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Revision Memo

12/03 Added NO_x control matrix for boilers/heaters, gas turbines, internal combustion engines and FCCU. Minor editorial changes.

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SCOPE

This DP focuses on technologies and methods that can be selected, and the considerations that must be addressed, for an effective NO_x control strategy. NO_x control methods and technologies, which have been successfully applied in other industries, such as the utility power industry, are not covered in this DP. Depending on the nature of the NO_x control problem, users of this Design Practice may want to consult experience in these other industries as an additional resource.

Specific combustion applications found and suitable control methods and technologies for particular applications are covered in this subsection. The material in this subsection is presented in several parts, which are:

1. Background
2. Fired heaters and boilers
3. Stationary gas turbines
4. Stationary internal combustion engines
5. Fluid Catalytic Cracking Unit regenerators
6. Post combustion controls

The first part provides background material applicable to NO_x control technology selection. The next four parts deal with prevention of NO_x formation. The sixth part, post combustion controls, deals with NO_x control after NO_x has been formed.

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DEFINITIONS AND ACRONYMS

DEFINITIONS

Acid rain - Precipitation having an acid pH, that is, a pH level below 7.0. The acidity sometimes results from carbon dioxide, nitrogen oxides or sulfur oxides dissolved in rainwater.

Ammonia slip - The amounts of unreacted ammonia in the exiting exhaust gas. It can result from introducing excess NH₃ or from poor mixing.

Boiler or steam generator - Any combustion equipment used to produce steam or heat water.

British Thermal Unit (Btu) - The amount of heat required to raise the temperature of one pound of water from 59 °F to 60 °F at one atmosphere pressure.

Catalyst matrix or substrate - Device coated or impregnated by the active ingredients of the catalyst. The catalyst matrix can be made from ceramic honeycomb, pellets, metal plates or mesh.

Catalyst space velocity - The quantity of gas (at standard conditions) flowing per volume of catalyst per unit time.

CO boiler - Any boiler or furnace which processes the off-gases from a catalytic cracking unit regenerator

Combustion modification - Any modification of the burner, combustion air flow (including flue-gas recirculation), or fuel-flow system which reduces nitrogen oxide emissions

Duct burner - A device used in the exhaust stream of a gas turbine to allow firing of additional fuel for the heat recovery steam generator (HRSG).

Flue gas recirculation (FGR) - The return of a portion of the products of combustion and their mixture with the combustion air to dilute the combustion air to a burner.

Fuel NOx - Nitrogen oxides that are formed by the oxidation of nitrogen contained in the fuel.

Greenhouse gas - An atmospheric gas that captures infrared radiation thereby preventing re-radiation of energy absorbed by the earth with the subsequent increase in the temperature of the earth.

Ground level ozone - An atmospheric pollutant formed by reaction of nitrogen dioxide and reactive hydrocarbons in the lower levels of the atmosphere.

ISO conditions - A set of reference conditions for temperature, pressure and ambient humidity agreed to by the International Organization for Standardization. Nitrogen oxide emission regulations for gas turbines are sometimes referenced to this standard.

Low NOx burner (LNB) - A burner especially designed to produce less NOx emissions.

Nitrogen oxides (NOx) - The sum of nitric oxide (NO) and nitrogen dioxide (NO₂), collectively expressed as nitrogen dioxide.

Nitrous oxide (N₂O) - One of the oxides of nitrogen. Also a greenhouse gas.

Ozone (O₃) - A triatomic molecule formed from an oxygen diatomic molecule and an atom of oxygen.



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Process heater - Any combustion equipment that transfers heat from combustion to raise the temperature of, change the state of, or promote chemical reactions in a process stream.

Prompt NOx - NO_x that is formed at low-temperature, fuel-rich conditions and short residence times.

Reduction efficiency - The percentage of NO_x removed from the exhaust gas stream by the NO_x control process.

Refinery fuel gas - A mixture of hydrogen and gaseous hydrocarbons generated by petroleum refinery processes and used by the refinery for on-site combustion in boilers, process heaters, turbines, and other combustion equipment.

Refinery-wide emission rate - The ratio of the total mass of discharge into the atmosphere of nitrogen oxides, in pounds, to the sum of the actual heat input to those units in million Btu (measured at high heating value), calculated over a twenty-four-(24) hour operating day.

Residence time - The time period the reactants are in contact at reaction temperature.

Staged air burner - A low NO_x burner design where the air is added in stages thereby providing an initial fuel-rich combustion zone.

Staged fuel burner - A low NO_x burner where the fuel is added in stages thereby providing an initial lower temperature fuel-lean combustion zone.

Standard conditions - A sea level atmospheric pressure and a temperature of 70°F (21°C).

Standard dry cubic meter - One m³ of gas free of water vapor and at standard conditions.

Stationary internal combustion engine - Any spark or compression ignited internal combustion engine that is operated at a specific site for more than one year or is attached to a foundation at that site.

Stratospheric ozone - Ozone that is found in the extreme upper levels of the atmosphere. Greenhouse gases destroy this ozone, that is responsible for interception of harmful ultraviolet rays.

THERMAL DENOX - An ExxonMobil proprietary SNCR NO_x removal technology applicable to fired heaters, boilers and FCCU regenerators.

Thermal NOx - Nitrogen oxides that are formed by the thermal fixation of nitrogen in the combustion air.

Ultra low NOx burner (ULNB) - A low NO_x burner incorporating internal flue gas recirculation, thereby further reducing NO_x emissions.

ACRONYMS

The following acronyms are used throughout this design practice.

BHP - Brake horsepower; a unit of energy used in discussing internal combustion engines

BSFC - Brake-specific fuel consumption; a term used to describe the fuel consumption required for a given power output in an internal combustion engine.

Btu - British thermal unit, a measure of energy.

DeNOx - A generic term for NO_x removal.

EPA - U.S. Environmental Protection Agency

FBN - Fuel bound nitrogen, that is, nitrogen contained in the fuel that is burned.

