

Analysis of NO_x Reduction Techniques on an Ethylene Cracking Furnace

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Background

This paper will investigate a dilemma Ethylene Producers currently face: which NO_x reduction technology to select for their ethylene cracking furnaces.

Operators may utilize Process Adjustments which include Unit Turndown, Fuel Switching and Steam Injection to gain incremental relief. While these operational changes offer some NO_x relief, they negatively impact unit economics and for most operators are not tempting to implement.

If 80% or higher NO_x reduction levels are required, like those proposed for the Houston/Galveston area along the Texas Gulf Coast, then operators are forced to consider Technology like Low NO_x Burners, Ultra Low NO_x Burners and SCR (Selective Catalytic Reduction). As these technologies are very different, one must consider the value of the differences in terms of Operating Flexibility, Maintenance Intensity, and Impact on the furnace's main mission: to efficiently produce olefins on a large commercial scale.

Commercial ethylene production occurs in relatively small diameter (1 inch ~ 6 inches) closely arranged reaction tubes where ethane reacts with steam in a high temperature (1,300 °F ~ 2,000 °F) environment. These tubes are constructed from alloys containing 25% - 35% Cr specifically designed for the high temperature environment. Special furnaces containing hundreds of closely aligned burners covering the floor and the walls are used to create and maintain the high temperature environment for these reaction tubes.

Meeting ever-changing environmental requirements is a challenge facing many industrial facilities worldwide. Keeping industrial facilities economically viable long-term is another on-going challenge. Current environmental requirements are directing specified NO_x reduction standards, which may in the future be enhanced to require even greater NO_x reductions. Making the appropriate decisions to meet current and future environmental requirements is a dilemma that impacts environmental compliance, economic viability, and



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operational flexibility. Consideration of all potential solutions, from process and fuel adjustments, to enhanced technology is crucial to making the best decision regarding NO_x emissions compliance.

Process Adjustments

There are several process adjustments that could be initiated to reduce NO_x emissions, and some of these are relatively easy to implement. Turndown is always an option for operators but not if they want to remain economically competitive. For this reason, Turndown will not be expanded further.

Switching to a “clean fuel” like natural gas may offer some relief but potentially at significant incremental fuel costs and product yield shifts. Steam injection is also an inexpensive experiment to learn how much NO_x reduction can be achieved along with the overall impact it has on the process (yield impact, steam cost).

Fuel Switching

Substituting a cleaner fuel for a heavier fuel directionally will lower NO_x emissions but there are other impacts that are not so desirable. These include operational impacts affecting the firing rate and thus the overall efficiency of the unit to produce the desired yield and product quality. Fuel costs will also increase as natural gas prices continue to climb above historical averages. Switching from a waste stream to a high value commodity like natural gas can easily double the fuel cost of the manufacturing ethylene.

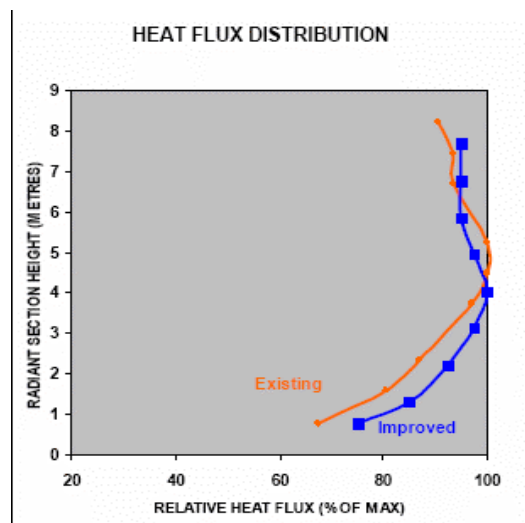
One operator implemented a program to clean the fuel gas in order to create less NO_x during combustion. This involved tightening the fuel quality specifications and removing the species heavier than CH₄ through a cryogenic process. While this program recovered additional co-products and by-products from the fuel, which makes good economic and environmental sense; however, in practice it is a very costly and challenging method to reduce NO_x emissions.

If the fuel gas comes from a neighboring refiner, it is assumed that every step has been taken to maximize the recovery of higher valued species from the fuel gas pool. Sometimes, when refinery upsets occur, the quality of the fuel gas is impacted and the furnace operator has to work under these dynamic conditions. Also, since the fuel source is external, very little quality control is afforded to the end user beyond the terms mentioned in the Supply Contract.

Steam Injection

The introduction of steam in the combustion zone has shown to reduce thermal NO_x formation by 5 – 20% through a quenching effect. However, the same quenching effect to inhibit NO_x formation opposes the primary function of the heater’s existence: to drive the cracking reaction towards olefins. The internal floor and walls of the furnace are covered with burners that endeavor to produce a firebox temperature of 2200 °F and thereby maintain the heat of reaction. Thus, steam injection to control NO_x works against the olefin furnace. Also, the cost to produce additional steam for NO_x emissions control must be considered.

