Air Pollution Control Technology Review for the Chemical and Fertilizer Sectors

March 24, 2017
Air Pollution Control Technology Review for the Chemical and Fertilizer Sectors

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for
Alberta Environment and Parks

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<td>AQ</td>
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<td>Auto-Thermal Reformer</td>
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<td>BAAQMD</td>
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<td>BACT</td>
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<td>BATEA</td>
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<td>BATNEEC</td>
<td>Best Available Techniques Not Entailing Excessive Cost</td>
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<td>BC MOE</td>
<td>British Columbia Ministry of Environment</td>
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<td>BFW</td>
<td>Boiler Feed Water</td>
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<td>BREF</td>
<td>BAT Reference Document</td>
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<td>CAA</td>
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<td>CAC</td>
<td>Criteria Air Contaminant</td>
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<td>CCME</td>
<td>Canadian Council of Ministers of the Environment</td>
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<td>CEMS</td>
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<td>GACT</td>
<td>Generally Available Control Technology</td>
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<td>GCP</td>
<td>Good Combustion Practice</td>
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<td>Guideline for the Implementation of Air Standards in Ontario</td>
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<td>HAP</td>
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<td>IPPC</td>
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<td>LAER</td>
<td>Lowest Achievable Emission Rate</td>
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<td>Linear Alpha Olefin</td>
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<td>Leak Detection And Repair</td>
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<td>Oxidation Temperature Minimization</td>
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<td>POL</td>
<td>Production of Polymers (European Union)</td>
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<td>PREPA</td>
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<td>Pressure Swing Adsorption</td>
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<td>PSD</td>
<td>Prevention of Significant Deterioration</td>
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<td>RACT</td>
<td>Reasonably Available Control Technology</td>
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<td>Regenerative Thermal Oxidizer</td>
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<td>Transfer Line Exchanger</td>
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<td>TOC</td>
<td>Total Organic Compound</td>
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<td>TRE</td>
<td>Total Resource Effectiveness</td>
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<tr>
<td>UAN</td>
<td>Urea and Ammonium Nitrate</td>
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<td>Pollutant Species</td>
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<td>PM</td>
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<td>PM₁₀</td>
<td>Particulate matter with aerodynamic diameter less than 10 μm</td>
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<tr>
<td>PM₂.₅</td>
<td>Particulate matter with aerodynamic diameter less than 2.5 μm</td>
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Summary

The province of Alberta’s current air quality management system relies on a variety of policy tools to successfully balance environmental protection with industrial development. New and evolving pollution prevention and control technologies provide opportunities for continuous improvement in emission reductions from anthropogenic sources, while still maintaining the environmental and development balance.

Alberta Environment and Parks (AEP) is currently reviewing policy tools to accommodate growth in the chemical and fertilizer sectors. Several existing chemical and fertilizer plants may proceed with major upgrades and/or large expansions over the next decade. Through the continuous improvement concept, industry growth can be accommodated by utilizing appropriate pollution control technologies to minimize environmental impacts.

In this study, Ramboll Environ Canada Inc. (Ramboll Environ) completed a review of the current commercially available pollution prevention and control technologies for major air emission sources at chemical and fertilizer plants. The chemical and fertilizer plants considered in the work included the following.

- **Chemical plants:**
  - Ethylene plants;
  - Polyethylene plants;
  - Ethylene oxide plants;
  - Ethylene glycol plants;
  - Methanol plants;
  - Ethanol plants; and
  - Stand-alone hydrogen plants.

- **Fertilizer plants:**
  - Ammonia plants;
  - Urea plants;
  - Nitric acid plants; and
  - Ammonium nitrate plants.

Several major air emission sources at the chemical and fertilizer plants listed above were identified with details provided for the largest emitting sources in terms of criteria air contaminants (CACs), volatile organic compounds (VOCs), and greenhouse gases (GHGs). The appropriate combustion controls and add-on air pollution emission control technologies were discussed including process, level of air pollution control, removal efficiency and associated cost. The effects of air preheat and different fuel types on the air emissions from these plants were also discussed.

In addition, a jurisdictional review of current environmental regulatory requirements by leading authorities as they apply to air emissions and technologies implemented at new and existing chemical and fertilizer plants was summarized.
1.0 Introduction

The province of Alberta’s current air quality management system relies on a variety of policy tools to successfully balance environmental protection with industrial development. New and evolving pollution prevention and control technologies provide opportunities for continuous improvement in emission reductions from anthropogenic sources, while still maintaining the environmental and development balance.

The concept of continuous improvement through the evolution of technologies recognizes it is more cost effective and simpler to design emission control equipment into production equipment at the time of initial construction than it is to engage in costly retrofits in the future.

Alberta Environment and Parks (AEP) is currently reviewing policy tools to accommodate growth in the chemical and fertilizer sectors. Several existing chemical and fertilizer plants may proceed with major upgrades and/or large expansions over the next decade. Through the continuous improvement concept, industry growth can be accommodated by utilizing appropriate pollution control technologies to minimize environmental impacts.

To support the continuous improvement concept, AEP contracted with Ramboll Environ Canada Inc. (Ramboll Environ) to report on the range of commercially available pollution prevention and control technologies currently available for major air emission sources at chemical and fertilizer plants. In addition, the report includes a jurisdictional review of current environmental regulatory requirements enacted by leading authorities as they apply to air emissions and technologies implemented at new and existing chemical and fertilizer plants.

1.1 Goals and Objectives

Our study was conducted in accordance with the following AEP goals:

- To understand the range of commercially available pollution prevention and control technologies available for major air emission sources at chemical and fertilizer plants; and
- To understand how the different technologies are incorporated by leading jurisdictions into environmental regulatory requirements.

In light of these goals, our study focused to achieve the following objectives:

- Identify and describe major emission sources from select chemical and fertilizer industries;
- Identify and describe the individual pollution prevention and control technologies applied to major air emission sources at chemical and fertilizer plants;
- Discuss the effects of air preheat and different fuel types on the air emissions from chemical and fertilizer plants; and
- Jurisdictional review to identify, describe, and discuss the air emissions requirements associated with the chemical and fertilizer sector in leading jurisdictions.
1.2 Scope and Methodology

Chapters that discuss major air emissions sources focused on the following chemical and fertilizer plants:

- Chemical plants:
  - Ethylene plants;
  - Polyethylene plants;
  - Ethylene oxide plants;
  - Ethylene glycol plants;
  - Methanol plants;
  - Ethanol plants; and
  - Stand-alone hydrogen plants.

- Fertilizer plants:
  - Ammonia plants;
  - Urea plants;
  - Nitric acid plants; and
  - Ammonium nitrate plants.

Major air emission sources at these plants were identified using publically-available information including, but not limited to: air permits and applications; emission estimation documents; regulatory agency documents; industry reports and factsheets; and research papers.

The Chapter that discusses major air emissions sources in greater detail was limited to the following sources:

- Pyrolysis furnaces (or cracking furnaces);
- Steam methane reformers;
- Boilers and heaters;
- Flares and thermal incinerators; and
- Cooling towers.

The chapter on air pollution prevention and control technologies was limited to the following major technologies implemented at chemical and fertilizer:

- Selective Non-Catalytic Reduction (SNCR);
- Selective Catalytic Reduction (SCR);
- Burner Technology;
- Flares and Thermal Incinerators; and
- Wet Scrubbers.

Information on these air pollution prevention and control technologies was compiled using publically-available information including, but not limited to: air permits and applications; emission estimation documents; regulatory agency documents; industry reports and factsheets; technology vendor reports and factsheets; and research papers.

The jurisdictional review focused on leading jurisdictions with well-developed air quality regulatory programs that are currently used to encourage and/or enforce evolving technologies at chemical and fertilizer plants. A complete list of jurisdictions discussed in this report is presented in Table 1.
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<th>Report Section</th>
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<td>Belgium</td>
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<td>The Netherlands</td>
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<td>Spain</td>
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<tr>
<td>United Kingdom</td>
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</tr>
</tbody>
</table>

Iceland, which is not the part of European was also reviewed. There is no specific regulation for chemical and fertilizer plants in Iceland that are different from European Union. Therefore Iceland was not considered in the report.
2.0 Identification of Air Emission Sources from Chemical and Fertilizer Plants

Chapter 2 provides a brief overview of production processes at several types of chemical and fertilizer plant. Major air emission sources are identified and briefly described for each type of plant.

2.1 Chemical Plants

The chemical sector includes a wide range of industrial activities resulting in the manufacturing and/or processing of a diverse variety of products. The purpose of any chemical plant is to convert raw materials into desired products using the appropriate chemical reactions and physical changes. Using detailed industrial-scale methods, the core activities of an industrial site consist of the following five basic steps as identified in Figure 1 (European Commission, 2003).

1) Raw material supply and preparation – The receipt and storage of raw material and ancillary reagents along with their placement into the reactors.
2) Synthesis – The core of every process where raw materials are transformed into crude product by means of a chemical reaction – often with the aid of a catalyst.
3) Product separation and refinement – The product is separated from other reaction components (e.g. unreacted feed, by-products, solvents and catalysts) and purified of contaminants to achieve the necessary product specifications.
4) Product handling and storage – The storage, packaging and export of the product.
5) Emission abatement – The collection, re-use, treatment and disposal of unwanted liquids, gases and solids for those pollutants that have not been addressed by process-integrated measures.

Figure 1 Schematic of five basic steps at a chemical plant.

Although chemical plants are extremely diverse and complex, there are typical combinations of similar activities and equipment based on similar scientific principles used at individual industrial sites. This
report focuses on the commonalities among the chemical plants and examines the air pollution prevention and control technologies that could apply within Alberta.

An important subset of the chemical sector prominent in Alberta is petrochemical plants. These industrial sites use chemicals from petroleum as a raw material or feedstock to produce final chemical products. For example, propane (a derivative of petroleum) may be used as a raw material to produce polypropylene (a plastic material) for sale and use in manufacturing a range of products from automobile parts to Canadian bank notes. These manufacturing facilities produce a wide variety of petrochemicals. Some products are used as primary building blocks for other petrochemicals; while others are specialty products including plastics, resins, fibres, and chemicals.

It is impossible to cover all the manufacturing processes used in the petrochemical sector. Therefore, the focus is on ethylene manufacturing and its derivatives since ethylene is the most common petrochemical found in Alberta and is also produced in the largest quantity world-wide (Zimmermann and Walzl, 2005). Ethylene itself has virtually no direct end use; but, is the building block for several plastics, solvents, surfactants, rubbers, etc. (European Commission, 2003). The specific petrochemical plants to be included in this report are:

- ethylene plants;
- polyethylene plants;
- ethylene oxide plants; and
- ethylene glycol plants.

Other chemical plants included in the report that are found within Alberta and utilize similar manufacturing techniques; but, are not considered petrochemical plants include:

- methanol;
- ethanol; and
- stand-alone hydrogen production plants.

The following parts of Section 2 identify and describe the processes and major air emission sources associated with the specified chemical plants.

### 2.1.1 Ethylene Plants

An ethylene plant is considered part of the petrochemical industry that is responsible for producing ethylene via steam cracking. This means the bonds between the hydrocarbons in the feedstock are heated to a high temperature in the presence of steam to break the molecule bonds.

Steam cracking is essentially a non-catalysed, thermal process used to break down hydrocarbons. A variety of thermal cracking technologies and processes are used at individual plants; but, the general approach can be summarized in four sections:

- The feed and furnace section – used to pre-condition and “crack” hydrocarbons into ethylene, other olefins and diolefins;
- The quench and fractionator section – used to cool the product mix after the furnace and remove some heavier compounds;
- The compressor and condensate section – needed to pre-condition the product mix for distillation; and
- The hydrocarbon separation section – used to distill the hydrocarbon fractions and react acetylene to ethylene.
Figure 2 displays a typical process flow diagram for thermal cracking at a steam ethylene plant.
An overview of a typical ethylene plant is provided below.

The feed section of an ethylene plant is used to isolate and pre-condition the raw material (feedstock) to be delivered to the furnace section. It can differ greatly depending on the type of feedstock used and the amount of upstream processing required for the feedstock. In Alberta, ethylene plants receive natural gas, ethane, and an ethane/propane mix as feedstocks.

After pre-conditioning, the hydrocarbon stream, along with steam, enter the furnace section. In the furnace, saturated hydrocarbons undergo a thermal pyrolysis reaction to produce ethylene and to a lesser extent, other olefins and diolefins. The high thermal energy requirement for the reaction is met in a fired tubular reactor (referred to as the cracking furnace or pyrolysis furnace). Typically, more than ten cracking furnaces in parallel are used in a single ethylene plant. However, the number of cracking furnaces at each plant is determined on a case-by-case basis.

The gas stream exiting the cracking furnaces (or cracked gas stream) is rapidly cooled to preserve the desired product composition. Vertically-oriented transfer line exchangers (TLE) equipped on each furnace remove heat from the cracked gas stream by generating high pressure steam for plant processes.

Coke is produced from the pyrolysis reaction and accumulated in the tubular reactors. Coking in the tubular reactors affects their performance and eventually, the furnace must be taken out of operation and decoked. Decoking occurs by passing pure steam, followed by an air/steam mixture through the tubular reactors, which removes the coke by reaction or spalling. Typically, one of the ten or more furnaces will be decoking at all times (Linde, 2010).

The gas stream from the TLE enters the quench and fractionator section, which consists of a tall column or series of columns depending on the type of feedstock processed at the plant. The first column can be an oil quench primary fractionator (or pyrolysis fractionator) or a water quench column, again depending on the type of feedstock processed at the plant (Kolmetz et al., 2007). The columns function as a quench, fractionation, and coke removal system.

Further cooling of the cracked gas stream is performed in the quench tower by a circulating water stream to minimize the possibility of further cracking. The quench tower also operates as a partial condenser for steam as well as C5 and heavier compounds components in the cracked products stream.

Gases from the quench tower overhead enter the compression section of the ethylene plant, which consists of a 4 or 5 stage compressor train with interstage drums. The compressor train is used to optimize the gas pressure for separating it into various components. In the train, water, hydrocarbon liquids, and acid gases are removed from the product stream, some of which are recycled to various stages of the process.

The process gas stream then enters a sequence of fractionator towers, collectively entitled hydrocarbon separators, in which the various products are successively separated.

The deethanizer tower (i.e., second tower in the sequence) separates the C2 fraction (ethylene, ethane, and acetylene) from heavier fractions. The isolated C2 fraction is sent to an acetylene converter to hydrogenate the acetylene (C2H2) to ethylene (C2H4).
The effluent from the acetylene converter is sent to another hydrocarbon separator called the C2 splitter tower. This tower operates at high pressure to cause the ethane in the stream to drop to the bottom of the tower and the ethylene to rise to the top of the tower. Ethane is collected and recycled back to the feed section of the plant.

All ethylene is further conditioned by removing any remaining impurities and routed by pipeline to storage or consumers.

**Other Plant Equipment**

Ethylene plants have steam boiler(s) and heaters to supply steam and heat energy to process equipment. Some ethylene plants also have separately-fired steam superheater(s) (e.g. natural gas-fired) to superheat steam needed for the feed and furnace section. These boilers and heaters can be major air emission sources, either individually or cumulatively.

Please note: some chemical plant complexes with ethylene production capabilities also have natural gas-fired cogeneration plants. The cogeneration plants are used to supply some of the steam and energy needs for the ethylene plant and other areas within the complex. At the same time, excess steam generated in the pyrolysis furnace can be routed to the cogeneration plant to produce power. The cogeneration plant offsets some / all of the need for steam boilers and heaters at the plant. While a cogeneration plant is a major air emission source at some petrochemical complexes, the emissions resulting from the electricity generation are auxiliary to the chemical production process. Therefore, cogeneration plants are not discussed further in this report.

Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. As a safety device, flares are considered the best control option when the heating value of the emission stream cannot be recovered due to uncertain or intermittent flow during process upsets or emergencies. They are primarily used for burning flammable gas released via pressure relief valves during unplanned, overpressuring of plant equipment. During plant start-ups and shutdowns, flares are also used for planned combustion of gases over relatively short periods of time while equipment is being brought into production or being taken off-line. They are designed and operated to handle large fluctuations in flow rate and VOC content.

Thermal incinerators are another choice of combustion devices typically used to destroy hazardous air pollutants and VOCs from industrial air streams. They are preferable to flares when halogenated or sulphur-bearing compounds are present. Three main factors critical to achieve effective design and operation of a thermal oxidizer are temperature, residence time, and turbulence. Although they can accommodate minor flow fluctuations, thermal incinerators are not well suited to streams with highly variable flow because of reduced residence time and poor mixing during increased flow conditions.

Cooling towers provide necessary process cooling and are integral components to chemical plants. They are basic heat exchangers operating on a wet or dry basis and are capable of dissipating large heat loads to the atmosphere.

Wet cooling towers direct a portion of a warm recirculating water stream entering the tower to come into contact with and evaporate into air passing through the tower. This significantly lowers the temperature of the remaining water stream as heat is liberated during evaporation and becomes
The non-evaporated water is collected in tower basins and recycled back into the industrial system to recover more process heat.

Dry cooling towers represent extended type radiator cooling. However, wet cooling towers are more commonly used in industrial applications because the cooling potential of a wet surface is much better than a dry one. Therefore, the report will focus on air emission releases from wet cooling towers.

Major Air Emission Sources

A list and brief description of the major air emission sources at ethylene plants is provided in Table 2.

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis Furnace</td>
<td>The pyrolysis furnace is used to “crack” saturated hydrocarbons into ethylene, other olefins, and diolefins. The cracking process has high thermal energy requirements, which are partly met by burners inside the furnace. The pyrolysis furnace is a major source of nitrogen oxides (NOₓ) and, to a lesser extent, other combustion by-products and volatile organic compounds (VOCs) at an ethylene plant. Combustion in the pyrolysis furnace also generates greenhouse gas (GHG) emissions, mostly CO₂. During furnace decoking, steam and air removes the coke by reaction or spalling resulting in particulate matter (PM) emissions being vented from the pyrolysis furnace.</td>
</tr>
<tr>
<td>Steam Superheater</td>
<td>Separately-fired steam superheaters can be used to superheat steam needed for the feed and furnace section. NOₓ and, to a lesser extent, other combustion by-products are released from the steam superheaters. Fuel combustion in the heater also generates GHG emissions, mostly CO₂.</td>
</tr>
<tr>
<td>Steam Boiler and Heaters</td>
<td>Steam boilers and heaters produce process steam and provide heat for the ethylene plant. NOₓ and, to a lesser extent, other combustion by-products are released from the steam boilers or heaters. Fuel combustion in the boilers or heaters also generates GHG emissions, mostly CO₂.</td>
</tr>
<tr>
<td>Flare/Thermal Incinerator</td>
<td>Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. NOₓ and, to a lesser extent, other combustion by-products; as well as, SO₂ and VOCs are released from flares and thermal incinerators. Combustion of fuel and other hydrocarbons in the flare/incinerator generate GHG emissions, mostly CO₂.</td>
</tr>
<tr>
<td>Cooling Towers</td>
<td>Cooling towers significantly lower the temperature of cooling water recirculated to various process units at the ethylene plant. PM emissions result from the total dissolved solids in the circulating water becoming trapped within liquid drift droplets entrained in the air and are directly discharged from the tower into the atmosphere. VOC emissions are generated from cooling towers by: 1) leakage from process heat exchangers that service the hydrocarbon process streams; and 2) use of chemicals containing VOCs that are added to the circulating water for treatment. Please note: VOC emissions are expected from cooling towers used at chemical plants where the circulating waters cool down process streams and NOT from cooling towers used in conjunction with heating, ventilating and air conditioning (HVAC) units.</td>
</tr>
<tr>
<td>Equipment Leaks (Fugitives)</td>
<td>Equipment (e.g. valves, flanges, connectors, pumps, etc.) on the process units and piping network at an ethylene plant will leak small quantities of their contents directly to the atmosphere. Collectively, the small leaks can amount to a significant source of VOC emissions at the ethylene plant.</td>
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</table>

a) Combustion by-products include nitrogen oxides (NOₓ) carbon monoxide (CO), particulate matter (PM), volatile organic compounds (VOCs); as well as, trace amounts of sulphur oxides (SOₓ), metals, and polycyclic aromatic hydrocarbons (PAHs)
b) Greenhouse gases include carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O)

* Natural gas-fired co-generation plants located at ethylene plants are a major source of NOₓ emissions, and, to a lesser extent, other combustion by-products. Even though it is critical to include them in a chemical plant’s emissions profile; co-generation and its associated air emissions are beyond the scope of this project and are excluded from the report.
2.1.2 Polyethylene Plants

Polyethylene (PE) is a polymer product resulting from the polymerization of ethylene. PE is a general term given to a family of PE resin representing the most widely used plastics in the world. Its classification is based mostly on its density and is categorized into groups that include: low density polyethylene (LDPE), linear low density polyethylene (LLDPE), medium density polyethylene (MDPE) and high density polyethylene (HDPE). All PE resins are produced by polymerizing ethylene with comonomers; however, the comonomers and the production process can vary significantly for different PE resins.

LLDPE, MDPE, and HDPE Plants

LLDPE, MDPE, and HDPE are mainly produced by either a gas-phase or liquid-phase processes (Siemens AG, 2007). Several plants exist that have multiple lines of production (i.e. one or two) to increase PE production capacity.

Figure 3 displays a typical process flow diagram for a gas-phase (e.g. fluidized-bed) polyethylene plant.
Feedstock materials and additives must be purified and catalyst material must be prepared prior to entering the polymerization reactor section of the plant. Compressor(s) or coolers are often used to purify the gas. Comonomers are typically linear alpha olefins (LAO), such as 1-butene, 1-hexene, and 1-octene. The comonomer is sent through a degasser with a cooling water-steam loop to remove impurities. Catalyst from a catalyst feed tank is mixed with a nitrogen stream and fed to the reactor.

The reactor, which can be either a gas-phase or liquid-phase type, is used to carry out the ethylene polymerization process.
The most common type of gas-phase reactor is termed a fluidized-bed reactor. The fluidized-bed reactor is a vertical tower, where polymer seed particles and catalyst are fed down through the reactor. The gaseous ethylene (monomer) and comonomers are fed through a perforated distribution plate at high speeds toward the bottom end of the reactor, which travels upward in a counter-current direction to the polymer and catalyst feds (Vahidi et al., 2008). The high speed gas addition is needed to achieve bed fluidization, which in turn, ensures that polymers do not agglomerate on the distribution plate. Unreacted ethylene is recycled back to the inlet of the distribution plate. Granular polyethylene particles are extracted from the reactor near the distribution plate.

The polymerization reaction is exothermic, and the heat produced is sufficient to maintain a constant temperature in the reactor under steady-state conditions.

The liquid-phase process is typically performed in a loop reactor. In this process, ethylene, comonomer, catalyst, and a diluent are fed into the loop reactor. The diluent is typically a light, inert solvent, such as butane or propane. It is circulated through the reactor and is needed to keep the mixture in suspension (Siemens AG, 2007). The polymerization reaction takes place in the loop reactor resulting in a polyethylene slurry. Temperature and pressure are increased in the reactor to maintain a supercritical state.

A portion of the slurry is extracted from the loop and fed to a flash tank. The flash tank is used to separate the gases from the polyethylene and diluent. The gases are collected and recycled back to the loop. Diluent is separated from the polyethylene and recovered for reuse. The molten polyethylene is sent onto an extruder.

Some advanced plants use a liquid-phase reactor in series with a gas-phase reactor (Larsson et al., 2011). The liquid phase reactor is used to produce the polymer seed particles in a pre-polymerization step for the gas-phase reactor.

Polyethylene leaving the reactor section is often sent to an extruder, where it is heated and additives can be incorporated into the polymer. The extruder, then, forces the molten polymer through a die plate and cuts into pellets using a pelletizer knife assembly. Water is used to cool the pellets after being cut.

The pellets and water are sent to dewatering boxes and spin dryers. The dewatering boxes remove the bulk of the water and the spin dryers use forced air to remove any remaining moisture on the pellets.

From the spin dryers, the pellets are screened by pellet size and appropriate-sized pellets are aerated to degas any unreacted monomer. The PE pellets are then stored in silos prior to loading onto railcars or trucks.

**LDPE Plants**

LDPE is commonly produced using a high pressure process (Siemens AG, 2007).

Figure 4 displays a typical process flow diagram for a polyethylene plant using a high pressure process.
Many of the major steps in the high pressure process are similar to the gas-phase and liquid-phase process, in that they require initial compression, followed by polymerization and polymer separation from the ethylene feed.

Initial compression is needed to purify the ethylene gas and prepare the feedstock for the high pressure reactor. At this compression stage, initiators (e.g. oxygen or hydrogen peroxide) and co-polymers (e.g. vinyl acetate) are introduced to the ethylene feed (Siemens AG, 2007).

After compression, the feedstock enters the high pressure reactor. High pressure reactors are either an autoclave or tubular reactor. The tubular reactor typically consists of several hundred meters of jacketed high-pressure tubing arranged as a series of straight sections connected by 180° bends. (Siemens AG, 2007). In the reactor, a portion of the ethylene is polymerized to PE.

After the reactor, the PE needs to be separated from the unreacted ethylene. This is accomplished using high and low pressure separators in series. The unreacted ethylene from the high pressure separator is recycled to the final compressor prior to entering the reactor, while the recycle stream from the low pressure is looped back to the fresh ethylene feed at the primary compressor.

Like other PE processes, the molten polyethylene leaving the separators is often sent to an extruder, where it is cut into pellets using a pelletizer knife assembly.
**Other Plant Equipment**

Polyethylene plants have steam boiler(s) and heaters to supply steam and heat energy to process equipment. These boilers and heaters can be major air emission sources, either individually or cumulatively.

Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. As a safety device, flares are considered the best control option when the heating value of the emission stream cannot be recovered due to uncertain or intermittent flow during process upsets or emergencies. They are primarily used for burning flammable gas released via pressure relief valves during unplanned, over-pressuring of plant equipment. During plant start-ups and shutdowns, flares are also used for planned combustion of gases over relatively short periods of time while equipment is being brought into production or being taken off-line. They are designed and operated to handle large fluctuations in flow rate and VOC content.

Thermal incinerators are another choice of combustion devices typically used to destroy hazardous air pollutants and VOCs from industrial air streams. They are preferable to flares when halogenated or sulphur-bearing compounds are present. Three main factors critical to achieve effective design and operation of a thermal oxidizer are temperature, residence time, and turbulence. Although they can accommodate minor flow fluctuations, thermal incinerators are not well suited to streams with highly variable flow because of reduced residence time and poor mixing during increased flow conditions.

