

CHAPTER 5 UNDERSTANDING ATMOSPHERIC EMISSIONS

The Major Concerns

It was pointed out in Chapter 1 that the combustion processes that underpin our society have negative consequences (see Table 5-1). Fortunately, not all fuels produce all these contaminants, and much can be done to avoid or minimize emissions. It is also fortunate that natural gas, Canada's most common fuel for residential, commercial and industrial purposes, has inherently low emissions potential, especially when paired with appropriate equipment, such as low-NO_x burners. Nonetheless, it is important to understand what the emissions are and what effects they have if the efforts to mitigate them are to be understood and supported.

Table 5-1 Emissions from Combustion Systems and Their Effects

Emission	Source	Effect
CO ₂ (carbon dioxide)	Complete combustion of carbon in fuel	Global warming
CO (carbon monoxide)	Incomplete combustion of carbon in fuel	Smog
SO ₂ (sulphur dioxide)	Combustion of sulphur in fuel	Acid rain Smog
NO _x (nitrogen oxides)	By-product of most combustion processes	Acid rain Smog
N ₂ O (nitrous oxide)	By-product of some combustion processes	Global warming
VOCs (volatile organic compounds)	Leakage and evaporation of liquid fuels (vehicles, fuel tanks, fuel pumps, refineries)	Smog
CH ₄ (methane)	Leakage from gas wells, pipelines and distribution systems	Global warming
H ₂ O (water vapour)	Combustion of hydrogen in fuel	Localized fog
Particulates (dust, soot, fumes)	Unburned or partially burned carbon or hydrocarbons, also ash and dirt in fuel	Smog Respiratory hazard
Trace elements	Impurities in fuel	Potential carcinogens
Chlorinated compounds	Chlorine compounds (e.g., salt) in fuel or combustion air	Potential carcinogens

This chapter describes the three major categories of atmospheric pollution, and then discusses at length the issue of NO_x control. NO_x being an important emission of combustion systems that can be substantially mitigated by manipulating the combustion process.

Smog

Smog, also referred to as urban air pollution, is a combination of nitrogen oxides (NO_x), volatile organic compounds (VOCs), and ground-level ozone. Smog is most severe in summer and where traffic is concentrated. If other pollutants are added, such as sulphur dioxide (SO_2) and particulates composed of ash and soot, air quality is rapidly degraded.

Often the most dangerous component of smog is ozone (O_3), a highly reactive form of oxygen containing three atoms instead of the more common and more stable two-atom configuration (O_2). In the upper atmosphere, the troposphere, a very small amount of ozone, the "ozone layer," protects the earth by absorbing the most harmful ultraviolet waves radiated by the sun. However, at ground level, short-term exposure to ozone concentrations of a few hundred parts per billion (ppb) can cause lung damage, particularly in children, while long-term exposure to concentrations of about 50 ppb can reduce crop yields by up to 12%.

Ground-level ozone is formed by oxides of nitrogen and volatile organic compounds reacting in the presence of sunlight at summer temperatures. Two oxides of nitrogen, nitric oxide (NO) and nitrogen dioxide (NO_2), collectively referred to as NO_x , are produced by nearly all combustion processes, including engines, in concentrations of a few dozen to a few hundred parts per million (ppm). NO_2 , of itself, aggravates breathing difficulties in people suffering from asthma and bronchitis but it also contributes to ozone formation. Volatile organic compounds (VOCs) result mostly from leakage and evaporation of liquid fuels such as gasoline and diesel fuel.

While smog is generated in localized areas it often downgrades air quality in downwind suburban and rural areas.

Acid Rain

This has its origins in acid gas emissions, primarily sulphur dioxide (SO_2) from combustion of sulphur-bearing fuels, and nitrogen oxides (NO_x) formed during most combustion processes. These react by various means with moisture in the air, to form sulphuric and nitric acids. It is normal for precipitation to be slightly acidic but in eastern North America and much of Europe it is often ten times more acidic than normal, due to acid rain. The resulting direct damage to the environment is enormous; forests and crops die back or grow poorly, lakes become too acidic to support fish or other aquatic forms of life; structures and machinery suffer accelerated corrosion. Respiratory problems such as bronchitis and asthma may also be aggravated. Prevailing winds can carry the precursors, or building blocks, of acid rain huge distances; more than half the acid rain in eastern Canada originates from acid gas emissions in the United States.