FCCU - Fluid catalytic cracking unit

FD - Forced draft

FHB -Fired heaters and boilers

GJ -Giga joule; a unit of energy

GT -Gas turbine

GTC - Gas turbine combustor

HC - HydroCarbons

HRSG - Heat recovery steam generator

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ICE - Internal combustion engine

ID - Induced draft

IFGR -Internal flue gas recirculation

ISO - International Organization for Standardization

LEA - Low excess air

LNB - Low NO_x burner

M - Designation for million (10⁶). Note, that this International System of Units differs from the MM designation for million used in earlier Exxon reports.

MBtu - Million of British thermal units; a unit of energy

MD/ND - Mechanical draft/Natural draft

NSCR - Non-selective catalytic reduction

PIC - Pre-ignition cell; a type of combustion modification NO_x control for internal combustion engines.

PM - Particulate matter

PM 2.5 - Particle matter with size less than 2.5 microns diameter.

ppb - Parts per billion. Used to express concentration. As used in this document ppb is always expressed on a volumetric basis unless otherwise specified.

ppm - Parts per million. Used to express concentration. As used in this document ppm is always expressed on a volumetric basis unless otherwise specified.

ppmvd - Parts per million volume dry. Used to express concentration, without including water.

PSC - Pre-stratified charge; a type of combustion modification NO_x control for internal combustion engines.

RQL - Rich/quench/lean; a description of a combustion modification process for NO_x control in internal combustion engines.

SCR - Selective catalytic reduction

SI - Steam injection

SNCR - Selective non-catalytic reduction

ULNB - Ultra low NO_x burner

WFR - Water to fuel ratio, a term used in water and steam injection for NO_x control in gas turbines.

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BACKGROUND

Three oxides of nitrogen (NO_x): nitric oxide (NO), nitrogen dioxide (NO₂) and nitrous oxide (N₂O) are considered important in atmospheric pollution. The predominant NO_x emissions from petroleum refineries and chemical plants, in terms of concentration, are nitric oxide (NO) and nitrogen dioxide (NO₂). The predominant sources of NO_x emissions from these facilities are combustion sources. The concentration of uncontrolled nitrogen oxides emitted from refinery and chemical plant combustion sources is typically in the range of 100 to 500 ppm (at 3% O₂ dry). Values as high as 3000 ppm can be found from some equipment, such as diesel engines.

ENVIRONMENTAL IMPACT

Nitric oxide (NO), the most prevalent of the oxides of nitrogen emitted from refineries and chemical plant combustion sources is not regarded as a significant pollutant from either a health or economic welfare standpoint. Its significance as an air pollutant results from the chemical reactions in which it participates once it leaves the source. These reactions result in several environmental concerns, which include nitrogen dioxide (NO₂) levels, ground level ozone, acid rain, and small particulate formation. These concerns are the reasons for the high degree of controls that have been placed on nitrogen oxides and for the emission tax which has been levied by some countries.

NO₂ ambient concentrations

As indicated above, some nitrogen dioxide (NO₂) is emitted directly from combustion sources. However, NO₂ is predominantly formed at ambient temperatures by the reaction of nitric oxide emissions in the atmosphere. The direct reaction of nitric oxide with molecular oxygen, while thermodynamically favored, is slow and most of the conversion to nitrogen dioxide occurs through reactions of nitric oxide with oxygen containing fragments of volatile organic compounds.

Nitrogen dioxide is an irritant to the nose and throat, especially in people who suffer from asthma. It causes respiratory system damage since its low solubility allows it to penetrate deep into the lungs where tissue damage occurs. It attacks foliage, resulting in economic damage to vegetation. Current NO₂ annual ambient concentration standards vary from one nation to another but range between 50 and 135 ppb (100 to 270 micrograms/cubic meter). Most areas easily achieve the standards, with ambient levels of 30 to 40 ppb being common place.

Nitrogen dioxide is also a precursor for ambient ground level ozone, acid rain, and the formation of fine particulate (PM 2.5).

Ground level ozone

Ozone is a compound of oxygen with a molecular formula of O₃. It is formed by attachment of an oxygen atom (O) to an oxygen molecule (O₂), often by very complicated chemical paths. It is multifaceted in that it is both essential and detrimental for human health.

Ozone in the stratosphere interacts with ultraviolet radiation impinging on the earth, thereby reducing the potential cancer causing level of ultraviolet radiation reaching the earth's surface and is essential for human health. This upper atmosphere ozone, located 2 to 6 miles above the earth's surface, is not a concern for our discussion of control of nitrogen oxides.

Ground level ozone is the ozone that is formed in the troposphere in the first few hundreds of feet (meters) above the earth surface by a complicated series of photochemical induced interactions involving nitrogen dioxide, volatile reactive organic compounds and sunlight. The role of NO_x in ozone formation is clear, leading nearly all ozone ambient level control plans to target NO_x reduction as part of their ozone mitigation strategy.

The reactive organics necessary for ground level ozone formation are found in the vicinity of petroleum operations and petrochemical plants as a result of the fugitive emissions from storage tanks and process units. They are even more prevalent in urban areas as a result of unburned hydrocarbons from hydrocarbon-fueled mobile transportation sources. Sunlight is a key ingredient for these photochemical reactions and the ground-level ozone problem is more prevalent in those urban areas favored by higher ambient temperatures and stagnant air masses.

Ground-level ozone causes "smog" and has been shown to result in serious respiratory and cardiovascular problems and injuries to plant tissues. Ozone irritates the lungs and breathing passages, causing coughing and pain in the chest and throat. It increases susceptibility to respiratory infections and reduces the ability to exercise. Effects are more severe in people with asthma and other respiratory illnesses. Long term exposure may lead to scarring of the lung tissue and lowered lung efficiency.