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<tbody>
<tr>
<td>Reactor Furnace</td>
<td>Reactor types that require heat input to keep the slurry in a supercritical state (e.g. loop reactors) will generate NOX and, to a lesser extent, other combustion by-products' emissions from burning fuels. Burning fuels to heat the reactor also generates greenhouse gas (GHG)b emissions, mostly CO₂.</td>
</tr>
<tr>
<td>Steam Boilers and Heaters</td>
<td>Steam boilers and heaters produce process steam and provide heat for the PE plant. NOX and, to a lesser extent, other combustion by-products' are released from the steam boilers or heaters. Fuel combustion in the boilers or heaters also generates GHG emissions, mostly CO₂.</td>
</tr>
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</tr>
<tr>
<td>PE Finishing Stack</td>
<td>PM generated from the finishing steps (drying, degassing, and storage / handling) are directed to cyclones and / or filters, prior to venting to atmosphere.</td>
</tr>
<tr>
<td>Equipment Leaks (Fugitives)</td>
<td>Equipment (e.g. valves, flanges, connectors, pumps, etc.) on the process units and piping network at a PE plant will leak small quantities of their contents directly to the atmosphere. Collectively, the small leaks can amount to a significant source of VOC emissions at the PE plant.</td>
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b) Greenhouse gases include carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O)
2.1.3 Ethylene Oxide Plants

Ethylene oxide (EO) is one of the most important raw materials used in large-scale chemical production because it is a key chemical intermediate in manufacturing many other prominent products such as glycols, detergent ethoxylates, ethanol amines, glycol ethers and polyols. EO is largely used for the synthesis of ethylene glycols (EG) – including diethylene glycol and triethylene glycol – and accounts for approximately 75% of global consumption (European Commission, 2003). As a result, many EO plants take an integrated approach and generate both EO and EG at the same site; although, each chemical can be manufactured separately.

EO is produced by reacting ethylene with oxygen. The major steps in an EO plant include:

- **EO Reactor** - ethylene is reacted with oxygen over a silver oxide catalyst to produce EO. A secondary reaction also occurs, whereby ethylene and oxygen react to produce carbon dioxide (CO₂) and water;
- **CO₂ Removal** - CO₂ and other trace contaminants are purged and absorbed from the EO stream; and
- **EO Recovery** – EO is distilled from water and any remaining CO₂ for recovery. The EO can be then be purified for direct sale or sent directly to an EG plant.

Figure 5 displays a typical schematic process flow diagram of an EO plant using a pure oxygen feed.
The oxygen needed for the EO reaction is supplied either by air or a pure oxygen stream. Since the oxygen process was first commercialized in 1969, it has been the preferred method because it contains fewer inerts that need to be purged from the stream (McKetta, 1984). By the mid-1980’s, newly constructed EO plants tended to use pure oxygen for feedstock (United States Environmental Protection Agency (US EPA), 1986). The air-based and oxygen-based processes are similar, so this report focuses on the oxygen-based process due to its prevalence.

Purified ethylene gas and compressed pure oxygen are piped to the EO reactor. The exothermic EO reaction occurs in several tubes running the length of the reactor, each packed with a silver oxide catalyst (European Commission, 2003). Some plants utilize multiple EO reactors in parallel to handle a larger gas flow (US EPA, 1986).

Ethylene can also react with oxygen to produce CO₂ and water. This secondary reaction can represent 20% to 30% of the overall ethylene consumed in the reactor.

Only a small percentage of the ethylene delivered to the reactor is actually consumed in a single pass. As such, the effluent stream from the reactor contains a mix of EO, CO₂, unreacted ethylene, and other trace reaction products (e.g. acetaldehyde, formaldehyde).

The reactor effluent is, therefore, sent through a primary absorber containing water to dissolve the EO, trace contaminants, and most of the CO₂ (US EPA, 1986). The unreacted ethylene and some CO₂ are recycled back to the EO reactors and combined with the new ethylene feed.

A portion of the recycle stream is purged to prevent the build-up unabsorbed CO₂ in the reactor. The purge stream passes through a CO₂ absorber to remove CO₂. CO₂ is then desorbed from the absorbent in a secondary unit using steam and then vented.

The aqueous mixture of EO, CO₂, and trace contaminants are sent to a distillation unit to recover the water, which can be reused in the primary absorber. The EO and CO₂ stream is, then, piped to a CO₂ stripper to remove the CO₂ and trace contaminants. The EO stream is then sent either for finishing to be converted into a final product or as feedstock to the EG plant.

Other Plant Equipment

EO plants have steam boiler(s) and heaters to supply steam and heat energy to process equipment. These boilers and heaters can be major air emission sources, either individually or cumulatively.

Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. As a safety device, flares are considered the best control option when the heating value of the emission stream cannot be recovered due to uncertain or intermittent flow during process upsets or emergencies. They are primarily used for burning flammable gas released via pressure relief valves during unplanned, overpressuring of plant equipment. During plant start-ups and shutdowns, flares are also used for planned combustion of gases over relatively short periods of time while equipment is being brought into production or being taken off-line. They are designed and operated to handle large fluctuations in flow rate and VOC content.

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Dry cooling towers represent extended type radiator cooling. However, wet cooling towers are more commonly used in industrial applications because the cooling potential of a wet surface is much better than a dry one. Therefore, the report will focus on air emission releases from wet cooling towers.

**Major Air Emission Sources**

A list and brief description of the major air emission sources at EO plants is provided in Table 4.

<table>
<thead>
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<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Vent</td>
<td>The ethylene recycle stream looping back to the EO reactor contains some CO₂ so it is purged to prevent a build-up of CO₂ in the reactor. The CO₂ from the purge stream is collected on an absorbent. The absorbent is sent for reactivation, which is accomplished by desorbing the CO₂. As a major source of GHGs, desorbed CO₂ (a GHG) and trace VOCs are then released from the CO₂ vent.</td>
</tr>
<tr>
<td>Main Process Vent</td>
<td>Gaseous impurities from the oxygen feed, such as argon, are purged from the recycle gas stream through the main process vent (aka argon purge vent). VOCs are released from this vent.</td>
</tr>
<tr>
<td>Steam Boilers and Heaters</td>
<td>Steam boilers and heaters produce process steam and heat for the EO plant. NOₓ and, to a lesser extent, other combustion by-products are released from the steam boilers or heaters. Fuel combustion in the boilers or heaters also generates GHG emissions, mostly CO₂.</td>
</tr>
<tr>
<td>Flare / Thermal Incinerator</td>
<td>Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. NOₓ and, to a lesser extent, other combustion by-products; as well as, SO₂ and VOCs are released from flares and thermal incinerators. Combustion of fuel and other hydrocarbons in the flare/incinerator generate GHG emissions, mostly CO₂.</td>
</tr>
<tr>
<td>Cooling Towers</td>
<td>Cooling towers significantly lower the temperature of cooling water recirculated to various process units at the EO plant. PM emissions result from the total dissolved solids in the circulating water becoming trapped within liquid drift droplets entrained in the air and are directly discharged from the tower into the atmosphere. VOC emissions are generated from cooling towers by: 1) leakage from process heat exchangers that service the hydrocarbon process streams; and 2) use of chemicals containing VOCs that are added to the circulating water for treatment. Please note: VOC emissions are expected from cooling towers used at chemical plants where the circulating waters cool down process streams and NOT from cooling towers used in conjunction with heating, ventilating and air conditioning (HVAC) units.</td>
</tr>
<tr>
<td>Equipment Leaks (Fugitives)</td>
<td>Equipment (e.g. valves, flanges, connectors, pumps, etc.) on the process units and piping network at an EO plant will leak small quantities of their contents directly to the atmosphere. Collectively, the small leaks can amount to a significant source of VOC emissions at the EO plant.</td>
</tr>
</tbody>
</table>
2.1.4 Ethylene Glycol Plants

Ethylene Glycol (EG) is produced by reacting ethylene oxide (EO) and water. As a major derivative of EO, EG production is typically produced at the same industrial complex as EO production.

Figure 6 displays the major steps in an EG plant.

EO and a water stream are fed into an EG reactor (or hydrolyzer). The EG reactor can be designed for either a non-catalysed or catalysed hydrolysis reaction.

In the non-catalysed process, EG reactors are maintained at elevated temperatures between 150°C and 250°C to promote the formation of ethylene glycol without the use of a catalyst (European Commission, 2003). The ethylene glycol reaction is relatively fast, such that all EO will react to EG on a single pass through the reactor.

a) Greenhouse gases include carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O)
b) Combustion by-products include nitrogen oxides (NOₓ) carbon monoxide (CO), particulate matter (PM), volatile organic compounds (VOCs); as well as, trace amounts of sulphur oxides (SOₓ), metals, and polycyclic aromatic hydrocarbons (PAHs)
In the catalysed process, the hydrolysis reaction can proceed with either an acidic or basic catalyst; although, higher yields of EG are achieved using an acid catalyst (MEGlobal, 2016). Like the non-catalysed process, all of the EO will react to EG on a single pass through the reactor.

In either process, EO and water will react to form monoethylene glycol (MEG), and to a lesser extent higher glycols (di-, tri-, and tetraethylene glycol).

The product stream leaving the reactor contains MEG, higher glycols, and water, which must be separated. A series of evaporators / vacuum distillation units are used to first separate the water and dry the EG (i.e., EG de-watering) and subsequently, fractionate the EG products into MEG and various higher glycols streams.

**Other Plant Equipment**

EG plants have steam boiler(s) and heaters to supply steam and heat energy to process equipment. These boilers and heaters can be major air emission sources, either individually or cumulatively.

Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. As a safety device, flares are considered the best control option when the heating value of the emission stream cannot be recovered due to uncertain or intermittent flow during process upsets or emergencies. They are primarily used for burning flammable gas released via pressure relief valves during unplanned, overpressuring of plant equipment. During plant start-ups and shutdowns, flares are also used for planned combustion of gases over relatively short periods of time while equipment is being brought into production or being taken off-line. They are designed and operated to handle large fluctuations in flow rate and VOC content.

Thermal incinerators are another choice of combustion devices typically used to destroy hazardous air pollutants and VOCs from industrial air streams. They are preferable to flares when halogenated or sulphur-bearing compounds are present. Three main factors critical to achieve effective design and operation of a thermal oxidizer are temperature, residence time, and turbulence. Although they can accommodate minor flow fluctuations, thermal incinerators are not well suited to streams with highly variable flow because of reduced residence time and poor mixing during increased flow conditions.

Cooling towers provide necessary process cooling and are integral components to chemical plants. They are basic heat exchangers operating on a wet or dry basis and are capable of dissipating large heat loads to the atmosphere.

Wet cooling towers direct a portion of a warm recirculating water stream entering the tower to come into contact with and evaporate into air passing through the tower. This significantly lowers the temperature of the remaining water stream as heat is liberated during evaporation and becomes absorbed into the air. The non-evaporated water is collected in tower basins and recycled back into the industrial system to recover more process heat.

Dry cooling towers represent extended type radiator cooling. However, wet cooling towers are more commonly used in industrial applications because the cooling potential of a wet surface is much better than a dry one. Therefore, the report will focus on air emission releases from wet cooling towers.
Major Air Emission Sources

A list and brief description of the major air emission sources at EG plants is provided in Table 5.

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporator Vents</td>
<td>Distillation columns / evaporators are used to isolate the EG products. Condensers on each of the units are used to recover the product. Uncondensed VOCs are released from these vent(s).</td>
</tr>
<tr>
<td>Steam Boilers and Heaters</td>
<td>Steam boilers and heaters produce process steam for the EG plant. NOX and, to a lesser extent, other combustion by-products(^a) are released from the steam boilers or heaters. Fuel combustion in the boilers or heaters also generates GHG(^b) emissions, mostly CO(_2).</td>
</tr>
<tr>
<td>Flare / Thermal Incinerator</td>
<td>Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. NOX and, to a lesser extent, other combustion by-products(^a); as well as, SO(_2) and VOCs are released from flares and thermal incinerators. Combustion of fuel and other hydrocarbons in the flare/incinerator generate GHG(^b) emissions, mostly CO(_2).</td>
</tr>
<tr>
<td>Cooling Towers</td>
<td>Cooling towers significantly lower the temperature of cooling water recirculated to various process units at the EG plant. PM emissions result from the total dissolved solids in the circulating water becoming trapped within liquid drift droplets entrained in the air and are directly discharged from the tower into the atmosphere. VOC emissions are generated from cooling towers by: 1) leakage from process heat exchangers that service the hydrocarbon process streams; and 2) use of chemicals containing VOCs that are added to the circulating water for treatment. Please note: VOC emissions are expected from cooling towers used at chemical plants where the circulating waters cool down process streams and NOT from cooling towers used in conjunction with heating, ventilating and air conditioning (HVAC) units.</td>
</tr>
<tr>
<td>Equipment Leaks (Fugitives)</td>
<td>Equipment (e.g. valves, flanges, connectors, pumps, etc.) on the process units and piping network at an EG plant will leak small quantities of their contents directly to the atmosphere. Collectively, the small leaks can amount to a significant source of VOC emissions at the EG plant.</td>
</tr>
</tbody>
</table>

\(^a\) Combustion by-products include nitrogen oxides (NO\(_X\)), carbon monoxide (CO), particulate matter (PM), volatile organic compounds (VOCs); as well as, trace amounts of sulphur oxides (SO\(_X\)), metals, and polycyclic aromatic hydrocarbons (PAHs)

\(^b\) Greenhouse gases include carbon dioxide (CO\(_2\)), methane (CH\(_4\)), and nitrous oxide (N\(_2\)O)
2.1.5 Methanol Plants

Methanol, also known as methyl alcohol or wood alcohol, is the simplest of all alcohols with the chemical formula CH₃OH. It is biodegradable and non-carcinogenic. Methanol can be used as a fuel, but is more commonly used as an essential ingredient in chemical and manufacturing processes for products, including paint, particle board, plastics, carpets, pharmaceuticals, laminated lumber, and windshield wiper fluid.

The methanol production generally consists of following steps:

- The first step in making methanol is to create synthesis gas, which is a mixture of CO, CO₂ and hydrogen gas. Methanol can be produced from small-scale plants units (few hundred liters per day) to large-scale methanol plants producing a million liters each day (Methanol Institute, 2016).
- The reformed gas then passes through a methanol conversion process, to produce crude methanol; and
- Finally, crude methanol is distilled through a multi-stage distillation process to produce a chemical grade methanol.

Figure 7 shows an overview of methanol production plant (Methanex, 2013); while, Figure 8 presents the process flow diagram for a typical methanol plant using natural gas as a feed stock.

![Figure 7 Overview of methanol production.](image-url)
An overview of a standard methanol plant using natural gas as a fuel is provided below. Since methanol is mainly synthesized from natural gas, the following discussion focuses on this process; although, methanol can be produced using other feedstocks such as coal and biomass.

Natural gas is first treated to remove sulphur compounds. The catalysts used in the reforming step of the process can be poisoned by sulphur compounds and natural gas typically contains trace quantities of sulphur, mostly as hydrogen sulphide (H₂S). Therefore, natural gas desulphurization is a necessary step in the methanol synthesis process. Desulphurization is accomplished using heat and a catalyst to convert sulphur compounds to H₂S, which can subsequently be removed by reaction on an adsorption bed. Most desulphurization units associated with a steam methane reformer (SMR) use a zinc oxide bed, which converts the H₂S to zinc sulphide (ZnS) and water.

The sweetened natural gas is then compressed and saturated with process water prior to entering the reformer. The treated water-rich natural gas is partially reformed with steam as a primary step, and completely reformed with oxygen in a secondary step using a reformer.

The primary reformer is used to complete the steam reforming process. The reformer consists of a radiant box containing hundreds of alloy tubes filled with a reforming catalyst. The radiant box needs to be heated because the overall chemical reaction with natural gas is highly endothermic. The reforming process generates CO, CO₂, and hydrogen gas (H₂).

Some plants are designed such that not all natural gas will react in the primary reformer. In these plants, a secondary reformer is needed to react most of the remaining natural gas (up to 99% of the feed). In the secondary reformer, oxygen is added to the mix to produce a syngas with the optimum composition for methanol synthesis.
The reformed synthesis gas leaving the reformer section is then cooled and compressed in multiple stages (Jackson, 2006). The compressed syngas then enters a methanol converter (or series of converters in some plants) where crude methanol is created (Ramboll Environ, 2016). The heat energy in the syngas remaining from the reformer section is sufficient for the methanol reaction. In the converter, hydrogen is reacted with CO and CO$_2$ over a catalyst bed to produce methanol, and water in the case of the CO$_2$ reaction (Jackson, 2006). The hot gas mixture leaving the converters flows through a series of coolers to allow methanol product to condense, and to recover and reuse waste process heat to improve energy efficiency. Condensed crude methanol is sent to the methanol distillation unit, and the non-condensed gas mixture is compressed and recycled back to the converters to enhance methanol production.

Crude methanol from the synthesis process is sent to the distillation unit where it is distilled to the required purity. Water and several other hydrocarbon by-products are synthesized at the same time as methanol. These by-products are separated from the methanol through a separation vessel and a series of distillation columns. The refined methanol is then directed to on-site storage tanks, the light hydrocarbon by-products are recovered and used as fuel for the boilers, and the heavy by-products (mainly water) are recycled to the reforming step for use in saturating the natural gas feedstock with process water.

Other Plant Equipment

Methanol plants have steam boilers and heaters to supply steam and heat energy to process equipment. Some methanol plants also have a gas-fired heater to preheat feedstock. Waste heat boilers (WHB) are used at some methanol plants to cool the syngas and recover the heat energy. These boilers and heaters can be major air emission sources, either individually or cumulatively.

It should also be noted that some chemical plant complexes with methanol production capabilities also have natural gas-fired cogeneration plants. The cogeneration plants are used to supply some of the steam and energy needs for the methanol plant and other systems within the complex. At the same time, excess steam generated at the methanol plant can be routed to the cogeneration plant to produce power. The cogeneration plant would offset some / all of the need for steam boilers and heaters at the plant. While a cogeneration plant is a major air emission source at some chemical plants, the emissions resulting from the electricity generation are auxiliary to the chemical production process. Therefore, cogeneration plants are not discussed further in this report.

Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. As a safety device, flares are considered the best control option when the heating value of the emission stream cannot be recovered due to uncertain or intermittent flow during process upsets or emergencies. They are primarily used for burning flammable gas released via pressure relief valves during unplanned, overpressuring of plant equipment. During plant start-ups and shutdowns, flares are also used for planned combustion of gases over relatively short periods of time while equipment is being brought into production or being taken off-line. They are designed and operated to handle large fluctuations in flow rate and VOC content.

Thermal incinerators are another choice of combustion devices typically used to destroy hazardous air pollutants and VOCs from industrial air streams. They are preferable to flares when halogenated or sulphur-bearing compounds are present. Three main factors critical to achieve effective design and operation of a thermal oxidizer are temperature, residence time, and turbulence. Although they can
accommodate minor flow fluctuations, thermal incinerators are not well suited to streams with highly variable flow because of reduced residence time and poor mixing during increased flow conditions.

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Wet cooling towers direct a portion of a warm recirculating water stream entering the tower to come into contact with and evaporate into air passing through the tower. This significantly lowers the temperature of the remaining water stream as heat is liberated during evaporation and becomes absorbed into the air. The non-evaporated water is collected in tower basins and recycled back into the industrial system to recover more process heat.

Dry cooling towers represent extended type radiator cooling. However, wet cooling towers are more commonly used in industrial applications because the cooling potential of a wet surface is much better than a dry one. Therefore, the report will focus on air emission releases from wet cooling towers.

**Major Air Emission Sources**

A list and brief description of the major air emission sources at methanol plants is provided in Table 6.
Table 6  Major air emission sources at methanol plants*

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reformer</td>
<td>Natural gas is partially reformed with steam as a primary step, and completely reformed with oxygen in a secondary step using a reformer. The reforming process has high thermal energy requirements, which are partly met by burners inside the reformer. A reformer is a major source of NOX and, to a lesser extent, other combustion by-products released from the reformer stack. Fuel combustion in the reformer also generates GHG emissions, mostly CO2.</td>
</tr>
<tr>
<td>Distillation Unit Vent</td>
<td>Synthesized methanol is purified in a multi-stage distillation process. The resulting methanol vapour is condensed and directed to on-site storage tanks. Uncondensed methanol and other hydrocarbon by-products (e.g. dimethyl ether [CAS number 115-10-6] (US EPA, 2008)) are released from the distillation unit vent.</td>
</tr>
<tr>
<td>Steam Boiler</td>
<td>Steam for the primary stage of the reforming process that produces syngas uses gas-fired boilers. The light hydrocarbon by-products recovered from the methanol distillation process may also be the primary fuel combusted by the boilers. The steam boiler is a major source of NOX and, to a lesser extent, other combustion by-products released from the units. Fuel combustion in the boilers also generates GHG emissions, mostly CO2.</td>
</tr>
<tr>
<td>Waste Heat Boiler</td>
<td>Waste heat boilers can be used to recover heat energy to produce steam. Some waste heat boilers are gas-fired to support efficient steam production. These gas-fired units will generate NOX and, to a lesser extent, other combustion by-products released from the units. Fuel combustion in a waste heat boiler also generates GHG emissions, mostly CO2.</td>
</tr>
<tr>
<td>Steam Boilers and Heaters</td>
<td>Steam boilers and heaters produce process steam for the methanol plant. NOX and, to a lesser extent, other combustion by-products are released from the steam boilers or heaters. Fuel combustion in the boilers or heaters also generates GHG emissions, mostly CO2.</td>
</tr>
<tr>
<td>Desulphurization Unit</td>
<td>The natural gas feedstock is first run through a desulphurization reactor to remove sulphur and other compounds that would damage the catalyst of the reactors. SO2 emitted from the desulphurization unit should occur in minimal quantities.</td>
</tr>
<tr>
<td>Flare / Thermal Incinerator</td>
<td>Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. NOX and, to a lesser extent, other combustion by-products, as well as, SO2 and VOCs are released from flares and thermal incinerators. Combustion of fuel and other hydrocarbons in the flare/incinerator generate GHG emissions, mostly CO2.</td>
</tr>
<tr>
<td>Cooling Towers</td>
<td>Cooling towers significantly lower the temperature of cooling water recirculated to various process units at the methanol plant. PM emissions result from the total dissolved solids in the circulating water becoming trapped within liquid drift droplets entrained in the air and are directly discharged from the tower into the atmosphere. VOC emissions are generated from cooling towers by: 1) leakage from process heat exchangers that service the hydrocarbon process streams; and 2) use of chemicals containing VOCs that are added to the circulating water for treatment. Please note: VOC emissions are expected from cooling towers used at chemical plants where the circulating waters cool down process streams and NOT from cooling towers used in conjunction with heating, ventilating and air conditioning (HVAC) units.</td>
</tr>
<tr>
<td>Equipment Leaks (Fugitives)</td>
<td>Equipment (e.g. valves, flanges, connectors, pumps, etc.) on the process units and piping network at a methanol plant will leak small quantities of their contents directly to the atmosphere. Collectively, the small leaks can amount to a significant source of VOC emissions at the methanol plant.</td>
</tr>
</tbody>
</table>

a) Combustion by-products include nitrogen oxides (NOX), carbon monoxide (CO), particulate matter (PM), volatile organic compounds (VOCs); as well as, trace amounts of sulphur oxides (SOX), metals, and polycyclic aromatic hydrocarbons (PAHs)
b) Greenhouse gases include carbon dioxide (CO2), methane (CH4), and nitrous oxide (N2O)

* Natural gas-fired co-generation plants located at methanol plants are a major source of NOX emissions, and, to a lesser extent, other combustion by-products. Even though it is critical to include them in a chemical plant’s emissions profile; co-generation and its associated air emissions are beyond the scope of this project and are excluded from the report.
2.1.6 Ethanol Plants

Ethanol is the chemical name for ethyl alcohol (CH₃CH₂OH) and represents a grain alcohol that can be blended with gasoline for use in motor vehicles. As an additive to gasoline, it extends the volume and boosts octane levels. The most common source of ethanol is corn; but, it can be produced from a variety of feedstocks including; but not limited to: wheat, sugar, and municipal solid waste (MSW). Using sophisticated equipment and complicated wet or dry milling processes, the carbohydrates in the various feedstocks are converted into glucose or cellulose which is fermented and distilled into ethanol. A typical process flow diagram for ethanol production is presented in Figure 9.

![Process flow diagram for ethanol production.](image)

The ethanol plants in Alberta rely mostly on cellulosic, sugar, and starch platforms. Overviews of typical ethanol plants using these platforms are provided below.

Cellulosic processes use biomass mostly composed of cellulose, hemicellulose, and lignin. Generally, the cellulosic feedstock (e.g. MSW), is separated and pre-treated prior to thermochemical or biochemical conversion. Biochemical conversion consists of fermentation which results in a mixture of ethanol and water which is then distilled and condensed. Thermochemical conversion uses heat to gasify and convert biomass to alcohol with the use of chemicals or a combination of heat and pressure. During gasification, feedstock is heated and partially oxidized or reformed resulting in the production
of synthetic gas (syngas). This syngas is made up of carbon dioxide and hydrogen gas which is then cleaned and converted through chemical reactions to chemicals and biofuels, including ethanol (Jones, 2010).

Sugar and starch processes typically involve a pre-treatment or liquefaction followed by hydrolysis or saccharification. These steps are necessary to convert the starch into a sugar which is able to be fermented and then turned into ethanol (Babu et al., 2013).

Table 7 outlines the major ethanol production processes and their associated feedstocks.

<table>
<thead>
<tr>
<th>Process</th>
<th>Raw Feedstock Options</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermochemical cellulosic conversion</td>
<td>Municipal solid waste, wood waste, straw</td>
</tr>
<tr>
<td>Biochemical cellulosic conversion</td>
<td>Municipal solid waste, wood waste, straw</td>
</tr>
<tr>
<td>Sugar / Starch processing</td>
<td>Corn, grains, sugar, wheat, barley</td>
</tr>
</tbody>
</table>

Many of the ethanol plants also incorporate other production processes and make use of their by-products within the system to form an overall integrated process. Examples of these complementary sites include animal feedlots and grain mills.

**Other Plant Equipment**

Many ethanol plants have steam boilers and heaters to supply steam and heat energy to process equipment. These boilers and heaters can be major air emission sources, either individually or cumulatively.

Ethanol plants typically have flare systems and/or thermal incinerators to dispose of vent gases resulting from either a number of minor process sources or are generated as intermediate gases during the process. Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. As a safety device, flares are considered the best control option when the heating value of the emission stream cannot be recovered due to uncertain or intermittent flow during process upsets or emergencies. They are primarily used for burning flammable gas released via pressure relief valves during unplanned, over-pressuring of plant equipment. During plant start-ups and shutdowns, flares are also used for planned combustion of gases over relatively short periods of time while equipment is being brought into production or being taken off-line. They are designed and operated to handle large fluctuations in flow rate and VOC content.

Thermal incinerators are another choice of combustion devices typically used to destroy hazardous air pollutants and VOCs from industrial air streams. They are preferable to flares when halogenated or sulphur-bearing compounds are present. Three main factors critical to achieve effective design and operation of a thermal oxidizer are temperature, residence time, and turbulence. Although they can accommodate minor flow fluctuations, thermal incinerators are not well suited to streams with highly variable flow because of reduced residence time and poor mixing during increased flow conditions.

In the case of sugar / starch processing plants, gas-fired dryers are used to dry distilled grains, which can be used as animal feed (Brady and Pratt, 2007). VOC emissions from dryers are often controlled with thermal oxidizers (Brady and Pratt, 2007).
Major Air Emission Sources

Sources of air emission differ at each site due to varying production processes at ethanol plants. However, one of the largest VOC emission sources for the chemical sector in Canada is ethanol production. Over the past 5 years, the ethanol production industry has more than doubled. This rapid growth is due, in part, to the Government of Canada’s Renewable Fuels Regulations, published on September 1, 2010. These regulations require that as of December 15, 2010, gasoline must contain an average renewable fuel (ethanol) content of five per cent.

