Duplex™ Technology Demonstrates Sub-5 PPM NO_x and CO Simultaneously Without SCR, FGR, or High Excess Air

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Abstract

Unlike traditional combustion concepts in which the flame is anchored via either swirl and/or bluff body stabilization techniques and the principal mode of heat transfer to the incoming cold charge is via conduction, within the porous ceramic flame holder, additional heat transfer mechanisms are at play to enhance the incoming enthalpy of the reactants to create "excess enthalpy burning" (Min, 1991; Hackert, 1999). *Recirculating heat to the incoming mixture without more traditional means as external Flue Gas Recirculation (FGR) extends the flammability limits for superior turndown with emissions compliance, promotes greater flame stability and enables the burner to be a technology enabler for opportunity fuels (low BTU fuels or the like) which may exhibit wide fluctuations in Wobbe Index and other key chemical characteristics (chemical constituents, flame speed, autoignition delay times, etc.). Further and more importantly, the porous ceramic burner radiates more effectively than a conventional flame due to its ability to emit as a black body, rather than in distinct spectral regimes as with traditional flames. The net effect is a system with higher combustion and thermal efficiencies, wider operating envelops and ultra-low emissions performance, all in a highly compact and cost effective package. Seattle based ClearSign Combustion Corporation has pioneered and commercialized this innovative and disruptive technology, referred to as Duplex Technology and has routinely demonstrated sub-5ppm NO_x and CO simultaneously in industrial applications and installations.*

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Introduction to Duplex Technology

Duplex technology, is a new or retrofit strategy for achieving ultralow NO_x and CO emissions in combustion equipment including boilers and process heaters. Duplex technology comprises a porous surface (Duplex surface) downstream of the burner which stabilizes combustion and radiates heat with near perfect black body emissivity (ε=1). Duplex technology is applicable to new and retrofit process heaters, boilers, and once-through steam generators (OTSGs) without the need for expensive and complex flue gas recirculation (FGR), selective catalytic reduction (SCR), high excess air, or other traditional NOx reduction technologies. In its simplest form, a Duplex surface is placed downstream of a conventional diffusion burner via supports. The burner initially ignites and fires in the normal way. After a few minutes, the Duplex surface achieves its "Transition Temperature", at which time the flame is safely transitioned from the burner to the Duplex surface (Figure 1), achieving sub-5 ppm of NO_x and CO emissions (corrected to 3% O_2).

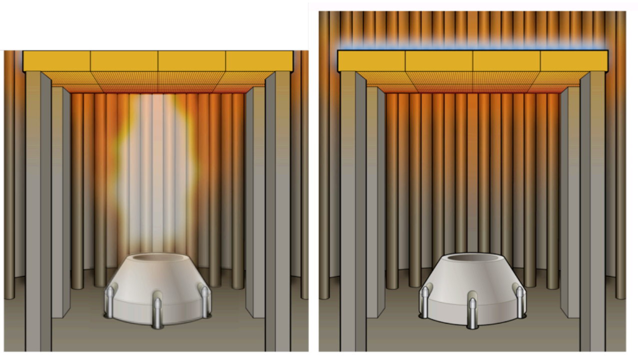


Figure 1: The Duplex surface is first brought to transition temperature (left) and then the flame is transitioned to the Duplex surface (right).

Operationally, the porous surface offers little flow resistance or pressure drop due to its large effective flow area (ACd) and is equally compatible with both natural draft and forced draft systems with no required modification to induced- and/or forced-draft fans and/or their respective controls. In essence, the traditional diffusion style burner is transformed into a premixed, porous ceramic burner with all its emissions and performance benefits – to be discussed.

Mechanism of NO_x Reduction

For gaseous fuels such as natural and refinery fuel gases, NO_x is primarily generated according to the Zeldovich (Thermal) mechanism (Glassman, 1977); the reduced mechanism of which appears below.