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Current ambient level ozone standards vary from one nation to another, but are generally in the range of 80 to 120 ppb (180 to 235 micrograms/cubic meter) as the maximum hourly or daily average ozone concentration. Normal concentrations found in rural areas are about 40 ppb, with concentrations in urban areas in the vicinity of 100 ppb. Pressures continue to mount for even greater reductions in allowed ambient levels of ozone.

Ozone has a long half-life, about 80 hours, and can be transported by the movement of air masses for long distances from where it was originally formed. This durability makes ozone a trans-boundary or regional air pollutant. Such trans-boundary pollutants can be evidenced hundreds and even thousands of miles downwind from the emission source.

Acid rain

Nitrogen dioxide is removed from the atmosphere by reactions which eventually form nitric acid (HNO_3). Soluble in water, the formed nitric acid dissolves in rainwater. This makes nitrogen dioxide one of several air pollutants deemed responsible for the acid rain problem, that is, acidic precipitation which causes acidification of lakes and streams, and damage to mortar, building stones and metal coatings. About 35% of the acid rain is attributed to NO_x .

Acid rain is also a trans-boundary pollutant whose effects can be seen hundreds of miles from the emission source. The acid rain problem has been particularly severe in the northeast of the United States and in northern Europe, both of which are situated downwind from major coal burning electric generation regions.

Fine particulates (PM 2.5)

Attention has recently been focused on fine particulates, those smaller than 2.5 micrometers (microns) in diameter. These particles, identified as PM 2.5, form largely from gaseous precursors including NO_x , tend to be acidic and are aerodynamically stable, i.e., do not have the tendency to settle out as do larger particles. Fine particulates are generated directly from combustion and indirectly from secondary chemical reactions in the atmosphere involving several different air pollutants. Ammonium nitrate from ammonia and nitric acid (from NO_2) in the atmosphere are significant sources of fine particulate.

PM 2.5 is associated with a number of health problems. The foremost concern is evidence that acute and chronic exposure to particulate matter causes premature mortality from respiratory diseases and heart attacks, particularly among the elderly and those with heart and lung diseases. Additional health problems attributed to PM 2.5 include aggravated asthma, increased illness, and respiratory problems among children, and increased hospital and emergency room visits.

Regional haze and diminished visibility are the principal welfare impacts of PM 2.5. These concerns are receiving increased attention in the United States and some other nations.

In the USA, the Environmental Protection Agency has added a new PM 2.5 national ambient air quality standard of annual $15 \mu\text{g}/\text{m}^3$ and 24-hour $50 \mu\text{g}/\text{m}^3$. The new standard involves a new control regime. While existing PM controls focus on scrubbers, electrostatic precipitators, and bag filters and preventing dust dispersion, the new controls would also focus on control of precursor gases, including NO_x .

Nitrous oxide

Nitrous oxide (N_2O) is not a threat to human health or vegetation, being employed extensively as an anesthetic, under the common name "laughing gas." It is however, a potent "green house" gas, being long-lived and having 90 times the effectiveness of carbon dioxide for destruction of essential high-level ozone. It accounts for 6% of the anthropogenic contribution of green house gas emissions. With the continuing interest in reducing "green house" gases to combat global warming, additional attention to nitrous oxide emissions may be a possibility in the future. Currently there are no ambient or emission level standards for N_2O emissions.

NO_x FORMATION MECHANISMS

Nitrogen oxides are generally classified as thermal NO_x , fuel NO_x or prompt NO_x . Thermal NO_x is formed by fixation of molecular nitrogen at combustion temperatures, fuel NO_x by direct oxidation of fuel bound nitrogen species in fuel, and prompt NO_x by reactions of molecular nitrogen with hydrocarbon fragments under rich combustion conditions.

Thermal NO_x

Thermal NO_x is the primary source of the NO_x emissions from gas-fired refinery and petrochemical heaters, boilers and other combustion equipment.

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Nitrogen oxides form at combustion temperatures through a complex chain of chemical reactions involving atomic and dissociated chemical species. The thermal fixation of molecular nitrogen becomes significant at temperatures exceeding 2800 °F (1540 °C) . While a complete discussion of the mechanisms of thermal NO_x formation is outside the content of this Design Practice, several observations, which are important to the control methods and techniques to be discussed later, bear mentioning.

Thermal NO_x formation is commonly described using the Zeldovich mechanism. This mechanism shows that the concentration of nitric oxide (NO), the most prevalent oxide of NO_x formed during combustion, depends on the concentrations of oxygen and nitrogen, the reaction temperature and the time in the peak temperature zone. The oxygen dependence is on the square root of the oxygen concentration and a definite peak in nitric oxide formation occurs slightly above the stoichiometric ratio of air (oxygen) to fuel. However, the most significant dependence is that of temperature, with nitric oxide concentrations rising exponentially as the temperature is raised above 2800°F (1540°C). For an increase of about 100°F (55°C) , the concentration of NO_x predicted by the Zeldovich mechanism increases by one order of magnitude. At temperatures encountered in the flame zone when burning commonly used fuels in the petroleum and chemical industry equilibrium concentrations of thermal NO_x can easily reach 3,000 ppm. While reaction kinetics limit the approach to equilibrium, uncontrolled thermal NO_x levels of about 100 ppm to 200 ppm are typically found.

Within the combustion zone nitrogen dioxide (NO₂) is formed from the reaction of nitric oxide with oxygen containing species. This reaction is favored by lower temperatures and, in general, less than 10% of the oxides of nitrogen leaving a combustion device are in the form of nitrogen dioxide. However higher levels of NO₂ emissions are encountered in the exhaust from gas turbines and duct burners, where high levels of excess air and low temperature promote the oxidation of NO to NO₂. However, most of the reaction of nitric oxide to nitrogen dioxide occurs at ambient conditions after the combustion gases have left the combustion device.

