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Nitrogen oxide emissions control from biomass and kraft recovery boilers in the pulp and paper industry

Scope

This TIP provides basic information on nitrogen oxide (NO_x) formation and control technologies. After years of limited interest in applying NO_x regulations on industrial boilers that fire biomass derived fuel (hog fuel, bark, wood chips, saw dust, sander dust, railroad ties, pulp mill clarifier sludges, construction and demolition debris, and red and black pulping liquors), regulators in some states are establishing NO_x emissions limits on boilers that are strict enough to impact boiler operations. Informed decisions on fuel usage, operating parameters, NO_x control technology implementation, and impact on other pollutant generation will be needed. This TIP offers background information to help engineers, operating staff, and managers understand the issues and the options that are available to meet compliance requirements.

Safety precautions

In addition to the safety standards and recommended practices generally applicable to combustion equipment employed in the pulp and paper industry, such as National Fire Protection Association (NFPA) 85, NFPA 499 and NFPA 654, the following safety precautions should be taken when applying NO_x emissions control processes.

Low excess air operation to suppress NO_x emissions can lead to generation of carbon monoxide (CO) and other combustible gases in large quantities if boiler combustion air and oxygen trim controls are not properly designed and functioning properly. Large pockets of combustible gases can lead to explosive conditions in the boiler's upper furnace or back passes when mixed with air and exposed to an ignition source. Also, leaking of flue gas containing high CO concentrations into the boiler house can be hazardous to operating personnel. Inhaling CO can cause headache, dizziness, lightheadedness and fatigue. Higher exposure to CO can cause sleepiness, hallucinations, convulsions, loss of consciousness, and, with extremely high exposure, collapse, coma and death. The Occupational Safety and Health Administration (OSHA) legal airborne permissible exposure limit (PEL) for CO is 50 ppm averaged over an 8-hour workshift. CO is rated as a moderate health hazard (NFPA 2 rating), but a severe flammability hazard (NFPA 4 rating).

Some **selective non-catalytic reduction** (SNCR) and **selective catalytic reduction** (SCR) systems utilize aqueous or anhydrous (gaseous) ammonia injection into the boiler or its back passes. Exposure to gaseous ammonia in relatively small quantities can be harmful to personnel. The OSHA legal airborne PEL for ammonia is 50 ppm averaged over an 8-hour workshift. Ammonia is rated as a serious health hazard (NFPA 3 rating) and exposure can cause skin, eye, nose, throat, and lung irritation. High concentration exposure may cause a build-up of fluid in the lungs (pulmonary edema). Precautions should be taken to prevent leakage in ammonia storage and handling systems,

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to properly train operating personnel, and to provide appropriate personal protective equipment (including access to NIOSH approved respirators). OSHA standard 1910.111 addresses the storage and handling of anhydrous ammonia. In addition, the Department of Homeland Security identifies in Appendix A of 6 CFR Part 27 (Appendix to Chemical Facility Anti-Terrorism Standards; Final Rule) "Chemicals of Interest", which include anhydrous ammonia and aqueous solutions of ammonia in concentrations greater than or equal to 20%.

See also the New Jersey Department of Health Hazardous Substance Fact Sheets for Ammonia and Carbon Monoxide: <http://nj.gov/health/eoh/rtkweb/documents/fs/0084.pdf> and <http://nj.gov/health/eoh/rtkweb/documents/fs/0345.pdf>.

Types of nitrogen-oxygen compounds

NO_x refers to various nitrogen oxides that are present in the atmosphere, primarily nitric oxide (NO) and nitrogen dioxide (NO₂), and, less commonly, nitrous oxide (N₂O). In typical boiler combustion processes, over 90% of the NO_x is generated as NO, less than 10% is NO₂, and less than 1% is N₂O.

Necessity for NO_x emission control

NO_x Health Hazards

NO can cause eye and throat irritation, chest tightness, nausea, and headache. NO₂ vapors are a strong irritant to the pulmonary tract.

Ozone formation

NO oxidizes in the atmosphere to form NO₂. This reaction produces ozone (O₃), which is also a health hazard. O₃ is an eye, nose and throat irritant, and can also cause damage to crops.

Acid rain

NO₂ can be absorbed by rain and form nitrous acid (HNO₂) and nitric acid (HNO₃), which are highly corrosive. Acid rain is destructive to plants, trees, and man-made structures.

Photochemical smog

Contact of sunlight with NO₂ and unburned hydrocarbons produces photochemical smog in the atmosphere, consisting of aldehydes, peroxyacyl nitrates, O₃, and volatile organic compounds (VOC). Photochemical smog causes impaired visibility and potentially acidic fog.

Greenhouse gas formation

N₂O, commonly known as laughing gas, is a greenhouse gas that is 300 times stronger in global warming potential than carbon dioxide (CO₂) on a mass basis. With an average life of 114 years in air, N₂O is more stable than many other air pollutants and therefore more likely to build up in the atmosphere. N₂O emissions require attention also because of its interactions with both NO formation and reduction processes.

NO_x formation mechanisms

NO_x is most commonly formed from combustion processes. There are three predominant mechanisms: Thermal NO_x, Fuel NO_x, and Prompt NO_x.

Thermal NO_x

Thermal NO_x is the high temperature reaction of nitrogen and oxygen in the air (the Zeldovich mechanism). As with all chemical reactions, the rate increases exponentially with temperature. Thermal NO_x becomes a significant generator of NO_x above about 2,800°F (1,538°C).