N_2 + O = NO + N *(rate limiting step)*
N + O_2 = NO + O

For the rate-limiting step, the kinetic rate law (differential form) is d[NO] = $k[N_2][O]dt$ where the brackets [ ] denote the molar concentrations of the enclosed species, k is the forward rate constant, and t is time. In the foregoing equation, the reverse reactions have been neglected because [NO][N] is orders of magnitude less than $[N_2][O]$ and the forward reaction. Making use of a partial equilibrium, ½ O_2 = O, allows one to substitute $K\sqrt{[O_2]}$ for [O] where K is the partial equilibrium constant. This leads to $d[NO] = kK[N_2][O]dt$. Finally, kK may be recast in Arrhenius form to yield $d[NO] = Ae^{-b/T}[N_2][O_2]dt$. Since $[N_2]$ is nearly constant over the combustion reaction, the integral form reduces to Equation (2).

$$[NO] = A[N_2]\int_0^{\theta} e^{-b/T}\sqrt{[O_2]}dt \quad (2)$$

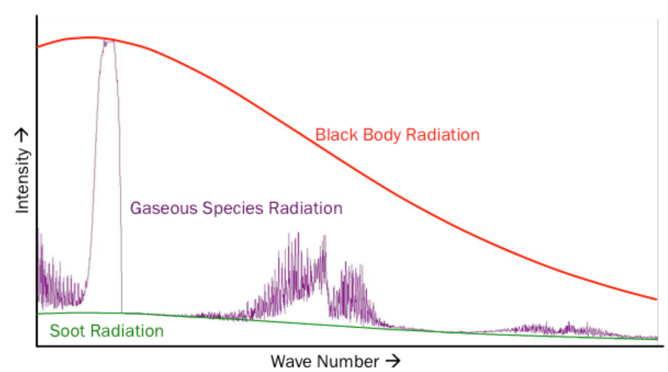


Figure 2: A black body radiates with significantly more intensity compared to a normal flame, greatly reducing flame temperature and consequential NO_x formation.

Equation (2) shows that NO_x concentration is an exponential function of temperature, is a linear function with time, and varies with the square root of oxygen concentration.

As will be shown, the Duplex technology reduces NO_x via all three of the foregoing mechanisms. Because the incoming air is diluted/mixed by fuel and flue gas prior to combustion on the Duplex surface, the initial O_2 concentration is minimized; moreover, flame length is largely limited by mixing rather than via chemical effects which are notoriously fast. Since mixing occurs prior to reactions, the entire combustion reaction is predominantly confined within the Duplex surface itself, substantially reducing the flame length and concurrently reducing the amount of time at high temperatures during which Thermal NO_x is formed. More importantly, the combustion temperature is much lower than the adiabatic flame temperature at the prevailing equivalence ratio because the Duplex surface is a nearly perfect black body radiator while the flame is a relatively poor one (Temperature and Measuremenet of thermal radiation, 2015) (Figure 2). As such, heat generated within the flame zone is quickly and efficiently radiated away from the surface to the cooler surrounding furnace walls, thereby greatly increasing thermal efficiency in the radiant section of the furnace and/or boiler.

NO_x Reduction in Practice

Owing to the shorter residence time, lower reaction temperature, and superior radiant heat transfer to the process, NO_x is greatly reduced and found to be at ultra-low, single digits - 5 ppm or less in both laboratory and field demonstrations. It is important to emphasize that such reduced NO_x does not require external FGR, alterations in the nominal air/fuel ratio, or post combustion strategies such as SCR, but is wholly accomplished via the Duplex technology – the economic and hence operational merits of the technology are therefore staggering. Figure 4 shows the results of lab experiments (Figure 3) at 2MMBtu/hr using a synthesis fuel composed of up to 50%/50% hydrogen/methane (by volume). As can be seen from the plot, the initial NO_x is approximately 65ppm but when the flame is transitioned to the surface, the NO_x drops precipitously to ultra-low levels, and at some points, both NO_x and CO reach near zero levels. During these excursions, the furnace “Bridgewall” temperature is around 1600F. ClearSign has successfully demonstrated the technology using a myriad of fuels including natural gas, propane and fuel blends including the aforementioned with hydrogen.

Figure 3: A process heater simulator fires natural gas at 2 MMBtu/hr. The right image shows a view of the Duplex surface in operation within the furnace as viewed by a high temperature camera.

In normal Duplex operation, the modified burner is allowed to ignite and burn as normal for several minutes as the Duplex surface gradually heats up to temperature. When the “Bridgewall” temperature – furnace gas temperature as measured downstream of the radiant section – exceeds approximately 1200F (“Transition Temperature”), the burner is switched off and the Duplex fuel injection system is engaged. Fuel, air and some flue gases mix in the new mixing zone formed between the injection plane and Duplex surface, thereby transforming the combustor to a substantially premixed variant with all its inherent emissions benefits. The reactants which receive some preheating from its surrounding and the tile itself then ignites and burns within the ceramic matrix with greater robustness, stability and efficiency than before.