Nitrous oxide (N₂O) is also formed by thermal reactions, although at temperatures of 1470 to 1650°F (800 to 900°C), considerably lower temperatures than those required for formation of nitric oxide. Nitrous oxide emissions are low for all combustion sources except for fluidized bed combustion, where the large volume of the bed solids helps to maintain lower temperatures than those encountered in flames. Within the petroleum industry, the only applications where nitrous oxide emissions might be a concern are cogeneration units burning coke or other residuals from coking operations. Nitrous oxide levels of 150 ppm have been reported for petroleum coke fired fluidized bed combustors. While it might be expected that fluid catalytic cracking (FCCU) regenerators would be a source of nitrous oxides, tests on a full-burn FCCU regenerator showed only 3 to 25 ppm of nitrous oxide.

Fuel NO_x

The direct oxidation of nitrogen containing species in fuels is a fast reaction, which, for high nitrogen containing fuels, can result in NO_x levels considerably higher than those produced thermally. Above a fuel nitrogen content of 0.2 wt.%, NO_x emissions from the direct oxidation of nitrogen in the fuel usually surpasses thermal NO_x emissions.

In petroleum operations, fuel nitrogen sources range from ammonia and amines in gaseous fuels to nitrogen containing compounds in liquid fuels and in the char from catalyst regeneration and catalytic cracking reactor burners.

Fuel NO_x is the result of the reactions between chemically bound nitrogen in the fuel and oxygen in the combustion air. The N bond in solid, liquid and gaseous fuels is not as strong as the N-N bond in the nitrogen molecule. Therefore, in the combustion process chemically bound N atoms contained in the fuel are released and rapidly converted to NO at temperatures well below those needed to form thermal NO_x. Intermediate species, such as HCN, HOCN and NH₂, are postulated to be involved in the gas phase reactions leading to NO. The conversion of fuel bound nitrogen to NO_x ranges from 10 to 30%. Fuels with very low nitrogen content have essentially all the bound nitrogen converted to NO_x, while the nitrogen in a fuel with 1.0 wt % nitrogen content undergoes about a 30% conversion to NO_x.

Prompt NO_x

The mechanisms by which prompt NO_x is formed are not well understood, but its formation appears significant in fuel rich combustion conditions. Formation appears to depend not on the fuel bound nitrogen content as much as it does on the conditions of the flame and tends to occur in the rich zones in the flame front. Prompt NO_x becomes an important consideration when emission levels are 20 to 30 ppm or below. Oxygen availability is another important factor; high levels of excess air can reduce prompt NO_x formation. Similar to gas phase fuel NO_x formation, prompt NO_x is formed from the products of intermediate reactions.

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NO_x REDUCTION AND CONTROL CONSIDERATIONS

In considering NO_x reduction methods and technologies, there are several points to emphasize. First, nitric oxide (NO) is the predominant form of NO_x that is formed in the combustion zone and emitted from the combustion device. Second, the formation of nitric oxide is very dependent on the concentration of available oxygen and on the reaction temperature. Third, fuel-bound nitrogen is a major contributor of NO_x.

The NO_x reduction control technologies discussed in the subsequent subsections concentrate on preventing the formation of NO_x during the combustion process, either by reducing the nitrogen content in the fuel, by limiting the access of the reaction to oxygen or by reducing the reaction temperature. For those cases where this approach is not successful, the alternative option is to consider control technologies that destroy the NO_x after combustion but before the combustion products leave the facility.

In general a NO_x reduction program is undertaken in response to regulatory requirements mandating temporary reductions in NO_x emissions or implementation of permanent reductions to meet plant wide bubble limits and/or source specific emission limits. The limits may require controlling the NO_x emissions from new installations and/or reducing the NO_x from existing facilities. The methods and technology options to address most effectively and economically the required control or reduction of NO_x emissions will differ, but in all cases the options involve either operating changes/combustion modifications to limit the formation of NO_x or post-combustion controls to destroy NO_x that is formed. In some cases, a combination of these basic options is used to maximize NO_x reduction.

Temporary Reductions on Existing Equipment -Temporary reductions on existing equipment may be imposed for a short period of time in response to an air pollution episode whose magnitude can be expected to be lowered quickly through immediate reduction in the NO_x emissions. An example would be a regulatory request to reduced NO_x emissions in response to an expected high concentration of ambient ground level ozone incident. If such episodes are infrequent, and if the regulatory agencies are in agreement, reduction measures that carry an economic operating penalty, but do not require investment in NO_x reduction technologies, may be more appropriate and acceptable.

Permanent Reductions on Existing Equipment - Permanent reductions on existing equipment are mandated as part of a national or regional plan to reduce the ambient level of an air pollutant or to meet agreed reductions on the emission of the oxides of nitrogen. One example is the Houston Galveston State Implementation Plan to reduce NO_x emissions. Another example is the United States and European Union targets to achieve specific percentage reductions in NO_x emissions by a given date. In general, these mandated reductions reflect the current perceptions as to technical and economical viability of achieving specific reduction levels on certain classes of emission producing facilities. In some cases, the physical layout of the existing facilities will prevent or hinder the application of the NO_x reduction options.

Controls On New Installations - Controls on new installations are mandated by regulatory agencies as a condition for obtaining the construction and operating permits necessary to install equipment for a new facility or to expand an existing facility. These mandates result from laws or administrative rulings that require specific control technologies, specific reduction levels or specific emission levels to be applied to or achieved from any new facilities as part of a national or regional plan to reduce the ambient level of an air pollutant. NO_x control has been practiced since the late 1970's and manufacturers have developed control equipment which in most cases can meet the required NO_x emission levels for new installations.

REGULATORY REQUIREMENTS

In this background section reference has been made to several ambient level concentrations of NO_x related air pollutants that have been established by local, national or regional authorities. While of interest in understanding the driving forces behind NO_x control requirements, the ambient requirements are generally not the direct concern for the owner/operator of combustion equipment. Rather, it is the level of NO_x emission reduction that is established by the regulatory authorities to enable them to achieve the desired ambient level concentration. These levels may reflect the level of NO_x reduction that can be achieved, although at times the cost of compliance is very high. Combustion modifications on existing installations can often achieve 60% reduction in NO_x and exceed 90% reduction on new installations. Post-combustion technologies can often reduce NO_x by greater than 90%.