Global Warming

The potential impact of human activity on global warming lies in the emission of so-called "greenhouse gases" associated with our use of fuels. Greenhouse gases have the effect of trapping heat that reaches the earth from the sun, preventing it from being

radiated back into space. Without the greenhouse effect the average temperature of the earth's surface would be -20°C , too cold to sustain most of the life forms we know. But if the greenhouse effect is increased, and the earth becomes warmer by even a few degrees, many things change, often unpredictably and with negative results. Global warming is indeed global in scope; activities on the other side of the earth ultimately affect us; what we do here ultimately affects the whole earth. It is an issue that requires international cooperation in encouraging local action.

The major greenhouse gases are carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), tropospheric ozone (O_3) and chlorofluorocarbons (CFCs). Carbon dioxide results primarily from the combustion of carbon, partly from the human use of fossil fuels but also from forest fires. Human activities that release methane into the atmosphere are mostly related to the industries of fuel production, transportation and distribution, for example, leakage from oil and gas wells, pipelines and refineries. A very substantial natural source is rotting vegetation in wetlands, and yes, the digestive processes of ruminant animals such as cattle also make a contribution. Human sources of nitrous oxide stem from some combustion systems and from use of ammonia-based fertilizers. Stratospheric ozone may have its origins at ground level, as already described. At high altitudes it acts as a greenhouse gas, but also provides some shielding from ultraviolet radiation. The chlorofluorocarbon refrigerants and aerosol propellants, now banned in Canada, are the only greenhouse gas having wholly man-made origins. While their concentrations are low, their heat-trapping ability is very high, and they break down very slowly, unless exposed to harsh ultraviolet radiation at high altitude, in which case they damage the ozone layer! On a per-molecule basis, other compounds have hundreds or thousands of times the heat-trapping ability of carbon dioxide, but it is the most important greenhouse gas simply because it is the most abundant. It is also the most abundant by-product of our combustion systems. Water vapour is also a greenhouse gas, but clouds reflect the sun's radiation away from the earth, and the net effect is not clear.

NO_x Emissions Guidelines

Under the auspices of the Canadian Council of the Ministers of the Environment (CCME), national guidelines for NO_x emissions were set for newly installed and newly modified fossil-fuel-fired boilers and heaters. The current emission limits are shown in Table 5-2. Capacity is determined by fuel input, and equipment firing less than 10 million Btu/h is excluded.

The guideline provides higher limits for equipment that can be shown to have higher efficiency than normal, and therefore burns less fuel. Enforcement is a provincial responsibility, and provinces may enact stricter limits. The extent to which the guideline is applied to boilers or heaters undergoing modification or overhaul is also a provincial responsibility. The Province of Ontario is presently conducting public review of a policy that would require meeting the limits in Table 5-2 as a condition for issuance of a Certificate of Approval by the Ministry of Environment. (See Chapter 6 for a more

This is because the ways by which NO_x is formed, and the amounts formed, are somewhat fuel dependent and the guideline limits are based on the NO_x control technology currently available.

There are two main types of NO_x analyzer in common use. One, intended for continuous duty, is often installed in large plants. When equipped with an adequate sample conditioning system to prevent dirt and moisture from fouling the detection cell and when regularly calibrated by means of span gases of known concentration, it gives very reliable results. The other type is conveniently portable, and intended only for spot checks because sampling conditioning is usually limited to a dust filter and perhaps a water trap. It gives satisfactory results if it is calibrated frequently and used as directed. The portable analyzers usually have the advantage of being able to measure other components of the flue gas, such as CO_2 , O_2 and SO_2 . However, they may measure on a wet gas basis in which case correction to dry gas basis may be necessary, as discussed in Appendix 1.

How NO_x Forms

There are three ways in which NO_x forms during combustion, and it is necessary to have some understanding of them to see why different fuels have different emission limits and to grasp why certain measures are undertaken to minimize NO_x formation. The three formation mechanisms are called, for convenience, thermal NO_x , fuel NO_x , and prompt NO_x .