ClearSign has successfully proven the technology in furnace and boiler applications, and at both laboratory and commercial scales. Furthermore, the Duplex technology has recently been scaled up in the field and applied to a 62.5 MMBtu/hr OTSG (Once Through Steam Generator – Figure 5) with similar results at a Southern Californian oil and gas producer. Here, ClearSign has installed a six foot square Duplex surface within the radiant section of the OTSG, itself measuring eleven feet in diameter and forty feet long. Figure 6 shows the startup and operating modes of the surface. As shown, the start-up process gradually transforms the tile's surface to a brilliant orange hue when in full operation.

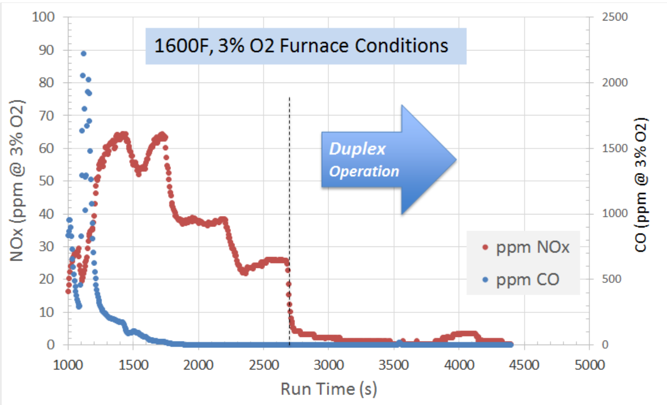


Figure 4: A standard burner generates 65 ppm NO_x (red symbols) in startup mode and near zero ppm with zero CO (blue symbols) under Duplex operation.

NO_x performance is typically between 3 to 5 ppm depending on the firing rate and configuration. At the normal firing rate and Duplex location, the OTSG generates 3 to 4 ppm while operating continuously and unattended at nominally 3% O_2 (wet conditions) without FGR. It should be noted that the fuel at this site is natural gas.

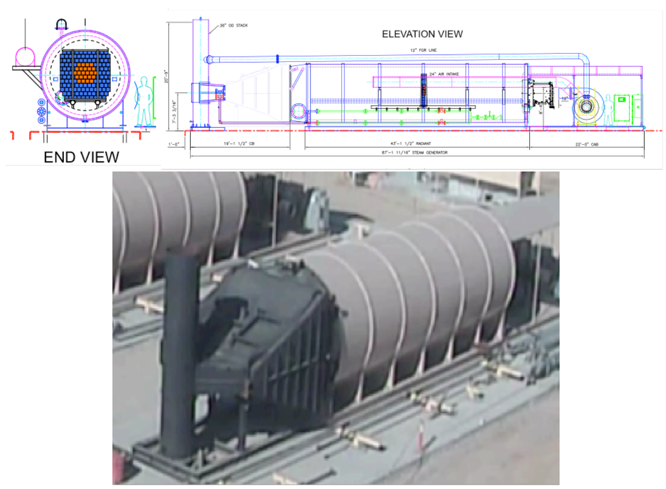


Figure 5: OTSG with Duplex surface installed. Left/top image shows the end view of the Duplex surface having a profile area of 6 feet by 6 feet. The surface is mounted on rails to allow for testing at a variety of distances from the burner. The right/top image shows the elevation view of the steam generator while the bottom image shows an actual OTSG. Its radiant section is approximately 40 feet long with a shell diameter of around 11 feet.