OVERVIEW OF EXXONMOBIL APPLICATIONS EXPERIENCE

Within ExxonMobil, many fired heaters and boilers have either been initially installed with or retrofitted with combustion modifications to reduce NO_x. Scores of stationary internal combustion engines have been modified to reduce NO_x emissions. Many stationary gas turbine installations have undergone steam injection or post-combustion modifications to achieve NO_x reductions.

The experience from these applications provide the guidelines for the NO_x reduction methods and technologies recommended in this Design Practice.

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FIRE HEATERS AND BOILERS

This subsection covers NO_x reduction and control for fired heaters and boilers. Generally, a refinery or chemical plant will have a number of these units and they collectively are the primary source of NO_x emissions. This subsection details NO_x control options for fired heaters and boilers, which are summarized in a table that follows.

OVERVIEW

In principle, a fired heater or boiler is a device consisting of a combustion zone and an associated heat transfer surface that transfer the energy to a process fluid for the purpose of increasing the temperature, vaporizing the fluid, and/or promoting a chemical reaction. A primary distinction between the two units is that process fluid in the fired heater can be a variety of gases and liquids, usually including a hydrocarbon, while the process fluid in a boiler is water.

There are many different fired heater and boiler types, or arrangements, available and have been used over the years. These units are all made up of four basic components: box (or enclosure), burners, coil, and stack. The reader is referred to the Design Practice, Section VIII for further details on fired heaters. Much of the description in this section can be extended to boilers.

As the combustion device, burners are the source of NO_x emissions in fired heaters and boilers. They are subject to all the conditions that promote the formation of NO_x described in the Background section: temperature, oxygen and nitrogen concentrations, and the time the reactants spend in the combustion zone. Reducing or controlling the NO_x emissions therefore involves changes to the operating conditions in the burners or modifications to the burners.

Burners fall into two main categories: natural draft or forced draft (sometimes referred to as mechanical draft because a fan is used to provide the combustion air). While either category is used in fired heaters, most fired heater burners utilize burners designed for natural draft service. Almost all boilers are supplied with forced draft systems. Most fired heaters and boilers in ExxonMobil service are fired with gas but some units can also be liquid-fuel fired or combination gas/liquid-fuel fired. Most gas-fired burners fire raw-gas, but some pre-mixed burners are used in fired heaters where special flame characteristics are needed to meet process heat transfer requirements. These different burner and fuel system design arrangements can affect the ability to make the modifications needed to reduce NO_x and must be considered when evaluating options for mitigating NO_x formation. For more specifics on burners, refer to subsection VIII-F of the ExxonMobil Design Practices which covers fired heater burners.

NO_x reduction options for fired heaters and boilers cover a wide number of options. These include pre-combustion options, combustion modifications, post-combustion options and a combination of the first three. These different options are discussed below.

PRE-COMBUSTION CONTROL OPTIONS

Pre-combustion options use the understanding of the NO_x formation mechanisms discussed in the Background section to modify the combustion conditions to mitigate the formation of NO_x. While these mitigation measures reduce the formation of NO_x with minimal or no plant investment to modify existing combustion equipment, they usually incur a significant operating debit. As a result of this operating penalty, the pre-combustion options are generally used only in temporary or short-term applications.

Operation at Reduced Load

As mentioned in the Background section, the rate of formation of thermal NO_x increases exponentially with increasing flame temperature. Operating the combustion device at a load lower than its design capacity reduces the heat release rate and results in a lower overall temperature. Because of the strong temperature dependence of the NO_x formation reactions, this results in lower NO_x emissions. For this NO_x reduction strategy to be effective, load cannot be reduced below the point where excess O₂ in the products of combustion might increase to the point where air control difficulties are introduced.

Fuel Switching

In the Background section two influences of the fuel used were discussed. The fuel composition was seen to influence the flame temperature, with fuels of high hydrogen content resulting in high flame temperatures and correspondingly higher NO_x formation rates. The presence of nitrogen-bound compounds in the fuel was also shown to result in fuel NO_x.

With refinery and petrochemical plant combustion devices sometimes fueled with by-product and waste, fuel type and the nitrogen content of the fuels becomes an important consideration in establishing the levels of NO_x emitted. Typically, heaters burn either liquid or gaseous fuels and sometimes both fuels in combination. Liquid fuels used include liquid butanes and pentanes, light fuel oils, such as diesel and No. 2 fuel oil, and heavy fuel oils, such as No. 6 residual oil. Gas fuels such as hydrogen, methane, ethane, propane and butane are usually burned in a variety of blends, often referred to as refinery fuel-gas. Natural gas, consisting predominantly of methane, is also a common fuel for refinery and petrochemical plant burners, and is often blended into refinery fuel-gas before combustion.

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CONTROL OF NITROGEN OXIDES

Combustion of liquid fuels often produces uncontrolled NO_x emissions higher than does the combustion of fuel gases at identical conditions of heat release rates, excess air levels and combustion air preheat. This arises from the higher nitrogen content in many liquid fuels.

High hydrogen content refinery fuel gases cause a hotter flame, resulting in greater NO_x formation. A conventional burner fired with fuel gas containing 50% or more hydrogen can increase NO_x emissions 20 to 50% over the same burner firing natural gas.

Often temporary relief from high NO_x emission levels can be achieved by changing the fuel to the combustion devices, with particular emphasis on replacing high hydrogen containing fuels and using fuels with low fuel-bound nitrogen content. However, the effectiveness of fuel switching will depend on the refinery or chemical plant flexibility to accommodate different fuels in the combustion equipment.