The graph shows how the temperature profile of the furnace is altered by employing steam injection



to curtail NO_x formation. Notice that the profile has shifted away from the original pattern thus effecting unit conversion and product yields.

Combustion Adjustments

Tests have shown that the internal peak temperature of the flame is lowered by reducing the quantity of air supplied for combustion. By limiting the amount of combustion air, the amount of excess O₂ is minimized thereby lowering the formation of NO_x. A consequence of this strategy is greater flame instability followed by the formation of additional CO though incomplete combustion.

Staged combustion is another consideration where air or fuel is added in increments to control flame temperature. In air staging, the flame is developed in a fuel rich atmosphere and air is introduced at the tip to consume any remaining fuel. In fuel staging, the flame is created in a fuel – lean environment. Fuel combined with air is delivered at the flame tip to complete combustion and thus achieve the desired temperature. The challenge is continually executing this option with precision on a commercial furnace.

Another option for furnaces with conventional burners is modification to create a larger flame. This alteration produces a lower flame temperature which directionally lowers NO_x emissions. The issues with this proposal include the time and expense to modify hundreds of burners as well as permanently altering the temperature profile of the furnace. Longer flame lengths also create an enhanced environment for coil elongation to occur.

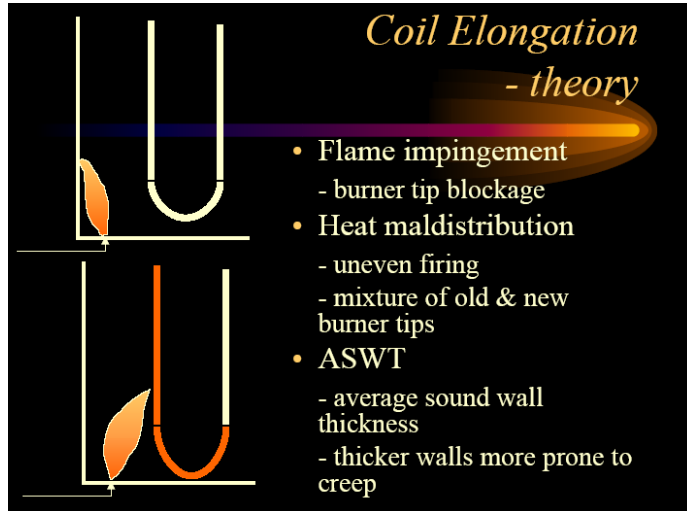
A more challenging and capital intensive consideration involves modifying or replacing an inefficient (undersized) heater. A heater that fires well above design conditions also has an undersized convection section. The savings in fuel consumption and heat recovery are immediate benefits of improved heater efficiency with NO_x reduction being a side benefit.

A correct analysis of these process adjustments must not be limited to NO_x reduction but should also include the impact they have on the primary reason these heaters are operated in the first place: to make olefins. The unit's operating flexibility in terms of turndown ratio, throughput and efficiency is very much a part of the decision. A burner should be designed with a turndown ratio of 4:1 or higher to reduce costs as well as the number of shutdown cycles. Some NO_x reduction options require furnace derating to achieve the reductions thereby impacting overall unit economics. The various methods requiring lower flame temperatures decrease the overall firebox temperature which lowers product yield, conversion and thus efficiency. Air preheating offers some relief but will increase fuel consumption, increase NO_x and change the heat integration of the furnace.

Technology

Of interest to ethylene furnace operators are burners and selective catalytic reduction.

Burners used to be mundane ancillary equipment that did not



stir much interest. Today, burners have evolved and are differentiated between Low NO_x and Ultra Low NO_x varieties. Burner suppliers have invested heavily in the development of their technology that they now extend guarantees of 0.01 lbs. NO_x/MMBTU. Ultra Low NO_x burners use internal flue gas recirculation to reduce NO_x production. This technology and its associated benefits do, however, come at a cost.

Low NO_x Burners and Ultra Low NO_x Burners

Low NO_x burners offer up to a 60% reduction in NO_x while Ultra Low NO_x burners offer higher reductions compared to conventional burners. These performance levels require the combination of premix combustion and fuel staging or flue gas recirculation which makes the operation of the furnace much more difficult. The heater then becomes more challenging to operate as even a subtle change to the Air – to – Fuel ratio may cause NO_x emissions to spike. Once installed, these burners require more tuning maintenance than the older less sophisticated types.