Thermal NO_x

Thermal NO_x is formed by free nitrogen and oxygen from the combustion air combining with each other. This only happens at the high temperatures encountered in flames; the normally stable molecules of nitrogen dissociate into atoms, which are very reactive, and readily join with similarly dissociated oxygen atoms to form NO. The higher the temperature the more readily this happens, so to minimize thermal NO_x various means are employed to reduce flame temperature and especially to avoid pockets of peak flame temperature.

Fuel NO_x

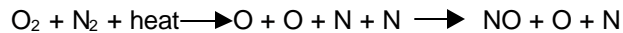
Fuel NO_x forms from the oxidation of nitrogen-containing compounds such as amine and pyridine which are found in some fuels such as residual oil and coal. These compounds are referred to as fuel-bound nitrogen. As they are broken down by the combustion process, a number of chemical reactions can occur to produce NO. The more fuel-bound nitrogen in the fuel, the more likely is the formation of NO, which is why the NO_x emissions standards for residual fuel oil are related to fuel nitrogen content. The reactions by which fuel-bound nitrogen forms NO are not very temperature-sensitive, so the measures that minimize thermal NO_x are ineffective against fuel NO_x . Instead, the combustion process must be managed to create an oxygen-deficient zone that inhibits NO

HOW NO_x HAPPENS

NO_x is nitric oxide (NO) and nitrogen dioxide (NO₂)
There are three ways it forms in flames

Thermal NO_x

At very high temperatures oxygen and nitrogen molecules in the combustion air “dissociate” into atoms. Some combine with each other, the hotter the faster.



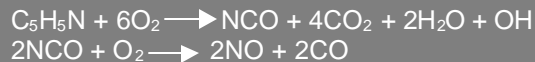
This happens slowly at 1500 °C but quickly at 1800 °C

As flame temperatures drop the NO starts to break down, but at slower and slower rates, so there is still some left in the stack gas.

We can reduce thermal NO_x by doing things to reduce flame temperature.

Fuel NO_x

Fuel oil and coal usually contain some nitrogen in the form of organic compounds such as pyridene (C₅H₅N). The amount is small, usually less than 0.5 %. As these compounds break down in combustion, some of the nitrogen may combine with oxygen to form NO, e.g.;



This can happen in the lower range of flame temperatures, so reducing flame temperature doesn't help.

We can reduce fuel NO_x by:

- 1) using fuels that have little organic nitrogen, like distillate oil, or none, like natural gas, and
- 2) staging the combustion process so the first part is fuel-rich, which works against the formation of NO.

Prompt NO_x

As hydrocarbon fuels begin to break down in combustion, products like CH may occur briefly. These may react with atmospheric nitrogen, and through several steps, form NO.

Usually not much forms this way, but it is hard to control.

formation, followed by a burnout zone. This is difficult to achieve when there are rapid load changes and high turndown requirements.

Prompt NO_x

Prompt NO_x results from nitrogen in the combustion air uniting with hydrocarbon radicals created in the early stages of combustion as fuel molecules break down. It is called prompt NO_x because it forms early in the combustion process and, although the amounts are usually small, they are difficult to avoid. This formation mechanism operates at the low end of combustion temperatures and so does not respond to measures that reduce thermal NO_x. On the other hand, prompt NO_x is promoted by the fuel-rich combustion conditions which combat fuel NO_x.

Typical NO_x Emissions

While natural gas usually contains some nitrogen, it is in the form of nitrogen gas, not the organic compounds that lead to fuel NO_x. So NO_x emissions from boilers and heaters burning natural gas derive mostly from the thermal NO_x mechanism, with perhaps a small contribution via the prompt NO_x mechanism. Crude oils contain varying amounts of fuel-bound nitrogen, which the refining processes tend to concentrate in the residual oil.