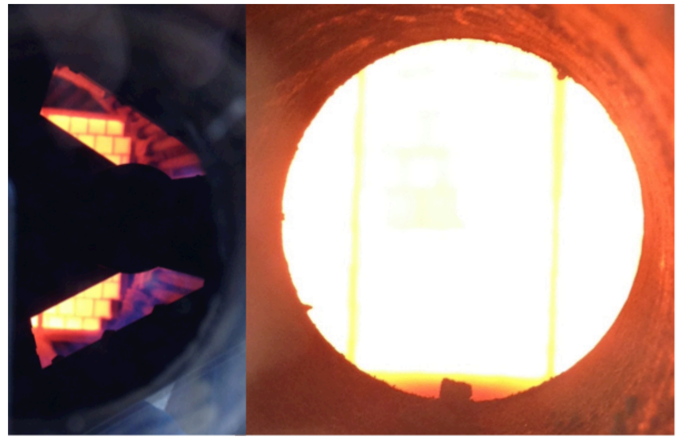


Figure 6: Left image shows the view through the burner sight port during warm up at 42.5 MMBtu/hr in the OTSG while the right image shows the Duplex surface in full operation.

Another interesting observation at the same OTSG was made by comparing the NO_x performance both before and after the Duplex installation (Figure 7). In the figure, the OEM's ULN (Ultra Low NO_x) burner's NO_x performance is compared to the Duplex at the same firing rate. As evident, the NO_x levels drop to one third at two stack oxygen levels (3% and 3.5%). The tile is further fired at an elevated rate (55MMBtu/hr) and the emission levels rise only minimally from their 45MMBtu/hr levels.

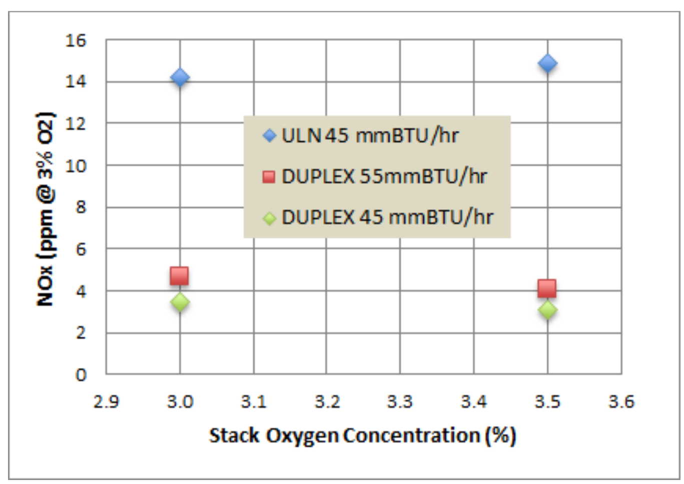


Figure 7: NO_x comparison between Duplex and the OEM ULN Burner.

More interesting, however, is how the overall thermal efficiency changes with and without Duplex operation.

As shown in Figure 8, the tile affords approximately a 2% increase in thermal efficiency over the OEM ULN burner – significant when this efficiency gain is amortized over the life of the unit.

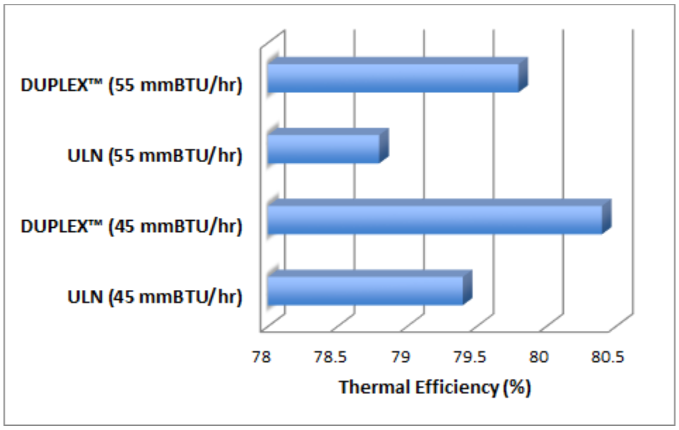
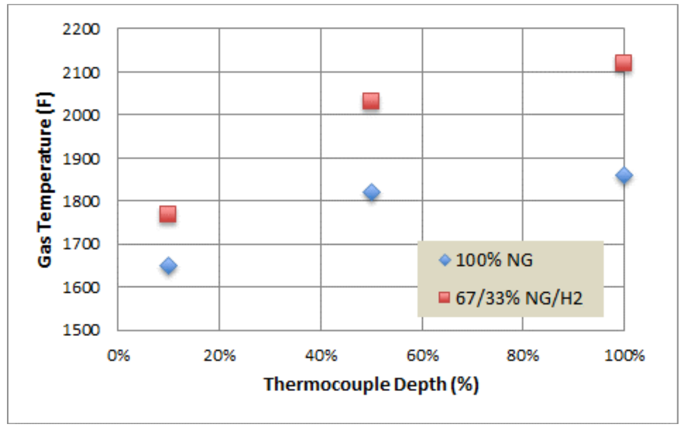


Figure 8: Thermal efficiency comparison between Duplex and the OEM burner.