Reducing Air Preheat

Combustion air preheat is often used in conjunction with mechanical draft boilers/heaters to improve thermal efficiency. Thermal efficiency for heaters of this type can be as high as 92% (LHV). With the strong dependence of NO_x formation on temperature, the use of air preheat for fuel efficiency works counter to NO_x mitigation. An increase in air preheat from ambient to 500°F (260°C) increases NO_x formation by a factor of approximately two. The temporary cessation of air preheat can be an effective temporary NO_x control measure, but it comes at the expense of increased fuel consumption and the associated increased operating cost. This loss of thermal efficiency can be partially offset by adding a convection section heat recovery unit or increasing the size of the existing one. NO_x emissions from radiant burners appear to be unaffected by combustion air preheat.

Operating Considerations

As mentioned above, many of the pre-combustion methods lower the flame temperature, thereby reducing the amount of heat that can be transferred by radiative or convective heat transfer. This reduces the capacity of furnaces and boilers and results in an operating penalty. The use of these methods then requires a trade-off between the cost of NO_x mitigation and plant operating requirements. The pre-combustion options can be particularly effective in those few situations where NO_x mitigation requirements are indeed temporary in nature and the investment cost in NO_x control modifications can be avoided.

Effect On Other Emissions

Reducing the flame temperature and/or reducing the oxygen concentration, while important for reducing the formation rate of nitric oxide, can result in incomplete combustion of carbon fragments, with the result that the levels of other air pollutants of concern, i.e., carbon monoxide (CO), unburned hydrocarbons and particulates can be increased.

COMBUSTION MODIFICATIONS

Like the pre-combustion options, combustion modification technologies use the understanding of the NO_x formation mechanisms discussed in the Background section to modify the combustion conditions to mitigate the formation of NO_x. Unlike the pre-combustion methods, combustion modification technologies generally require that permanent changes be made to the combustion equipment. In most cases, plant investment is required that involves selection of lower NO_x producing combustion equipment on new installations or modification and/or replacement of combustion equipment at existing installations. The advantage of the combustion modification technologies is that they can reduce the formation of NO_x without incurring a continuing operating penalty; although temporary operating losses can exist while the equipment is shut down for modification.

Minimizing Excess Air

While operation with excess air is used to ensure completion of combustion, it can result in added NO_x emissions. Since NO_x emissions peak at excess air levels about 30 to 50% above the stoichiometric air to fuel ratio, reducing the excess air toward the stoichiometric air to fuel amount can reduce NO_x emissions. On average, a 9% increase in NO_x accompanies each 1 vol.% increase in stack oxygen up to about a 6 vol.% excess oxygen level. Above this level the NO_x formation begins to decrease due to the flame cooling effect of the excess air which reduces the formation of thermal NO_x.

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Decreased local oxygen concentration in the combustion zone inhibits the formation of thermal NO_x. The effectiveness of low excess air (LEA) controls in reducing NO_x depends on the long-term average excess air level that can be maintained in the combustion device. The lowest excess air level that can be practically maintained depends on the burner type, fuel type, the degree of air leakage into the fired heater or boiler, and on the ability of the excess air control system to react quickly to changes in fuel composition. Burner type influences the excess air level attainable by affecting the degree of fuel/air mixing. Forced draft burners, generally operate with a higher pressure drop than natural draft burners resulting in improved fuel to air mixing. Consequently, forced draft burners can achieve complete combustion at lower excess air levels than natural draft burners, especially with more difficult to burn liquid fuels. Forced draft burners are more likely encountered in packaged boilers than in fired heaters used in refinery operations, making LEA more applicable to NO_x control from boilers. While most of the fired heater applications which are encountered in the petroleum and chemical industry are of the natural draft type, there are enough forced draft burners in fired heater applications to make LEA worth considering.

The fuel type also affects the minimum excess air level. Gas fired burners generally can operate at a lower excess air level than oil fired burners to achieve complete combustion. Variations in fuel composition, often associated with refinery gas, may affect the ability of the LEA control system to continuously maintain lower stack oxygen levels.

Current practice is to control excess air to improve combustion efficiency. However, retrofitting old heaters/boilers that lack LEA equipment may require a large capital investment to achieve optimal excess air operation. Excess O₂ levels of approximately 2 to 4 vol%(dry) appear to provide the best balance of maximum thermal efficiency and NO_x and CO emissions.

In many ExxonMobil refineries and chemical plants, excess air is already minimized as an energy conservation operating practice. Therefore, control of excess air should be viewed as an expected standard operating procedure, not as a potential retrofit to provide a significant NO_x reduction. However, in some locations where fuel is inexpensive, energy conservation may not have a high priority. In such situations, the incremental NO_x reduction benefit may provide an additional incentive for minimizing excess air.

External Flue Gas Recirculation

Flue gas recirculation (FGR) generally involves forced return of flue gas to the burner and introducing the air/flue gas mixture into the combustion zone. This technique, referred to as external flue gas recirculation, recycles about 15 to 30% of the products of combustion (flue gas) to the primary combustion zone. The recirculation of flue gas dilutes the combustion reactants, reduces the peak flame temperature and reduces the local oxygen concentration, thereby inhibiting thermal NO_x formation. It is believed that the technique has only a small effect on fuel NO_x formation. Therefore, FGR may not be as effective on oil fired heaters as on gas fired heaters. Where applicable, FGR is an effective NO_x reduction technique and when used in combination with low NO_x burners, NO_x reductions up to 80% of baseline NO_x have been reported.

Several inherent drawbacks include a large capital outlay because of the need for high temperature fans and extensive ductwork and piping modifications. Furthermore, it may not apply to all types of fired heaters. The low flame temperature and susceptibility to flame instability limits FGR usage in high temperature applications. In addition, FGR can only be used on mechanical draft heaters. Boilers, with their generally fewer and larger burners, have been more amenable to FGR modifications than fired heaters, with their more numerous and smaller burners.