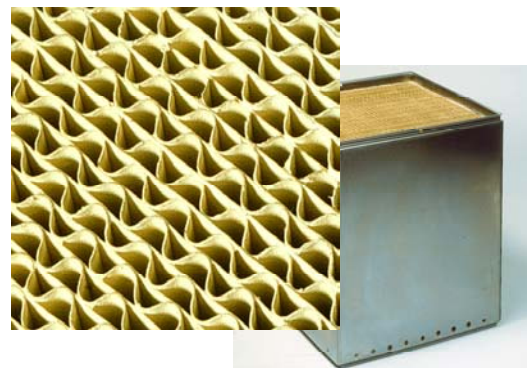
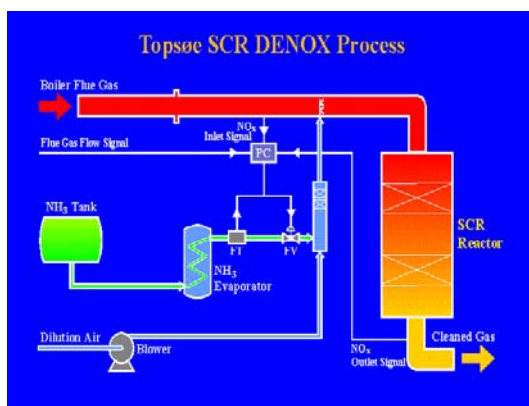
Low NO_x and especially Ultra Low NO_x burners typically have smaller-diameter burner tips and are therefore more susceptible to plugging. Plugging could result in flame impingement and uneven heating which could lead to thermal shock as well as coil elongation (creep). In general, Low NO_x generation burners exhibit longer flame lengths and larger – diameter burners. Ultra Low NO_x burners have shorter flame lengths but still have larger diameters.

Both types of burners offer their lowest NO_x levels at lean O₂ concentrations but at a cost of flame stability and a change to the temperature profile of the heater. Thus, aside from modifying the heater for a new burner type retrofit, the objectives may shift away from optimizing unit efficiency to accommodate the heater's narrower operating range.

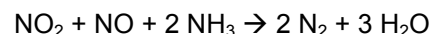
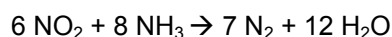
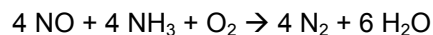
Selective Catalytic Reduction

Selective Catalytic Reduction (SCR) is the reaction of NO_x with ammonia NH₃ that occurs on a catalytic surface to produce N₂ and H₂O. The typical temperature range of an SCR is 400 °F to 950 °F with guaranteed NO_x removal rates of 95+%. The catalytic metals are oxide forms of vanadium and tungsten. Commercial applications of SCR range from very clean service firing natural gas to ultra high particulate loadings (>20,000 mg/Nm³) in coal – fired utility boilers.

The general process flow diagram and catalyst are illustrated below:



The reactions that occur are as follows:



Ethylene cracking furnaces pose several challenges that influence the design of the SCR. These include chromium deposition and coke ash loading during the intermittent decoking procedure. Selecting an active catalyst with a high Cr tolerance and large hydraulic diameter is recommended.

Haldor Topsoe's reference list includes the installation of SCR NO_x control at 13 Ethylene cracking furnaces located in the U.S. Gulf Coast. The open literature contains others' claims of their ability to control NO_x and NH₃ slip to single digits parts per million at two European Ethylene Production facilities.

Based upon knowledge gained from years of SCR experience in multiple industries, SCR suppliers can design and guarantee the system to operate for up to 5 years of continuous service in the Ethylene Cracking furnace.

Conclusion

Selective Catalytic Reduction (SCR) is the best proven technology to achieve maximum NO_x reduction in Ethylene Cracking Furnaces. As Ethylene furnaces cycle between olefin production and decoking, the SCR system is able to smoothly accommodate the transition. This back – end technology offers 95%+ NO_x reduction across a wide operating range requiring little or no maintenance while essentially remaining transparent to the rest of the furnace operation. SCR was installed on some ethylene cracking furnaces, after originally installing Low NO_x burners, to regain operating flexibility.

The process adjustments such as fuel switching, steam injection and existing burner modifications offer the Ethylene Furnace operator limited NO_x reduction at the risk of eroding the unit's efficiency and reducing the operating window. Higher costs may also result due to the rising cost of natural gas which also influences the value of steam. A switch away from Fuel Gas to Natural Gas also creates another problem: what to do with the Fuel Gas? Economic alternative dispositions for waste streams are difficult to identify.

Low NO_x burners and Ultra Low NO_x burners initially seem to be the obvious choice for NO_x reduction technology especially for furnaces. This may not be the case as these burners are designed to combust fuel at lower temperatures to inhibit the formation of NO_x preferably in a lean excess O₂ environment with staged combustion. Low NO_x burners have longer flames which is undesirable. Flame impingement on the pyrolysis tubes combined with uneven heat dispersion result in coil elongation. Lower flame temperature works against the fundamental purpose of the furnace: to efficiently produce olefins on a large commercial scale.

The overall NO_x reduction strategy must consider many factors. Choosing the most appropriate strategy will have long – range implications on the economic viability of facilities worldwide.

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