## TRADE-OFFS AND CO-BENEFITS ACCOMPANYING NOx CONTROL

## **Power Boiler NOx**

Apart from recovery furnaces, the pulp and paper industry draws upon power boilers to generate the steam and electrical energy required to sustain the manufacturing process. In the U.S., the industry uses nearly 1,000 of these auxiliary power boilers. Approximately one-third of these boilers are larger than 250 million Btu per hour; only 17 have heat capacities larger than  $1000 \times 10^{6}$  Btu/hr. The largest is 1,400 x  $10^{6}$  Btu/hr. Approximately one-half of the industry's power boilers were installed prior to 1970, and 292 were installed between 1971 and 1990. Fewer than 1 in 5 were installed in 1991 or later.

Wood products boilers are typically much smaller than boilers at pulp and paper plants, with the majority of boilers less than  $100 \times 10^6$  Btu/hr and very few over 250 x  $10^6$  Btu/hr.

The most important determinant of NOx emissions from power boilers is the choice of fuel. Also influential are features of the boiler's design and the combustion conditions with which it can be operated. As for external controls, many of the same control technologies for utility boilers are candidates for consideration on industrial boilers in the pulp and paper industry. These include selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) technology for NOx. In practice, however, their application has been limited due to skewed economics resulting from the much smaller sizes of industrial boilers relative to their utility counterparts. Furthermore, control performance is often diminished by the dynamic nature of industrial boiler operation (CIBO 2003).

#### How does fuel choice affect emissions of SOx and NOx?

Coal, residual oil, distillate oil, natural gas, and wood residues account for the bulk of the fuels burned in conventional steam generating boilers. Boilers are commonly configured to burn multiple fuels to ensure that steam demands can be met at the most favorable fuel cost.

A comparison of the relative nitrogen content of various fuels is shown in Table S3b.

Fuel	Nitrogen, %
Natural Gas	Insignificant
Distillate Oil	0.05 or less
Residual Oil	0.1 to 1.0
Coal	0.5 to 2.0
Bark and Wood Residue	0.1 to 0.4

## Table S3b. Relative Nitrogen Content of Fuels (Source: USEPA 1998)

At pulp and paper mills in 2005, wood fuels accounted for 39% of the total fuel heat input to boilers, followed by coal (28%), natural gas (24%) and fuel oil (10%) (Pinkerton 2007). Wood is most often burned in combination with fossil fuels in these boilers. Wood products mills that burn coal are rare and only a small percentage burn oil. Thus, their related  $NO_x$  emissions are primarily from combustion of wood and natural gas.

Combustion conditions are particularly influential on NOx formation. The amount of nitrogen available in the fuel is relatively small compared with the amount of nitrogen available in the combustion air. Though a significant portion of the fuel nitrogen can be converted to NOx during combustion, the amount of nitrogen

available in the fuel is relatively small compared with the amount of nitrogen available for conversion in the combustion air. Peak combustion temperatures influence the magnitude of that conversion.

The combustion of wood brings advantages beyond its relatively low sulfur and nitrogen content. The composition and greater moisture content of wood fuels affects combustion conditions in ways that yield NOx reductions. There are other emission dividends as well. CO<sub>2</sub> from wood fuel combustion is considered "neutral" (see tab on Greenhouse Gases, on this website). Moreover, mercury emissions associated with biomass combustion are far lower than those associated with coal.

## What factors constrain beneficial fuel substitutions on existing power boilers?

Fuel switching is an attractive option for reducing releases to the environment, but its application cannot be considered in isolation from a host of site-specific factors of importance to boiler performance, boiler integrity, and overall emissions control capability.

Oland (2002) cites as an example a switch from a) eastern bituminous coal, with a high heat value and low ash content, to b) a low-sulfur western sub-bituminous coal with a lower heating value and high ash content. Though beneficial for reducing SOx emissions, the change comes with potentially adverse effects:

- flame stability impacts consequential to boiler efficiency and pollutant emissions;
- diminished energy efficiency due to deposition and slagging on heat transfer surfaces;
- increased ash loading; and
- unsatisfactory performance of emissions control equipment.

Natural gas is recognized as a clean burning fuel, but its higher hydrogen content yields water vapor during combustion that contributes to greater heat loss out the stack. Biomass and wood are favorable fuels from the standpoint of NOx emissions, but firing them has been observed to lead to accelerated corrosion of boiler components. Fuel properties are best taken into account at the time of boiler design.