Table 8 presents the major air emissions sources that are commonly found at ethanol plants. Please note: Ethanol is the final product of the plant and will always be present. In most cases, it does represent the most prevalent VOC from the process.

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fermentation Vents</td>
<td>A major source of VOCs results from the formation process with wet scrubbers being installed on the fermentation vents to control their releases. The VOCs are generated by the natural actions of the enzymes and yeast interacting with the various constituents of the feedstock i.e. corn, wheat, grain, etc. that have been milled and added to the fermenters. The type and quantity of the VOCs generated depend on: 1) conditions of fermentation; and 2) the ratio of compounds upon which the specific enzymes and yeast strains are applied to.</td>
</tr>
<tr>
<td>CO2 Vent</td>
<td>The fermentation process can be used to convert sugars in the feedstock to ethanol, other alcohols, and CO2 (a GHG) with the addition of enzymes and yeast. The CO2 is vented to atmosphere. Trace amounts of alcohols not collected by beer wells / distillation units can also be vented through the CO2 vent.</td>
</tr>
<tr>
<td>Fabric Filters and Cyclones</td>
<td>Some ethanol plants utilize various grains and starches as feedstock resulting in PM emissions from the handling of the materials.</td>
</tr>
<tr>
<td>Ethanol By-product Processing Equipment</td>
<td>Many ethanol plants incorporate other processes that utilize by-products from ethanol production. Resulting products include wet distilled grains, dried distilled grains, and animal feed. Associated equipment needed for the post-ethanol processes include centrifuges, dryers, and coolers. Processing equipment associated with the ethanol by-products is a major source of VOCs. If a gas-fired dryer is used, NOX and to a lesser extent, other combustion by-products are released from the dryer. Fuel combustion in the dryer also generates GHG emissions, mostly CO2.</td>
</tr>
<tr>
<td>Steam Boilers and Heaters</td>
<td>Boilers can be used to produce the heat and steam necessary to form syngas, and the fermentation and distillation processes. Steam boilers and heaters also produce steam for the ethanol plant. NOX and, to a lesser extent, other combustion by-products are released from the steam boilers or heaters. Fuel combustion in the boilers or heaters also generates GHG emissions, mostly CO2.</td>
</tr>
<tr>
<td>Handling and Drying Area</td>
<td>Additional VOCs are emitted during the handling and drying of the distillers dried grains with solubles and are typically controlled by a regenerative thermal oxidizer (RTO).</td>
</tr>
<tr>
<td>Flare / Thermal Incinerator</td>
<td>Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. NOX and, to a lesser extent, other combustion by-products; as well as, SO2 and VOCs are released from flares and thermal incinerators. Combustion of fuel and other hydrocarbons in the flare/incinerator generate GHG emissions, mostly CO2.</td>
</tr>
<tr>
<td>Equipment Leaks (Fugitives)</td>
<td>Equipment (e.g. valves, flanges, connectors, pumps, etc.) on the process units and piping network at an ethanol plant will leak small quantities of their contents directly to the atmosphere. Collectively, the small leaks can amount to a significant source of VOC emissions at the ethanol plant.</td>
</tr>
</tbody>
</table>

a) Combustion by-products include nitrogen oxides (NOX) carbon monoxide (CO), particulate matter (PM), volatile organic compounds (VOCs); as well as, trace amounts of sulphur oxides (SOX), metals, and polycyclic aromatic hydrocarbons (PAHs)

b) Greenhouse gases include carbon dioxide (CO2), methane (CH4), and nitrous oxide (N2O)
2.1.7 Hydrogen Production Plants

Hydrogen can be produced from a variety of feedstocks using a number of different processes. Any hydrogen-containing compounds can be a source of hydrogen production such as fossil fuels, biomass, and water.

Thermochemical processes use heat and chemical reactions to release hydrogen from organic materials such as fossil fuels and biomass. Steam methane reforming (SMR), also known as natural gas reforming, is the most widely used process for the generation of hydrogen, and will be discussed in detail following the identification of other hydrogen production practices. Requiring a large heat input, the SMR process is a highly energy intensive method producing hydrogen from heating methane in natural gas with steam in the presence of a catalyst.

Electrolytic processes use electricity to split water into hydrogen and oxygen.

Direct solar water splitting, or photolytic, processes use light energy to split water into hydrogen and oxygen.

In biological processes, microbes such as bacteria and microalgae can produce hydrogen through biological reactions, using sunlight or organic matter. These process technologies are at an early stage of research.

Table 9 presents the major hydrogen production processes along with feedstock, energy requirement and associated emissions (adapted from Sustainable Development Technology Canada (SDTC), 2006).
### Table 9 Major hydrogen production processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Raw Feedstock Options</th>
<th>Energy Required</th>
<th>Catalyst Required</th>
<th>Scale/Load</th>
<th>Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thermal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam Reformation</td>
<td>Natural gas, other gaseous or light hydrocarbons</td>
<td>High temperature steam</td>
<td>Yes</td>
<td>Medium to Large / Steady load (small systems have been demonstrated)</td>
<td>Mainly CO₂, NOₓ and other combustion by-products⁸ and GHG⁹</td>
</tr>
<tr>
<td>Gasification</td>
<td>Coal Heavy Hydrocarbons</td>
<td>Steam &amp; oxygen at high temperature &amp; pressure</td>
<td>No</td>
<td>Large / Steady load</td>
<td>Mainly CO₂, NOₓ and other combustion by-products⁸ and GHG⁹</td>
</tr>
<tr>
<td>Autothermal Reformulation (Partial Oxidation)</td>
<td>Natural gas, other gaseous or light hydrocarbons</td>
<td>Steam - generated by heat from the exothermic process</td>
<td>No</td>
<td>Medium to Large / Steady load (small systems have been demonstrated)</td>
<td>Mainly CO₂, NOₓ and other combustion by-products⁸ and GHG⁹</td>
</tr>
<tr>
<td>Catalytic Reforming</td>
<td>Naphthas from oil refining</td>
<td>Heat from the oil refining process</td>
<td>Yes</td>
<td>Large / Variable load</td>
<td>Mainly CO₂, NOₓ and other combustion by-products⁸ and GHG⁹</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>Biomass</td>
<td>Moderately high temperature steam</td>
<td>No</td>
<td>Medium / Steady load</td>
<td>Mainly CO₂, NOₓ and other combustion by-products⁸ and GHG⁹</td>
</tr>
<tr>
<td>Thermo-chemical Water Splitting</td>
<td>Water</td>
<td>High temperature heat (e.g. from gas cooled nuclear reactor)</td>
<td>No</td>
<td>Large / Steady load</td>
<td>No emissions during electrolysis process</td>
</tr>
<tr>
<td><strong>Electrochemical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrolysis</td>
<td>Water</td>
<td>Electricity from renewable sources</td>
<td>Depends on Technology Used</td>
<td>Small / Variable load</td>
<td>No emissions during electrolysis process</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>Water</td>
<td>Electricity from fossil fuel sources</td>
<td>Depends on Technology Used</td>
<td>Small / Variable load</td>
<td>Mainly CO₂, NOₓ and other combustion by-products⁸ and GHG⁹ from fossil fuel sources</td>
</tr>
<tr>
<td>Thermal Catalytic Dry Reformation</td>
<td>Methane, landfill gas, water</td>
<td>Heat (solar energy or other heat source)</td>
<td>Yes</td>
<td>Small to Medium / Variable load</td>
<td>Mainly CO₂, NOₓ and other combustion by-products⁸ and GHG⁹ (depending on feedstock)</td>
</tr>
<tr>
<td>Plasma Dissociation</td>
<td>Biomass, Natural Gas</td>
<td>Electricity (plasma discharge)</td>
<td>No</td>
<td>Small / Variable load</td>
<td>No emissions</td>
</tr>
<tr>
<td><strong>Byproduct Recovery</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recover H₂ from Another Process</td>
<td>No specific feedstock for hydrogen production</td>
<td>Incremental energy required for gas clean-up and possible compression</td>
<td>No</td>
<td>Small to Medium / Steady load (matched to main production process)</td>
<td>No emissions from collection of hydrogen</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Process</th>
<th>Raw Feedstock Options</th>
<th>Energy Required</th>
<th>Catalyst Required</th>
<th>Scale/Load</th>
<th>Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Biological</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Photo-biological</td>
<td>Water and algae strains</td>
<td>Direct sunlight</td>
<td>No</td>
<td>Small load matched to availability of sunlight</td>
<td>No emissions</td>
</tr>
<tr>
<td>Anaerobic Digestion</td>
<td>Biomass</td>
<td>High temperature steam: methane produced by process must be converted to hydrogen by another process (e.g. SMR)</td>
<td>Yes</td>
<td>Medium / Steady load</td>
<td>Mainly CO₂, NOₓ and other combustion by-products&lt;sup&gt;a&lt;/sup&gt; and GHG&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Fermentive Microorganisms</td>
<td>Biomass</td>
<td>High temperature steam: methane produced by process must be converted to hydrogen by another process (e.g. SMR)</td>
<td>Yes</td>
<td>Medium / Steady load</td>
<td>Mainly CO₂, NOₓ and other combustion by-products&lt;sup&gt;a&lt;/sup&gt; and GHG&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Combustion by-products include nitrogen oxides (NOₓ) carbon monoxide (CO), particulate matter (PM), volatile organic compounds (VOCs); as well as, trace amounts of sulphur oxides (SOₓ), metals, and polycyclic aromatic hydrocarbons (PAHs)

<sup>b</sup> Greenhouse gases include carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O)

### Hydrogen Production from Steam Methane Reforming

Figure 10 presents a generic process flow diagram for hydrogen production from steam methane reforming.

![Figure 10 Process flow diagram for hydrogen production from steam methane reforming.](image)

An overview of hydrogen production by a SMR is provided below.

Steam methane reforming is the most widely used process for the generation of hydrogen. Part of its popularity is attributed to its cost effectiveness in obtaining a high level of purity in its produced hydrogen. The hydrogen obtained from an SMR can be used in industrial processes and in fuel cells because of its purity. However, the steam methane reforming process requires vast amounts of heat causing it to be highly energy intensive.

The basic steps leading from the natural gas feedstock to a highly purified hydrogen product are: pretreatment of the raw feed; reforming to synthesis gas; conversion to a hydrogen-rich gas; and purification to hydrogen product specifications.
Reformer limitations dictate minimum quality requirements (composition standards) for the natural gas feed. Reforming is a catalytic operation, and the catalysts employed are poisoned by even trace amounts of sulphur. Hence, for economical operation, sulphur compounds are removed by pre-treatment. Desulphurization is accomplished using heat and a catalyst to convert sulphur compounds to H₂S, which can subsequently be removed by reaction on an adsorption bed. Most desulphurization units associated with SMR use a zinc oxide bed, which converts the H₂S to zinc sulphide (ZnS) and water.

Removal of non-methane components along with recycling of hydrogen rich steams are also considered part of raw feed pre-treatment. Since reforming is a reaction between methane and steam, non-methane hydrocarbons must be converted to methane and all liquid phase components are removed. Hydrogen, which is recycled from a hydrogen rich process stream (after CO₂ separation by MDEA but before final purification by pressure swing adsorption (PSA)) is introduced to the gaseous feed for use in downstream hydrogenation processes.

Sweetened natural gas is then mixed with process steam and further heated prior to entering the reformer.

During the steam methane reforming process, methane supplied by natural gas is heated with steam in the presence of a catalyst. Methane reacts with high-temperature steam (700°C-1,000°C) under 3-25 bar pressure in the presence of a catalyst to produce hydrogen, carbon monoxide and a relatively small amount of carbon dioxide. Since steam reforming involves an endothermic reaction, heat must be supplied to the process for the reaction to proceed. This is supported by heat from the reformer furnace. This support is direct, through the heating of the catalyst-filled tubes that form the reactor, and indirect, through raising steam with a heat recovery steam generator. Note that gas conversion, which is exothermic, also provides heat for raising steam. The furnace consumes natural gas as fuel and process gas, which is a residual from the hydrogen purification process.

A fired tubular reformer is used to complete the steam reforming process. The reformer consists of a radiant box containing hundreds of alloy tubes filled with a nickel-based reforming catalyst. The radiant box needs to be heated because the overall chemical reaction with natural gas is highly endothermic. The reforming process generates the hydrogen gas as well as CO and CO₂ by-products (syngas).

The syngas leaving the reformer is cooled in a waste heat steam boiler or boiler/superheater.

The synthesis gas from the reformer is rich in H₂ and in CO. Subsequently, in what is called the "water-gas shift reaction," the carbon monoxide and steam are reacted using a catalyst to produce carbon dioxide and more hydrogen. Therefore, after cooling, the syngas enters a medium temperature CO shift (MTS) converter. The MTS converter is filled with copper-based catalyst, which promotes the conversion of CO to CO₂ and in the process, generates additional H₂ gas (Rostrup-Nielsen and Rostrup-Nielsen, 2002).

The process gas and water leaving the MTS converter is further cooled and condensed to remove excess steam / water and trace constituents (e.g. methanol) from the bulk stream in a knockout drum.

The process gas stream then enters a PSA unit. In a final process step called "pressure-swing adsorption," carbon dioxide and other impurities are removed from the gas stream, leaving essentially pure hydrogen. The PSA unit contains an adsorbent to separate the CO₂ and unreacted methane from...
the hydrogen. The unreacted off-gas from the PSA unit can be reused in the reformer (Rostrup-Nielsen and Rostrup-Nielsen, 2002). Alternatively, the CO₂ can be removed using an amine solution in an adsorption tower (see section 2.2.1 for more details).

The hydrogen stream leaving the PSA unit is a high purity product (e.g. 99.9% pure or higher) (Rostrup-Nielsen and Rostrup-Nielsen, 2002).

**Other Plant Equipment**

Hydrogen plant equipment will depend on the type of production process. Again, this section focuses on hydrogen production by SMR.

Hydrogen plants have steam boilers and heaters to supply steam and heat energy to process equipment. Some hydrogen plants also have a gas-fired heater to preheat feedstock. Waste heat boilers (WHB) are used at some hydrogen plants to cool the syngas and recover the heat energy. These boilers and heaters can be major air emission sources, either individually or cumulatively.

It should also be noted that some chemical plant complexes with hydrogen production capabilities also have natural gas-fired cogeneration plants. The cogeneration plants are used to supply some of the steam and energy needs for the hydrogen plant and other systems within the complex. At the same time, excess steam generated at the hydrogen plant can be routed to the cogeneration plant to produce power. The cogeneration plant would offset some/all of the need for steam boilers and heaters at the plant. While a cogeneration plant is a major air emission source at some chemical complexes, the emissions resulting from the electricity generation are auxiliary to the chemical production process. Therefore, cogeneration plants are not discussed further in this report.

Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. As a safety device, flares are considered the best control option when the heating value of the emission stream cannot be recovered due to uncertain or intermittent flow during process upsets or emergencies. They are primarily used for burning flammable gas released via pressure relief valves during unplanned, overpressuring of plant equipment. During plant start-ups and shutdowns, flares are also used for planned combustion of gases over relatively short periods of time while equipment is being brought into production or being taken off-line. They are designed and operated to handle large fluctuations in flow rate and VOC content.

Thermal incinerators are another choice of combustion devices typically used to destroy hazardous air pollutants and VOCs from industrial air streams. They are preferable to flares when halogenated or sulphur-bearing compounds are present. Three main factors critical to achieve effective design and operation of a thermal oxidizer are temperature, residence time, and turbulence. Although they can accommodate minor flow fluctuations, thermal incinerators are not well suited to streams with highly variable flow because of reduced residence time and poor mixing during increased flow conditions.

Cooling towers provide necessary process cooling and are integral components to chemical plants. They are basic heat exchangers operating on a wet or dry basis and are capable of dissipating large heat loads to the atmosphere.

Wet cooling towers direct a portion of a warm recirculating water stream entering the tower to come into contact with and evaporate into air passing through the tower. This significantly lowers the
temperature of the remaining water stream as heat is liberated during evaporation and becomes absorbed into the air. The non-evaporated water is collected in tower basins and recycled back into the industrial system to recover more process heat.

Dry cooling towers represent extended type radiator cooling. However, wet cooling towers are more commonly used in industrial applications because the cooling potential of a wet surface is much better than a dry one. Therefore, the report will focus on air emission releases from wet cooling towers.

**Major Air Emission Sources**

A list and brief description of the major air emission sources for hydrogen production by steam methane reforming is provided in Table 10.
Table 10 Major air emission sources for hydrogen production* by steam methane reforming

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reformer</td>
<td>Natural gas is reformed with steam using a tubular reformer. The reforming process has high thermal energy requirements, which are partly met by burners inside the reformer. The reformer is a major source of NOx and, to a lesser extent, other combustion by-products released from the reformer stack. Fuel combustion in the reformer also generates GHG emissions, mostly CO2.</td>
</tr>
<tr>
<td>CO2 Vent</td>
<td>CO2 is produced in the reformer and additional CO2 is generated in the MTS. The CO2, a GHG, is removed from the process gas stream by absorption. During regeneration of the absorbent, the CO2 is commonly released and vented to atmosphere (Ebrahimi et al., 2009).</td>
</tr>
<tr>
<td>Steam Boilers and Heaters</td>
<td>Steam boilers and heaters produce process steam and heat for the hydrogen plant. NOX and, to a lesser extent, other combustion by-products are released from the steam boilers or heaters. Fuel combustion in the boilers or heaters also generates GHG emissions, mostly CO2.</td>
</tr>
<tr>
<td>Waste Heat Boiler</td>
<td>Waste heat boilers can be used to recover heat energy to produce steam. Some waste heat boilers are gas-fired to support efficient steam production. These gas-fired units will generate NOX and, to a lesser extent, other combustion by-products emissions. Fuel combustion in a waste heat boiler also generates GHG emissions, mostly CO2.</td>
</tr>
<tr>
<td>Desulphurization Unit</td>
<td>The natural gas feedstock is first run through a desulphurization reactor to remove sulphur and other compounds that would damage the catalyst of the reactors. SO2 should be emitted from the desulphurization unit in minimal quantities.</td>
</tr>
<tr>
<td>Flare / Thermal Incinerator</td>
<td>Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. NOX and, to a lesser extent, other combustion by-products; as well as, SO2 and VOCs are released from flares and thermal incinerators. Combustion of fuel and other hydrocarbons in the flare/incinerator generate GHG emissions, mostly CO2.</td>
</tr>
<tr>
<td>Cooling Towers</td>
<td>Cooling towers significantly lower the temperature of cooling water recirculated to various process units at the hydrogen plant. PM emissions result from the total dissolved solids in the circulating water becoming trapped within liquid drift droplets entrained in the air and are directly discharged from the tower into the atmosphere. VOC emissions are generated from cooling towers by: 1) leakage from process heat exchangers that service the hydrocarbon process streams; and 2) use of chemicals containing VOCs that are added to the circulating water for treatment. Please note: VOC emissions are expected from cooling towers used at chemical plants where the circulating waters cool down process streams and NOT from cooling towers used in conjunction with heating, ventilating and air conditioning (HVAC) units.</td>
</tr>
<tr>
<td>Equipment Leaks (Fugitives)</td>
<td>Equipment (e.g. valves, flanges, connectors, pumps, etc.) on the process units and piping network at a hydrogen plant will leak small quantities of their contents directly to the atmosphere. Collectively, the small leaks can amount to a significant source of VOC emissions at the hydrogen plant.</td>
</tr>
</tbody>
</table>

a) Combustion by-products include nitrogen oxides (NOx) carbon monoxide (CO), particulate matter (PM), volatile organic compounds (VOCs); as well as, trace amounts of sulphur oxides (SOX), metals, and polycyclic aromatic hydrocarbons (PAHs)
b) Greenhouse gases include carbon dioxide (CO2), methane (CH4), and nitrous oxide (N2O)

* Natural gas-fired co-generation plants located at hydrogen production plants are a major source of NOx emissions, and, to a lesser extent, other combustion by-products. Even though it is critical to include them in a chemical plant’s emissions profile; co-generation and its associated air emissions are beyond the scope of this project and are excluded from the report.

2.2 Fertilizer Plants

Chemical fertilizer manufacturing is divided into three groups of fertilizers based on the main element in the product, specifically nitrogen (N), phosphorous (P), and potassium (K). This report focuses only on chemical fertilizer manufacturers under the NAICS code 325313, “Chemical Fertilizer (except Potash) Manufacturing”, and more specifically, the N-type fertilizer manufacturers.
Within the N-type fertilizers, there are several manufactured fertilizer products in plant-available forms. Fertilizer products are classified by the percentage of the three main elements by mass, as \((N - P \text{ [commonly as } P_2O_5] - K \text{ [commonly as } K_2O])\). For example, synthetic ammonia (NH\(_3\)) fertilizer has 14gN/mol per 17gNH\(_3\)/mol which is 82% N and is therefore a (82-0-0) fertilizer under the classification system.

Ammonia is the N-type fertilizer product produced in the largest quantity by mass. This is because ammonia can be used directly as an applied fertilizer or as a building block for all other N-based fertilizer products. Stored as a liquid under pressure or refrigerated, it becomes a gas when exposed to air and is injected into the soil as a gas (Canadian Fertilizer Institute, 2011).

Other common N-based fertilizers include urea, ammonium nitrate, ammonium sulphate, and urea and ammonium nitrate (UAN) solution. Each fertilizer varies in terms of the form of fertilizer (i.e. solid granules, prill, or liquid fertilizers), handling/application methods, solubility, and the nitrogen release time.

Figure 11 depicts the boundaries and links between large volume inorganic chemical plants producing ammonia, acids and fertilizers (adapted from European Commission, 2007). As illustrated, fertilizer plants are often integrated to produce a combination of fertilizer and non-fertilizer products.

This report will not explore all the possible processes and products found at a given fertilizer plant, whether independent or integrated; but, will focus on:

- Ammonia plants;
- Urea plants;
- Nitric acid plants (needed for ammonium nitrate production); and
2.2.1 Ammonia Plants

Most ammonia manufacturing plants produce ammonia (NH₃) by catalytic steam reforming of natural gas. In this process, synthetic NH₃ is generated from nitrogen gas in air, and hydrogen gas obtained from the decomposition of methane in natural gas. A typical process flow diagram for NH₃ production by catalytic steam reforming of natural gas is presented in Figure 12.

An overview of a typical ammonia plant using natural gas reforming is provided below.

The catalysts used in the reforming step of the process can be poisoned by sulphur compounds. Since the natural gas used as feedstock typically contains trace quantities of sulphur (mostly as hydrogen sulphide (H₂S)); it is necessary for the gas stream to undergo desulphurization. This aids in preserving...
the catalysts and is a critical pre-treatment step in the ammonia synthesis process. Desulphurization is accomplished using heat and a catalyst to convert sulphur compounds to H₂S, which can subsequently be removed by reaction on an adsorption bed. Most ammonia plants use a zinc oxide bed, which converts the H₂S to zinc sulphide (ZnS) and water.

Sweetened natural gas is then mixed with process steam and delivered to the first of two reformers. The primary reformer is used to complete the steam reforming process. The reformer consists of a radiant box containing hundreds of alloy tubes filled with a nickel-based reforming catalyst. The radiant box needs to be heated because the overall chemical reaction with natural gas is highly endothermic. The reforming process generates CO, CO₂, and hydrogen gas (H₂).

Not all natural gas will react in the primary reformer, so a secondary reformer is needed to react most of the remaining natural gas (up to 99% of the feed). In the secondary reformer, air is added to the mix (air reforming). The air serves two purposes: it is needed for internal combustion in the reformer and it provides the necessary nitrogen gas (N₂) for the final ammonia synthesis reaction, which occurs downstream of the reformers in the ammonia converter(s).

The process gas leaving the reformer is cooled in a waste heat steam boiler or boiler/superheater.

After cooling, the process gas enters a high temperature CO shift (HTS) converter. The HTS converter is filled with chromium oxide and iron oxide initiator/catalyst, which promotes the conversion of CO to CO₂ and in the process, generates additional H₂ gas (European Fertilizer Manufacturers’ Association (EFMA), 2000a).

The process gas leaving the HTS converter is further cooled and then passed through a low temperature shift (LTS) converter. This LTS converter is filled with a copper oxide/zinc oxide-based catalyst to reduce the residual CO content to 0.2% to 0.4% (dry gas basis) (EFMA, 2000a).

The effluent stream from the LTS is then condensed to remove excess steam and trace constituents (e.g. ammonia and methanol) from the bulk stream in a knockout drum (European Commission, 2007).

The main process gas stream now contains mostly H₂, N₂, and CO₂. The CO₂ is most commonly removed using aqueous amine solutions, such as Monoethanolamine (MEA) and activated Methyl Diethanolamine (aMDEA), in an adsorption tower. The amine solution can be regenerated using steam stripping and heat in a reactivation tower. The CO₂ gas from the regeneration process is either vented or used for chemical feedstock in other parts of the plant complex, such as urea production.

Any remaining CO and CO₂ in the main process stream is removed by reacting it in a methanator. The methanator converts CO and CO₂ back to methane using pressure, heat, and a nickel catalyst. Methane is inert in the ammonia synthesis process so the trace quantities remain in the gas stream.

The H₂ and N₂ stream (now referred to as synthesis gas stream) is condensed and preheated prior to entering an ammonia converter. The ammonia converter contains an iron oxide catalyst, which, at the operating pressure and temperature, converts the synthesis gas to ammonia. This reaction is highly exothermic and therefore, extensive heat exchangers are needed to maintain the converters operating temperature and the conversion to NH₃.

Even at an ideal operating temperature for the catalyst, only 20 to 30% of the synthesis gas is reacted per pass in the converter due to the unfavourable equilibrium conditions. The ammonia that is formed...
is separated from the synthesis gas by cooling and condensation in a let-down separator. Unreacted synthesis gas is recycled and combined with newly formed synthesis gas.

From the let-down separator, ammonia is sent to storage or other on-site fertilizer plants, such as a urea plant.

**Other Plant Equipment**

Ammonia plants have steam boilers and heaters to supply steam and heat energy to process equipment. Some ammonia plants also have a gas-fired heater to preheat feedstock. Waste heat boilers (WHB) are used at some ammonia plants to cool the syngas and recover the heat energy. These boilers and heaters can be major air emission sources, either individually or cumulatively.

Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. As a safety device, flares are considered the best control option when the heating value of the emission stream cannot be recovered due to uncertain or intermittent flow during process upsets or emergencies. They are primarily used for burning flammable gas released via pressure relief valves during unplanned, over-pressuring of plant equipment. During plant start-ups and shutdowns, flares are also used for planned combustion of gases over relatively short periods of time while equipment is being brought into production or being taken off-line. They are designed and operated to handle large fluctuations in flow rate and VOC content.

Thermal incinerators are another choice of combustion devices typically used to destroy hazardous air pollutants and VOCs from industrial air streams. They are preferable to flares when halogenated or sulphur-bearing compounds are present. Three main factors critical to achieve effective design and operation of a thermal oxidizer are temperature, residence time, and turbulence. Although they can accommodate minor flow fluctuations, thermal incinerators are not well suited to streams with highly variable flow because of reduced residence time and poor mixing during increased flow conditions.

Cooling towers provide necessary process cooling and are integral components to chemical plants. They are basic heat exchangers operating on a wet or dry basis and are capable of dissipating large heat loads to the atmosphere.