Table 5-3 Typical NO_x Emissions for Different Fuels and Boilers Without NO_x Control Equipment

Fuel and Boiler Type	Typical NO_x Emissions ppm at 3% O₂
<u>Natural gas</u>	
Firetube	75-115
Package watertube	40-90
Field-erected watertube	45-105
<u>No. 2 Oil</u>	
Firetube	70-140
Package watertube	90-150
Field-erected watertube	40-115
<u>No. 4 Oil</u>	
Package watertube	160-310
Field-erected watertube	140-190
<u>No. 6 Oil</u>	
Package watertube	200-360
Field-erected watertube	190-330

Refined oils, such as No. 2 distillate oil, generally contain less than 0.05% fuel-bound nitrogen, No. 4 residual oil and some No. 6 residual oils contain less than 0.35% fuel-bound nitrogen, while other residual oils from high-nitrogen crude may contain between 0.35% and 0.6% fuel-bound nitrogen. In the absence of NO_x control measures these fuels produce fuel NO_x more or less in proportion to their fuel-bound nitrogen content, in addition to thermal NO_x according to flame temperature conditions. Fuel oil may also produce more prompt NO_x than natural gas because it contains more complex hydrocarbons.

Strategies for NO_x Control

It is possible to minimize NO_x emissions by switching fuels or by chemically scrubbing it from the flue gas, but most NO_x reduction strategies involve modification of the combustion process. Some are only effective in reducing thermal NO_x, others combat both thermal NO_x and fuel NO_x and perhaps reduce prompt NO_x as well. Used in various ways, singly or in combinations, these strategies are the usual means by which compliance with NO_x regulations is achieved.

It is useful to begin this discussion with a review of some of the terminology that will be used. Chemists apply the term “stoichiometric” to a reaction which has exactly enough of each reactant for the process taking place. Thus, “stoichiometric combustion” means that there is exactly enough air to burn all the fuel, with no excess air or fuel left over. If there is more fuel than air it may be called “sub-stoichiometric combustion” or “fuel-rich combustion” and the combustion zone may be called “chemically reducing”. If there is an excess of air, then the combustion zone is called “fuel-lean” or “oxidizing”.

Fuel Switching

One obvious way to reduce NO_x emissions is to switch from a fuel with a high fuel-bound nitrogen content to one that has little or none; for example, from residual fuel oil to natural gas. This eliminates fuel NO_x but additional measures may be required to achieve compliance with the regulations, since different standards apply to each fuel.

NO_x Scrubbing

It is also possible to reduce NO_x to very low levels by employing selective catalytic reduction (SCR) or synthetic non-catalytic reduction (SNCR) to scrub the NO_x from the flue gas. However, these processes involve installing and operating a chemical treatment plant between the boiler and the stack. Some systems employ ammonia and others employ urea as reactants, both of which present their own environmental problems. To date these processes have had only a few applications in Canada. Worldwide, they have been used with large boilers in areas where air quality problems are severe.

Water or Steam Injection

As already explained, the formation of thermal NO_x increases sharply with increasing flame temperature, so strategies for controlling it involve reducing flame temperature or reducing the length of time that high temperatures exist. A simple way to do this is to inject water or steam with the fuel, as is now the routine practice for reducing NO_x emissions from gas turbines. In boilers fired with natural gas, injecting water at 25% to 75% of fuel weight has achieved NO_x reductions of 50% to 77%, but of course boiler efficiency is reduced by one or two percent. Other negative side effects are increases in CO emissions, plume visibility, and fireside corrosion. Inadequate control of water injection could also impair flame stability and damage furnace refractory. However, being effective and inexpensive to install, water injection is sometimes used to bring a boiler having a low utilization factor into compliance with regulations.

Accelerated Combustion and Flame Chilling

Two other techniques for reducing thermal NO_x are accelerated combustion and flame chilling. Both are usually applied to natural gas, and usually the fuel and air are premixed at the entrance to the burner. With accelerated combustion the burner itself has a large surface, sometimes made of porous ceramic or sintered metal, on which is established a very large number of very short flames, only a few millimetres in length. These little flames are quickly cooled by radiation to the furnace waterwalls, so the residence time at high temperature is simply too short for much NO_x to form. With flame chilling, gridlike burners are placed behind closely spaced watertubes and fire between the tubes, so the flames, short to begin with, are immediately chilled to a level where thermal NO_x formation is slow. Generally speaking, these techniques are not applied to liquid fuels due to problems with soot and CO.