### What is the magnitude of boiler NOx emissions?

Emissions depend on the composition of the fuel, the type and size of the boiler, boiler load, and firing conditions in the boiler. Representative emissions of SOx and NOx for various fuels and boiler configurations are shown in Table S4b.

Fuel Option	NOx Emissions	Comment
Natural Gas	0.27	
Distillate Oil (0.5% S)	0.17	
Residual Oil (1%)	0.21 to 0.31	
Pulverized Coal (1% S)	0.32 to 1.19	Assumed Btu content of 13000 Btu per pound
Pulverized Coal (2% S)		
Stoker Fed Coal (1% S)	0.28 to 0.42	
Stoker Fed Coal (2% S)		
Wet Wood	0.22	
Dry Wood	0.49	

### Table S4b. Representative Emissions of NOx for Various Fuels and Boiler Configurations

The representative emission levels in Table S4 were derived from data compiled by EPA (USEPA 1998). The values were selected from those deemed most credible and reflective of performance for boilers that pre-date emission standards applicable to new or reconstructed sources that were adopted in the 1970s. As such, they reflect a baseline level of performance.

## Trade-offs and Co-benefits Accompanying NOx Control

### **Power Boiler NOx**

Values in the table support a number of observations.

- NOx emissions associated with natural gas, given the fuel's low nitrogen content, can be attributed to thermal conversion of nitrogen in combustion air (thermal NOx).
- NOx emissions from coal combustion exceed those for oil and natural gas.
- NOx emissions from pulverized coal boilers exceed those from stoker fed systems.
- Higher NOx emissions are a penalty associated with combustion of the more energy-efficient dry wood.

In the wood products sector, bark, panel trim, and wood residuals other than sanderdust and fines are typically combusted in boilers or thermal oil heaters at temperatures low enough that little thermal NO<sub>x</sub> is formed. (Thermal NO<sub>x</sub> is formed from conversion of atmospheric nitrogen at high temperatures.) For these wood materials, the amount of nitrogen in the wood is the primary variable affecting NO<sub>x</sub> emissions. Sanderdust and fines are small wood particles that can be burned in suspension. The suspension burners that combust these wood materials operate at high enough temperatures to generate thermal NO<sub>x</sub>. NO<sub>x</sub> emissions from suspension burners are then due to both thermal NO<sub>x</sub> and fuel NO<sub>x</sub> (NO<sub>x</sub> generated from the nitrogen in the fuel). Suspension burners are utilized in boilers, thermal oil heaters, and as separate burners to direct fire wood dryers. Sanderdust generated at particleboard and medium density fiberboard (MDF) plants generally contains polymerized urea formaldehyde resin. Since urea is rich in nitrogen, NO<sub>x</sub> emissions from suspension burners burning urea formaldehyde containing sanderdust are the highest in the wood products industry.

## What control options exist for reducing NOx emission levels?

Apart from choice of fuel, NOx emissions may be reduced either by manipulation of combustion conditions or treatment of flue gas in the post-combustion regions of the furnace. Various approaches are characterized in Table S5b. Applicability of individual options and performance will depend upon boiler design and configuration, fuels being burned, and the dynamic character of boiler loading. Greater opportunity for NOx reduction exists when the capability is designed into newly constructed boilers as opposed to retrofitting existing boilers.

In part, the appropriateness of various combustion control measures depends upon whether the principal source of NOx originates with fuel nitrogen content ("fuel NOx") or is derived from thermal conversion of nitrogen in combustion air ("thermal NOx"). The firing of natural gas typifies the latter, whereas the firing of coal and oil typifies the former. Fuel NOx represents approximately 50% of the total uncontrolled emissions when firing residual oil and more than 80% when firing coal.

Thermal NOx formation is commonly controlled by reducing peak and average flame temperatures, an approach contrary to measures typically employed to ensure complete fuel combustion. Thus, a compromise is exacted between effective combustion and NOx formation. Conversion of fuel-bound nitrogen is more dependent upon fuel-air proportions than it is variations in combustion zone temperatures. Overall, NOx control involves a delicate balance of air distribution and combustion temperature control that invites a risk of combustion inefficiency and potential release of pollutants associated with incomplete combustion.