Wet cooling towers direct a portion of a warm recirculating water stream entering the tower to come into contact with and evaporate into air passing through the tower. This significantly lowers the temperature of the remaining water stream as heat is liberated during evaporation and becomes absorbed into the air. The non-evaporated water is collected in tower basins and recycled back into the industrial system to recover more process heat.

Dry cooling towers represent extended type radiator cooling. However, wet cooling towers are more commonly used in industrial applications because the cooling potential of a wet surface is much better than a dry one. Therefore, the report will focus on air emission releases from wet cooling towers.

**Major Air Emission Sources**

A list and brief description of the major air emission sources at ammonia plants is provided in Table 11.
### Table 11  Major air emission sources at ammonia plants

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reformer Stack</strong></td>
<td>Natural gas is partially reformed with steam as a primary step, and completely reformed with air in a secondary step using a reformer. The reforming process has high thermal energy requirements, which are partly met by burners inside the reformer and steam superheaters. The reformer and steam superheaters are a major source of NOX and, to a lesser extent, other combustion by-products(^a) being released from their associated stacks. Fuel combustion in the reformer and boiler also generates GHG(^b) emissions, mostly CO(_2).</td>
</tr>
<tr>
<td><strong>CO(_2) Vent</strong></td>
<td>CO(_2) is removed from the process gas stream by absorption. During regeneration of the absorbent in the reactivation tower, the CO(_2) is released and vented to atmosphere. It must be noted that several ammonia plants have on-site urea plant, which utilize the CO(_2) instead of venting it, so this source is plant dependent.</td>
</tr>
<tr>
<td><strong>Process Condensate Vent</strong></td>
<td>Methanol is generated during the shifting reaction at ammonia plants. The methanol and other trace contaminants are removed along with steam when condensed. Methanol and other trace contaminants are stripped from the water, and steam is vented. Any trace VOCs remaining in the steam will be emitted.</td>
</tr>
<tr>
<td><strong>Desulphurization Unit</strong></td>
<td>The natural gas feedstock is first run through a desulphurization reactor to remove sulphur and other compounds that would damage the catalyst of the reactors. SO(_2) should be emitted from the desulphurization unit in minimal quantities.</td>
</tr>
<tr>
<td><strong>Flare / Thermal Incinerator</strong></td>
<td>Flare systems and/or thermal incinerators are combustion devices used at many fertilizer plants to decompose hazardous gases at high temperatures prior to atmospheric release. NOX and, to a lesser extent, other combustion by-products(^a); as well as, SO(_2) and VOCs are released from flares and thermal incinerators. Combustion of fuel and other hydrocarbons in the flare/incinerator generate GHG(^b) emissions, mostly CO(_2).</td>
</tr>
<tr>
<td><strong>Steam Boilers and Heaters</strong></td>
<td>Steam for the primary stage of the reforming process that produces syngas using gas-fired boilers. Steam is also required for various processes at the ammonia plant. Heaters are also used to provide heat throughout the plant. NOX and, to a lesser extent, other combustion by-products(^a) are released from the steam boilers or heaters. Fuel combustion in the boilers or heaters also generates GHG(^b) emissions, mostly CO(_2).</td>
</tr>
<tr>
<td><strong>Waste Heat Boiler</strong></td>
<td>Waste heat boilers can be used to recover heat energy to produce steam. Some waste heat boilers are gas-fired to support efficient steam production. These gas-fired units will generate NO(_X) and, to a lesser extent, other combustion by-products(^a) emissions. Fuel combustion in a waste heat boiler also generates GHG(^b) emissions, mostly CO(_2).</td>
</tr>
<tr>
<td><strong>Cooling Towers</strong></td>
<td>Cooling towers significantly lower the temperature of cooling water recirculated to various process units at the ammonia plant. PM emissions result from the total dissolved solids in the circulating water becoming trapped within liquid drift droplets entrained in the air and are directly discharged from the tower into the atmosphere. VOC emissions are generated from cooling towers by: 1) leakage from process heat exchangers that service the hydrocarbon process streams; and 2) use of chemicals containing VOCs that are added to the circulating water for treatment. Please note: VOC emissions are expected from cooling towers used at chemical plants where the circulating waters cool down process streams and NOT from cooling towers used in conjunction with heating, ventilating and air conditioning (HVAC) units.</td>
</tr>
<tr>
<td><strong>Equipment Leaks (Fugitives)</strong></td>
<td>Equipment (e.g. valves, flanges, connectors, pumps, etc.) on the process units and piping network at an ammonia plant will leak small quantities of their contents directly to the atmosphere. Collectively, the small leaks can amount to a significant source of ammonia and VOC emissions at the ammonia plant.</td>
</tr>
</tbody>
</table>

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2.2.2 Urea Plants

Urea fertilizer manufacturing facilities can typically have on-site ammonia fertilizer plants. This is because both the ammonia and carbon dioxide generated at the ammonia plant are necessary ingredients in urea production.

The urea production by mass at each fertilizer complex is comparable to its ammonia production with one exception. Those facilities utilizing ammonia for other N-type fertilizer products such as ammonium nitrate, ammonium sulphate, mono-ammonium phosphate may not have comparable production of their urea and ammonia.

Urea (CO\(\text{[NH}_2\text{]}_2\)) is generated by the following steps:
First, ammonia (\(\text{NH}_3\)) and carbon dioxide (\(\text{CO}_2\)) are reacted to form ammonium carbamate (\(\text{NH}_2\text{CO}_2\text{NH}_4\)) and urea directly;
- The ammonium carbamate by-product is dehydrated to form urea and water; and
- The resulting urea solution can then be concentrated and formed into solid fertilizer, as prill or granules.

A typical process flow diagram for urea production and solids formation is presented in Figure 13.

![Figure 13. Process flow diagram for urea production and solid formation.](image-url)
An overview of a typical urea plant is provided below.

Liquid NH₃ and CO₂ at a molar ratio of between 3:1 and 4:1 enter the synthesis reactor. In the reactor, two reactions can occur: 1) NH₃ and CO₂ converts to ammonium carbamate and 2) NH₃ and CO₂ converts to urea. The first reaction is fast, while the second is slow. Urea plants will add heat to the reactor to dehydrate the first reaction, and drive the reactor effluent to a solution containing 70 to 80% urea. Some urea plants use a series of two reactors, whereby the second reactor’s main function is to decompose the ammonium carbamate to urea using heat.

Some fertilizer plants will use this urea solution directly as an ingredient in other fertilizer mixtures (e.g. different concentrations of urea and ammonium nitrate [UAN] solution), while other plants may choose to concentrate the urea to form a solid urea fertilizer product (National Pollutant Inventory (NPI), 2004).

More efficient plants will strip unconverted NH₃, CO₂, and ammonium carbamate in the reactor effluent before sending the urea solution to the next stage of production. A couple of different stripping systems exist, but in each case, the unconverted reactants and remaining ammonium carbamate are removed from the product stream and recycled to the synthesis reactor.

The urea and water solution stream is then concentrated, most commonly using a series of evaporators to remove excess water. Alternative methods to concentrate the urea exist, such as vacuum concentration and crystallization, but these methods are used infrequently in North America. The goal in any method is to concentrate the urea to levels from 95% to greater than 99%. This high purity urea stream is referred to as urea “melt”. At this point, additives can be incorporated in the urea melt to enhance its fertilizer properties. The urea melt is now ready for solids formation.

Solid urea is available in two forms, prill or granules, which are produced using two separate methods referred to as prilling and granulation. In North America, granulation is used more frequently than prilling in producing solid urea for fertilizer.

Urea granulation is completed in pan granulator(s) or the more common type of granulator, rotating drum granulator(s). In drum granulation, urea solids are built up in layers on seed granules placed in a rotating drum granulator. Urea melt is sprayed onto the seed granules and allowed to move through the rotating drum. Cool air is passed through the granulator in a countercurrent direction to solidify the molten urea to the seed granules and increase their diameter. Solid granules leaving the granulator are screened, where small particles are recycled back to the start of the granulator to be used as seed particles, oversized granules are crushed and recycled, and appropriately-sized particles are conveyed to storage warehouses for shipping.

Other Plant Equipment

Urea plants have steam boilers and heaters to supply steam and heat energy to process equipment. These boilers and heaters can be major air emission sources, either individually or cumulatively.

Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. As a safety device, flares are considered the best control option when the heating value of the emission stream cannot be recovered due to uncertain or intermittent flow during process upsets or emergencies. They are primarily used for burning flammable gas released via pressure relief valves during unplanned, over-
pressuring of plant equipment. During plant start-ups and shutdowns, flares are also used for planned combustion of gases over relatively short periods of time while equipment is being brought into production or being taken off-line. They are designed and operated to handle large fluctuations in flow rate and VOC content.

Thermal incinerators are another choice of combustion devices typically used to destroy hazardous air pollutants and VOCs from industrial air streams. They are preferable to flares when halogenated or sulphur-bearing compounds are present. Three main factors critical to achieve effective design and operation of a thermal oxidizer are temperature, residence time, and turbulence. Although they can accommodate minor flow fluctuations, thermal incinerators are not well suited to streams with highly variable flow because of reduced residence time and poor mixing during increased flow conditions.

Cooling towers provide necessary process cooling and are integral components to chemical plants. They are basic heat exchangers operating on a wet or dry basis and are capable of dissipating large heat loads to the atmosphere.

Wet cooling towers direct a portion of a warm recirculating water stream entering the tower to come into contact with and evaporate into air passing through the tower. This significantly lowers the temperature of the remaining water stream as heat is liberated during evaporation and becomes absorbed into the air. The non-evaporated water is collected in tower basins and recycled back into the industrial system to recover more process heat.

Dry cooling towers represent extended type radiator cooling. However, wet cooling towers are more commonly used in industrial applications because the cooling potential of a wet surface is much better than a dry one. Therefore, the report will focus on air emission releases from wet cooling towers.

**Major Air Emission Sources**

A list and brief description of the major air emission sources at urea plants is provided in Table 12.
### Table 12 Major air emission sources at urea plants

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea Synthesis Process Vent</td>
<td>Ammonia and trace amounts of PM are typically emitted from the solution synthesis process due to non-condensable vent streams in the ammonia carbamate decomposition process. The stripping process used to recover and recycle unconverted reactants and remaining ammonium carbamate is not 100% efficient. The vent stream(s) from the stripping process is often combined with the vent stream from the synthesis process and exhausted from a single stack. Likewise, the evaporators produce a vent stream containing some ammonia, which is combined with the streams and exhausted from a single stack (Synthesis Process Vent).</td>
</tr>
<tr>
<td>Granulation Stack</td>
<td>Off-gas ammonia and PM are generated from mechanical agitation in the granulator(s), conveying urea granules, and crushing oversized granules. These sources are combined into one exhaust stream and emitted to atmosphere through a granulation stack. If additives are combined in the urea melt, the granulation stack can contain VOCs, mainly formaldehyde and methanol.</td>
</tr>
<tr>
<td>Flare / Thermal Incinerator</td>
<td>Flare systems and/or thermal incinerators are combustion devices used at many fertilizer plants to decompose hazardous gases at high temperatures prior to atmospheric release. NOX and, to a lesser extent, other combustion by-products; as well as, SO₂ and VOCs are released from flares and thermal incinerators. Combustion of fuel and other hydrocarbons in the flare/incinerator generate GHG emissions, mostly CO₂.</td>
</tr>
<tr>
<td>Steam Boilers and Heaters</td>
<td>Heat needed for the dehydration reaction is often supplied using gas-fired boilers. Steam is also required for other processes at the urea plant. Heaters are also used to provide heat throughout the plant. NOX and, to a lesser extent, other combustion by-products are released from the steam boilers or heaters. Fuel combustion in the boilers or heaters also generates GHG emissions, mostly CO₂.</td>
</tr>
<tr>
<td>Cooling Towers</td>
<td>Cooling towers significantly lower the temperature of cooling water recirculated to various process units at the urea plant. PM emissions result from the total dissolved solids in the circulating water becoming trapped within liquid drift droplets entrained in the air and are directly discharged from the tower into the atmosphere. VOC emissions are generated from cooling towers by: 1) leakage from process heat exchangers that service the hydrocarbon process streams; and 2) use of chemicals containing VOCs that are added to the circulating water for treatment. Please note: VOC emissions are expected from cooling towers used at chemical plants where the circulating waters cool down process streams and NOT from cooling towers used in conjunction with heating, ventilating and air conditioning (HVAC) units. Cooling towers at urea plants are not expected to be a significant source of volatile compounds (e.g. ammonia, VOCs).</td>
</tr>
<tr>
<td>Equipment Leaks (Fugitives)</td>
<td>Equipment (e.g. valves, flanges, connectors, pumps, etc.) on the process units and piping network at a urea plant will leak small quantities of their contents directly to the atmosphere. Collectively, the small leaks can amount to a significant source of ammonia, urea, and VOC emissions at the urea plant.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Combustion by-products include nitrogen oxides (NOₓ), carbon monoxide (CO), particulate matter (PM), volatile organic compounds (VOCs); as well as, trace amounts of sulphur oxides (SOₓ), metals, and polycyclic aromatic hydrocarbons (PAHs)</td>
</tr>
<tr>
<td>b) Greenhouse gases include carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O)</td>
</tr>
</tbody>
</table>

#### 2.2.3 Nitric Acid Plants

In the context of fertilizer plants, nitric acid is produced as an intermediate to be used in the production of solid ammonium nitrate fertilizer; as well as, urea and ammonium nitrate (UAN) solution fertilizers.

The major steps in a nitric acid plant are:
- Reacting ammonia and oxygen to produce primarily nitric oxide (NO) and water;
- The NO and water is cooled and condensed and in doing so, NO is reacted with residual oxygen to produce nitrogen dioxide (NO₂) and nitrogen tetroxide (N₂O₄); and
The NO₂ is hydrated in an adsorption column using process water to produce nitric acid (HNO₃) and NO. Air is also added to the column to re-oxidize the NO formed in the hydration reaction back to NO₂.

Figure 14 displays a typical process flow diagram for a general nitric acid plant using the catalytic ammonia oxidation process (adapted from US EPA, 1998a).

Figure 14 Process flow diagram for typical weak nitric acid plant.

An overview of a typical nitric acid plant for downstream fertilizer production is provided below.

Ammonia and preheated air enter an ammonia oxidation reactor, which forms NO and water in the presence of heat and a platinum/rhodium alloy catalyst. Trace amounts of nitrogen gas and nitrous oxide (N₂O) are also produced in the reaction.

Heat energy exiting the reactor with the process stream is partly recovered using a waste heat boiler and/or air preheater.

The process stream is then further cooled and pressurized to condense the water; while at the same time, causing NO to react non-catalytically with residual oxygen to form NO₂ and N₂O₄.
The process stream is piped to the absorption tower. Condensed process water is sprayed down through the tower in a countercurrent direction to the process stream. The NO\textsubscript{2} reacts to form nitric acid and NO. Air is also added to the column to re-oxidize the NO formed in the hydration reaction back to NO\textsubscript{2}.

The acid leaving the absorption contains dissolved nitrogen oxides (NO\textsubscript{X}). Air is added to a bleaching unit to remove the NO\textsubscript{X} for the crude acid. The air and NO\textsubscript{X} are recycled to the absorption tower inlet.

**Other Plant Equipment**

Nitric acid plants have steam boilers and heaters to supply steam and heat energy to process equipment. Nitric acid plants can use a gas-fired heater to preheat air. Waste heat boilers (WHB) are also used at some nitric acid plants to recover the heat energy from the reactor. These boilers and heaters can be major air emission sources, either individually or cumulatively.

Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. As a safety device, flares are considered the best control option when the heating value of the emission stream cannot be recovered due to uncertain or intermittent flow during process upsets or emergencies. They are primarily used for burning flammable gas released via pressure relief valves during unplanned, over-pressuring of plant equipment. During plant start-ups and shutdowns, flares are also used for planned combustion of gases over relatively short periods of time while equipment is being brought into production or being taken off-line. They are designed and operated to handle large fluctuations in flow rate and VOC content.

Thermal incinerators are another choice of combustion devices typically used to destroy hazardous air pollutants and VOCs from industrial air streams. They are preferable to flares when halogenated or sulphur-bearing compounds are present. Three main factors critical to achieve effective design and operation of a thermal oxidizer are temperature, residence time, and turbulence. Although they can accommodate minor flow fluctuations, thermal incinerators are not well suited to streams with highly variable flow because of reduced residence time and poor mixing during increased flow conditions.

Cooling towers provide necessary process cooling and are integral components to chemical plants. They are basic heat exchangers operating on a wet or dry basis and are capable of dissipating large heat loads to the atmosphere.

Wet cooling towers direct a portion of a warm recirculating water stream entering the tower to come into contact with and evaporate into air passing through the tower. This significantly lowers the temperature of the remaining water stream as heat is liberated during evaporation and becomes absorbed into the air. The non-evaporated water is collected in tower basins and recycled back into the industrial system to recover more process heat.

Dry cooling towers represent extended type radiator cooling. However, wet cooling towers are more commonly used in industrial applications because the cooling potential of a wet surface is much better than a dry one. Therefore, the report will focus on air emission releases from wet cooling towers.
Major Air Emission Sources

A list and brief description of the major air emission sources at nitric acid plants is provided in Table 13.

Table 13  Major air emission sources at nitric acid plants

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tail Gas Stack</td>
<td>Tail gas, consisting mainly of NO₂, unreacted NO and N₂O with trace amounts of nitric acid and ammonia, exit the absorption tower. The tail gas is often treated using catalytic reduction prior to being emitted from the tail gas stack.</td>
</tr>
<tr>
<td>Air Preheater</td>
<td>Gas-fired heaters can be used to preheat the process air for the ammonia oxidation reactor. NOₓ and, to a lesser extent, other combustion by-products are released from the steam boilers. Fuel combustion in the boiler also generates GHG emissions, mostly CO₂.</td>
</tr>
<tr>
<td>Waste Heat Boiler</td>
<td>Heat needed for the dehydration reaction is often supplied using gas-fired boilers. Steam is also required for other processes at the urea plant. NOₓ and, to a lesser extent, other combustion by-products are released from the steam boilers. Fuel combustion in the boiler also generates GHG emissions, mostly CO₂.</td>
</tr>
<tr>
<td>Steam Boilers and Heaters</td>
<td>Steam boilers and heaters produce process steam and heat for the nitric acid plants. NOₓ and, to a lesser extent, other combustion by-products are released from the steam boilers or heaters. Fuel combustion in the boilers or heaters also generates GHG emissions, mostly CO₂.</td>
</tr>
<tr>
<td>Flare / Thermal Incinerator</td>
<td>Flare systems and/or thermal incinerators are combustion devices used at many fertilizer plants to decompose hazardous gases at high temperatures prior to atmospheric release. However, flares are not often used at nitric acid plants due to large gas volumes and low initial NOₓ concentrations. However, where there is intermittent discharge of NOₓ in concentrations of 1% or more, flaring may be the best means of abatement. (United States Department of Health, Education, and Welfare, 1966). NOₓ and, to a lesser extent, other combustion by-products; as well as, SO₂ and VOCs are released from flares and thermal incinerators. Combustion of fuel and other hydrocarbons in the flare/incinerator generate GHG emissions, mostly CO₂.</td>
</tr>
<tr>
<td>Cooling Towers</td>
<td>Cooling towers significantly lower the temperature of cooling water recirculated to various process units at the nitric acid plant. PM emissions result from the total dissolved solids in the circulating water becoming trapped within liquid drift droplets entrained in the air and are directly discharged from the tower into the atmosphere. VOC emissions are generated from cooling towers by: 1) leakage from process heat exchangers that service the hydrocarbon process streams; and 2) use of chemicals containing VOCs that are added to the circulating water for treatment. Please note: VOC emissions are expected from cooling towers used at chemical plants where the circulating waters cool down process streams and NOT from cooling towers used in conjunction with heating, ventilating and air conditioning (HVAC) units. Cooling towers at nitric acid plants are not expected to be a significant source of emissions (e.g. ammonia, VOCs).</td>
</tr>
<tr>
<td>Equipment Leaks (Fugitives)</td>
<td>Equipment (e.g. valves, flanges, connectors, pumps, etc.) on the process units and piping network at a nitric acid plant will leak small quantities of their contents directly to the atmosphere. Collectively, the small leaks can amount to a significant source of ammonia and VOC emissions at the nitric acid plant.</td>
</tr>
</tbody>
</table>

a) Combustion by-products include nitrogen oxides (NOₓ) carbon monoxide (CO), particulate matter (PM), volatile organic compounds (VOCs); as well as, trace amounts of sulphur oxides (SOₓ), metals, and polycyclic aromatic hydrocarbons (PAHs)
b) Greenhouse gases include carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O)

2.2.4  Ammonium Nitrate Plants

Ammonium nitrate (NH₄NO₃) is produced by reacting nitric acid with ammonia. The ammonium nitrate solution can be combined with urea to produce a urea and ammonium nitrate (UAN) solution
fertilizer or it can be concentrated and solidified (typically as prill) to be sold directly as ammonium nitrate fertilizer. This section focuses on the production of ammonium nitrate prills.

The three main steps in ammonium nitrate production are:
- Neutralization;
- Evaporation; and
- Solidification.

Figure 15 displays a typical process flow diagram for a generic ammonium nitrate plant with a prill tower.

Figure 15  Process flow diagram for typical ammonium nitrate plant with a prill tower.

An overview of a common ammonium nitrate production process is provided below.
Nitric acid and ammonia are reacted in a neutralizer system to produce ammonium nitrate and steam. There are several different types and designs for the neutralization system, including vessels, circulating systems, and pipe reactors (EFMA, 2000b). The exothermic neutralization of nitric acid with ammonia gas produces ammonium nitrate solution and steam. The nitric acid is commonly preheated using equipment of suitable corrosion resistance; especially, if the available concentration of nitric acid is towards the lower limit of the range 50-70%. Preheating can best be performed (i.e., Best Available Technique (BAT)) by using steam or hot condensate from the ammonium nitrate process (EFMA, 2000b). Please note: the steam produced from the exothermic reaction can be used either to preheat the feedstocks or used in downstream processes (e.g. evaporators).

The ammonium nitrate solution stream from the neutralizer needs to be concentrated before prilling or granulating the fertilizer product. This can be accomplished by an evaporator unit, which uses steam to reduce the water content to 1% to 8%, depending on the requirement for the particular type of solidification process used at the plant (EFMA, 2000b).

Concentrated ammonium nitrate solution leaving the evaporator is piped to the top of a prill tower. It is sprayed down into the tower, where a countercurrent air stream cools and solidifies the droplets into spherical prills (US EPA, 1995a).

Cooled prills are screened, where over- and under-sized prills are dissolved and recycled to the evaporator. Appropriately-sized prills can be sent directly to storage or coated in a rotary drum to prevent agglomeration during storage. The most common coating materials are clays and diatomaceous earth (US EPA, 1995a).

Other Plant Equipment

Ammonium nitrate plants may require steam boilers and heaters to supply steam and heat energy (beyond the recycle stream from the neutralizer) for various plant processes (e.g. evaporators). WHB are used at some ammonium nitrate plants to cool the ammonium nitrate solution and recover the heat energy. These boilers and heaters can be major air emission sources, either individually or cumulatively.

Flare systems and/or thermal incinerators are combustion devices used at many chemical plants to decompose hazardous gases at high temperatures prior to atmospheric release. As a safety device, flares are considered the best control option when the heating value of the emission stream cannot be recovered due to uncertain or intermittent flow during process upsets or emergencies. They are primarily used for burning flammable gas released via pressure relief valves during unplanned, over-pressuring of plant equipment. During plant start-ups and shutdowns, flares are also used for planned combustion of gases over relatively short periods of time while equipment is being brought into production or being taken off-line. They are designed and operated to handle large fluctuations in flow rate and VOC content.

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Cooling towers provide necessary process cooling and are integral components to chemical plants. They are basic heat exchangers operating on a wet or dry basis and are capable of dissipating large heat loads to the atmosphere.

Wet cooling towers direct a portion of a warm recirculating water stream entering the tower to come into contact with and evaporate into air passing through the tower. This significantly lowers the temperature of the remaining water stream as heat is liberated during evaporation and becomes absorbed into the air. The non-evaporated water is collected in tower basins and recycled back into the industrial system to recover more process heat.

Dry cooling towers represent extended type radiator cooling. However, wet cooling towers are more commonly used in industrial applications because the cooling potential of a wet surface is much better than a dry one. Therefore, the report will focus on air emission releases from wet cooling towers.

Major Air Emission Sources

A list and brief description of the major air emission sources at ammonium nitrate plants is provided in Table 14.
Table 14  Major air emission sources at ammonium nitrate plants

<table>
<thead>
<tr>
<th>Emission Source</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutralizer</td>
<td>Trace quantities of ammonia, nitric acid, and PM (as fine ammonium nitrate droplets) are present in the steam produced in the neutralization reaction. The steam is often condensed and purified for re-use. A portion of the contaminants are not recovered in the condensation and purification steps, and are emitted to air.</td>
</tr>
<tr>
<td>Evaporator</td>
<td>During evaporation, ammonia volatilizes from the ammonium nitrate solution. The steam from the evaporator will be contaminated with the ammonia and droplets of ammonium nitrate. Similar to the neutralizer, a portion of the contaminants are not recovered, and are emitted to air (EFMA, 2000b).</td>
</tr>
<tr>
<td>Prill Tower</td>
<td>The countercurrent air stream in the prill tower picks up ammonia and ammonium nitrate prill. A large portion of the contaminants are removed from the air stream; however, fine ammonium nitrate particles will be emitted from the prill tower.</td>
</tr>
<tr>
<td>Steam Boiler and Heaters</td>
<td>Steam, beyond the recycle stream from the neutralizer, may be required for various processes at the ammonium nitrate plant (e.g. feedstock preheat, evaporators). Steam boilers and heaters produce process steam and heat for the ammonium nitrate plant. NOX and, to a lesser extent, other combustion by-products are released from the steam boilers or heaters. Fuel combustion in the boilers or heaters also generates GHG emissions, mostly CO2.</td>
</tr>
<tr>
<td>Waste Heat Boiler</td>
<td>Waste heat boilers can be used to recover heat energy to produce steam. Some waste heat boilers are gas-fired to support efficient steam production. These gas-fired units will generate NOX and, to a lesser extent, other combustion by-products emissions. Fuel combustion in a waste heat boiler also generates GHG emissions, mostly CO2.</td>
</tr>
<tr>
<td>Flare / Thermal Incinerator</td>
<td>Flare systems and/or thermal incinerators are combustion devices used at many fertilizer plants to decompose hazardous gases at high temperatures prior to atmospheric release. NOX and, to a lesser extent, other combustion by-products; as well as, SO2 and VOCs are released from flares and thermal incinerators. Combustion of fuel and other hydrocarbons in the flare/incinerator generate GHG emissions, mostly CO2.</td>
</tr>
<tr>
<td>Cooling Towers</td>
<td>Cooling towers significantly lower the temperature of cooling water recirculated to various process units at the ammonium nitrate plant. PM emissions result from the total dissolved solids in the circulating water becoming trapped within liquid drift droplets entrained in the air and are directly discharged from the tower into the atmosphere. VOC emissions are generated from cooling towers by: 1) leakage from process heat exchangers that service the hydrocarbon process streams; and 2) use of chemicals containing VOCs that are added to the circulating water for treatment. Please note: VOC emissions are expected from cooling towers used at chemical plants where the circulating waters cool down process streams and NOT from cooling towers used in conjunction with heating, ventilating and air conditioning (HVAC) units.</td>
</tr>
<tr>
<td>Equipment Leaks (Fugitives)</td>
<td>Equipment (e.g. valves, flanges, connectors, pumps, etc.) on the process units and piping network at an ammonium nitrate plant will leak small quantities of their contents directly to the atmosphere. Collectively, the small leaks can amount to a significant source of ammonia and VOC emissions at the ammonium nitrate plant.</td>
</tr>
</tbody>
</table>

a) Combustion by-products include nitrogen oxides (NOx) carbon monoxide (CO), particulate matter (PM), volatile organic compounds (VOCs); as well as, trace amounts of sulphur oxides (SOx), metals, and polycyclic aromatic hydrocarbons (PAHs)  
b) Greenhouse gases include carbon dioxide (CO2), methane (CH4), and nitrous oxide (N2O)
3.0 Major Air Emission Sources

Several major air emission sources at chemical and fertilizer plants are identified in Chapter 2. This chapter provides detail descriptions of the largest emitting sources in terms of criteria air contaminants (CACs), VOCs, and greenhouse gases (GHGs). However, it does not mean that any of the other air emission sources identified in Section 2 should not be addressed or are any less important. All air emissions identified in Section 2 need to be considered when assessing air emissions from individual sources at any given chemical and fertilizer plant and/or choosing the most appropriate air pollution prevention and control technologies.