Fuel NO_x

Fuel NO_x is formed from the oxidation of organically bound nitrogen in the fuel from precursors such as ammonia (NH₃) and hydrogen cyanide (HCN). Fuel NO_x is not generated from the combustion of natural gas or propane since these fuels do not contain fuel bound organic nitrogen, but is a significant contributor when burning oil, coal, biomass and other fuels that contain organic nitrogen. In many biomass combustion technologies that operate at relatively low temperatures, Fuel NO_x becomes the dominant NO_x formation mechanism.

Prompt NO_x

Prompt NO_x is the oxidation of nitrogen and oxygen in the air when interacting with hydrocarbon radicals. It is typically much less important than Thermal NO_x at typical combustion temperatures in industrial boilers.

In biomass combustion processes, NO_x generation is dominated by Fuel NO_x. The temperatures during biomass combustion are typically low enough to form a limited amount of Thermal NO_x, and Prompt NO_x is a very small contributor. Biomass has a small nitrogen content relative to heavy fuel oil and coal, but enough nitrogen is present to generate NO_x emissions in excess of some regulatory limits. Biomass derived from hardwood species typically has higher nitrogen content than from softwood species, and bark has higher nitrogen content than clean wood chips. Some biomass fuels have elevated nitrogen contents, such as paper mill clarifier sludges, municipal sewage sludge, and construction and demolition debris that include particle board, siding, or plywood that contains urea-based glues. Sander dust from wood products that contain urea-based resins and glues can also have elevated nitrogen content. Table 1 below summarizes typical nitrogen content ranges for a number of biomass and fossil fuels.

The low nitrogen contents of some biomass fuels require special attention when having fuel samples analyzed for nitrogen. A standard elemental analyzer typically provides adequate accuracy for fuels with nitrogen content equal to or higher than approximately 0.2% unless the sample size is increased to lower the detection limit. Alternatively, the Kjeldahl digestion and titration technique can be used with larger sample sizes to obtain a lower detection limit and improve measurement accuracy.

Table 1: Typical nitrogen content ranges for some biomass and fossil fuels.

<i>Fuel Type</i>	<i>Nitrogen Content (mass %, dry)</i>
Bark	0.10 to 0.20
Wood Chips	0.03 to 0.10
Black Liquor – Softwood	0.05 to 0.10
Black Liquor – Hardwood	0.10 to 0.14
Primary Sludge	0.2 to 0.5
Secondary Sludge	1.5 to 5.0
Sander Dust	0.4 to 3.3
Fuel Oil	0.02 to 1.0
Coal	0.9 to 1.6

NO_x emissions regulations

NO_x is one of six “criteria” pollutants – along with O₃, Particulate Matter (PM), CO, Sulfur Dioxide (SO₂), and Lead (Pb) - that were identified in the Clean Air Act (originally promulgated in 1970 and revised in 1990). The Clean Air Act requires that the Environmental Protection Agency (EPA) establish National Ambient Air Quality Standards (NAAQS) for these six criteria pollutants.

Environment Canada is the regulatory body in Canada for emissions control under the mandate of the Canadian Environmental Protection Act (CEPA, 1999). In addition to the six criteria pollutants mentioned above, the criteria air contaminants (CAC) identified in the CEPA also include VOC and NH₃.

Individual states are tasked with developing plans to meet the NAAQS in their jurisdictions. The State Implementation Plans (SIPs) are developed by state and local air quality management agencies and submitted to EPA for approval. The SIPs typically include emissions limits from stationary sources, such as power plants and industrial facilities. Efforts to reduce NO_x emissions has resulted in more than a 40% reduction in ambient NO_x concentrations since 1980, such that all areas monitored in the US have average NO_x concentrations below the NAAQS.

Few industrial boilers burning biomass derived fuels currently have NO_x emissions limits

NO_x emissions from industrial sources have previously been of lesser importance compared to mobile sources (passenger cars, trucks, locomotives, planes, ships, etc.) and power plants. Of the industrial sources, emissions of NO_x from boilers firing biomass derived fuels was a small fraction. Not only are there a fewer number of biomass-fired boilers compared to fossil fuel-fired units, but they also have lower uncontrolled NO_x emissions than oil- or coal-fired boilers since biomass typically contains significantly less fuel bound nitrogen and burns at lower temperatures than oil or coal. Consequently, state and local regulators focused first on the largest contributors to NO_x and did not enforce limits on many industrial boilers firing biomass derived fuels.

Although the US has been slow to implement NO_x emissions regulations on industrial biomass boilers, Europe began requiring strict NO_x emissions limits more than 15 years ago.

NO_x emissions limits are becoming more common

Although the NO_x NAAQS level is being met, a number of regions in the US do not meet the required O₃ ambient air level. Since NO is a precursor to the formation of O₃, regulatory limits for NO_x emissions have become more common. The EPA is currently reviewing the O₃ NAAQS level and has proposed to lower the level from 75 parts per billion (ppb) to the 65 ppb to 70 ppb range. It is anticipated that this will trigger a large increase in the number of industrial boilers that will require NO_x emissions limits, as well as the lowering of existing NO_x emissions limits.

Despite the fact that total NO_x emissions from the pulp and paper industry have been declining since 1995 due to lower pulp and paper production rates, increased boiler and plant efficiency, and reductions in fossil fuel firing, there is a high probability that the remaining boilers in the industry will face NO_x emissions limits in the future.

Most common NO_x control technologies

The following lists are the most commonly applied NO_x control technologies utilized by industrial boilers, categorized into combustion related and flue gas treatment related technologies or approaches:

Combustion related control technologies

- Lower excess air
- Overfire air (OFA)/staging
- Low-NO_x burners
- Fuel switching
- Flue gas recirculation (FGR)
- Reburning