Flue Gas Recirculation

A common technique for reducing thermal NO_x has been flue gas recirculation, usually referred to as FGR. It involves mixing flue gas from the boiler exit into the combustion air stream or sometimes, with a gaseous fuel, into the fuel stream. The recirculated flue gas lowers flame temperature by adding more gases around the flame to absorb heat and by slowing down fuel/air mixing, thus creating a larger flame with more heat transfer to boiler surfaces.

Most often, a separate high-temperature blower drawing flue gas from the boiler breeching and injecting it into the burner windbox accomplishes FGR. This is called forced FGR. Sometimes the suction of the forced draft fan is used to move the flue gas, and this is called induced FGR. In any case there must be means to control FGR according to boiler load. FGR systems generally recirculate 10% to 30% of the flue gas and thereby, in boilers fired with natural gas, achieve NO_x reductions of 50% to 70%. Higher rates of FGR may achieve higher NO_x reduction, but are likely to have a negative effect on flame stability.

Because it has little effect on fuel NO_x , FGR is most effective with natural-gas-fired boilers, less effective but still useful with boilers firing distillate oil, and of little benefit with boilers firing residual oil. Results can be improved by combining FGR with low- NO_x burners, as will be discussed later.

FGR has a minimal detrimental effect on efficiency because, with the cooler flame temperatures, more air is required to ensure complete combustion. At a given firing rate, this marginally raises the minimum air flow with a corresponding efficiency penalty. Forced FGR and, to a much lesser extent, induced FGR have an additional penalty in the electrical energy used by the fan motor to recirculate the flue gases. Forced FGR has further costs associated with installing and maintaining the fan and its control.

Fuel Staging and Air Staging

These are two other techniques that manipulate the combustion process to minimize NO_x formation. Both aim to create the chemically reducing zones which inhibit the formation of fuel NO_x ; one through control of the fuel supply, the other through control of the air supply. Often they employ burner designs that draw flue gas from the rear of the furnace up to the front, to mix it with the fresh fuel and air. This is called internal FGR.

In fuel staging, a small, primary fuel supply is provided with enough air to ensure a stable, reliable source of ignition. Around it, secondary fuel nozzles create a fuel-rich, and therefore reducing, zone into which secondary air mixes slowly, resulting in relatively low flame temperatures, inhibiting thermal NO_x formation. Sometimes tertiary fuel is injected through nozzles completely outside the flame envelope.

Air staging may have only one fuel nozzle or one set of gas spuds, provided with enough air to stabilize ignition and support fuel-rich combustion, with the rest of the air mixed in slowly downstream via secondary air ports. In field-erected boilers with multiple burners, air staging is sometimes accomplished by firing some burners fuel-rich and other burners fuel-lean.

Both fuel staging and air staging require a large furnace volume to be most effective, which limits their applicability to firetube and package watertube boilers. Getting secondary fuel and air nozzles into such boilers also presents problems. Nonetheless, several so-called low- NO_x burners have been developed which incorporate fuel and/or air staging, and have been successfully applied to package boilers. Some suppliers have also redesigned boilers to provide furnace configurations that support the requirements of NO_x reduction.

Low- NO_x Burners

In recent years low- NO_x burners have become the most common means for minimizing NO_x emissions. Employing the strategies described in the foregoing, primarily fuel staging and air staging, and sometimes incorporating flue gas recirculation, manufacturers of boilers and burners have made the emissions guidelines in Table 5-2

routinely achievable. Some have developed low-NO_x burners that can be retrofitted to existing boilers and heaters; others have developed complete systems, integrating burner and furnace design for best effect. Some of these proprietary designs are shown in Appendix 2.

Burner Tuning

To control fuel NO_x it is necessary to modify the combustion process in ways that provide a fuel-rich or chemically reducing zone in which the nitrogen-bearing compounds in the fuel break down to form compounds other than NO. Such modifications often have the effect of lowering flame temperature as well, and so have a beneficial effect on thermal NO_x.