3.1 Pyrolysis Furnace

Pyrolysis furnaces (or cracking furnaces) are used to “crack” saturated hydrocarbons, such as ethane and propane, through pyrolysis reactions into smaller molecules – primarily ethylene, propylene, other olefins and diolefins. These pyrolysis reactions are highly endothermic and require substantial heat energy inputs.

3.1.1 General Description

Pyrolysis furnaces are designed to: 1) provide the necessary energy to crack the feedstock; 2) rapidly cool the cracked gas stream to prevent further reactions; and 3) efficiently reclaim the heat energy. To perform these functions, pyrolysis furnaces are comprised of the following sections/components:

- Convection section;
- Radiant section;
- Transfer line exchanger (TLE); and
- Steam drum.

A generic configuration of a pyrolysis furnace is shown in Figure 16 (adapted from European Commission, 2003).
Figure 16  Configuration of a generic pyrolysis furnace.

The convection section is used to preheat the hydrocarbon feedstock, steam, and saturated hydrocarbon stream to an incipient temperature for the pyrolysis reactions. This section is essentially an elongated chamber carrying the hot exhaust gases of the radiant section to the pyrolysis furnace stack. Heat exchangers run through the convection section to preheat the hydrocarbon feedstock and superheat the steam by recovering the heat energy contained in the flue gas stream. In addition to preheating the feedstock and steam, the convection section is often equipped with a few extra heat exchangers to recover more heat energy by preheating other streams including boiler feed water (BFW), combustion air, etc.

New plants are designed for 93% to 95% thermal efficiency, and revamping of older ones can increase efficiencies to 89% to 92% (Zimmermann and Walzl, 2005). In other words, a well-designed pyrolysis furnace will only lose roughly 5% of the heat input through the stack (Zimmermann and Walzl, 2005). Heat loses through the furnace walls is minimal (e.g. roughly 1.5% of heat input).
In the convection section, the hydrocarbon feedstock is also mixed with steam to lower the hydrocarbon partial pressure, thus improving olefin yields and limiting the formation of less desirable secondary products (e.g. C₄ to C₇ products) (Fisher, 2010). The steam also reduces the amount of coke depositing in the radiant section of the furnace and other downstream equipment, by: 1) limiting the formation of coke; and 2) reacting with coke already deposited on surfaces. The amount of steam added to the hydrocarbon feed (referred to as dilution steam) depends on the furnace design, feedstock type, and desired product yields.

The preheated, saturated hydrocarbon feedstock (e.g. 500 to 680°C) leaves the convection section and enters the radiant section of the furnace. The radiant section consists of a refractory-lined firebox with coiled radiant tubes hung vertically in the firebox. The saturated hydrocarbon feedstock is fed through the tubes to gain heat energy and crack the hydrocarbons into ethylene, propylene, and other olefins and diolefins.

The radiant coils are heated externally, largely by radiation. The firebox is heated to 1000°C - 1200°C, typically using natural gas-fired burners (Zimmermann and Walzl, 2005). Burners can be floor-mounted, wall-mounted, and / or mounted on a terraced wall.

The number of coils, their configuration (e.g. single plane, double-row, etc.), and dimensions (e.g. diameter, length) determine the residence time and temperature and pressure profiles along the coils to ultimately achieve the desired product yields. Burner arrangements will differ depending on the coil arrangements in the firebox.

The residence time of feedstock in the radiant section is typically less than 0.5 to 1 second. Short residence times limit the amount of time for secondary reactions to occur (e.g. formation of aromatics, C₄ products, C₅ products, etc.). It does, however, prevent some feedstock from reacting in the pyrolysis furnace. The feedstock must, therefore, be recovered downstream of the furnace and recycled.

Flue gases generated in the radiant section are drawn upward and through the convection section using induced draft fans prior to emission from the stack.

The cracked gas stream leaving the radiant section is typically between 750°C - 875°C. It must be cooled rapidly to prevent degradation of primary olefins to secondary products. Transfer-Line Exchangers (TLEs) perform this function by indirect heat transfer from the product stream to high-pressure BFW on the shell side of the TLE. The heat vaporizes the BFW to high-pressure steam, which is recovered and re-used in various plant processes. TLEs can lower the cracked gas temperature from 750°C - 875°C down to 550°C - 650°C (European Commission, 2003).

TLEs are usually mounted vertically, along the side of the pyrolysis furnace; although, other designs and arrangements exist. Some furnace designs utilize two or more TLE in series to perform the cooling function.

A steam drum is connected to the TLE to separate and recover the high-pressure steam generated in the TLE. The recovered steam is often returned to the convection section of the furnace to be superheated and used as dilution steam.
Decoking Operation

Periodically, the furnace needs to be decoked to remove the coke deposits that build-up in the radiant tubes and TLE from the pyrolysis reactions. The coke acts as a thermal insulator, which inhibits heat transfer to the feedstock, and reduces the flow area in the tubes (Zimmermann and Walzl, 2005). Both affect the efficiency of the system and increase fuel demands for the furnace.

Likewise, coke deposited in the TLE reduces the heat transfer to the BFW and thus, the amount of high-pressure steam generated in the process. This, also, increases the need to burn more fuel for the process.

A couple of different methods are used to decoke a pyrolysis furnace.

In an air-steam process, the furnace is, first, taken off-line from downstream processes. A steam and air mixture is, then, fed through the radiant coils to burn off the coke, and to a lesser extent, by spalling the coke. Steam reacts with coke to produce CO₂, CO, and hydrogen. The firebox burners remain on-line to enhance the burn-off process. The air to steam ratio increases over the duration of the decoke operation to prevent the radiant tubes from overheating (Zimmermann and Walzl, 2005). After the radiant tubes are decoked (approx. 20 hours), the TLE is decoked. The process is similar, but the air to steam ratio differs from the radiant tubes to achieve the necessary burn-off in the TLE. The total decoking process takes roughly 36 hours (Zimmermann and Walzl, 2005).

In the steam-only process, the furnace can remain connected to downstream processes. A steam stream is fed through the radiant coils to react the coke deposits to CO₂, CO, and hydrogen. Again, the burners are used to maintain the high temperature in the radiant coils. The steam, along with the reaction products, continues through the TLE to partially decoke them. Downstream equipment will be designed accordingly to handle the steam and carbon monoxide loads. The steam-only process is typically followed by a relatively brief air-steam stream to finish the decoking process. Steam-only decoking is less effective than the air-steam process, but protects the radiant coils from overheating (Zimmermann and Walzl, 2005).

The decoking process produces a vent gas steam, which contains CO₂, CO, and coke particulates. The vent gas is typically directed to pollution control device to lower emissions, usually with a specific focus on particulate control. These devices include, but are not limited to (European Commission, 2003):

- Wet de-dusting (e.g. water spray tower, water scrubber);
- Dry de-dusting (e.g. cyclone, bag filters); or
- Re-routing the vent gas to the firebox to promote complete combustion of coke particulates.

After control, the vent gas can be exhausted from a separate vent or the pyrolysis furnace stack.

3.1.2 Associated Emissions

The major air emissions associated with a pyrolysis furnace are presented in Table 15.
<table>
<thead>
<tr>
<th>Pollutant</th>
<th>CAS Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Criteria Air Contaminants</td>
<td></td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>630-08-0</td>
</tr>
<tr>
<td>Nitrogen Oxides</td>
<td>11104-93-1</td>
</tr>
<tr>
<td>Particulate Matter, PM (Total)</td>
<td>n/a</td>
</tr>
<tr>
<td>PM ≤ 10µm (PM_{10})</td>
<td>n/a</td>
</tr>
<tr>
<td>PM ≤ 2.5µm (PM_{2.5})</td>
<td>n/a</td>
</tr>
<tr>
<td>Sulphur Dioxide</td>
<td>7446-09-5</td>
</tr>
<tr>
<td>Volatile Organic Compounds</td>
<td>n/a</td>
</tr>
<tr>
<td><strong>Greenhouse Gases</strong></td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>124-38-9</td>
</tr>
<tr>
<td>Methane</td>
<td>74-82-8</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>10024-97-2</td>
</tr>
<tr>
<td><strong>Individual Volatile Organic Compounds</strong></td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td>74-85-1</td>
</tr>
<tr>
<td>Propylene</td>
<td>115-07-1</td>
</tr>
<tr>
<td>Isobutane</td>
<td>75-28-5</td>
</tr>
<tr>
<td>Propane</td>
<td>74-98-6</td>
</tr>
<tr>
<td>Heptane</td>
<td>142-82-5</td>
</tr>
<tr>
<td>Ethane</td>
<td>74-84-0</td>
</tr>
<tr>
<td>Pentane</td>
<td>109-66-0</td>
</tr>
<tr>
<td>Butane</td>
<td>106-97-8</td>
</tr>
<tr>
<td>Hexane</td>
<td>110-54-3</td>
</tr>
<tr>
<td>Benzene</td>
<td>71-43-2</td>
</tr>
<tr>
<td>Isopentane</td>
<td>78-78-4</td>
</tr>
<tr>
<td>Toluene</td>
<td>108-88-3</td>
</tr>
<tr>
<td>Styrene</td>
<td>100-42-5</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>100-41-4</td>
</tr>
<tr>
<td>Methanol</td>
<td>67-56-1</td>
</tr>
</tbody>
</table>

(a) Individual VOCs are generally sorted by magnitude of emissions (largest to smallest) for a furnace using natural gas liquids (NGL) feedstocks. Specific pyrolysis furnaces might generate more or less of individual VOCs, such that the order might vary from that presented above.

The data sources for individual VOC species include the National Pollutant Release Inventory (NPRI), US EPA (2008), and European Monitoring and Evaluation Programme/European Environment Agency (EMEP/EEA, 2006).

The pollutants emitted during normal furnace operation and decoking are expected to be similar; but, the magnitude of emissions will differ. For example, PM emissions are expected to be higher during decoking, due to coke spalling, compared to normal furnace operation. Also, high carbon monoxide emissions are expected during the initial stages of decoking compared to normal furnace operation (European Commission, 2003). Conversely, VOC emissions are expected to be greater during normal furnace operation compared to the decoking operation.

### 3.2 Steam Methane Reformer

A Steam Methane Reformers (reformer) is used to convert methane and steam into “synthesis gas” or “syngas” – a combination of CO, CO₂, and hydrogen gas (H₂). The syngas is used in a number of chemical and fertilizer plants including methanol plants, high-purity hydrogen plants, and ammonia
plants. The reaction is highly endothermic and requires substantial heat energy inputs. A reformer functions similar to a pyrolysis furnace, in that it provides the necessary energy to react the feedstock; while, recovering much of the energy in the vent gas stream prior to release. However, the reformer is fundamentally different from the pyrolysis furnaces because of the type of reactions occurring in the radiant tubes, specifically a catalysed, “controlled” reaction in the reformer and a number of non-catalysed, “uncontrolled” reactions in the pyrolysis furnace (i.e., uncontrolled, in that ethylene is one of many products formed through the pyrolysis reaction). This fundamental difference may appear insignificant; but, it affects many aspects of their design and function, including; but not limited to the following.

- **Pyrolysis furnaces** must focus on short residence time in the tubes because they rely on the reaction kinetics of various olefins and secondary products to partially control and maximize ethylene yields. As a consequence, a significant amount of ethane (or other feedstock) remains unreacted. The reforming reaction is controlled, and therefore design can have a stronger focus on maximizing syngas yield and thermal efficiency.
- **Since** there is a catalyst in the reformer tubes and natural gas feedstock contains sulphur compounds, the reformer design must consider desulphurization to prevent poisoning the catalyst.
- **Coke** is not produced in the reformer (i.e., not a pyrolysis reaction) and therefore, the reformer doesn’t need to be designed for decoking operations.

More details on the design differences are presented below.

### 3.2.1 General Description

Steam methane reformers are designed to: 1) provide the necessary preheat to support removal of sulphur compounds from the natural gas; 2) effectively pass large volumes of feedstock over a catalyst; 3) provide the necessary energy to convert the methane and steam to syngas; and 4) efficiently reclaim the heat energy. To perform these functions, steam methane reformers are comprised of the following sections / components:

- Convection section;
- Inlet and outlet manifolds; and
- Radiant section.

A generic configuration of a reformer is shown in Figure 17 (adapted from European Commission (2007) and ThyssenKrupp Uhde (2011) documents).
The reformer has a convection section used to heat various process and feed streams using the energy in the vent gas stream. The convection section is typically a long horizontal tunnel that links the firebox (or radiant section) to the reformer stack. A number of heat exchangers run through the length of the tunnel to recover the heat energy.

The feed (methane) stream preheat provides an essential function - to preheat the feed to 350°C - 400°C for the desulphurization vessel. Without this preheat step, the desulphurization process will not function well, and sulphur can remain in the feed. Sulphur can poison the catalyst in the reformer and inhibit the fundamental chemical reactions.

Other stream preheat are not as essential, but improve the thermal efficiency of the reformer. These streams can include combustion and process air, steam, and high pressure superheated steam.

After desulphurization, but still in the convection section, the methane feedstock is mixed with steam, at a steam to carbon ratio of roughly 3 (EFMA, 2000a). This mixture stream contains both reactants needed to produce the synthesis gas. It is preheated to a temperature of 500°C - 600°C, and then sent to the inlet manifold of the reformer (EFMA, 2000a).

New or revamped reformers can include a pre-reformer, that partially reacts the feed and steam over a catalyst bed (European Commission, 2007). Since the reaction is endothermic, the gas stream is cooled, and must be reheated in the reformer’s convection section prior to entering the radiant section. Overall though, the pre-reformer reduces the primary reformer’s duties, and thus lowers the overall burner firing needs (European Commission, 2007). The steam reforming process can occur at lower steam to carbon ratio, thus reducing the overall energy needs of the plant (European Commission, 2007). This provides fuel savings and an overall emission reduction to the plant.
The radiant section consists of a refractory-lined firebox with hundreds of catalyst-filled tubes (reformer tubes) running vertically through the length of the firebox. The catalyst in the tubes is nickel-based (e.g. nickel oxide), and the tubes themselves are typically made of a high–nickel chromium alloy.

Ceiling-mounted and possibly wall-mounted burners supply the necessary thermal energy to heat the reformer tubes and sustain the endothermic reaction. The burners are usually natural gas-fired and capable of heating the radiant section to temperatures in excess of 900°C (EFMA, 2000a).

The number and configuration of reformer tubes is proprietary; but, must fundamentally be arranged to supply the necessary pressure and temperature for the steam reforming process. Similarly, burner arrangements can differ depending on the tube arrangements in the radiant box.

The inlet manifold atop the reformer distributes the methane and steam mixture into the reformer tubes. As the mixture travels down through the reformer tubes, it gains heat energy and in the presence of the nickel-based catalyst, the methane and steam react to form the synthesis gas. At the outlet of the reformer tubes, the process gas stream is typically heated to 780°C - 830°C (EFMA, 2000a).

The process gas stream from the tubes collects in an outlet manifold located below the reformer. This stream will contain synthesis gas, unreacted methane, and steam; and is typically sent to a secondary reformer to complete the synthesis gas formation.

Flue gases generated in the radiant section are drawn downward through the radiant section and across the convection section using induced draft fans located toward the reformer stack. Typically, chemical and fertilizer plants will combine other exhaust streams (e.g. secondary reformer flue gases) into the reformer stack to take advantage of its height for optimal pollutant dispersion.

### 3.2.2 Associated Emissions

The major air emissions associated with a steam methane reformer are presented in Table 16.
<table>
<thead>
<tr>
<th>Pollutant</th>
<th>CAS Number</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Criteria Air Contaminants</strong></td>
<td></td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>630-08-0</td>
</tr>
<tr>
<td>Nitrogen Oxides</td>
<td>11104-93-1</td>
</tr>
<tr>
<td>Particulate Matter, PM (Total)</td>
<td>n/a</td>
</tr>
<tr>
<td>PM ≤ 10µm (PM$_{10}$)</td>
<td>n/a</td>
</tr>
<tr>
<td>PM ≤ 2.5µm (PM$_{2.5}$)</td>
<td>n/a</td>
</tr>
<tr>
<td>Sulphur Dioxide</td>
<td>7446-09-5</td>
</tr>
<tr>
<td><strong>Volatile Organic Compounds</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Greenhouse Gases</strong></td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>124-38-9</td>
</tr>
<tr>
<td>Methane</td>
<td>74-82-8</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>10024-97-2</td>
</tr>
<tr>
<td><strong>Individual Volatile Organic Compounds</strong>&lt;sup&gt;(a)&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Hexane</td>
<td>110-54-3</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>50-00-0</td>
</tr>
<tr>
<td>Benzene</td>
<td>71-43-2</td>
</tr>
<tr>
<td>Toluene</td>
<td>108-88-3</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>110-82-7</td>
</tr>
<tr>
<td>Hexane</td>
<td>110-54-3</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>50-00-0</td>
</tr>
<tr>
<td>Toluene</td>
<td>108-88-3</td>
</tr>
</tbody>
</table>

(a) Individual VOCs are generally sorted by magnitude of emissions (largest to smallest) for a reformer using natural gas-fired burners. Specific reformers might generate more or less of individual VOCs, such that the species and order presented above might differ.

The data sources for individual VOC species include the NPRI, NPI (1999), and US EPA (2008).

The reformer stack may also contain exhausts from other emission sources, such as the desulphurization vessel. Therefore, the reformer exhaust may contain other pollutants including methanol, trace metals, and hydrogen sulphide (H$_2$S), etc. These pollutants will differ depending on the type of chemical or fertilizer plant utilizing the reformer.

### 3.3 Boilers and Heaters

Boilers and heaters are used at a wide variety of facilities (industrial/commercial/institutional) and can use a number of different fuels including natural gas, coal, fuel oil, biomass (wood residue, bagasse), liquefied petroleum gas, a variety of process gases, and waste materials. The report focuses on boilers and heaters burning either natural gas or alternate gaseous fuel including refinery fuel gas, produced gas, etc.

Using the definition as per the Canadian Council of Ministers of the Environment document (CCME, 1998), a boiler is defined as:

> Any combustion equipment fired with fossil fuel, biomass or a by-product derived from fossil fuel, for the purpose of generating hot water or steam. This definition excludes equipment that:

1. has a thermal input capacity in excess of 73 megajoules per second (megawatts thermal) (this is approximately equal to 250 million British thermal units per hour) and is used by an electric power utility for the generation of electricity; or
2. recovers sensible heat from the exhaust of combustion equipment that is designed primarily for purposes other than to generate hot water or steam.

As per the CCME (1998) document, a heater is defined as:

Any combustion equipment fired with fossil fuel, or a by-product derived from fossil fuel, for the purpose of transferring heat directly or indirectly to material being processed, excluding equipment that comes under the definition of a “boiler”. A “heater” does not include any kiln or oven used for drying, baking, cooking, calcining or vitrifying; or any process used to chemically transform ore or intermediate products into bulk metallic products.

This section is limited to boilers and heaters with a heat input capacity of 10.5 GJ hr\(^{-1}\) (10 MMBtu hr\(^{-1}\)) or greater. This heat input rating is generally consistent with the US EPA’s New Source Performance Standards (NSPS), which set out emission standards, among other requirements, for “small” (i.e., between 10 to 100 MMBtu hr\(^{-1}\)) and “large” (i.e., in excess of 100 MMBtu hr\(^{-1}\)) boilers (Combustion Portal, 2016).

### 3.3.1 General Description

Industrial boilers are used by industry (e.g. chemical and fertilizer) to run processes, machinery or to produce heat or electricity. Most industrial boilers have a capacity between 10 and 250 million British thermal units (MMBtu hr\(^{-1}\)). Commercial and institutional boilers may also have similar capacities as industrial boilers; but, can also be smaller than the industrial units with heat input capacities below 10 MMBtu hr\(^{-1}\) (Combustion Portal, 2016). Within the context of this report, only industrial boilers are the main focus.

A process heater is an enclosed device using a controlled flame with the primary purpose of transferring heat indirectly to a process material or to a heat transfer material for use in a process unit instead of generating steam.

Figure 18 shows a process flow diagram of a typical industrial boiler system. As shown in the figure, combustion for heat generation begins in the boiler burner system and then heat is transferred to the water in the boiler. Boilers are available in a wide variety of designs and configurations. Boilers may use an economizer to preheat the process water before it is fed to the boiler using waste heat from the exhaust gas (US EPA, 2010).
Heaters are similar to boilers in that combustion for heat generation begins in the burner system. The heat is transferred – either directly or indirectly – to a process material, such as process air and feedstock, as is the case at chemical and fertilizer plants. In fact, the pyrolysis furnace and steam methane reformer are a specialized type of heater.

A variety of heater designs and configurations exist to heat different materials for various processes.

### 3.3.2 Associated Emissions

The combustion of gaseous fuels in boilers and heaters results in emissions of criteria air contaminants (CACs), most notably NOX, as well as various hazardous air pollutants (HAPs), including dioxins and furans, hydrochloric acid (HCl), and mercury (Hg). Fuel combustion in boilers and heaters also generates GHG emissions, mostly CO2, a product of complete combustion.

A complete list of major air emissions associated with boilers and heaters is presented in Table 17. Individual VOC species in Table 17 are distinguished by fuel type (US EPA, 2008).
### Table 17
Major air emissions from boilers and heaters

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>CAS Number</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Criteria Air Contaminants</strong></td>
<td></td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>630-08-0</td>
</tr>
<tr>
<td>Nitrogen Oxides</td>
<td>11104-93-1</td>
</tr>
<tr>
<td>Particulate Matter, PM (Total)</td>
<td>n/a</td>
</tr>
<tr>
<td>PM ≤ 10µm (PM\text{10})</td>
<td>n/a</td>
</tr>
<tr>
<td>PM ≤ 2.5µm (PM\text{2,5})</td>
<td>n/a</td>
</tr>
<tr>
<td>Sulphur Dioxide</td>
<td>7446-09-5</td>
</tr>
<tr>
<td><strong>Volatile Organic Compounds</strong></td>
<td>n/a</td>
</tr>
<tr>
<td><strong>Greenhouse Gases</strong></td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>124-38-9</td>
</tr>
<tr>
<td>Methane</td>
<td>74-82-8</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>10024-97-2</td>
</tr>
<tr>
<td><strong>Individual Volatile Organic Compounds(^{(a)})</strong></td>
<td></td>
</tr>
<tr>
<td>Natural Gas Combustion</td>
<td></td>
</tr>
<tr>
<td>Butane</td>
<td>106-97-8</td>
</tr>
<tr>
<td>Isomers of pentane</td>
<td>n/a</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>50-00-0</td>
</tr>
<tr>
<td>Pentane</td>
<td>109-66-0</td>
</tr>
<tr>
<td>Benzene</td>
<td>71-43-2</td>
</tr>
<tr>
<td>Propane</td>
<td>74-98-6</td>
</tr>
<tr>
<td>Toluene</td>
<td>108-88-3</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>110-82-7</td>
</tr>
<tr>
<td>Isomers of Hexane</td>
<td>n/a</td>
</tr>
<tr>
<td>Refinery Gas Combustion</td>
<td></td>
</tr>
<tr>
<td>Butane</td>
<td>106-97-8</td>
</tr>
<tr>
<td>Ethane</td>
<td>74-84-0</td>
</tr>
<tr>
<td>Propane</td>
<td>74-98-6</td>
</tr>
<tr>
<td>Propylene</td>
<td>115-07-1</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>50-00-0</td>
</tr>
<tr>
<td>Isobutane</td>
<td>75-28-5</td>
</tr>
<tr>
<td><strong>Other Contaminants</strong></td>
<td></td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>7647-01-0</td>
</tr>
<tr>
<td>PAHs(^{(b)})</td>
<td>n/a</td>
</tr>
<tr>
<td>Trace metals(^{(c)})</td>
<td>n/a</td>
</tr>
<tr>
<td>Dioxins &amp; furans</td>
<td>n/a</td>
</tr>
</tbody>
</table>

(a) Individual VOCs are generally sorted by magnitude of emissions (largest to smallest) for boilers and heaters. Specific boilers and heaters might generate more or less of individual VOCs, such that the species and order presented above might differ.

(b) PAHs include, but are not limited to: Benz(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Chrysene, Dibenzo(a,h)anthracene, Fluoranthene, Fluorene, and Phenanthrene.

(c) Trace metals include, but are not limited to: Mercury, Arsenic, Barium, Beryllium, Cadmium, Chromium, Cobalt, Copper, Lead, Manganese, Molybdenum, Nickel, Selenium, Vanadium, and Zinc.
The data sources for individual VOC and PAH species, along with the metals, include the US EPA (2008) database and Eastern Research Group (1998) document.

There are several numeric emission limits in place for boilers and process heaters such as: mercury (Hg), CO, filterable PM, HCl and air toxics. The quantities and compositions of CAC and GHG emissions emitted from a given boiler or heater depends upon the fuel source (e.g. natural gas, refinery fuel gas, produced gas, etc.). A further discussion on the types of fuel source used and their effects on air pollutants emitted by an industrial source is provided in Chapter 5.

### 3.4 Flares and Thermal Incinerators

Flares are control devices that destroy hydrocarbons or inorganic gases (e.g. ammonia) by combusting them. Flares are designed to route these gases to a burner tip and to burn these gases in an open flame (i.e. in open air). As a safety device, flares are considered the best control option when the heating value of the emission stream cannot be recovered due to uncertain or intermittent flow during process upsets or emergencies. They are primarily used for burning flammable gas released via pressure relief valves during unplanned, over-pressuring of plant equipment. During plant start-ups and shutdowns, flares are also used for planned combustion of gases over relatively short periods of time while equipment is being brought into production or being taken off-line. They are designed and operated to handle large fluctuations in flow rate and VOC content. At some plants with gaseous products (e.g. ethylene, ammonia, etc.), flares are connected on storage tanks and railcar loading areas to ensure that concentrated vapours are not released directly to atmosphere.