Field demonstrations are also in progress for several process heaters at various refineries having single and multiple burner configurations in vertical cylindrical (VC) and cabin-type heaters with individual burners ranging from 4 to 15 MMBtu/hr in size.

Recent CFD (Computational Fluid Dynamics) analyses calibrated via concurrent experimental work have been instrumental in uncovering the intricate details within the Duplex substrate itself (Figure 9). The bottom plot shows the gas temperatures within a single channel comprising the tile (flow is upwards) while the top plot relays some experimental results at similar conditions. As shown, the flame resides close to the inlet face as corroborated by others (Hackert, 1999), thereby enabling the products of combustion sufficient time to react, convect heat to its surrounding walls and permit CO burnout.



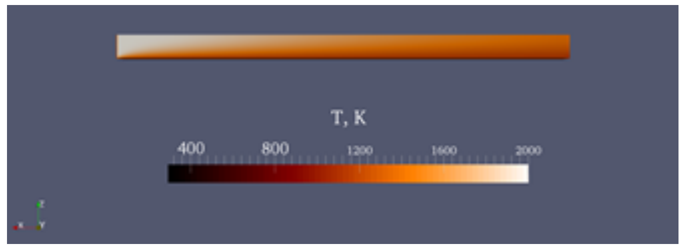


Figure 9: Experimental (top) and CFD (bottom) images depicting the gas temperature within a single flame channel. Flow is left to right.

Other Benefits of Duplex Technology

Enhanced CO Oxidation

CO oxidation requires catalysis (Kuo, 2005) by OH:

$$CO + OH = CO_2 + H$$

Typical NO_x reduction techniques seek to minimize O_2, reduce temperature, or both, which can impede OH formation and subsequent CO oxidization pathways. OH formation requires intimate mixing of oxygen and fuel so that OH can be generated by oxidation of fuel fragments; for example:

$$CH_4 = CH_3 + H$$

$$H + O_2 = OH + O$$

However, Duplex technology allows for intimate fuel and air mixing prior to the combustion process. Thus, ample oxygen is available for generation of OH. Furthermore, this mixing reduces fuel rich zones, thereby enabling reduced equilibrium CO production. Finally, the Duplex surface allows for increased heat transfer as compared with ordinary combustion schemes. These factors among others allow for CO to remain low even with sub-5 ppm NO_x.

Enhanced Radiative Heat Transfer

Heat transfer in the radiant section is enhanced because the Duplex surface is a nearly perfect blackbody radiator. Laboratory experiments show a measureable increase in heat transfer and field trials are currently under way to corroborate laboratory results.

Elimination of Flame Impingement

Flame length and dimensions are largely determined by air-fuel mixing, which is at least an order of magnitude slower than flame chemistry. Because combustion is largely confined to the Duplex surface, flames are well removed from process tubes. To the extent that unit capacity is limited by flame length and flame impingement on process tubes, Duplex technology promises to allow increased throughput and process capacity with existing assets.

Conclusions

NO_x and CO emissions of 5 ppm or less have been routinely demonstrated at heat release rates up to 40 MMBtu/hr, excess oxygen concentrations from 1 to 4% and furnace temperatures from 1200 to 1800 °F. The technology's ability to recirculate heat to the incoming cold charge without traditional means like external FGR extends traditional flammability limits, promotes reduced gaseous emissions and greater flame stability and enables the system to exploit low cost, opportunity fuels. Further, the Duplex system radiates more effectively than a traditional flame, greatly improving overall plant economics. The net effect is a system enabling higher combustion and thermal efficiencies, wider operating envelopes, increased throughput and ultra-low emissions performance, all in a highly compact and economic package.

To date, ClearSign Combustion Corp. has approximately 40 patents pending in the U.S. and worldwide regarding its Duplex technology for a variety of combustion equipment including heaters, furnaces, boilers and gas turbines – all serviceable markets for this highly innovative and disruptive technology.

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