Post-combustion flue gas controls involve chemical reduction of NOx to  $N_2$ . They entail the injection of ammonia-based compounds under suitable temperature conditions where flue gas exits the furnace. Because of the relatively narrow temperature windows required and reaction chemistry sensitivity to flue gas flow rates, these control options are ill-suited for application to industrial scale boilers that are subject to highly variable loads and fuel combinations.

Low-NOx burners, where boiler size and geometry permit, as well as flue gas recirculation, are the most widely applied techniques for boiler NOx reduction. Low-NOx burners are designed to control the mixing of fuel and air to achieve what amounts to staged combustion. This staged combustion reduces both flame temperature and oxygen concentration during some phases of combustion, lowering both thermal

NOx and fuel NOx formation. Flue gas recirculation reduces thermal NOx formation by reducing peak temperatures and limiting oxygen availability. Taken together, NOx reductions of 60-90% are achievable. Flue gas recirculation, however, is better suited to new boilers rather than retrofits, can reduce boiler heating capacity (Sustainability Victoria n.d.), and is difficult to justify economically for industrial-scale boilers.

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	CONTROL OPTION	DESCRIPTION	PERFORMANCE	APPLICATION
	Low Excess Air (LEA)	Reducing excess air in the combustion flame zone reduces fuel and thermal NOx formation	Little to moderate NOx reduction	Limited by-production of smoke, high CO emissions, and increased fouling and corrosion in boiler. Applied for energy efficiency.
	Staged Combustion			
Combustion Modifications	Overfire Air	Diversion of 10-20% of combustion air downstream of burners	15% to 30% NOx reduction	More attractive for new units than retrofit applications. May be used with all fuels and most combustion systems. Can decrease energy efficiency.
	Burners Out of Service	In multiple burner systems, fuel flow is blocked to upper burners allowing only air to pass		Useful in retrofit situations involving suspension-fired coal and oil/gas-fired boilers. Operational problems can include soot/slag formation.
	Biased Burner Firing	The furnace is divided into a lower, fuel-rich zone and an upper fuel-lean zone to complete the burnout	20% NOx reduction	Proven only for oil/gas- fired utility boilers
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	Flue Gas Recirculation (FGR)	Up to 20% of the combustion flue gas is brought into the combustion zone, acting as a heat sink, lowering combustion zone temperature	20% to 30% NOx reduction	Because only thermal NOx formation can be controlled by this technique, it is especially effective only in oil- and gas-fired boilers. Most effective when used in conjunction with air and/or fuel staging. More adaptable to new designs than as a retrofit application. Capital intensity and high operating and maintenance (O&M) costs are prejudicial to use on industrial-scale boilers.

## Table S5b. NOx Control Technologies (USEPA 2003; Srivastava 2000)

CONTROL OPTION	DESCRIPTION	PERFORMANCE	APPLICATION
Reduced Air Preheat (RAP)	Lowers the primary combustion zone peak temperature through reduced preheating of the combustion air		RAP only lowers thermal NOx, and thus is economically attractive only for natural gas and distillate fuel oil combustion. The energy penalty usually makes this option unfavorable.
Steam & Water Injection	Flame quenching by the addition of steam or water in the combustion zone		An effective control technology for oil/gas- fired burners, but one with a potentially significant energy penalty
Load Reduction	Reducing boiler capacity lowers flame temperatures and reduces thermal NOx formation		Can cause improper fuel-air mixing during combustion, creating carbon monoxide and soot emissions
Low-NOx Burners (LNB)	Burners designed to mix fuel and air in a controlled pattern that sustains local fuel-rich regions, keeps the temperatures down and dissipates heat quickly	Approximately 50% NOx reduction	Used in both gas/oil- fired and coal-fired units. Elongated flame configuration limits application in smaller boilers.
Fuel Staging	10% to 20% of the total fuel input is diverted to a second combustion zone downstream of the primary zone. Combustion of fuel in the fuel-rich secondary zone reduces NO formed in the primary zone to N <sub>2</sub> . Low nitrogen-containing fuels such as natural gas and distillate oil are typically used for reburning to minimize further NOx formation.	Claims of NOx reductions from 50% to 70% when combining this approach with overfire air and flue gas recirculation	Limited application in the U.S.