Steam Injection

The injection of steam makes use of both the dependence of nitric oxide formation on temperature and on the concentration of oxygen. The steam acts primarily as an additional heat sink to lower the flame temperature and it secondarily reduces the concentration of molecular oxygen. Both of these effects reduce the rate of nitric oxide formation thereby lowering NO_x emissions.

There are practical limitations on the amount of steam diluent that can be added without sacrificing operational stability. Up to 1 lb steam per lb of fuel has been demonstrated. ExxonMobil experience with steam addition to reduce the NO_x levels from fired heaters indicates that a ratio of steam to fuel of 0.8 lb/lb (0.04 lb steam per lb of dry air) reduces NO_x by about 60% from the no moisture case.

Substantial moisture injection can result from the humidity level of the combustion air. Combustion air at 90°F (32°C) and 80% relative humidity is equivalent to 0.02 lb water per lb of dry air and results in about a 35% reduction in NO_x from the no moisture case.

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Use of Air Lances to Achieve Staged Combustion

Early efforts to stage combustion used air lances to separate the combustion process and limit NO_x formation. In the primary combustion zone, a rich mixture is combusted while the air lances supply jets of air in the secondary combustion zone to complete the oxidation of the fuel. It has been demonstrated that nitrogen oxide reductions from uncontrolled levels using air lances for heaters firing refinery gas range from 12 to 71 percent. Reduction for heaters that combine firing of No.6 fuel oil and refinery gas range from 25 to 54 percent.

Although staged air combustion is potentially applicable to many fired heaters, its use may be restricted by several limitations. As the degree of staging is increased, the flame quality and temperature decrease, and the uniformity of the heat flux provided by the flame is impaired. In process heater applications where the process fluid flow may be seriously affected by variations from the design heat flux distribution, staged air lances may not be applicable. For example, reforming heaters and vacuum heaters often have process fluids of more than one phase or at high temperatures that require a uniform heat flux distribution. Other heater types, such as crude oil heaters, have been demonstrated to more readily tolerate changes in heat flux and temperature. Other limitations include the possible corrosive environment due to staged combustion within the heater, which leads to frequent replacement of air lances. A large flame zone would be required in some heaters to accommodate the longer flame associated with staged combustion.

The development of staged burners incorporating air staging or fuel staging has eliminated the need for extensive air supply piping and removed many of the flame difficulties associated with air lance staging. For this reason, air staging using air lances should not be considered a current NO_x control approach.

Low NO_x Burners

Principles Of Operation - Low NO_x burners (LNB) make use of design modifications that reduce the available oxygen or cool the combustion zone, thereby mitigating the emissions of NO_x. LNB's typically provide NO_x reduction in the range of 50 to 75% and some recently developed burners are achieving about 90% reduction. LNB's are competitive control technology when measured in cost per quantity of NO_x removed. Several different burner designs incorporating one or more of these features have been developed by burner manufacturers to achieve the desired operating conditions to mitigate NO_x formation. These designs are generally classified as staged-air, staged-fuel or internal flue gas recirculation burners. Often more than one feature is incorporated in a low NO_x burner (LNB) design.

Staged-Air Burners - Early LNB burner design centered on bypassing some of the combustion air around the conventional burner combustion zone. In this design, called staged-air operation, only a portion of the combustion air is available to the fuel in the primary flame zone. The theoretical basis for air staging is that the initial combustion of the fuel takes place in a fuel-rich zone in which N₂ is preferentially formed rather than NO. Also, the flame temperature in the primary combustion zone is reduced and the oxygen concentration is lowered, thereby further reducing thermal NO_x. The remaining portion of the combustion air (50 to 75%) is introduced downstream forming a secondary zone where combustion is completed. NO_x formation in the secondary zone is reduced because the inerts from the primary zone reduce the flame temperature.

For heavy fuel oil firing, staged-air burners are more suitable than staged-fuel burners due to difficulties in staging liquid fuels and the opportunity to reduce fuel NO_x. The reducing conditions prevailing in many staged air burners (particularly if they have long primary zone residence times) are thought to have a greater impact on fuel NO_x destruction than the staged-fuel burners which essentially affect only thermal NO_x formation. Fuel NO_x reduction, as we saw in the Background section, is the key issue in overall NO_x reduction for high nitrogen content liquid fuels, such as residual fuel oils.

NO_x emission reduction achieved by staged air LNB's range from 30 to 40% below the emissions from conventional burners.

Staged-Fuel Burners - Designed for gas firing, staged-fuel LNB's separate the combustion zone into two regions. The first is a lean primary region in which the total quantity of combustion air is supplied with a fraction of the fuel. In a typical staged fuel LNB, 40 to 70% of the fuel is bypassed around the primary combustion region. Combustion in the primary region therefore takes place in the presence of a large excess of oxygen at substantially lower temperatures than in conventional burners, which reduces the thermal NO_x. The remaining fuel is introduced downstream forming a secondary zone where combustion is completed by oxygen left over from the primary region. NO_x formation in the secondary zone is reduced because the inerts from the primary zone reduce the flame temperature. This technique inhibits the formation of thermal NO_x, but has little effect on fuel NO_x.

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Reductions in NO_x emissions over conventional burners up to 70% have been reported for staged-fuel LNB's. For gaseous fuels that do not contain fuel-bound nitrogen, NO_x reduction performance from fuel staging is better than from air staging. The lower temperature, high oxygen conditions of the staged fuel LNB have a stronger effect on NO_x reduction than do the higher temperature, low oxygen conditions of the staged air LNB. Staged fuel burners also have several operational advantages over staged air burners. First the improved fuel/air mixing due to pressurized injection of secondary region fuel reduces the excess air necessary to insure complete combustion. The lower excess air both reduces NO_x formation and improves overall fired heater thermal efficiency. Second, for a given peak flame temperature, staged fuel LNB's have a more compact flame than staged air LNB's.