Thermal incinerators (or thermal oxidizers) are another choice of combustion devices typically used to destroy hydrocarbons or inorganic gases by burning them. Some types of PM (e.g. PM from incomplete combustion, coke, and carbon residue) can be destroyed in the incinerator (US EPA, 2016a). The fundamental difference between flares and thermal incinerators is the gases are burned in a combustion chamber rather than an open flame. Thermal incinerators are preferable to flares when halogenated or sulphur-bearing compounds are present. Three main factors critical to achieve effective design and operation of a thermal oxidizer are temperature, residence time, and turbulence. Although they can accommodate minor flow fluctuations, thermal incinerators are not well suited to streams with highly variable flow because of reduced residence time and poor mixing during increased flow conditions. Thermal incinerators are often used at chemical and fertilizer plants to control waste streams from individual sources (e.g. main process vent at an EO plant, distilled grain dryer at an ethanol plant, etc.) or a number of minor vent sources (US EPA, 1986; Brady and Pratt, 2007).
3.4.1 General Description

Flares

There are two general types of flares: elevated and ground flares. Both are used at chemical and fertilizer plants. Elevated flares use a stack to route the waste gases to a burner tip (aka flare tip). Ground flares route waste gases to a large enclosure or isolated area and burn the gases within the enclosed area.

In either case, combustion occurs by means of a diffusion flame (US EPA, 2000a). A diffusion flame has an inner core of waste gases, which is enveloped by a flame zone. Air diffuses toward the center of the waste gas flow, which ignites with the gases on contact with the flame zone. This establishes a stable flame zone around the gas core above the burner tip (US EPA, 2000a). This inner waste gas core is also heated by diffusion of hot combustion products from the flame zone (US EPA, 2000a).

To achieve good combustion and smokeless burning, flares use an assist gas or pressure at the flare tip to educt and mix air with the waste gas (Bader et al., 2011). Flares are typically described by the method of assist, which include non-assisted, steam-assisted, air-assisted, or pressure-assisted flares. Elevated flares can be designed as any of these four types, while ground flares are either non-assisted or pressure-assisted flares (US EPA, 2000a).

Non-assisted flares do not use an assist gas. They are used for waste gas streams where the gas will burn readily without producing smoke (US EPA, 2000a).

Air-assisted flares use forced air at the flare tip to: not only promote turbulent mixing; but also, to protect the design of the flare tip and induce combustion air into the flame (US EPA, 2012). Air-assisted flares are used for waste gas streams where the gas stream pressure is low and steam is not readily available (Bader et al., 2011).

Steam-assisted flares use high-pressure steam at the flare tip to perform the same primary functions as the air-assisted flare listed above. The high-pressure steam-assist has more momentum than the forced air-assist, so it is generally more effective at inducing air, promoting gas-air mixing, and ultimately achieving smokeless burning (Bader et al., 2011). Therefore, the steam-assisted flare design is preferred over the air-assisted flare design when steam is readily available.

Pressure-assisted flares are designed to use the vent stream pressure to create a high exit velocity stream (at or near sonic) at the flare tip to induce and mix the combustion air (Varner, 2012). The high exit velocity should be able to achieve a smokeless burn (Varner, 2012). Pressure-assisted flares can be used with vent streams with at least 15 psig (103.42 kPa) (Varner, 2012). They do not have the operational costs associated with supplying forced air or high-pressure steam to the flare tip.

Overall, whichever flare type is used in a particular application, it should be capable of achieving a destruction and removal efficiency (DRE) of 98% or greater for combustible constituents in the waste gas stream (US EPA, 2015).
Thermal Incinerators

Thermal incinerators are designed to raise the waste gas stream temperature to a desired reaction temperature and maintain the temperature for a given reaction time (referred to as residence time) to achieve the necessary DRE (US EPA, 2000b). For most VOC streams, thermal incinerators are designed to achieve a combustion temperature of 870°C for a 0.75 second residence time (US EPA, 2016a).

The basic type of thermal incinerator (often referred to as a direct flame incinerator) consists of a dilution air feed, a combustion chamber, and a stack. The dilution air feed is mixed with the waste gas stream prior to entering the combustion chamber. The stream then enters the combustion chamber and ignites in the direct flame. An auxiliary fuel source (e.g. natural gas) is used to sustain the flame while the waste gas stream enhances the burn. The combustion chamber, and a portion of the stack in some case, shapes the flow pathway, such that the waste gas will achieve the necessary residence time at the reaction temperature. The combustion chamber is also designed to promote mixing.

Some thermal incinerators are designed with waste gas preheaters and, if possible, a secondary energy recovery heat exchanger (US EPA, 2000b). These incinerators are referred to as recuperative incinerators, or recuperative thermal oxidizers. With the waste gas preheat, the gas will reach the reaction temperature more quickly, and higher DRE have been reported in relation to the basic direct flame incinerator (US EPA, 2016a; US EPA 2016b).

Regenerative thermal incinerators or oxidizers (RTO) are another type of thermal incinerator design. A schematic diagram of an RTO is presented in Figure 19.

![Schematic diagram of a two bed regenerative thermal oxidizer.](Source: Banks Engineering, 2007)

RTOs pass the waste gas stream through a hot ceramic bed to heat the stream to its ignition temperature prior to entering the combustion chamber (US EPA, 2000b). Only a relatively small amount of auxiliary fuel is added to the combustion chamber to increase the temperature and sustain the necessary residence time. After the combustion chamber, the hot exhaust gas stream is passed through a second ceramic bed to absorb its heat energy. The inlet bed will begin to cool, so after a certain amount of time, the flow direction is reversed, such that the waste gas stream now passes...
through the bed that had been collecting the heat energy (Banks Engineering, 2007). This cyclic process provides a very efficient unit, with up to 95% heat recovery (US EPA, 2000b).

RTOs can contain more than two beds to improve the DRE of the unit (Banks Engineering, 2007). In these systems, one bed will absorb the heat energy while the others heat the waste gas.

There are certain waste streams that should not be controlled with an RTO. Waste streams with particles or aerosols can foul the ceramic beds (Banks Engineering, 2007). This can be resolved by pre-treating the inlet waste stream to remove PM and prevent fouling (US EPA, 2016c). Waste streams containing chlorinated hydrocarbons or sulphur compounds can form acid droplets once the stream is cooled on the exhaust-side ceramic bed. Finally, rich waste gas streams (~25% of the lower explosive limit or greater) can raise the combustion chamber temperature to levels that can damage the refractory (Banks Engineering, 2007).

Direct flame thermal incinerators and recuperative incinerators can achieve 98% - 99.99% DRE or greater for VOCs (US EPA, 2016a; US EPA, 2016b). RTOs are typically limited to 95% - 99.5% DRE for VOCs (Banks Engineering, 2007). At chemical plants, US EPA (2016a) reports that thermal incinerators can control between 50% and 99.9% of PM10 emissions.

3.4.2 Associated Emissions

Flares and thermal incinerators emit the portion of hydrocarbons or inorganic gases that remain unburned (i.e., not destroyed and removed). Therefore, the associated emissions are highly dependent on the waste gas stream fed to the flare or incinerator.

Greenhouse gases, mainly CO2, as well as CO and NOX will be generated in the combustion process. If sulphur compounds are present in the waste gas stream, flares and incinerators will emit SO2.

Flares and thermal incinerators can also emit partially reacted hydrocarbons that have been altered from the inlet waste gas stream (US EPA, 2015).

In the case of flares, if there is an oxygen deficiency and if the carbon particles are cooled below their ignition temperature, soot formation (i.e., PM emissions) will occur (US EPA, 2000a).

A list of major air emissions associated with flares and thermal incinerators is presented in Table 18. Individual VOC species in Table 18 were distinguished by waste gas source using data taken from the NPRI database, the Chemistry Industry Association of Canada (CIAC) National Emission Reductions Masterplan (NERM) database, and the US EPA (2008) database.
### Table 18  Major air emissions from flares and thermal incinerators

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>CAS Number</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Criteria Air Contaminants</strong></td>
<td></td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>630-08-0</td>
</tr>
<tr>
<td>Nitrogen Oxides</td>
<td>11104-93-1</td>
</tr>
<tr>
<td>Particulate Matter, PM (Total)</td>
<td>n/a</td>
</tr>
<tr>
<td>PM ≤ 10µm (PM$_{10}$)</td>
<td>n/a</td>
</tr>
<tr>
<td>PM ≤ 2.5µm (PM$_{2.5}$)</td>
<td>n/a</td>
</tr>
<tr>
<td>Sulphur Dioxide</td>
<td>7446-09-5</td>
</tr>
<tr>
<td>Volatile Organic Compounds</td>
<td>n/a</td>
</tr>
<tr>
<td><strong>Greenhouse Gases</strong></td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>124-38-9</td>
</tr>
<tr>
<td>Methane</td>
<td>74-82-8</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>10024-97-2</td>
</tr>
<tr>
<td>**Individual Volatile Organic Compounds$^{(a)}$</td>
<td></td>
</tr>
<tr>
<td><strong>Chemical Plant Flare</strong></td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td>74-85-1</td>
</tr>
<tr>
<td>Benzene</td>
<td>71-43-2</td>
</tr>
<tr>
<td>Propylene</td>
<td>115-07-1</td>
</tr>
<tr>
<td>Isomers of butene</td>
<td>n/a</td>
</tr>
<tr>
<td>Ethyl chloride</td>
<td>75-00-3</td>
</tr>
<tr>
<td>Methanol</td>
<td>67-56-1</td>
</tr>
<tr>
<td>Ethylene oxide</td>
<td>75-21-8</td>
</tr>
<tr>
<td>1-butene</td>
<td>106-98-9</td>
</tr>
<tr>
<td>Toluene</td>
<td>108-88-3</td>
</tr>
<tr>
<td>Styrene</td>
<td>100-42-5</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>107-13-1</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>67-63-0</td>
</tr>
<tr>
<td>Carbolic acid</td>
<td>108-95-2</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>110-82-7</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>50-00-0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>64-17-5</td>
</tr>
<tr>
<td>Propylene oxide</td>
<td>75-56-9</td>
</tr>
<tr>
<td>Xylenes</td>
<td>1330-20-7</td>
</tr>
<tr>
<td>Xylene base acids</td>
<td>n/a</td>
</tr>
<tr>
<td>Acetylene</td>
<td>74-86-2</td>
</tr>
<tr>
<td>Methyl chloride</td>
<td>74-87-3</td>
</tr>
<tr>
<td>Butyraldehyde</td>
<td>123-72-8</td>
</tr>
<tr>
<td>Ethyl acrylate</td>
<td>140-88-5</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>75-07-0</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>75-01-4</td>
</tr>
<tr>
<td>n-butyl alcohol</td>
<td>71-36-3</td>
</tr>
<tr>
<td><strong>Ethylene Plant Flare</strong></td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td>74-85-1</td>
</tr>
<tr>
<td>Benzene</td>
<td>71-43-2</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>106-99-0</td>
</tr>
<tr>
<td>Propylene</td>
<td>115-07-1</td>
</tr>
<tr>
<td>Butane</td>
<td>106-97-8</td>
</tr>
<tr>
<td>Propane</td>
<td>74-98-6</td>
</tr>
<tr>
<td>Isomers of butene</td>
<td>n/a</td>
</tr>
<tr>
<td>Acetylene</td>
<td>74-86-2</td>
</tr>
<tr>
<td>Toluene</td>
<td>108-88-3</td>
</tr>
<tr>
<td>1-pentene</td>
<td>109-67-1</td>
</tr>
<tr>
<td>Styrene</td>
<td>100-42-5</td>
</tr>
<tr>
<td>Pentane</td>
<td>109-66-0</td>
</tr>
<tr>
<td>Pollutant</td>
<td>CAS Number</td>
</tr>
<tr>
<td>---------------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>Xylenes</td>
<td>1330-20-7</td>
</tr>
<tr>
<td>Isomers of butene</td>
<td>n/a</td>
</tr>
<tr>
<td>Ethylene</td>
<td>74-85-1</td>
</tr>
<tr>
<td>1-hexene</td>
<td>592-41-6</td>
</tr>
<tr>
<td>Hexane</td>
<td>110-54-3</td>
</tr>
<tr>
<td>Butane</td>
<td>106-97-8</td>
</tr>
<tr>
<td>1-butene</td>
<td>106-98-9</td>
</tr>
<tr>
<td>Propane</td>
<td>74-98-6</td>
</tr>
<tr>
<td>Ethane</td>
<td>74-84-0</td>
</tr>
<tr>
<td>Propane</td>
<td>74-98-6</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>50-00-0</td>
</tr>
</tbody>
</table>

(a) Individual VOCs are generally sorted by magnitude of emissions (largest to smallest) for flares for general chemical manufacturing and a couple specific types of chemical plants. Specific flares will generate more or less of individual VOCs, such that the species and order presented above might differ.

The emissions from a particular flare or thermal incinerator will heavily depend on the composition of the waste gas stream. The above table is only intended to provide an indication of the type of pollutants that can be emitted from certain chemical and fertilizer plants. It is not an exhaustive list of all air emissions from flares and incinerators at every chemical and fertilizer plant.

### 3.5 Cooling Towers

Cooling towers are devices used to extract heat from process streams and reject the heat to atmosphere through water evaporation. At chemical and fertilizer plants, cooling towers are used for various process units, such as reactors, fractionators / evaporators, and condensers.

#### 3.5.1 General Description

Cooling towers provide necessary process cooling and are integral components to chemical and fertilizer plants. They are basic heat exchangers operating on a wet or dry basis, capable of dissipating large heat loads to the atmosphere.

Cooling towers can be classified either as wet or dry cooling towers. Wet cooling towers direct a portion of a warm recirculating water stream entering the tower to come into contact with and evaporate into air passing through the tower. This significantly lowers the temperature of the remaining water stream as heat is liberated during evaporation and becomes absorbed into the air. The non-evaporated water is collected in tower basins and recycled back into the industrial system to recover more process heat.

Dry cooling towers represent extended type radiator cooling. However, wet cooling towers are more commonly used in industrial applications because the cooling potential of a wet surface is much better than a dry one. Therefore, the report will focus on air emission releases from wet cooling towers.

The general configuration of cooling tower is presented in Figure 20.
Heat is extracted from a process stream using a fluid (e.g. water) in a heat exchanger. The heated fluid is sent to cooling tower to reject the heat to atmosphere. The method of heat rejection depends on the cooling towers design.

Direct contact cooling towers are designed to remove the process heat collected in water by spraying this water over a packing material called “fill” (US Department of Energy, 2011). Air flows through the fill (either counter-current or cross-current to water flow) to come in direct contact with the water to evaporate it and transport the heat and water vapour out of the tower. The cooled water is collected in a sump at the bottom of the cooling tower and then recirculated back to the heat exchanger to collect more process heat.

Indirect contact cooling towers are designed to remove the process heat collected in a fluid, typically water or a glycol mixture, by circulating it through a coil in the cooling tower (Cooling Tower Institute (CTI), 2016). A separate stream of cooling water is sprayed over the coil to reject the heat. Again, air flows across the coil and contacts the sprayed water to provide evaporative cooling and to transport the heat and water vapour out of the tower. The cooled water spray is collected in a sump at the bottom of the cooling tower and then recirculated to the top of the tower. In this case, the fluid collecting the heat from the process is not directly exposed to the atmosphere.

Cooling towers are further classified as either natural or mechanical draft towers, to signify whether or not fans are used to force air through the tower. Most chemical and fertilizer plants use mechanical draft towers.
In addition to evaporation, some cooling water is lost as water droplets that become entrained in the airstream and are carried out of the tower (referred to as drift). To prevent drift losses, cooling towers are equipped with “drift eliminators”, located above the water spray manifold. The drift eliminators are designed to capture large water droplets entrained in the cooling tower air stream. The eliminators prevent the droplets and mist from escaping the cooling tower by causing the droplets to change direction and lose velocity at impact on the blade walls and fall back into the tower. Efficient drift eliminators will keep drift losses to less than 0.001% of the re-circulating water flow rate.

### 3.5.2 Associated Emissions

Dissolved solids (i.e., impurities) in the drift are classified as particulate matter emissions (US EPA, 1995b).

In addition, VOC emissions are generated from cooling towers, which result from hydrocarbons in the process stream leaking into the recirculating fluid at the heat exchanger (Environment Canada, 2013).

A list of major air emissions associated with cooling towers is presented in Table 19.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>CAS Number</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Criteria Air Contaminants</strong></td>
<td></td>
</tr>
<tr>
<td>Particulate Matter, PM (Total)</td>
<td>n/a</td>
</tr>
<tr>
<td>PM ≤ 10µm (PM_{10})</td>
<td>n/a</td>
</tr>
<tr>
<td>PM ≤ 2.5µm (PM_{2.5})</td>
<td>n/a</td>
</tr>
<tr>
<td><strong>Volatile Organic Compounds</strong></td>
<td>n/a</td>
</tr>
<tr>
<td><strong>Other Contaminants</strong></td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>7664-41-7</td>
</tr>
</tbody>
</table>

The individual VOCs emitted from cooling towers depends entirely on the process stream being cooled. At certain fertilizer plants, it is reasonable to expect that some ammonia will also be emitted if an ammonia process stream is cooled.
4.0 Air Pollution Prevention and Control Technologies

Pollution prevention is the use of any processes, practices, materials, products, energy, etc. that avoids or minimizes the creation of pollutants or wastes at the source as a preferred approach over end-of-pipe treatment. With less pollution produced, there are fewer hazards posed to public health and/or the environment.

Pollution prevention is reflected in the selection of appropriate air pollution emission control technology. This choice depends upon the pollutant to be removed and the control efficiency required. It also inherently recognizes it is more cost effective and simpler to design emission control equipment into production equipment at the time of initial construction than it is to engage in future retrofits.

The three general ways pollutant emissions can be reduced are through: 1) process improvements, 2) combustion practices and controls, and 3) add-on pollution control technologies (Ramboll Environ, 2016). It should be noted that emission reductions through process improvements are site and plant specific. Therefore, it is impossible to address this aspect within the context of the report. The following sections instead focus on summarizing and briefly evaluating the most commonly used combustion controls and add-on air pollution control technologies currently applied in the chemical and fertilizer sectors. A more focused discussion occurs in subsequent sections regarding currently utilized air pollution prevention and control technologies.

1) Process Improvements

Process improvements such as on-line optimization, efficiency maximizations, process debottlenecking, etc. can result in a decrease of air emissions from a given chemical or fertilizer plant. As mentioned above, the appropriate process improvements applied to any plant is uniquely adapted and customized to the specific industrial site. However, the use of process improvements as the sole means of achieving air pollution reductions is unable to obtain the same level of reductions associated with applying proper air pollution prevention and control technology.

2) Combustion Practices and Controls

Commonly used combustion control practices or techniques frequently used in conjunction with commercially available combustion control technology include the following.

- Good Combustion Practices (GCP): GCPs include combustor design elements and operational strategies intended to control the amount and distribution of excess air in the combustion zone to ensure that enough oxygen is present for complete combustion.
- Oxidation Temperature Minimization (OTM): OTM techniques intended to reduce NOX emissions by reducing oxidation temperatures in the combustion zone include: flue gas recirculation (FGR), staged combustion, overfire air injection (OFA), and water/steam injection.
- Burner Technologies: Conventional burners were designed to inject the combined fuel and air/oxygen mix at the same place within the burner. By comparison, the commercially available low NOX burners or LNBs are designed to modify the means of introducing air and fuel into the burner allowing for delayed mixing. This approach results in a reduction in the availability of oxygen and a lowering of the peak flame temperature. These design changes in LNBs allow for controlled mixing of combustion air and fuel to reduce maximum flame temperatures; thereby, greatly minimizing NOX formation as compared to conventional burners.
The design of LNBs differs significantly from manufacturer to manufacturer and may incorporate one or more OTM techniques in the burner design. Nowadays, LNB designs that incorporate OTM techniques do not explicitly distinguish these techniques such as explicitly stating a low NOX burner is being supplied with flue gas recirculation (FGR). Instead, a low NOX burner incorporating FGR is considered part of the low NOX concept in burner technology, and is collectively termed LNB. For this reason, there are numerous variations of the LNB concept in addition to variations in the burner design itself. Burner manufacturers and vendors assign the term LNB, and occasionally ultra-low NOX burners (ULNB), to burner technologies and associated OTM techniques designed to meet reduced NOX emission levels ranging from 30 ppm to 4 ppm as discussed in subsequent sections of this chapter. Thus, the term LNB is assigned to a moving scale of NOX levels over time and regulatory geography.

For this study, the term LNB is used to refer to the current state of next generation, commercially available low NOX burners using any combination of LNB, GCP and OTM techniques designed to meet regulatory standards, which conforms to burner manufacturer convention. It does not at any time refer to or encompass traditional, conventional low NOX burner technology of the 1980’s or 1990’s.

3) Add-On Pollution Control Technologies

The commonly used add-on pollution control technologies include the following.

- **Selective Catalytic Reduction (SCR):** SCR is one of the most commonly used secondary methods to reduce or eliminate the emissions of NOX from industrial sources. In the SCR process, a reagent (usually NH₃) reacts with NOX to form N₂ and H₂O. SCR utilizes a catalyst matrix to increase the NOX removal efficiency, which allows the reduction reaction to take place at reduced temperatures compared to Selective Non-Catalytic Reduction (SNCR) discussed below (i.e., 315ºC to 375ºC for SCR, as opposed to 870ºC to 1,150ºC for SNCR).

  SCR technology can be used separately or in combination with other NOx combustion control technologies such as low NOX burners (LNB) and natural gas reburn (NGR). It can also be designed to provide NOX reductions year-round or seasonally, such as during summer months, when ozone concerns are greatest.

  SCR is discussed in more detail in Section 4.2.

- **Selective Non-Catalytic Reduction (SNCR):** Like SCR, SNCR is one of the most commonly used secondary methods to reduce or eliminate the emissions of NOX from industrial sources. In the SNCR process, ammonia is mixed with the exhaust from the combustion device or other industrial equipment and the NOX in the exhaust is minimized by reacting with the introduced ammonia to form N₂ and H₂O. As the name implies, no catalyst is used for the SNCR technology.

  Like SCR, SNCR technology can be used separately or in combination with other NOx combustion control technologies such as low NOX burners (LNB) and natural gas reburn (NGR). It can also be designed to provide NOX reductions year-round or seasonally, such as during summer months, when ozone concerns are greatest.
SNCR is discussed in more detail in Section 4.3.

- **Non-Selective Catalytic Reduction (NSCR):** NSCR is an add-on NOX control technology for exhaust streams with low O2 content. NSCR uses a three way catalyst to reduce NOX, CO, and HC to N2, CO2, and H2O. Because the CO and HC will more readily react with O2 than NOX, there must be little O2 in the exhaust (between 0.5% and 4%, depending upon the system). Excess oxygen is removed by the catalyst or, in some designs, an afterburner, which necessitates injecting additional hydrocarbons (i.e., natural gas) to act as the reducing agent.

- **Oxidation Catalysts (OC):** OC are processes that oxidize compounds using catalysts. Common applications involve oxidation of organic compounds by oxygen in the air. Catalytic oxidation does not rely on the introduction of additional chemical reagents to promote the desired reactions. The activation energy required for the oxidation reaction between O2, CO, and VOCs to proceed is reduced in the presence of a catalyst. Products of combustion are introduced into a catalytic bed, with the optimum temperature range for these systems being between 370°C and 600°C. The catalyst oxidizes CO to CO2, and VOCs to CO2 and H2O; but, it also can promote other, less desirable, oxidation reactions such as NH3 to NOX and SO2 to SO3. Consequently, the presence of an oxidation catalyst can cause emissions of other pollutants to increase, and therefore its design needs to be carefully considered.

- **EMx:** The EMx (formerly SCONOx) system is an add-on catalyst control device that reduces emissions of multiple pollutants. EMx control technology is provided by Emerachem, LLC (formerly Goal Line Environmental Technologies). EMx utilizes a single catalyst that significantly reduces SOX and PM emissions; while at the same time, reduces CO, VOC and NOX, by converting them to CO2, H2O and N2. EMx is considered a Lowest Achievable Emission Rate (LAER) technology for NOX abatements (RJ Mann & Associates Inc., 2017). EMx is capable of achieving NOX levels below 1.5 ppm.

The system does not use NH3, and operates most effectively at temperatures ranging from 150°C - 370°C. Operation of EMx requires natural gas, water, steam, electricity and ambient air, and no special reagent chemicals or processes are necessary. Steam is used periodically to regenerate the catalyst bed and is an integral part of the process.

- **Cyclone Separator:** A cyclone separator, also called simply a “cyclone”, is a method of removing PM from an air, gas or liquid stream via vortex separation that does not involve the use of filters. Cyclones provide a low-cost, low-maintenance method of removing large particulate matter from gas streams. Because cyclone operating costs and collection efficiency of fine PM are low, they are not sufficient on their own to meet stringent emission standards; but, are often used as “pre-cleaners” to remove larger particulate matter (e.g. >2.5 µm) prior to the exhaust reaching the primary control device such as an electrostatic precipitator (ESP) or fabric filter.

Actual collection efficiencies of a cyclone vary greatly based on the design of the cyclone, operating flow rate, and various properties of the gas and PM. The control efficiency range for a typical cyclone is estimated at 70% to 90% for PM, 30% to 90% for PM10, and 0% to 40% for PM2.5 (US EPA, 2003a).
• Electrostatic Precipitator (ESP): ESPs are capable of removing all size of particulate matter including PM, PM$_{10}$, and PM$_{2.5}$; along with HAPs that are in particular form, such as most metals. They remove PM from an exhaust stream by imposing an electrical charge on the particles and then attracting them to an oppositely charged plate. The dust collected on the charged plates is periodically removed by vibrating or rapping of the plates.

An ESP’s collection efficiency depends on several factors with ESP size being the most important, since size determines the amount of treatment time. In other words, the longer time a particle spends in an ESP, the greater its chance of being collected. Current, commercially available ESPs have design efficiencies between 99% and 99.9%; while older ones from the 1980’s or 1990’s have operating efficiencies of 90% to 95% (US EPA, 2003b).

• Fabric Filter: Also referred to as “baghouses”, due to the configured fabric bags used, fabric filters use various types of materials (generally fabrics) to trap PM (for example submicron size) while the gas passes through the voids in the material. PM particles form a more or less porous cake on the surface of the fabric. It is normally this cake that actually does the filtration. Depending on the performance of the fabric filter system, the manner in which the excess PM is removed from the fabric becomes a critical factor. If the dust cake is not adequately removed, the pressure drop across the system will increase to an excessive amount. If too much of the cake is removed, excessive dust leakage will occur while the fresh cake develops. In either case, the excess dust required to be removed from the fabric bags is periodically done by either shaking, blowing jets of air, or using sonic horns.

In the context of chemical and fertilizer plants, baghouses are generally considered a better choice over ESPs for control of PM, PM$_{10}$, and PM$_{2.5}$. The reason is an ESP required to achieve the same level of fine PM control as a fabric filter or baghouse typically requires a very large plate area resulting in a much higher cost. Also, a baghouse proves in most cases to be much more reliable than an ESP because of the availability of different fibres/fabrics, improvements in the design of the bag fabrics, and better cleaning techniques.

Fabric filter control is discussed in more detail in Section 4.5.