## Table S5b. NOx Control Technologies (continued)

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	CONTROL OPTION	DESCRIPTION	PERFORMANCE	APPLICATION	
Post-Combustion/Flue Gas Treatments	Selective Non- Catalytic Reduction (SNCR)	Involves the injection of urea, ammonium hydroxide, anhydrous ammonia, or aqueous ammonia into the furnace exit region where the flue gas is in the range of 1,600°F to 1,900°F. NOx is reduced to N <sub>2</sub> and H <sub>2</sub> O. Performance affected by inlet NOx level, temperature, mixing, residence time, reagent-to-NOx ratio, and fuel sulfur content.	NOx reduction as high as 60 to 70%	A portion of the NO reduction (about 5%) is due to $N_2O$ formation, a potent greenhouse gas. Process complexity prompts concern about ability to perform adequately under changing load and fuel conditions. Operating problems include optimizing chemical addition to prevent NH <sub>3</sub> emissions in the flue gas and, with higher sulfur fuels, salt deposits on downstream components that contribute to plugging and reduced heat transfer.	
	Selective Catalytic Reduction (SCR)	NOx is reduced to N <sub>2</sub> and H <sub>2</sub> O by the injection of ammonia into the flue gas at temperatures between 450° and 750°F in the presence of a catalyst. Performance is affected by NOx level at SCR inlet, flue gas temperature, NH <sub>3</sub> - to-NOx ratio, fuel sulfur content, gas flow rate, and catalyst condition.	70% to 90% NOx reduction	A proven technology, but not often applied to smaller industrial- scale boilers. Major problems with SCR processes include corrosion, formation of solid ammonium sulfate, and formation of salt deposits in high sulfur oil-fired or coal- fired boilers that reduce heat transfer efficiencies. Ammonia slippage is also a potential problem. Catalysts lose activity over time due to poisoning by trace metals or erosion by fly ash.	

## Table S5b. NOx Control Technologies (continued)

## What are the trade-offs and co-benefits from power boiler NOx control?

### **Combustion Modifications for Boilers:**

A number of combustion-related control options exist for reducing NOx formation and emissions. The effects of these modifications on boiler performance and secondary emissions depend upon unit-specific factors such as combustion chamber type and design, fuel type, and operating practices and restraints (USEPA 1994). Other factors include burner type and location, as well as the fuel delivery system. Thus, generalizations that are made below need to be taken in this context.

Combustion controls can be used to address NOx that originates with the fuel, as well as NOx formed from nitrogen in combustion air. The candidate modifications embody reducing peak flame temperatures and/or delaying the mixing of fuel with the combustion air. Inherent with these changes is the risk of a decrease in boiler combustion efficiency that can affect emissions of other pollutants and the performance of other emission control systems. Increases in carbon monoxide, CO, and unburned carbon are illustrative (USEPA 1994).

### Flue Gas Treatments for Boilers:

Selective Non-Catalytic Reduction (SNCR) and Selective Catalytic Reduction (SCR) are postcombustion techniques installed for NOx control. The retrofitting of SCR on industrial boilers is, however, difficult and costly. In retrofit application, capital costs are estimated to be 30 to 50% higher. Moreover, SCR systems are not very tolerant of constantly changing conditions, as a stable window of operation is required for optimum efficiency. Load swings make it particularly difficult to retrofit boilers with SCR or SCNR, as appropriate temperature windows are hard to maintain.

Both SCR and SNCR involve injection of a reducing agent such as ammonia or urea into the flue gas under conditions where the reagent can react with NOx to form N<sub>2</sub> and H<sub>2</sub>O. Urea or ammonia handling systems are an added complication for boiler operations. In addition, associated salt deposition on downstream boiler components contributes to plugging and reduced heat transfer efficiencies. Catalyst deterioration and poisoning in SCR systems are other impediments that must be taken into account.

Unreacted reagent that exits with the flue gas is known as ammonia slip and can negatively impact plume visibility and ash disposal. Secondary emissions that can result with SNCR include such intermediate reaction products as  $N_2O$ , a potent greenhouse gas.  $N_2O$  levels have been observed to equal up to 4% of the NOx reduction with ammonia injection, while urea injection yielded  $N_2O$  levels up to 25% of the NOx reduced (USEPA 1994). SCR enhances mercury removal.

*Multi-Pollutant Reduction* involving the use of SCR followed by wet flue gas desulfurization (FGD) has gained credence as a potential means of reducing not only NOx and SOx, but also mercury emissions. The contribution of SCR technology to mercury reduction comes from the fact that SCRs have been shown to oxidize elemental mercury. Wet scrubbers, in turn, have been shown to be effective in removing oxidized mercury (Tavoulareas and Jozewicz 2005).

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