Limitations of Low NO_x Burners

The major problem with high performance LNB retrofitting is that the flames tend to be larger and sometimes less well defined than those of the standard burners being replaced. The altered flame pattern is caused by diffusion mixing and delayed combustion resulting from the air staging. The tendency for larger, less well-defined flames is more pronounced for natural draft than for mechanical draft and more so for oil than for gas firing. However, one source³⁰ reports that problems resulting from flame pattern alteration can be minimized or eliminated if the burner system is properly designed. Design considerations that affect the flame characteristics include burner tip placement, burner tip hole sizes and angles, placement of the flue gas recycle ducts, and burner tile shape.

Another problem with LNBs is that retrofit operations may require extensive modifications to the heater itself. A large number of process heaters are floor fired with limited space under the heater. LNBs require larger air plenums than conventional burners, so may increase retrofit cost significantly. Other typical retrofit requirements may include multiple connections, steam header connections, and flue gas ducting alterations.

Spacing between burner center lines varies appreciably from one heater design to another, typically within a range of 2 to 5.6 feet (most are greater than 3.3 feet). In general, retrofitting heaters that have a spacing of less than 3.3 feet may not be practical because of potential flame impingement. In the case of heaters in critical services (i.e., those with high process temperatures or pressures) such as catalytic reforming, steam/methane reforming, hydrocracking, olefin cracking, etc., this minimum spacing may be as high as 4.6 feet because of the need to minimize heat flux variation around the tubes.

Another limitation on LNB applications is the existing burner design heat release rate. Most LNBs have a minimum design heat release of about 3 to 9 MBtu/h. Certain heaters, such as steam/methane reformers, are typically designed with a large number of small burners with duties that may fall below the minimum LNB heat release. LNB's in such low duty range are not readily available.

From the above discussions, it is apparent that not all process heaters are suitable for LNB retrofitting, although the majority will qualify. In the case of heaters with multiple small burners, the cost of a burner retrofit is high even when it is technically feasible, therefore alternative low NO_x solutions may have to be considered.

Internal flue gas recirculation burners - Both the staged fuel and the staged air low NO_x burners are further enhanced by designs that use a venturi effect to entrain a small amount of flue gas prior to entering the primary flame, in a process called internal flue gas recirculation (IFGR). Fuel gas injection via primary or secondary burner tips, and possibly, steam injection can be used to create the venturi effect. In this technique, like in the external flue gas recirculation technique discussed above, the entrained flue gas dilutes the oxygen concentration and reduces the local flame temperature, thereby reducing the rate of NO_x formation. Since reduced oxygen concentrations in the flame have a strong impact on fuel NO_x, IFGR burners are an effective NO_x control technique for burners firing N-containing fuel oil. This is especially the case when combined with staged-air combustion.

Ultra Low NO_x Burners - Most recent low NO_x burner designs make use of a combination of either air or fuel staging and internal flue gas recirculation. These burners, known as ultra low NO_x burners (ULNB) are capable of achieving lower NO_x emissions than LNB's. Retrofitting burner experience at Baytown Refinery demonstrates 10-30 ppmvd NO_x emissions from these burners. This can lead to NO_x reductions of about 90% compared with conventional uncontrolled raw gas burners. More details concerning burner design and ULNB's can be found in DP XVIII, Fired Heaters.

Limitation of Ultra Low NO_x Burners

Retrofit problems with ULNBs are similar to those encountered with LNB retrofits. Ultra low NO_x burners, in general, are larger in size and may require larger air plenums than the conventional burners. Modifications to the burner mounts may be required because ULNBs usually do not fit into conventional burner mounts. However, it is expected that this may not always be true because of the wide variety of burners available and the differing heater designs.

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Radiant burners

One company named Alzeta offers a gas burner that has a cube of ceramic fibers at the burner tip. The fibers act as a catalyst in oxidizing the fuel. As a result, combustion is accomplished at a temperature of approximately 1800°F. Thermal NO_x formation is reduced since this temperature is approximately 1830°F lower than the flame temperature in conventional burners. Radiant burners do not appear to be affected by high temperature air preheat, and NO_x is actually decreased by high excess air operation. This technique is available for new installations but is not considered practical in most cases for retrofit installation. The burner intrudes into the furnace space, and a retrofit would probably require retubing the process heater. Reported emissions have been 20 to 25 ppmv at 3 percent O₂. However, the reported emissions were tested for the heaters with capacity of less than 10 MBtu/h. Most of its applications are limited to relatively small sized packaged boilers. There is no reported experience with these burners within ExxonMobil.

Low NO_x Burner Application Considerations

Operating Considerations - LNB's tend to have longer flames than conventional burners and this needs to be considered when retrofitting low NO_x burners in existing fired heaters

Project Considerations - NO_x reduction modifications are not as simple as they first appear. Whether a new installation or a modification to an existing facility, they involve a "project" in the full context of the term. Modifications to existing equipment must be implemented during planned unit turn-around. Substantial modifications to the floor of the furnaces are often involved to accommodate the new burners and to the piping and control systems.

In general the following project steps must be considered:

- Evaluate historical fuel gas composition and flow rates. This will set the design basis for the burner heat release and allow the burner vendor to more accurately calculate emissions from the new burners. The table below lists fuel gas constituents and how they may affect LNB's and ULNB's.
- Modify existing furnace floor as required to accommodate new LNB's. In general, LNB are several inches larger in diameter than conventional burners of the same capacity.
- Purchase new burners and plenums. In some cases existing plenums can be modified.
- Provide new fuel and pilot gas piping from headers to burners. In some cases it may prove expedient to replace the headers.
- Install new emission monitoring and recording equipment as required by local regulations.
- Install new fuel gas treatment facilities to remove particulates not removed by the knockout drum. This typically consists of one or more filters and associated instrumentation. As the newer ULNB's have significantly smaller fuel ports, coalescing filters which remove sub-micron particulates may be required.

The reader is referred to Report EE.129E.92 for a more complete account of the project implementation required to assure a smooth transition to the Low NO_x combustion modifications.