On older boilers that have been converted to oil or natural gas from stoker firing of coal, a technique that sometimes works well is to adjust the excess air to the lowest level that gives clean combustion. This is called burner tuning or oxygen tuning. It works by slowing down the fuel/air mixing, which delays combustion, creates chemically reducing zones, and reduces flame temperature. The resulting flame envelope is much larger, which the older boilers usually have sufficient furnace volume to accommodate. In one case with residual oil as the fuel it was possible to reduce NO_x by 30% at 70% MCR, and by 50% at 40% MCR, but under conditions of fixed load and manual control. With firetube boilers and package watertube boilers, NO_x reductions by burner tuning are usually limited to 10% or 15% because as the flame envelope increases in size it begins to impinge on the furnace walls, causing carbon deposition and possible tube damage. High-quality combustion controls are necessary for continuous operation with burner tuning.

Reburning

Reburning is a NO_x reduction technique being applied to large industrial and utility boilers, primarily those firing coal and residual oil. It is a three-stage combustion process based on fuel staging. The main burner zone is operated at a fuel-lean condition with about 90% of the required fuel input. At the point where primary combustion is complete the balance of the fuel, the “reburn fuel”, is injected, and creates a chemically reducing zone which decomposes most of the NO and the chemical constituents likely to form NO. Tertiary air is then blended in slowly to complete the combustion process. The reburn fuel may be different than the primary fuel; often natural gas is chosen because of the ease with which it can be injected.

Reburning has been shown to reduce NO_x by 50% to 90%. In some cases even coal-fired boilers have achieved emissions of less than 100 ppm NO_x, corrected to 3% O₂. However, residence time for each stage of combustion is critical. The points of injection for reburn fuel and tertiary air must be accurately positioned, and perhaps varied with changes in boiler load. It is therefore best suited to large, base-loaded boilers.

NO_x CONTROL STRATEGY	AGAINST
<p><u>Flue Gas Recirculation (FGR)</u></p> <p>Feed 10% to 30% of the flue gas from the boiler exit back to the windbox. This dilutes the combustion air and imposes a thermal burden on the flame, reducing temperatures. FGR is a common means for reducing NO_x.</p>	Thermal NO _x
<p><u>Water or Steam Injection</u></p> <p>This lowers flame temperature by imposing a thermal burden as well as slowing down combustion.</p>	Thermal NO _x
<p><u>Accelerated Combustion</u></p> <p>Create a very short flame of very large area, in which the high-temperature zone exists for such a short time that thermal NO_x has little time to form.</p> <p>This technique is usually limited to gaseous fuels.</p>	Thermal NO _x
<p><u>Flame Chilling</u></p> <p>Sweep the flame over watercooled surfaces as quickly as possible so thermal NO_x has little time to form. This technique is usually limited to gaseous fuels.</p>	Thermal NO _x
<p><u>Fuel Switching</u></p> <p>Convert from a fuel with a high nitrogen content to one with little or none.</p>	Fuel NO _x
<p><u>Burner Tuning</u></p> <p>Adjust the burners to the minimum excess air that avoids excessive CO.</p> <p>This gives a bigger flame, lower temperatures and somewhat reducing conditions at the core of the flame.</p>	Thermal NO _x Fuel NO _x
<p><u>Air Staging</u></p> <p>Supply the combustion air in two or three stages, so the core of the flame is fuel-rich. This creates chemical conditions which discourage NO_x formation.</p> <p>Flame temperatures are also reduced.</p>	Fuel NO _x Thermal NO _x
<p><u>Fuel Staging</u></p> <p>Supply the fuel in two or more stages so there is a fuel-rich zone which discourages NO_x formation. Flame temperatures are also reduced.</p>	Fuel NO _x Thermal NO _x
<p><u>Low-NO_x Burners</u></p> <p>New burner designs combine fuel staging, air staging and FGR to reduce NO_x formation.</p>	Fuel NO _x Thermal NO _x
<p><u>Reburning</u></p> <p>This combines fuel staging and air staging. About 90% of the fuel is fired through the burners. At the point where combustion is nearly complete, the rest of the fuel is injected, creating chemically reducing conditions which break down NO_x. Then more air is added to complete combustion.</p> <p>This technique is only used on large boilers.</p>	Prompt NO _x Fuel NO _x Thermal NO _x

Poster 5-2 NO_x Control Strategies