Figure 4. NO_X vs zirconium oxide (wet) oxygen probe measurement: NO_X from DUPLEX technology is a weak function of excess oxygen, and generally shows a mild decrease at higher excess oxygen levels.

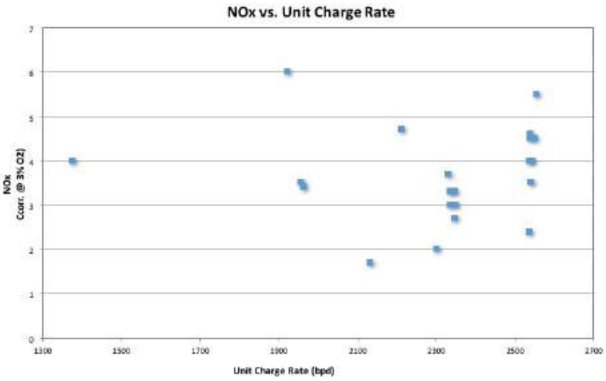

Figure 5. NO_X vs reformer unit charge rate: NO_X from DUPLEX technology is relatively insensitive to firing rate.

catalyst, a constant supply of ammonia or similar reagent, and the potential transport of hazardous material. SCR is also an order of magnitude more expensive than ULNBs. However, SCR can achieve sub-5 ppm NO_X levels, which typically requires the use of ammonia in excess. It is common for NH_3 to slip from the reactor through the stack and into the atmosphere. This is now regulated to less than approximately 5 ppm.

Distal surface architecture

Combustion emissions can be minimised at the source to sub-5 ppm NO_X levels, through a combustion reaction occurring distal (rather than proximal) to the burner. A flame in a typical process heater may be 10 or 20 ft long, depending on the time it takes to mix the fuel and the air in a combustion reaction. If combustion were to take place downstream of the burner, after where the fuel and air are mixed, the resulting combustion reaction could occur in inches rather than feet. However, this requires a downstream surface to hold the resulting flame.

Case study

A California refiner required a sub-6 ppm solution for a multiple-burner heater. ClearSign Combustion's DUPLEX^{TM} technology was selected for the project. The technology uses a porous ceramic matrix to provide a downstream combustion surface (Figure 1), which can retrofit to any existing conventional, low NO_X, or ultra-low NO_X burner. The technology reduces NO_X from every element of the Zeldovich mechanism. First, because the surface behaves nearly as a blackbody with an emissivity much higher than the flame, more heat is radiated to the process, cooling the flame and reducing NO_X. Moreover, since the combustion occurs in inches rather than feet, there is little time for NO_X to form. Finally, prior to combustion, the fuel and air have already entrained flue gas produced at the surface, thus lowering the initial oxygen concentration. The result is sub-5 ppm NO_X without any need for external flue gas recirculation, fans, SCR apparatus, long flame lengths or other associated but problematic issues associated with ULNBs.

A typical operating scenario for the technology requires two steps: first, heating the surface above the fuel's automatic ignition temperature; and second, transferring the combustion from the burner to the surface (Figure 2). The first step is typically accomplished with an existing burner. Once the wall is sufficiently warm, the flame transfer is brought about by a second set of nozzles designed to stabilise at the surface rather than the burner. A flame scanner with a view of the surface identifies flame transfer and combustion per design, resulting in sub-5 ppm NO_X. Moreover, because existing burners can be retrofit to work with the technology, it de-risks a retrofit – existing burners can always be re-utilised to generate process heat (albeit with higher NO_X).

Installation and results

Such was the case for the Californian refiner, whose permitted NO_X level was 6 ppm corrected to conditions of 3% dry excess oxygen. The technology was installed during a two-day shutdown (one day to cool the heater down and half a day to install the surface comprising a modular ceramic support structure and porous ceramic tiles).

Data were collected to verify NO_X performance under operating conditions using a Testo 350 analyser equipped with a low-NO_X cell. Flue gas samples were drawn from the furnace stack and conditioned using a sample dryer to give NO_X on a dry basis. Wet oxygen data were obtained using an in-situ zirconium oxide oxygen probe located downstream of the convection section. Over 100 data points were obtained during a six week period (Figures 3, 4 and 5) representing averaged daily data. Figure 3 shows the NO_X performance as a function of the process heater bridgewall temperature, while Figure 4 plots NO_X as a function of wet O_2.

Figure 6. DUPLEX surface glow: view from viewing port on furnace shell (left), and view from viewing port on furnace floor (right). The surface glow may be considered a qualitative measure of performance, where a relatively uniform glow indicates good distribution of fuel and air along the surface, leading to optimal NO_X performance.

The reboiler process heater serves a downstream reformer. As such, refinery operations requested a plot of NO_X from the technology's operation as a function of the reformer charge rate. Note that daily unit and reboiler charge rates were kept constant and experienced minor daily deviations (Figure 5).

NO_X results met or exceeded the project's objectives. In addition, average CO emissions were 25 ppm (corrected to conditions of 3% excess O_2 on a dry basis) and were consistently lower than the permitted level of 50 ppm in spite of the relatively low bridgewall temperature. Furthermore, performance of the surface was stable over all of the process conditions encountered during the evaluation period. Figure 6 shows the operating surface.

Conclusion

The technology was able to generate sub-5 ppm NO_X in the refinery heater without the need for additional excess air, FGR, or catalysts and reagents. As a retrofit strategy, it worked with the existing burner. With the flame stabilised on the surface, sub-5 ppm NO_X was demonstrated independent of the original burner NO_X and without additional production of CO.

Note

*Fuel-bound nitrogen refers to nitrogen-bound within the fuel molecule, in contrast to small concentrations of nitrogen in the fuel gas, which act merely to reduce the heating value slightly.