Duplex™ – A Creative Innovation in Industrial Combustion Technology

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Abstract
Duplex Technology has been installed in a Vertical Cylindrical (VC) reformer-splitter reboiler process heater with a maximum firing capacity of 11.25 MMBtu/hr at a California refinery. The technology has successfully demonstrated the capability to operate with unmatched NOx emissions of sub-6 ppm (corrected to 3% O_2), without external flue gas recirculation (EFGR) or selective catalytic reduction (SCR), over a wide range of refinery process conditions.

Background
Duplex is a revolutionary gaseous fuel combustion technology that has proven its capability to reduce environmental emissions of nitrogen oxides (NOx), a highly regulated pollutant in industrial applications, to the very low levels required by the most stringent regulations in the country, while enhancing heat transfer characteristics. The technology has been successfully implemented in Once-Through Steam Generators (OTSGs) in Enhanced Oil Recovery (EOR) applications[1], and more recently in refinery process heaters.

Duplex incorporates a high-temperature porous ceramic matrix (i.e., Duplex surface) positioned at a distance a few feet away from where the fuel and air are introduced in the furnace (Figure 1). Fuel and air are thoroughly mixed before reaching the Duplex surface. The fuel/air jet entrains internal flue gases diluting the mixture. The diluted mixture is then ignited by the hot, glowing Duplex surface where the bulk of the combustion process takes place within the matrix porous passages. Duplex provides an effective combustion stabilization, flame confinement and radiation source.

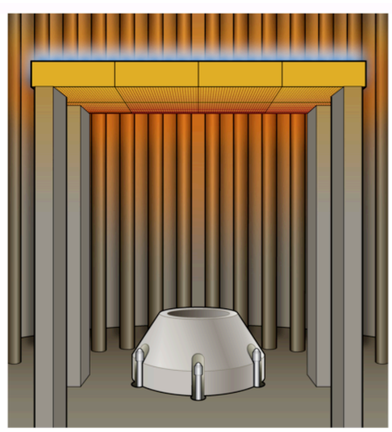

Figure 1. Schematic of Duplex in a VC heater

[1] "Duplex™ Technology Demonstrates Sub-5 PPM NOx and CO Simultaneously Without SCR, FGR, or High Excess Air" – D. Karkow, et.al., AFRC 2015 Symposium

The technology integrates several NOx reduction techniques that combine to deliver extremely low NOx emission levels:

- *Pre-mixed combustion behavior*. Fuel and air are introduced in the furnace in a manner consistent with a diffusion flame burner; however, in contrast with conventional raw gas burners in which ignition takes place at the burner throat immediately after the fuel and air start mixing, Duplex ignition does not take place until fuel and air reach the Duplex surface. Although fuel/air injection is configured as a diffusion system, fuel and air have the opportunity to thoroughly mix as they travel the distance before ignition occurs. The system behaves as a premixed system with its inherent NOx reduction benefits but without the disadvantages of pre-mixed combustion (i.e., flashback).
- *Fuel/air mixture dilution*. Internal flue gas is entrained along the length the fuel/air jet travels providing enhanced dilution of the jet. This dilution contributes to reduced peak flame temperatures for better control of thermal NOx.
- *Radiation cooling*. Because combustion primarily occurs within the Duplex surface, the majority of the energy transfer takes place as solid body radiation (gray body). Solid body radiation is a considerable more effective energy transfer mechanism than flame radiation, the primary energy transfer in conventional burners. This is because of the highly spectrally dependent manner in which gaseous fuel flames radiate energy. The enhanced radiation heat transfer by Duplex contributes to thermal NOx reduction by radiative cooling of the flame[2].

In addition to being able to operate with very low emissions of NOx, Duplex has also shown to provide other benefits[1]:

- *Elimination of flame impingement*. A NOx reduction strategy in the design of ultra-low NOx (ULN) burners incorporates delayed fuel/air mixing (i.e., flame stretching). Unfortunately, stretching flames creates buoyant flames that are often impacted by furnace currents or coalesce with adjacent flames leading to flame impingement on process tubes or shock tubes in the convection section. Duplex combustion is confined within the Duplex surface eliminating any possibility for flame impingement.
- *Enhanced CO oxidation*. With Duplex, fuel and air are thoroughly mixed prior to ignition, eliminating fuel rich and fuel lean zones that may contribute to CO production in conventional burners. Furthermore, Duplex provides very uniform temperature on the surface further enhancing CO oxidation.
- *Enhanced radiation heat transfer*. As previously described, Duplex provides a considerable enhancement in radiation heat transfer over conventional burner flames as it radiates energy as a gray body. In addition, radiation is further improved by the porous nature of the Duplex surface. The cavities in the porous surface enhance emissivity properties of the high-temperature ceramic material as a result of the apparent emissivity phenomena[3].
- *Noise reduction*. Laboratory experiments have demonstrated that sound pressures levels can be reduced from an average of 85 dB in burner mode to an average of 72 dB in Duplex mode. This is attributed to the fact that the turbulent nature of combustion is essentially eliminated in Duplex mode as laminar combustion takes place mostly within thousands of small cavities in the Duplex surface.

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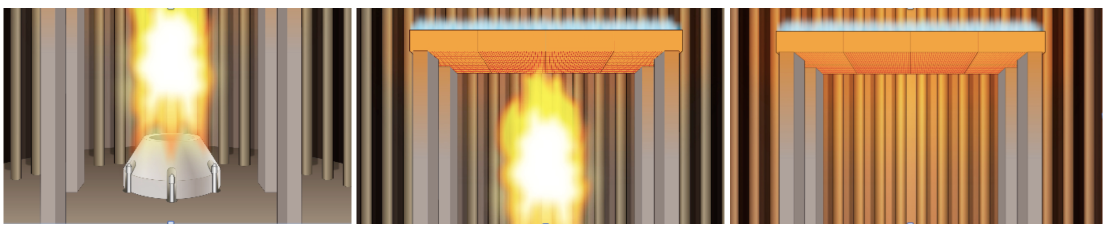
2 "Radiative cooling in a flame holder for NOx reduction" – Breidenthal, R.; et.al., American Physical Society Division of Fluid Dynamics Fall (2014). Bibliographic Code: 2014APS..DFDA34005B.

3 "Thermal Radiation Heat Transfer," R. Siegel & J. Howell, Published by Taylor & Francis, 4th Edition, 2002

Duplex Modes of Operation

- *Cold furnace start up and warm up (burner-mode operation)*. Conventional process heater start-up procedures are followed. That is, burner pilots are ignited followed by proof of ignition. Burner ignition follows according to standard refinery process heater and burner procedures. The heater operates in burner mode (i.e., flames stabilized at the burner throat/tile) during the furnace and Duplex surface warm up period. Standard burner ramp-up and furnace soaking periods should be followed.
- *Transition*. Once the standard heater warm up procedures have been met, Duplex surface temperature is verified to ensure it is above the ignition temperature of the gas. There is no direct ignition temperature measurement but the temperature is typically correlated to the heater bridge wall temperature and/or the Duplex surface glow. Once ignition temperatures are verified, fuel supply to the burner nozzles is interrupted and fuel supply to the Duplex fuel nozzles is started concurrently effecting transition to Duplex operation. A few seconds later and upon confirmation of Duplex operation, burner pilots are shut off.
- *Duplex-mode operation.* Once transition has been accomplished, the heater can be ramped-up to its design capacity.



Burner mode Transition Duplex mode

Figure 2. Modes of operation

Duplex Retrofit in a Refinery Process Heater

Duplex Technology was retrofitted in a VC reformer splitter reboiler process heater at a refinery in California. Project objective was to meet NOx emissions ≤ 6 ppm, corrected at 3% O_2 (≤ 0.007 lbs of NOx/MMBtu) over a wide range of refinery process conditions.

The reboiler VC furnace heats fluid fed from a distillation tower that fractionates process fluid fed from a reformer unit ("the unit"). The heater's radiant section dimensions are: outside shell diameter of 9' 6 ½" and height of 17' 8 ½". Three natural draft ULN burners with a maximum capacity of 3.75 MMBtu/hr each are installed on the furnace floor firing refinery fuel gas vertically up. Historical refinery fuel compositions obtained over a 24-week period immediately prior to the initiation of the testing activities was obtained. A summary of selected data is presented in the table below:

	H_2 (vol. % @ STP)	CH_4 (vol. % @ STP)	LHV (BTU/scf)
Maximum	68.7	55.6	1462
Minimum	22.8	12.3	636
Average	43.8	31.7	892