• Wet Scrubber: Wet scrubbers can be used to remove PM, inorganic gases or VOC.

PM control using wet scrubbers involves contacting or scrubbing the gases with a liquid, typically water or an aqueous solution, to capture PM (> 0.5 to 10 µm depending upon the configuration). Another way wet scrubbers are used to control PM is to increase the size of aerosol to facilitate capture in another control device. Depending on the design and application, wet scrubbers have collection efficiencies ranging from 50% to 95% for PM. It should be noted that spray tower scrubbers are not generally used for fine PM applications.

When used as control devices for inorganic gases, wet scrubbers can achieve removal efficiencies ranging from 95% to 99%.

Wet scrubbers can also be used to remove VOCs; however, the removal efficiency depends on each pollutant-solvent system and the type of absorber used. Most absorbers have removal efficiencies in excess of 90% with most having the ability to achieve efficiencies of greater than 99%. Lower control efficiencies represent flows containing relatively insoluble
compounds at low concentrations; while, the higher efficiencies are for flows which contain readily soluble compounds at high concentrations.

Wet scrubbers are discussed in more detail in Section 4.4.

- **Flue Gas Desulphurization (FGD):** FGD or SO₂ scrubbing process is a set of technologies used to remove SO₂ from exhaust flue gases typically using a calcium- or sodium-based alkaline reagent. The reagent is injected in the flue gas in a spray tower or directly into the exhaust duct. The SO₂ is absorbed, neutralized and/or oxidized by the alkaline reagent into a solid compound, either calcium or sodium sulphate. The resulting solid (i.e. particulate matter) is removed from the waste gas stream using downstream particulate control equipment.

  Current, commercially available FGD units are capable of reduction efficiencies easily in in excess of 90% for both wet and dry designs (US EPA, 2003i).

- **Flares and Thermal Incinerators:** Flares and thermal incinerators (or thermal oxidizers) are control devices that destroy hydrocarbons (e.g. VOCs) or inorganic gases (e.g. ammonia) bycombusting them. The main difference between flares and thermal incinerators is the gases are burned in a combustion chamber, rather than an open flame. Both flares and thermal incinerators are capable of achieving destruction efficiencies of over 99% depending on system requirements and characteristics of the contaminated stream.

  Flares and thermal incinerators are discussed in more detail in Section 4.6.

Table 20 presents various commercially available technologies with examples of documented use at some chemical and fertilizer plants. Table 20 does not represent a comprehensive list of control technologies; does not identify the only control options available; does not epitomize best available control technology; or denote a precedent of the only types of air pollution prevention or control technology to be applied to chemical and fertilizer plants. The table merely contains a list of documents on chemical and fertilizer plants that reference commonly used control technologies at these plants. The intent of Table 20 is to provide an indication of successfully implemented, commercially-available control technologies at these plants. All of the various technologies can be successfully applied to a wide range of applications and not solely to the plant types or emission sources identified in Table 20.

A detailed description of the most commonly used control technologies is described in detail after Table 20.
Table 20  Air pollution control technologies with documented use at chemical and fertilizer plants.

<table>
<thead>
<tr>
<th>Air Pollution Control</th>
<th>Primary Pollutants Controlled</th>
<th>Examples of Applicable Plant Types</th>
<th>Examples of Applicable Emission Sources</th>
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<td>Ethylene</td>
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<td>b</td>
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<tr>
<td></td>
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<td>Polyethylene</td>
<td>PE Finishing Stack</td>
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<td></td>
<td></td>
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<td></td>
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<tr>
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<td>Main Process Vent</td>
<td>m</td>
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<tr>
<td>Selective Non-catalytic Reduction</td>
<td>NOₓ</td>
<td>All Plants</td>
<td>Boilers</td>
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<td></td>
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<td></td>
<td></td>
<td>Ammonia, Methanol, Hydrogen</td>
<td>Reformer Stack</td>
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</tr>
<tr>
<td>Selective Catalytic Reduction</td>
<td>NOₓ</td>
<td>All Plants</td>
<td>Boilers</td>
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<td>All Plants</td>
<td>Process heaters</td>
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<td>Ethylene</td>
<td>Pyrolysis Furnace</td>
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<td>Nitric Acid</td>
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<tr>
<td>Thermal incineration</td>
<td>PM</td>
<td>Ethylene</td>
<td>Pyrolysis Furnace / Decoking Vent</td>
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<td>Ethylene Oxide / Ethylene Glycol</td>
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<td>Wet Scrubber</td>
<td>Ammonia, PM, VOC</td>
<td>Ethylene</td>
<td>Pyrolysis Furnace / Decoking Vent</td>
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<tr>
<td></td>
<td></td>
<td>Urea</td>
<td>Urea Synthesis Process</td>
<td>f</td>
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</tbody>
</table>

<sup>1</sup> Extended absorption reduces NOₓ emissions by increasing absorption efficiency and is achieved by either installing a single large tower, extending the height of an existing absorption tower, or by adding a second tower in series with the existing tower. Extended absorption can be applied to new and existing plants.
<table>
<thead>
<tr>
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<tr>
<td></td>
<td></td>
<td>Urea</td>
<td>Vent</td>
<td>f</td>
</tr>
</tbody>
</table>

a) Zimmermann, H.; Walzl, R., 2005.
c) NOVA Chemicals (Canada) Ltd., September 2012.
d) Texas Natural Resource Conservation Commission, 1996.
f) European Fertilizer Manufacturers’ Association, 2000b.
g) European Fertilizer Manufacturers’ Association, 2000c.
h) European Fertilizer Manufacturers’ Association, 2000d.
m) US EPA, 1986.
n) US EPA, 2003d.
o) US EPA, 2003e.

### 4.1 Burner Technologies

In conventional burners, the combined fuel and air/oxygen mix is entirely injected at the same place. The resulting flame is then composed of a hot and oxidising primary zone located at the flame root and a colder secondary zone located at the flame end. The primary zone generates most of the NO, which increases exponentially with temperature, whereas the contribution of the secondary zone is rather modest (IPCC, 2006). Low NOX burner (LNB) technologies modify the means of introducing air and fuel to delay the mixing, reduce the availability of oxygen, and reduce the peak flame temperature. As explained previously, LNBs may incorporate a combination of the NOX combustion control techniques in a single burner, for example low excess air, off-stoichiometric combustion, and/or combustion gas recirculation.

The level of NOX reduction that can be achieved by various combustion sources at a chemical or fertilizer plant such as pyrolysis furnaces, steam methane reformers, boilers and heaters, etc. depend on many factors including the size and type of application, range of operating conditions, fuel type, fuel quality, and burner control systems. Therefore, LNBs have been developed by a large number of manufacturers targeting particular emission limits. Based on a scan of NOX emission limits applied across a variety of combustion equipment at different chemical and fertilizer plants, the NOX emission limits are typically found to be 30 ppm or lower.

The commercially available LNBs from a large number of manufacturers are capable of targeting emission limits less than 30 ppm. Current LNB technologies are significantly improved as compared to the older designs of the 1980s and 1990s that were only able to achieve NOX emission levels in excess of 30 ppm. These older, conventional burner technologies would no longer qualify as LNBs.
The operating principle of LNBs is to maintain adequate combustion process efficiency, which means complete combustion of the fuel, a stable flame, and stable operation of the burner (BMA, 2016). LNBs design details differ significantly from manufacturer to manufacturer, and is focused on achieving a specified NOX concentration (ppm) level.

There is no strict definition of an emission level associated with the burner technology defined as LNBs or ULNBs. For this report, the emissions level for LNBs and ULNBs conform with the definition used by the Boiler Operators and Facility Managers (2010):

- **LNBs** achieve 30 ppm NOX or less and, at a minimum, have the following characteristics / design features:
  - Use FGR\(^2\)
  - Can maintain 3 to 5% excess O\(_2\) with good controls
  - Offer good turndown (> 8:1) and flame stability

- **ULNBs** achieve 7 to 15 ppm and, at a minimum, have the following characteristics / design features:
  - Use FGR, adjusted fuel/air ratios, and staging
  - May have (in some designs):
    - Higher excess O\(_2\) (anywhere from 5 to 9%)
    - Larger combustion air fans (15% to 50% increase in required HP)
    - Reduced turndown (3:1 or 4:1) and flame stability.

LNBs and ULNBs have been successfully used as a control devices in pyrolysis furnaces, steam methane reformers, boilers, and process heaters at chemical and fertilizer plants as discussed below. It is important to note that both LNBs and ULNBs can be used in combination with other technologies including other combustion control technologies and add-on technologies such as SCR and SNCR. These technologies (SCR and SNCR) are discussed in Sections 4.2 and 4.3, respectively.

### 4.1.1 Process Description

The three mechanisms of NOX formation that result from fuel combustion are as follows (HPAC Engineering, 2016; BOFM, 2010):

1. **Thermal NOX** is created by the reaction of atmospheric oxygen and nitrogen at elevated temperatures. Thermal NOX increases exponentially with temperature. The key to limiting thermal NOX is to reduce peak flame temperature and restrict oxygen availability and exposure at peak temperature. Thermal NOX is the largest contributor to overall NOX emissions.

2. **Prompt NOX** occurs through early reactions between nitrogen, oxygen and hydrocarbon radicals. The reduction in prompt NOX has been achieved by manufacturers by minimizing the formation of sub-stoichiometric regions in the flame.

3. **Fuel-bound NOX** is inherent in fuel and cannot be reduced, except via post-combustion processes. Fuel-bound NOX is not typically a concern with high-quality gaseous fuels like natural gas or propane, which normally have no organically-bound nitrogen. Fuel NOX may be

---

\(^2\) In FGR, a portion (10% to 30%) of the flue gas exhaust is recycled back into the main combustion chamber by removing it from the effluent gas stream and mixing it with the secondary air entering the windbox that supplies the burners. Rerouting the flue gas to mix with the combustion air brings about a reduction in the flame temperature; therefore, addressing the dormation of combustion NOX.
important when oil, for example residual fuel oil, coal, or waste fuels are used, which may contain significant amounts of organically-bound nitrogen.

LNBS control the mixing of fuel and air in a pattern that keeps the flame temperature low and dissipates the heat quickly. To accomplish this, LNBS provide a stable flame that has several zones serving different functions. For example, the first zone can be primary combustion; the second zone can be Fuel Reburning (FR) with fuel added to chemically reduce NOX; and the third zone can be the final combustion in low excess air to limit the temperature (US EPA, 1999).

An example of a typical LNBS utilizing FGR for industrial-style boiler is shown in Figure 21.

Figure 21   Typical low-NOX induced FGR flow for industrial-style boiler

4.1.2   Level of Air Pollution Control

The NOX emission levels achievable for LNBS are a function of design and operating factors. In practice, the design of the burner technology depends upon the level of NOX that needs to be achieved.

The output of new burner technologies range from 12 to 420 MMBtu hr⁻¹, while delivering NOX emissions well below 30 ppm, and as low as 9 ppm or less. (BMA, 2016).

Pyrolysis furnaces and steam methane reformers are unique in design which requires the use of specialized burners to control NOX emissions. Burner technology applied to these units has evolved since the 1970s with a progression from raw gas and oil fired burners to LNBS and ULNBs. LNBS currently available for both new and retrofitted pyrolysis furnaces or steam methane reformers can achieve NOX emissions between 10 and 15 ppm. For example, a steam methane reformer at a fertilizer
plant in New Orleans replaced its LNB which was emitting 26 ppm of NOX with an ULNB. The new ULNB lowered the NOX emission level from 26 ppm to 10 ppm.

For boilers and heaters found at chemical and fertilizer plants, the current state of next generation, commercially available LNBs can achieve NOX emissions of 9 ppm or less for both new and retrofitted units over 10.5 GJ hr⁻¹ with little to no additional cost or performance penalty.

The US EPA’s RACT/BACT/LAER Clearinghouse (RBLC) confirms this by providing information on the final best available control technology (BACT) determinations and the installed air pollution control technologies. The RBLC clearly demonstrates new or modified non-utility boilers and heaters in attainment areas show a trend of installing next generation LNBs that are achieving NOX emission levels of 9 ppm or less. Some industrial sites are achieving even lower emissions by installing add-on control technologies such as an SCR.

4.1.3 Minimum, Average and Maximum Amount of CACs Emitted

The information presented in this section is intended to provide a reasonable upper- and lower-bound and average quantity of CACs emitted; not the unqualified maximum and minimum quantity of CACs emitted, nor the actual mean quantity for this emission source across the industry.

ULNBs are designed to achieve average NOX levels of 9 ppm or less. They do have the ability to achieve levels as low as 5 ppm as demonstrated in the boiler requirements of the California’s San Joaquin Valley Air Pollution Control District. They require new and modified boilers with an input of 20 MMBtu h⁻¹ or greater to achieve a NOX emission limit of 5 ppm (BMA, 2016).

The lower the NOX emission level to be achieved, the more FGR must be added to the combustion-air supply. Typically, 15% to 20% FGR would be required to attain a NOX emission level of 30 ppm emissions. 20% to 25% FGR would be required to reach a NOX emission level of 9 ppm (HPAC Engineering, New Trends in Burner Technology, 2013).

Based on the definition for LNBs applied in this study, the maximum amount of NOX that could potentially be emitted from an LNB is 30 ppm. For example, a 100 MMBtu hr⁻¹ natural gas fired boiler, the average emission levels for a base (uncontrolled) burner, and LNB (with FGR) is reported to be approximately 85 ppm and 26 ppm, respectively (US EPA 1995b). However, there is little to no justification for using LNBs emitting NOX at a maximum level of 30 ppm given the vast choice of LNBs and ULNBs designed to emit NOX well below that level.

4.1.4 Minimum, Average and Maximum Amount of Associated GHGs Emitted

The information presented in this section is intended to provide a reasonable upper- and lower-bound and average quantity of GHGs emitted; not the unqualified maximum and minimum quantity of GHGs emitted, nor the actual mean quantity for this emission source across the industry.

The major GHG produced by chemical and fertilizer plants is carbon dioxide (CO₂). During combustion, carbon in the fuel oxidizes through a series of reactions to form CO₂. One of the best ways to minimize CO₂ production is fuel switching to use ones that produce less GHGs. For example, coal has much higher GHG emissions than natural gas with an average emission factor of 53.06 kg CO₂
MMBtu$^{-1}$ (US EPA, 2008). Fuel switching can reduce GHG emissions, particularly CO$_2$, on an average of 25% to 30%.

Another method used to decrease GHG emissions is to improve the efficiencies of combustion equipment such as pyrolysis furnaces, methane steam reformers, boilers and heaters, etc. Please note: all LNB designs include some degree of FGR use and excess air (i.e. O$_2$). When FGR is used, boiler efficiency may decrease, typically in the range of 0.25% to 1%, depending on the amount of FGR added. (HPAC Engineering, New Trends in Burner Technology, 2013). Also, it is estimated that for every 2% increase in O$_2$, there is a 1% loss in efficiency. This does not prevent the minimization of both NO$_X$ and CO$_2$ emissions from current burner technology.

The current state of next generation, commercially available LNBs and ULNBs reduces both NO$_X$ and CO$_2$ emissions over a wide range of operating conditions by using advanced fluid dynamic mixing and control techniques. Current burners have much wider turndown ratios and more compact flames allowing for low NO$_X$ and CO$_2$ emissions without sacrificing combustion efficiency during start-up, operation, and shutdown (Poe et al., 2007). For example, many of today’s burners operate between 4% and 6% O$_2$ with the goal of being between 3% and 4% O$_2$ to prevent efficiency loses (HPAC Engineering, New Trends in Burner Technology, 2013).

As mentioned, CO$_2$ is the major GHG produced during fuel combustion. However, 100% conversion of carbon to CO$_2$ is rarely achieved in practice. Some carbon only oxidizes to the intermediate step forming CO. CO itself is a very weak direct greenhouse gas; but, it reacts with hydroxyl (OH) radicals thus reducing their availability in the atmosphere. This indirectly increases the global warming potential of other gases as OH radicals help to reduce the lifetime of strong greenhouse gases, like methane. The other problem with CO emissions is it can lead to the formation of the tropospheric greenhouse gas ozone.

With newer, optimized LNB designs coupled with advanced controls technology, such as parallel positioning and O$_2$ trim, the majority of combustion equipment can meet very low NO$_X$ emission levels with minimum, if any, CO. This can be achieved with performance and efficiencies at or even better than comparable uncontrolled equipment (including FGD fan horsepower) only slightly larger than non-controlled units. New designs optimize combustion and heat transfer to get a more complete burn to reduce CO; have a lower uniform flame temperature to reduce NO$_X$; and achieve high efficiency to reduce CO$_2$.

CO emissions from the current state of next generation, commercially available LNBs and ULNBs applied to new installations and retrofitted units are typically less than 50 ppmvd under all conditions including start-up, operation and shutdown. Many burner manufacturers have current technology available that is guaranteed to achieve NO$_X$ emissions equal to or less than 9 ppm and CO emission equal to or less than 50 ppm over the full range of burner operations (Poe et al., 2007; Webster Combustion, 2017).

It is important to note that older equipment generally has higher levels of CO than new equipment because CO has only recently become a concern and older burners were not designed to achieve low CO levels. In present day equipment, high levels of CO emissions primarily result from incomplete combustion due to poor burner design or firing conditions (for example, an improper air-to-fuel ratio) or possibly a leaky furnace. Through proper burner maintenance, inspections, operation, upgrading
equipment or utilizing an oxygen control package, the formation of CO can be controlled at an acceptable level (Energy Solutions Center, 2016).

4.1.5 Percentage of Air Pollution Reduction

Assuming uncontrolled emissions of NO\textsubscript{X} as 85 ppm (US EPA 1995b), and emissions level achieved using LNB and ULNB as 30 ppm and 9 ppm or less, respectively, the minimum percentage reduction from LNBs and ULNBs is estimated as 65% and 89%, respectively.

For a 100 MMBtu hr\textsuperscript{-1} natural gas fired boiler, the average emission reduction for LNB (with FGR) is reported to be approximately 69% (US EPA 1995b).

A typical NO\textsubscript{X} reduction percentage reported from LNBs or technologies using LNBs for process heaters was reported to be 55% for LNB (with FGR), 80% for LNB with SNCR, and 88% for LNB with SCR (US EPA, 1999).

A typical NO\textsubscript{X} reduction percentage reported from LNBs or technologies used with LNB for reformers used in ammonia production was 60% for LNB (US EPA, 1999).

LNBs are also used in combination with other control technologies including combustion control and add-on technologies (US EPA, 1999).

4.1.6 Trade-offs between Minimizing CACs and Controlling GHGs

The current state of next generation, commercially available LNBs and ULNBs reduces both NO\textsubscript{X} and CO\textsubscript{2} emissions over a wide range of operating conditions as discussed in Section 4.1.4.

New burner designs use less FGR and excess air, optimize combustion and heat transfer to get a more complete burn to reduce CO and achieve high efficiency to reduce CO\textsubscript{2} (Cole Industries, 2017). However, this does not compromise the LNB’s or ULNB’s ability to minimise NO\textsubscript{X} emissions in the range of 9 ppm or less.

4.1.7 Associated Capital and Operating Costs

There is a wide range of technology and cost associated with LNBs and ULNBs; but, they still prove to be one of the least expensive air pollution prevention technologies. LNBs and ULNBs are often used in combination with other combustion control or add-on technologies to eliminate or further reduce air emissions compared to being used on their own.

In general, the cost of LNBs including retrofits are approximately $300 per ton of NO\textsubscript{X} removal for LNBs with no FGR with cost rising between $1,300 and $3,400 per ton of NO\textsubscript{X} removal for LNBs with FGR (Alberta Research Council, 2007; US EPA, 2016g).

The estimated cost of LNB (with FGR) varied from $1,375 to $4,026 per ton of NO\textsubscript{X} removal for catalytic cracking application in petroleum industry (US EPA, 2016g).
The cost of ULNBs including retrofitting cost is estimated from $2,419 to $2,638 per ton of NOX removal for natural gas-fired process heaters (US EPA, 2016g).

4.2 Selective Catalytic Reduction (SCR)

SCR is a widely used post-combustion control technology applied in industrial applications to reduce NOX emissions on stationary combustion units. It can be applied as a stand-alone NOX control, or in combination with other combustion control technologies (e.g. LNB) and/or add-on control technologies (e.g. SNCR) for improved NOX reduction (US EPA, 2016e).

As shown in Table 20, SCR has been successfully used as a control device in pyrolysis furnaces, steam methane reformers, nitric acid plant tail gas stacks, boilers, and process heaters at chemical and fertilizer plants. The US EPA currently recognizes SCR as BACT in attainment areas for new and modified pyrolysis furnaces and steam methane reformers (US EPA, 2017). In general, SCR is capable of achieving higher levels of NOX reduction than that achieved through SNCR or combustion controls alone.

4.2.1 Process Description

SCR is an advanced active emissions control technology system that injects a liquid-reductant agent through a special catalyst to significantly reduce NOX from an exhaust stream prior to atmospheric release. Either ammonia or urea are used as a liquid-reductant agent to remove NOX from a given gas stream.

Ammonia – either in a liquid aqueous or liquid anhydrous state – is stored at a facility site and used as a reagent. It is injected in such a manner as to mix with the treated process flue gas immediately upstream of the SCR’s catalysts. Urea can also be used as a reagent and is generally converted into ammonia prior to injection.

Regardless of which type of reagent is incorporated into the process gas; the mixture then reacts over a catalyst to reduce the NO and NO2 that is present into N2 and H2O. NOX and ammonia combine at the catalyst surface, forming an ammonium salt intermediate which then decomposes into the products as shown below. The main reactions that take place over the SCR catalyst are as follows:

\[
4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O
\]

\[
2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O
\]

Other reactions that occur at the same time as the two reactions above contribute minimally to the overall NOX reduction. The ratio of NH3 to NOX can be varied to achieve the desired level of NOX reduction. Typical SCR systems employ a ratio of 1.05 moles of ammonia per mole of NOX.

A range of materials can be used as the catalyst’s active surface contained in an SCR including: a precious metal such as platinum or palladium; a zeolite-based material; a base metal oxide such as titanium, vanadium or tungsten oxides; or a zeolite-based material. Whatever material is used for the
catalyst, the two predominant structural types of catalyst used in an SCR are honeycomb and plate to maximize the surface over which the reactions take place and ensure the maximum amount of NOX is removed.

Figure 22 presents a simplified process flow schematic diagram for an SCR (US EPA, 2016e).

Figure 22  SCR process flow diagram
(Source: US EPA, 2016e)

4.2.2 Level of Air Pollution Control

SCRs are capable of achieving NOX emission levels of 5 ppm or less. The high removal efficiencies of a given SCR system depend on the following aspects:

- A higher residence time;
- Sufficient mixing of the flue gas and reagent before entering the reactor;
- Higher uncontrolled NOX inlet concentrations;
- Higher catalyst activity;
- Sufficient amount of excess oxygen provided;
- Managing flue gas pressure drop and catalyst deactivation; and
• Consideration regarding type of fuel used i.e. process gas vs natural gas.

When using an SCR, consideration is given to a phenomenon known as ammonia slip. This occurs when unreacted ammonia passes through the SCR and could potentially be released into the atmosphere. Maintaining catalyst activity, along with proper catalyst maintenance and operation, ensures that the ammonia is completely reacted and does not pass through unreacted or ‘slip’ from the SCR. Other ways of avoiding ammonia slip are to prevent ammonia from being over-injected into the gas steam and ensuring temperatures remain high enough for all the ammonia to react. If ammonia slip does occur, it may indicate operational problems with the SCR.

### 4.2.3 Percentage of Air Pollutant Reduction

SCR is a cost effective technology capable of high NOX reduction efficiencies in the range of 70% to 98%. An air pollution reduction level of 70% for SCR is applicable to streams with low NOX concentrations (e.g. 20 ppm), where other control technologies are used in conjunction with SCR. An SCR applied as a stand-alone control (i.e., no other control technologies) should achieve a much higher NOX removal efficiency.

Theoretically, SCR systems can be designed for NOX removal efficiencies of close to 100% efficiency. In practice, commercial SCR systems are often designed to meet control targets of over 90% and if required, may be able achieve up to 98% efficiency.

### 4.2.4 Minimum, Average and Maximum Amount of CACs Emitted

The information presented in this section is intended to provide a reasonable upper- and lower-bound and average quantity of CACs emitted; not the unqualified maximum and minimum quantity of CACs emitted, nor the actual mean quantity for this emission source across the industry.

Many commercial SCRs have been operated with emissions of 5 to 10 ppm NOx. Current SCR designs are targeting less than 5 ppm NOx.

### 4.2.5 Minimum, Average and Maximum Amount of GHGs Emitted

SCR systems using ammonia as a reagent do not generate GHGs. However, SCR systems using urea may generate trace amounts of CO2 that are negligible.

### 4.2.6 Trade-offs between Minimizing CACs and Controlling GHGs

The application of an SCR greatly reduces NOX emissions released to the atmosphere; but, in some cases it may slightly reduce the overall efficiency of the system. This may result in small increases of emissions of other greenhouse gases, particulate matter and ammonia. However, the use of appropriate engineering, system knowledge and operational design can successfully balance maximum NOX removal with overall system efficiency so there is no significant trade-off between GHGs and any other air pollutant of concern. In other words, it is possible to accomplish reductions in both NOX and GHG with the use of an SCR.
It is critical that the reaction temperature of the SCR is not reduced below design to prevent the generation of:

- Increased CO emissions;
- Potential emissions of unburned VOCs; and
- Ammonia slip.

As noted above, the use of urea as a SCR liquid-reductant agent may lead to the generation of trace amounts of CO₂; but these levels are insignificant.

### 4.2.7 All Other Associated Emissions and Related Issues

Other related issues with using an SCR are described below.

#### Ammonia Handling and Storage

Suppliers and SCR technology users have reported no ammonia related handling, transportation, and storage issues with SCR installations. It is understood that any ammonia handling and storage would have safety measures such as leak detectors and deluge systems implemented; as well as, fire and explosion prevention safety measures.

Of the three commercially available forms of NH₃ – anhydrous NH₃, 19% aqueous NH₃, and 29% aqueous NH₃ – aqueous ammonia is the most common form used for SCRs in Alberta. The reason is it can be protected against freezing during the winter when ambient temperatures fall below 0°C.

#### Catalyst Disposal

The catalyst used in an SCR must be replaced and disposed of either after it has been spent or comes to its natural end of life. In general, the catalyst life expectancy is between 10 and 15 years.

Most used catalyst can be disposed of by landfilling in an industrial landfill.

#### Ammonia Slip

Ammonia slip refers to excess reagent that passes through the reactor without reacting and is emitted directly to atmosphere.

From the literature review, suppliers provide a range of 2 ppm to 20 ppm for ammonia slip values. Commercial SCRs have been operated with emissions of 5 to 10 ppm NOₓ while maintaining emissions of ammonia lower than 10 ppm. It is common practice for the SCR system to be designed to meet ammonia slip regulations which usually range between 5 ppm and 10 ppm, although slip values as low as 2 ppm can be achieved.