Table 1. Fuel Composition

The retrofit into the VC process heater took less than 2 days of furnace downtime and it encompassed the following:

- Modifications to the existing burners were made to make the existing UNL burners compatible with Duplex operation. The existing fuel manifolds, risers and tips were kept intact and separate Duplex fuel manifolds, risers and tips were installed. Figure 3 is a schematic representation of the burner modifications that were made to the existing ULN burners installed in the VC heater. A doughnut-shaped fuel manifold was added at the bottom of each burner. Each Duplex manifold delivers fuel to four risers with Duplex tips positioned in the burner throat within the core of the air supply. Valves in each burner fuel supply lines were installed to provide independent fuel supply to accommodate burner-mode operation and Duplex-mode operation.
- Duplex surface. A Duplex surface ceramic structure resting on supports welded to the furnace shell was installed. The high-temperature porous ceramic matrix rested on this structure (Figure 4).
- Instrumentation. Additional valving and instrumentation, as required for Duplex operation, was installed for proper control and safety monitoring. This included a UV scanner to detect flame on the Duplex surface, and oxygen control.

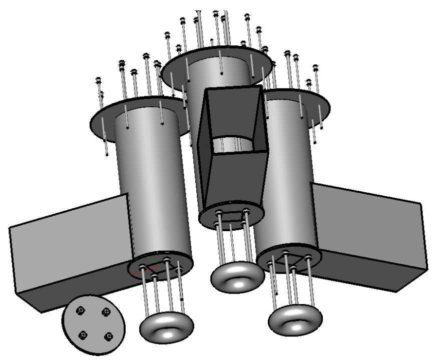


Figure 3. Duplex Burner Modifications

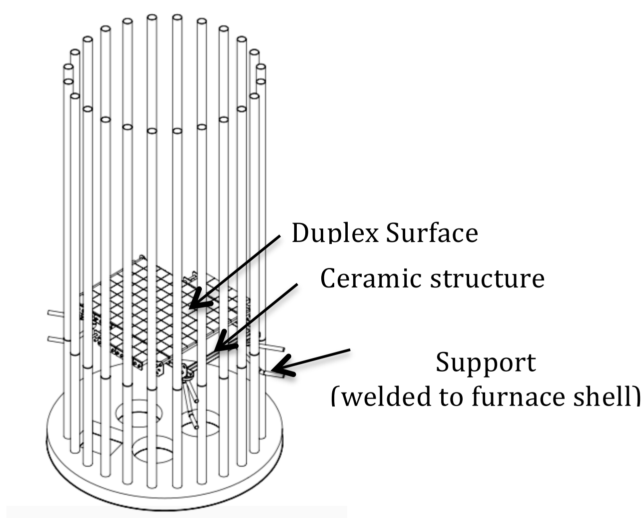


Figure 4. Duplex surface

Results

After Duplex was installed and commissioned, data was collected to verify NOx performance under typical process conditions experienced at the refinery. NOx data was obtained using a Testo 350 analyzer with a low-NOx cell. Flue gas samples were drawn from the furnace stack and were conditioned using a sample dryer with a fast loop. Wet oxygen data was obtained using an in-situ zirconium oxide oxygen probe installed downstream of the convection section.

More than 100 data points were obtained during a six-week period. Data points presented below represent averaged daily data.

The thermal load in the reboiler process heater is dependent on the reformer unit process conditions. Because of this, refinery operations requested to monitor Duplex operation as a function of the unit's charge rate (barrels per day – bpd).

Daily unit and reboiler charge rates were kept at constant values and experienced only minor daily deviations.

A summary of results is presented in the following graphs:

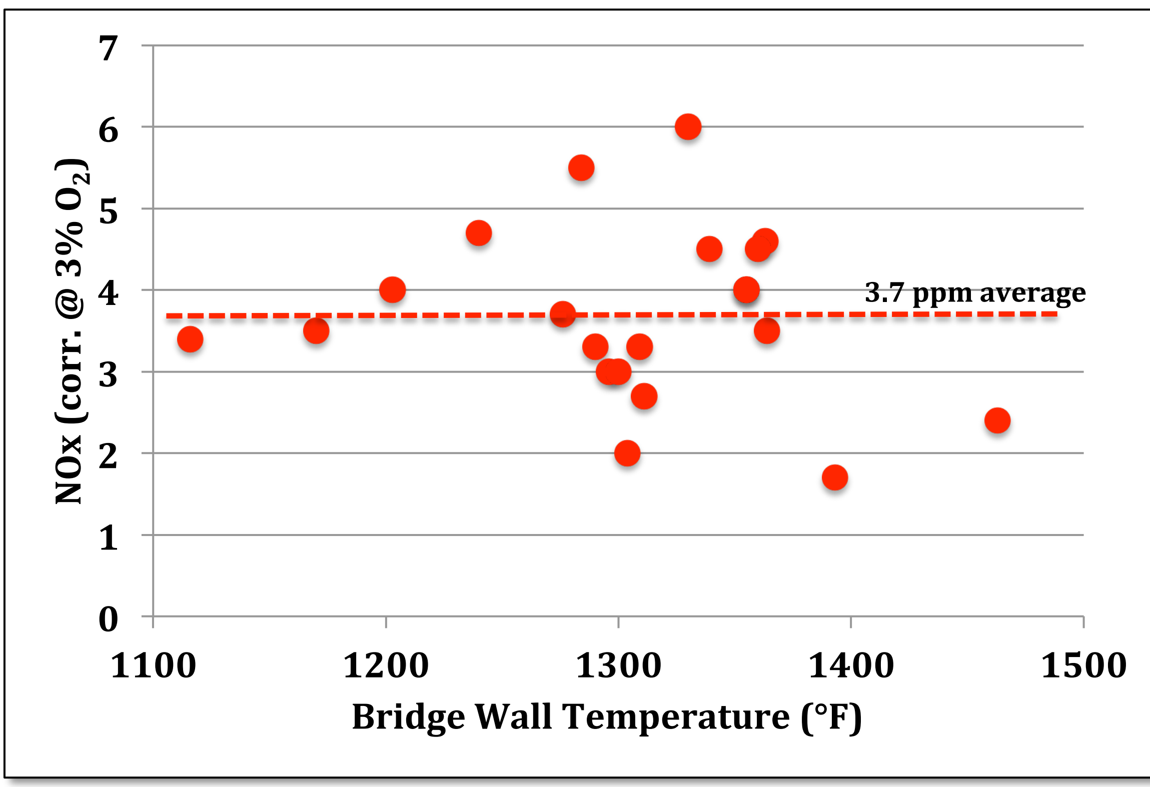


Figure 5. NOx vs. Bridge Wall Temperature

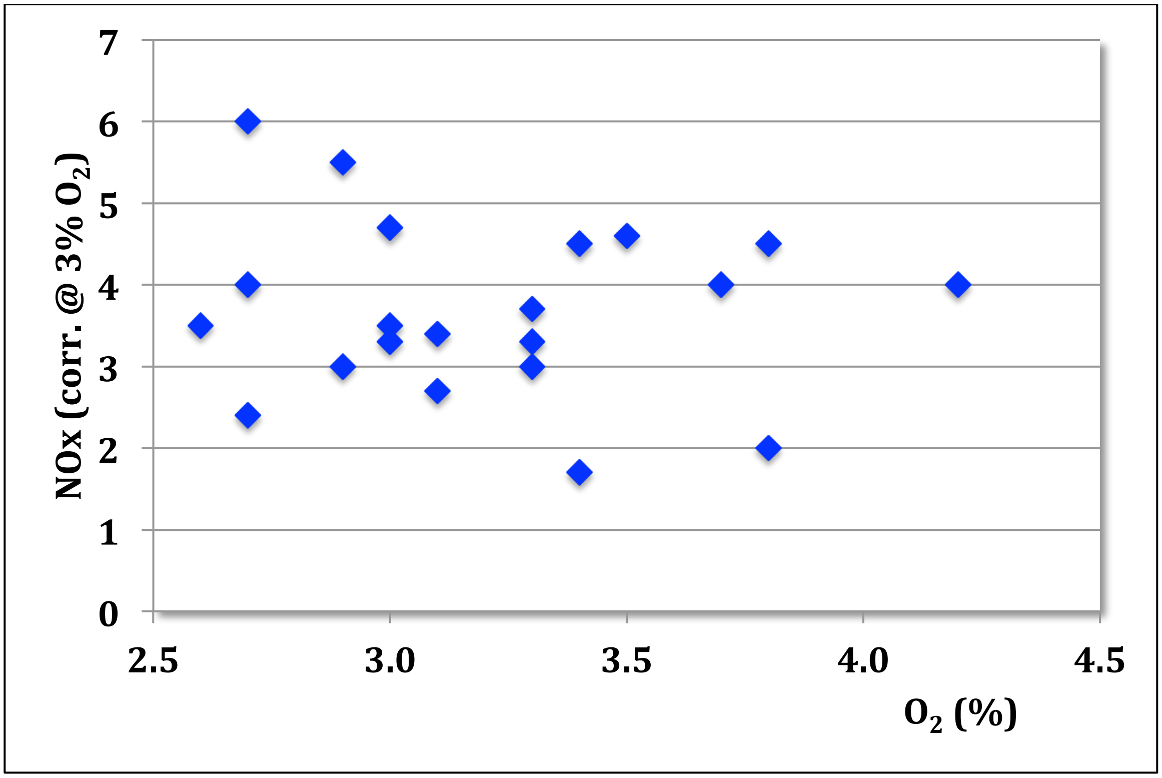


Figure 6. NOx vs. Zirconium Oxide Oxygen Probe Measurement

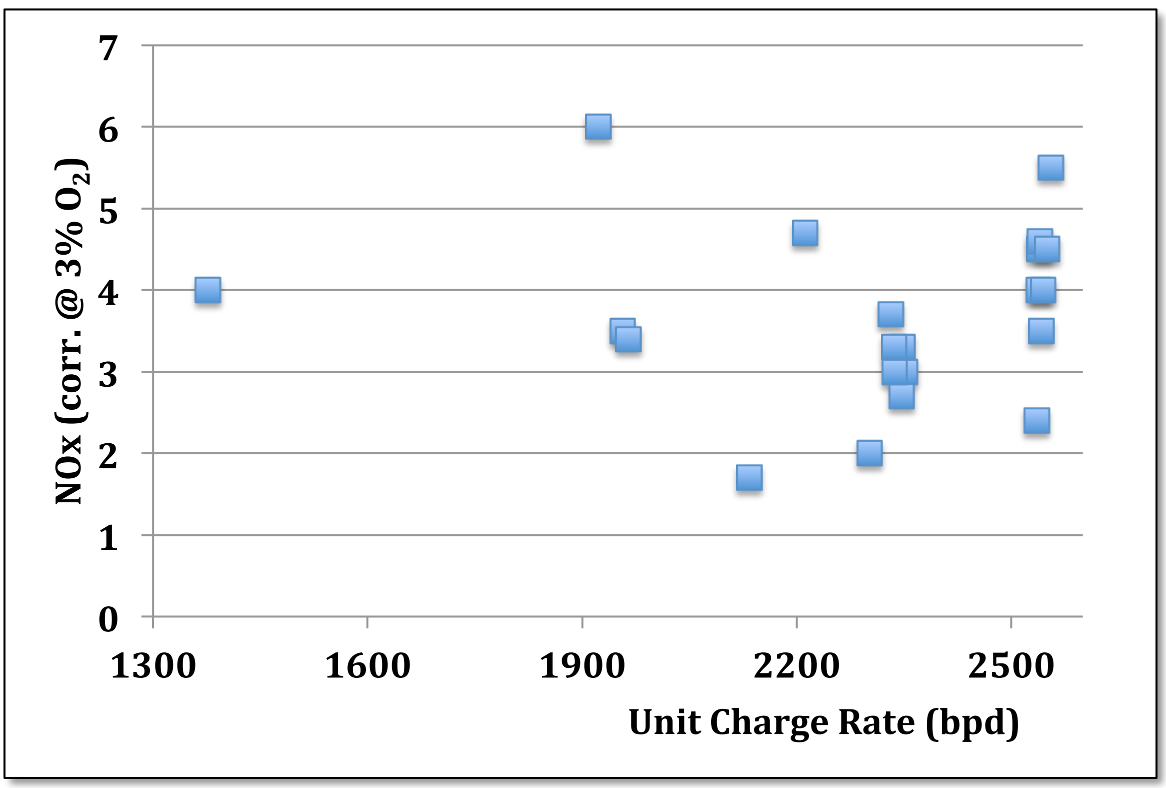


Figure 7. NOx vs. Reformer Unit Charge Rate

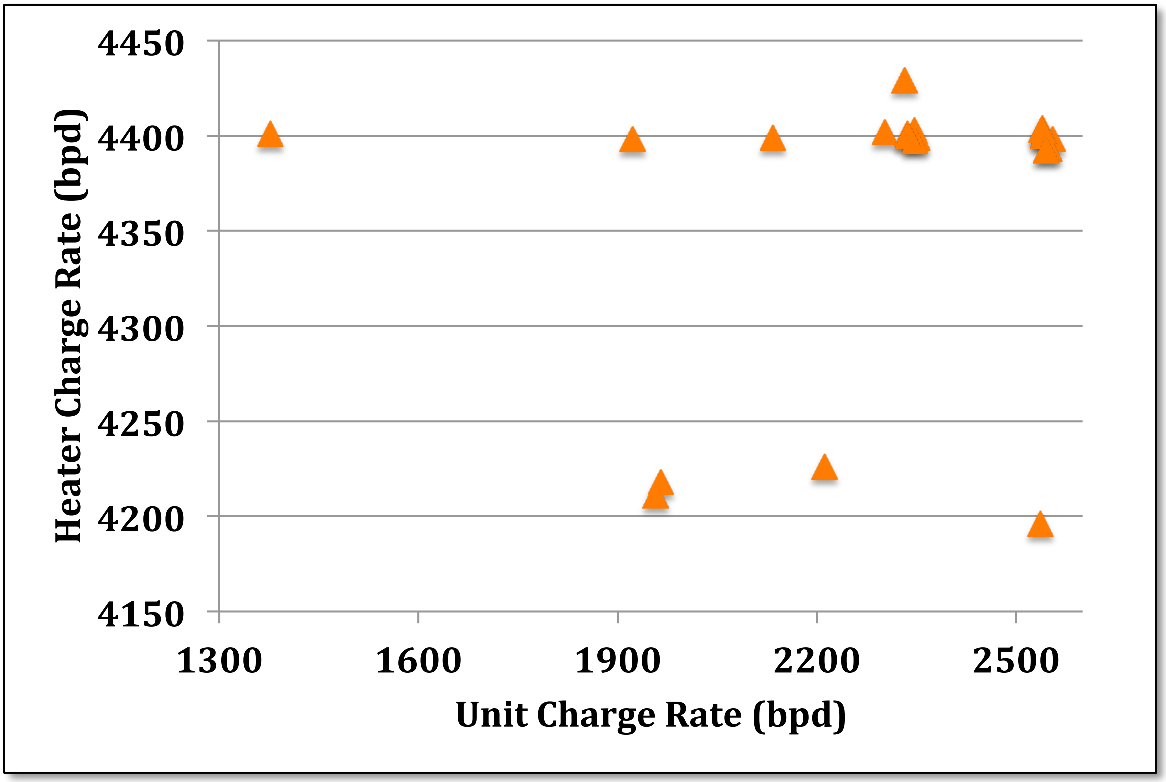


Figure 8. Reboiler Heater Charge Rate vs. Reformer Unit Charge Rate

NOx results met and exceeded project objectives. In addition, average CO emissions were 25 ppm (corrected @ 3% O_2) and were consistently lower than 50 ppm (below regulatory requirements) in spite of the relatively low bridge wall temperature conditions. Furthermore, Duplex performance was very stable over all process conditions encountered during the evaluation period.

The NOx data is scattered and does not appear to reveal any trends. However, the dynamic conditions typically encountered in refinery operations in which thermal loads, fuel heating values and other process variables that may change rapidly and may not be monitored continuously, make it difficult to establish any trends.

The pictures below document Duplex surface glow that can also be used as a qualitative measure of optimum Duplex performance.

Figure 9. Duplex Surface Glow.
Viewing port located on furnace shell (left) and viewing port located on furnace floor (right)

Conclusions

Duplex is a revolutionary and highly innovative technology that has been successfully implemented in a refinery VC process heater. Duplex demonstrated its capability to consistently operate with NOx emissions ≤ 6 ppm, corrected at 3% O_2 (≤ 0.007 lbs of NOx/MMBtu) over a wide range of process conditions. This emissions performance satisfies the most stringent NOx regulations and is un-matched by any other retrofit combustion technology. It also provides a very attractive and competitive option against SCR systems.

Duplex is also being considered by other refineries as a solution to eliminate flame impingement on furnace process tubes brought about by long and buoyant flames characteristic of ULN burners.