Low ammonia slip levels of 2 to 5ppm can be maintained by operating the SCR system close to the theoretical stoichiometry and supplying adequate catalyst volume. As catalyst activity decreases, ammonia slip increases. Other ways of avoiding ammonia slip are to prevent ammonia from being over-injected into the gas stream and ensuring temperatures remain high enough for all the ammonia to react. If ammonia slip does occur, it may indicate operational problems with the SCR.
Limits on ammonia slip are generally imposed as part of the SCR design requirements to avoid impacts on downstream equipment. For example, any ammonia in the flue gas can cause a number of problems including health effects, stack effluent visibility, and formation of ammonium sulphates.

While ammonia slip may partly offset the environmental benefits of SCR systems in reducing NOX, current SCR designs are targeting less than 5 ppm NOX and maintaining ammonia slip below 5 ppm.

**Presence of Sulphur**

If sulphur is present in the fuel, such as the use of process off-gas, this could limit SCR system performance via the formation of ammonium sulphate, ammonium bisulphate, and sulphuric acid.

Ammonium sulphate is the product of the reaction between NH₃ and sulphur trioxide (SO₃), which is formed through the oxidization of SO₂. Ammonium sulphate contributes to increased emissions of PM₁₀.

If ammonium bisulphate is formed, it condenses in response to lowering of the flue gas temperature. It then deposits on the SCR catalyst, as well as on downstream equipment including air heaters, ducts and fans.

Sulphuric acid (H₂SO₄) could also form in the SCR system, which could damage equipment because it is a highly corrosive substance. As a result, it is important to minimize the formation of SO₃ in the SCR system.

To prevent problems with the presence of sulphur, it is critical to: maintain appropriate SCR temperature control; use specified catalysts; and/or provide caustic scrubbing of the fuel to remove SO₂ prior to use. Suppliers also indicate the effect of the sulphur in an SCR can be minimized through design consideration and catalyst selection.

Further, methods to limit the impact of ammonia-sulphur salt deposition include: increased acid washing of downstream equipment; decreasing the sulphur content of the flue gas; firing natural gas as the preferred fuel; and raising flue gas temperature to prevent condensation.

### 4.2.8 Associated Capital and Operating Costs

US EPA (2016g) carried out a comprehensive study summarizing the current available information on NOX emissions and associated control measures. As part of the work, the US EPA used the Control Strategy Tool (CoST) to estimate the emission reductions and costs associated with NOX control technologies. CoST is the software tool the US EPA uses to estimate the emission reductions and total capital and operating costs associated with future year control strategies. The program tracks information about control measures, their costs, and the types of emissions sources to which they apply.

NOX reduction using an SCR system has a wide range of cost associated with it that varies by industry, fuel, source and process. The information has been summarized in Table 21.
Table 21  NO\textsubscript{X} reduction using SCR and associated cost

<table>
<thead>
<tr>
<th>Source Group or Relevant Industries</th>
<th>Control Technology Recommended by CoST</th>
<th>Current estimate of NO\textsubscript{X} removed $ per ton, CoST (2011US$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum Industry, Process Heaters, Process Gas- fired</td>
<td>SCR-95%</td>
<td>$1,406-$9,140</td>
</tr>
<tr>
<td>Boilers &amp; Process Heaters in several Industries</td>
<td>SCR</td>
<td>$2,235</td>
</tr>
<tr>
<td>Gas-Fired Process Heaters - Petroleum Industry</td>
<td>SCR-95%</td>
<td>$2,376</td>
</tr>
<tr>
<td>Chemical Manufacturing, Ammonia Production, Primary Reformer: Natural Gas Fired</td>
<td>SCR</td>
<td>$2,896</td>
</tr>
</tbody>
</table>

Using $10,000 per ton of NO\textsubscript{X} removed as an upper cost of effectiveness (US EPA, 2016g), the costs associated with using SCRs are substantially less.

The associated costs of installing an SCR system depend on the choice of catalyst and reagent for the system.

**Choice of Catalyst**

Catalyst is chosen based on performance requirements including reaction temperature range, flue gas composition and flow rate, fuel source, and the catalyst activity, selectivity and operating life. Other factors of consideration include catalyst cost.

New SCR catalyst has higher activity and can achieve greater than 90% NO\textsubscript{X} reduction. Over time, the catalyst activity decreases, which eventually creates a need to replace the catalyst. The catalyst life is the amount of time that the catalyst activity, for a given catalyst layer volume, maintains NH\textsubscript{3} slip below the design limit. When the slip level reaches this design limit, the catalyst must be replaced or new catalyst must be added. Typically, the catalyst life is expected to be 10 to 15 years, after which time it must be replaced and disposed of.

Catalyst cost is only a small part of total capital cost. Therefore, while 43% more catalyst volume is required for a 90% NO\textsubscript{X} reduction as compared to an 80% reduction, the total impact on capital cost for this increased removal is not significant. Other than the cost of catalyst replacement, there is virtually no impact on operating or maintenance costs for the catalyst system. Catalyst cost ranges from about $2,000 to $4,000 per tonne of catalyst.

Operators also have the option of using a catalyst management plan to schedule periodic catalyst replacement, such that a fraction, rather than the entire volume, of catalyst inventory is replaced at any one time, while maintaining NH\textsubscript{3} levels at or below the NH\textsubscript{3} slip requirements. This method helps to distribute replacement costs more evenly over the lifetime of the system and can decrease annual operating costs of the SCR system. Costs can also be reduced by using regenerated catalyst instead of new catalyst layers, as this would reduce the operator’s catalyst replacement cost and spent catalyst disposal costs.

Further, newer catalyst designs are available that have increases in catalyst activity, surface area per unit volume and the temperature range for the reduction reaction. As such, there is a decrease in the volume of catalyst required and an increase in the catalyst operating life. Applications using oil and natural gas have a SCR catalyst vendor guarantee of over 32,000 hours and in some cases, operational experience indicates the actual catalyst deactivation rates are lower than the design specifications.
Choice of Reagent

The capital cost and the annual cost are both affected by the reagent chosen for the SCR system. Urea systems have higher capital costs and energy consumption costs as compared to ammonia systems because of processing equipment complexity and the increased energy needed to hydrolyze urea, respectively.

By comparison, anhydrous ammonia systems typically have the lowest capital and operating costs with lower relative cost per ton of NOX removed. However, aqueous ammonia systems do have the highest overall operating costs due to higher transportation costs. Regardless of system used, reagent price ranges from $200 to $400 per tonne of reagent.

Estimated SCR Costs

Total capital costs for purchasing and installing a SCR system include an NH3 injection skid, NH3 storage equipment, and instrumentation.

The operating and maintenance costs include the cost of reagent, electrical power usage and catalyst replacement.

The literature indicates that other than NH3 unloading weekly and catalyst replacement every 10 to 15 years, SCR systems require very little operating and maintenance activities unless specifically required by regulation on a special case basis. Therefore, these costs are typically considered to be negligible.

The catalyst replacement cost is a significant portion of the operating cost, at about 25% to 30% of initial cost.

A Note on Retrofit Costs

Retrofitting an existing piece of equipment with a SCR system has higher capital costs as compared to installing a SCR on a new piece of equipment. This is primarily due to modifications to existing ductwork, the cost of structural steel and reactor construction, auxiliary equipment costs and engineering costs, and in some cases making space for the reactor. These costs can account for over 30% of the capital costs associated with SCR. The capital cost range for retrofitting is from $2,000 to $14,000 per MMBtu hr⁻¹.

4.3 Selective Non-Catalytic Reduction (SNCR)

SNCR is post-combustion control technology applied in industrial applications to reduce NOX emissions. As shown in Table 20, SNCR has been successfully used as a control device in steam methane reformers, boilers, and process heaters at chemical and fertilizer plants. However, this does not limit the application of SNCR only to those plant types and emission sources identified in Table 20. SNCR can be applied as a stand-alone NOX control or in combination with other technologies such as combustion controls technologies LNB and FGR. The SNCR system can be designed for seasonal or year-round operation (US EPA, 2016f).
4.3.1 Process Description

The SNCR technology relies on a non-catalysed chemical reaction facilitated by injecting either ammonia or urea into the post combustion gas stream. The effective temperature ranges for ammonia and urea are 870 to 1100°C and 900 to 1150°C, respectively. The reagent (ammonia or urea) can react with a number of flue gas components; but, the NO\textsubscript{X} reduction reaction is favoured for a specific temperature range and in the presence of oxygen. To drive the reaction, adequate heat must be available. At lower temperatures, reaction kinetics are slow and ammonia passes through the exhaust system unreacted, leading to ammonia slip. At higher temperatures, the reagent can oxidize and additional NO\textsubscript{X} is generated. Therefore, SNCR is only effective in a relatively high and narrow temperature range.

The SNCR process is similar to SCR, in that it begins with ammonia (or urea) being vaporized either before injection by a vaporizer or after injection by the heat of the boiler within an appropriate temperature range. The gas-phase urea or ammonia, then, decomposes into free radicals including NH\textsubscript{3} and NH\textsubscript{2}. The overall reactions with urea and ammonia are as follows (US EPA, 2016f):

**For ammonia:**

\[
\begin{align*}
4\text{NO} + 4\text{NH}_3 + O_2 & \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \\
2\text{NO}_2 + 4\text{NH}_3 + O_2 & \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O}
\end{align*}
\]

**For urea:**

\[
\begin{align*}
2\text{NO} + \text{CO(NH}_2)_2 + \frac{1}{2}O_2 & \rightarrow 2\text{N}_2 + \text{CO}_2 + 2\text{H}_2\text{O} \\
2\text{NO}_2 + 2\text{CO(NH}_2)_2 + O_2 & \rightarrow 3\text{N}_2 + 2\text{CO}_2 + 4\text{H}_2\text{O}
\end{align*}
\]

The two equations involving NO are predominant because 90 to 95% of NO\textsubscript{X} in flue gas from combustion units is NO (US EPA, 2016f).

Figure 23 presents a simplified system flow schematic diagram of a SNCR system. The design and equipment specifications for SNCR systems may have different configuration. For example, SNCR systems using anhydrous ammonia inject the reagent as a vapour, while systems using aqueous ammonia solutions and urea typically inject the reagent as an aqueous solution.
4.3.2 Level of Air Pollution Control

The NO\textsubscript{X} reduction efficiencies from SNCR vary over a wide range. Several design and operational factors affect the NO\textsubscript{X} reduction efficiency of the SNCR, such as the temperature reaction range, residence time, type of NO\textsubscript{X} reducing reagent, reagent injection rate, uncontrolled NO\textsubscript{X} concentration level, distribution of the reagent in the flue gas, and CO and O\textsubscript{2} concentrations.

SNCR is only effective in a relatively high, narrow temperature range and not suitable for sources where: 1) the residence time is too short, 2) temperatures are too low, 3) NO\textsubscript{X} concentrations are low, 4) the reagent would contaminate the product, or 4) a suitable location does not exist for installing reagent injection ports.

The highest levels of NO\textsubscript{X} reduction can be achieved for sources with stable temperatures of approximately 870 to 1320°C, uncontrolled NO\textsubscript{X} concentrations above 200 ppm, and residence times of 1 second or greater. SNCR tends to be less effective at lower levels of uncontrolled NO\textsubscript{X}. NO\textsubscript{X} control with an SNCR system alone is often limited by ammonia slip requirements (US EPA, 2016f and 2003b).
4.3.3 Percentage of Air Pollutant Reduction

SNCR performance is specific to each unique application. NOX reduction levels using SNCR alone ranges from 30% to 50%. Higher NOX removal efficiencies (e.g. 75%) can be obtained using SNCR with combustion control such as LNB. SNCR reduces NOX an additional 20% to 30% above LNB/combustion modifications.

A SNCR tends to be less effective at lower levels of uncontrolled NOX. When SNCR is applied to larger combustion units greater than 3,000 MMBtu h⁻¹, it typically achieves much lower NOX removal efficiencies (<40%) due to mixing limitations.

4.3.4 Minimum, Average and Maximum Amount of CACs Emitted

The information presented in this section is intended to provide a reasonable upper- and lower-bound and average quantity of CACs emitted; not the unqualified maximum and minimum quantity of CACs emitted, nor the actual mean quantity for this emission source across the industry.

SNCR performance is specific to each unique application. In general, SNCR is used in situations where less NOX control is required than could be achieved using SCR. Exhaust concentrations of NOX from an SNCR systems are much greater than 5 ppm (as can be achieved with SCR). For example, at the high end, an SNCR on its own can control NOX at 40 ppm with the capability to achieve lower NOX levels.

When used in combination with other low NOX technologies such as the current state of next generation, commercially available LNBs; NOX levels of 10 ppm or less can be achieved.

4.3.5 Minimum, Average and Maximum Amount of GHGs Emitted

The information presented in this section is intended to provide a reasonable upper- and lower-bound and average quantity of GHGs emitted; not the unqualified maximum and minimum quantity of GHGs emitted, nor the actual mean quantity for this emission source across the industry.

The primary by-product formed in using SNCR systems is N₂O, which is a GHG. The SNCR process using urea generates significantly more N₂O than ammonia-based systems. For example, Weijuan et al (2007) reported N₂O emissions up to 7 and 27.8 μmol mol⁻¹ in ammonia- and urea-based SNCR systems, respectively. The amount of N₂O formed depends on the reagent feed rate and temperature. An increase in N₂O formation correlates with increased NOX reductions. Use of proprietary additives for the urea-based SNCR process can reduce the N₂O formation.

4.3.6 Trade-offs between Minimizing CACs and Controlling GHGs

The SNCR system design is a proprietary technology. The design of SNCR is highly site-specific and is generally undertaken by providing all of the plant and equipment specific data to the SNCR system supplier.
Similar to SCR, appropriate engineering, system knowledge and operational design can address the balance between NOX and GHG emissions such that no significant trade-off between the two pollutants of concern is required. In other words, it is possible to accomplish reductions in both NOX and GHG with the use of an SNCR.

4.3.7 All Other Associated Emissions and Related Issues

Other related issues with using an SNCR are described below.

Retrofit Considerations

The primary concern of an SNCR retrofit is adequate wall space within the equipment (e.g. boiler) for installation of injectors; as well as, space adjacent to the equipment must be available for the distribution system equipment and for performing maintenance. It is not impossible, but retrofit work associated with a SNCR most often requires modifications or relocation of other equipment, such as ductwork.

Ammonia Handling and Storage

One potential issue with an SNCR is the associated ammonia handling and storage (US EPA, 2016f). Suppliers and SNCR technology users have reported no ammonia related handling, transportation and storage issues with SNCR installations. It is understood that any ammonia handling or storage would have safety measures such as leak detectors and deluge systems implemented; as well as, fire and explosion prevention safety measures.

Ammonia Slip

Ammonia slip is another identified issue associated with utilizing an SNCR (US EPA, 2016f). Ammonia slip results from excess reagent injection to obtain the desired level of NOX reduction where a portion of the reagent passes through unreacted and could potentially be emitted into the atmosphere. For any individual SNCR, the NOX reduction and ammonia slip are established by the reagent injection rate, i.e. an operational setting that can be adjusted based on the desired NOX reduction and allowed ammonia slip.

Presence of Sulphur

If sulphur is present in the fuel, such as the use of process off-gas, this could limit SNCR system performance. Sulphur trioxide (SO₃) forms during the combustion of fuels that contain sulphur. It reacts with ammonia in the flue gas downstream of the combustion equipment that the SNCR is applied to, such as a boiler, to form ammonium bisulphate and ammonium sulphate. The amount formed depends on the sulphur content of the fuel and the amount of ammonia slip. Ammonia-sulphur salts can plug, foul, and corrode downstream equipment such as the air heater, ducts, and fans.

Depending on the rate of ammonia-sulphur salt deposition on downstream equipment, more frequent acid washing of this equipment may be warranted. However, increased acid washing generates additional wastewater that must be disposed of or treated by the plant.
Choice of Reagents

Ammonia is generally less expensive than urea as a SNCR reagent since urea is derived from ammonia. However, the choice of reagent is based not only on cost, but also on physical properties, reagent characteristics, and operational considerations.

Generally, anhydrous ammonia, which is typically used in conventional SNCR, is the least costly reagent, with a nominal cost one-half that of 50% urea. A 29.4% aqueous ammonia solution costs 150% more than anhydrous ammonia, and a 70% urea solution costs 175% more than anhydrous ammonia.

4.3.8 Associated Capital and Operating Costs

The mechanical equipment required to install an SNCR system is less complex in comparison to a SCR system. The capital cost associated with an SNCR system is generally low due to the small amount of capital equipment required. Most of the cost associated with using an SNCR system is operating expenses. The primary operating expense is for the NOX reduction reagent. Thus, the total annual costs vary directly with the NOX reduction requirements.

Overall, the general costs of SNCR installed and used continuously throughout the year is between $400 and $2,500 per ton of NOX removed (US EPA, 2003d). For SNCR that are only used on a seasonal basis, the general costs are $2,000 to $3,000 per ton of NOX removed (US EPA, 2003d).

There is very little information available regarding the cost of new installations versus retrofits of SNCR. One study suggested retrofit installation of an SNCR system generally requires additional expenditures in the range of 10% to 30% of the total cost (US EPA 2016f).

Figure 24 presents the actual installed capital costs on industrial sources. The capital costs per unit of output decreases as the size of the source increases. A typical breakdown of annual costs is 25% for capital cost recovery and 75% for operating expense (ICAC, 2008; US EPA 2016f). Reagent costs currently account for a large portion of the annual operating expenses associated with SNCR. Based on 30 industrial boilers, annual operation of a SNCR is reported to be less than $3,000 per ton of NOX removed.
Wet scrubbers can be distinguished by the type of air pollutant(s) being controlled. For example, acid gas scrubbers are typically used to control inorganic gases such as H₂S, and flue-gas desulphurization (FGD) units are used to specifically control SO₂ (US EPA, 2003f).

Wet scrubbers are available in many different designs from a wide variety of vendors. The versatility of wet scrubbers makes them popular in many industries including chemical and fertilizer plants. The specific configurations and operations of wet scrubbers may differ, but the basic components are similar across all industries.

4.4.1 Process Description

In wet scrubbers, the removal of pollutants in the gaseous stream is done by absorption. Absorption is a mass transfer process by which the soluble components of a gas mixture are dissolved in a liquid that
has low volatility under the process conditions. The pollutant diffuses from the gas into the liquid when the liquid contains less than the equilibrium concentration of the gaseous component. The difference between the actual concentration and the equilibrium concentration provides the driving force for absorption. (US EPA, 1995c).

A properly designed gas scrubber provides thorough contact between the gas and the solvent in order to facilitate diffusion of the pollutant that needs to be removed. The design of a scrubber depends on the following parameters:

- Waste gas flow rate;
- Waste gas composition and concentration of the air pollutants in the gas stream;
- Required removal efficiency;
- Equilibrium relationship between the air pollutants and solvent; and
- Properties of the air pollutant(s), waste gas, and solvent, such as:
  - diffusivity,
  - viscosity,
  - density, and
  - molecular weight.

The scrubbing liquid, usually water, is used to absorb the pollutant. Other liquids, such as dimethylaniline or amines, may be used as the absorbent for gases with low water solubility (i.e., HCs or H₂S). The chosen absorbent should have a high solubility for the gaseous stream and should be relatively inexpensive.

Water is the preferred solvent used to remove inorganic contaminants and VOCs with relatively high water solubility. For organic compounds with low water solubility, solvents such as hydrocarbon oils are used – particularly in industries where large volumes of these are readily available such as petrochemical plants. Caustic solution (sodium hydroxide) is the most common scrubbing liquid used for acid-gas control (e.g. HCl, SO₂). In addition, sodium carbonate (Na₂CO₃) and calcium hydroxide (Ca[OH]₂) are also used as scrubbing liquid for acid-gas control (US EPA, 2003f).

The most common types of wet scrubbers used are spray towers. Spray towers use a liquid spray produced by nozzles to contact particulate-laden air that passes into a chamber. The water droplets capture the particles suspended in the gas flow through impaction, interception and diffusion. Figure 25 shows a schematic diagram of a wet scrubbing process in a spray tower scrubber system.
Wet scrubbers are often used as part of FGD systems.

### 4.4.2 Level of Air Pollution Control

Typical gaseous pollutant concentrations for spray towers range from 250 to 10,000 ppmv while gas flow rates are 0.7 to 47 standard m$^3$ s$^{-1}$ and 1.3 to 2.6 L m$^{-3}$, respectively (US EPA, 2003f).

The removal efficiency of wet scrubbers varies for each pollutant-solvent system and with the type of absorber used. The collection efficiency can range from 50% to 99%; although, most wet scrubbing processes achieve removal efficiencies greater than or 90% – depending on the pollutant absorbed.

The key parameters influencing scrubber efficiency include the following:

- **Velocity/Gas Flow Rate:** The collection efficiency depends on the velocity of the gas stream through the liquid contacting section of the scrubber vessel. Increasing the relative velocity between the gas and the liquid droplets increases the momentum of the particulate, allowing smaller particles to be collected by impaction. However, increasing relative velocity generally increases the pressure drop. It should be noted that the volumetric flow rate of a high-temperature gas stream decreases as the gas is being cooled by the scrubbing liquid, and may impact the collection efficiency.
- Liquid-to-Gas (LG) Ratio: The LG ratio is the volume of liquid injected per volume of waste gas treated. It is a function of inlet gas temperature, inlet solids content, and method of water introduction. In general, a higher LG ratio increases collection efficiency since the density of droplets increase across a given cross-section of the scrubber. A typical value for LG flow rate range from 0.3 to 5 L m\(^{-3}\) of inlet gas. If the LG ratio falls below design value, removal efficiency will be reduced.

- Pressure Drop: The collection efficiency depends upon the designed pressure drop. An increase in pressure drop may be caused by plugging or an increase in waste stream flow rates, while a decrease in pressure drop may be caused by a decrease in gas or liquid flow.

- Temperature: Wet scrubber inlet and outlet temperatures need to be monitored. For example, an increase in temperature may be due to failure of the cooling equipment which would result in decreased removal efficiency.

- Particle Size Distribution: Removal efficiency of PM emissions depends on the gas stream particle size distribution. Spray tower scrubbers are not generally used for fine PM applications because of high liquid to gas ratios needed (> 3 L m\(^{-3}\)).

4.4.3 Percentage of Air Pollution

The extreme range of removal efficiencies for a spray tower wet scrubber is reported to be 50% to 99% for most applications of inorganic gases, VOC and PM removal. Although, most wet scrubbing processes achieve removal efficiencies greater than or equal to 90% depending on the pollutant absorbed. Removal efficiencies of the pollutants vary for each pollutant-solvent type and type of absorbent used.

The removal efficiency of wet scrubbers is estimated as follows.

- Inorganic gases: range from 95% to 99%
- VOC: range from 70% to greater than 99%
- PM: range from 50% to 95%. It should be noted that wet scrubbers are typically not used in applications of removing fine particulate matter.

4.4.4 Minimum, Average and Maximum CACs Emitted

The information presented in this section is intended to provide a reasonable upper- and lower-bound and average quantity of CACs emitted; not the unqualified maximum and minimum quantity of CACs emitted, nor the actual mean quantity for this emission source across the industry.

The minimum, average, and maximum CAC emission levels post-treatment is dependent on site-specific or regulatory requirements. With removal efficiencies at 99% or greater, a scrubber can be designed and sized to meet virtually any required level.

4.4.5 Minimum, Average and Maximum GHGs Emitted

Wet scrubbers do not generate GHGs. Therefore, this section is not relevant to wet scrubbers.
4.4.6 Trade-offs between Minimizing CACs and Controlling GHGs

Scrubbers are designed to remove pollutants (CACs such as VOCs, SO₂, CO, PM) in the gaseous stream by absorption. Wet scrubbers do not generate GHGs. Therefore, there are no trade-offs expected between CACs reductions and GHG emissions from wet scrubbers.

4.4.7 All Other Associated Emissions and Related Issues

Other related issues with using a wet scrubber are described below.

PM Characteristics

Wet scrubbers are particularly useful in the removal of PM with the following characteristics (US EPA, 2002):

• sticky and/or hygroscopic materials;
• combustible, corrosive and explosive materials;
• particles which are difficult to remove in their dry form;
• PM in the presence of soluble gases;
• large PM molecules; and
• PM in waste gas streams with high moisture content.

Solvent Generation

The liquid, water or other solvents, used in wet scrubbers to remove air pollutants from the gas stream, requires treatment to remove the captured pollutants from the solution prior to discharge. The effluent from the scrubbers may be recycled into the system and used again. This is usually the case if the solvent is costly, such as hydrocarbon oils and caustic solutions. Otherwise, the effluent becomes a waste stream that must be treated and disposed of appropriately.

Operational Challenges

Challenges with using wet scrubbers include the following (US EPA, 2002).

• The increased collection efficiency comes at a cost of increased pressure drop across the control system.
• They are limited to lower waste gas flow rates and temperatures as compared to ESPs or baghouses.
• They generate waste in the form of a sludge that requires both wastewater treatment and solid waste disposal.
• Downstream corrosion or plume visibility problems can result unless the added moisture is removed from the gas stream.

4.4.8 Associated Capital and Operating Costs

In comparison to ESPs and baghouses, wet scrubbers have smaller space requirements, lower capital cost, and comparable operation and maintenance costs. They also have the ability to process high acidity and high humidity flue gas streams. Scrubber costs, along with energy requirements, have continued to decrease, largely because of technical innovations helping to lower operating costs.
Spray towers have lower capital costs than other wet scrubbers. They also have lower operational costs because of the lower power consumption needs and less chance of fouling compared to other types of wet scrubbers. The estimated cost for a spray tower wet scrubber of conventional design under typical operating conditions in 2002 USD is as follows (ICAC, 2016).

- Capital Cost: $4,200 to $13,000 per m³ s⁻¹ ($2 to $6 per scfm);
- Annual Operational & Maintenance Cost: $3,200 to $64,000 per standard m³ s⁻¹ ($1.50 to $30 per scfm);
- Annualized Cost: $5,300 to $102,000 per standard m³ s⁻¹ ($2.5 to $48 per scfm)
- Annualized Cost Effectiveness: $50 to $950 per metric ton ($45 to $860 per short ton), cost per ton per year of pollutant controlled.

Using $10,000 per ton of NOₓ removed as an upper cost of effectiveness (US EPA, 2016g), the annualized cost effectiveness associated with using wet scrubbers is substantially less.

### 4.5 Fabric Filter (Baghouse)

A fabric filter, or baghouse, is a dust collection device that removes PM from the contaminated gas stream by depositing the particles on fabric material. Fabric filters are frequently referred to as baghouses because the fabric is usually configured in cylindrical bags. Fabric filters can collect particles ranging from submicron to several hundred microns in diameter with an efficiency greater than 99.9%. The layer of dust collected on the fabric (referred to as dust cake) is primarily responsible for such high efficiency (US EPA 1998b, 2003f).

As shown in Table 20, fabric filters have been used as a control device in a pyrolysis furnace, decoking vent, various stacks and prill tower at chemical and fertilizer plants. In general, fabric filters are used where moderate to stringent emission control measures are required.

#### 4.5.1 Process Description

Inside the fabric filter housing, flue gas passes through a tightly woven or felted fabric, causing PM in the flue gas to be collected on the fabric by sieving and other mechanisms. Each individual filter may be in the form of sheets, cartridges, or bags, and are often located together as a group of filters in a unit known as a baghouse (US EPA, 2003g). Fabric filters can be categorized by the following means (US EPA, 2003f).

- Type of filter cleaning (shaker, reverse-air, or pulse-jet)
- Direction of gas flow (from inside the bag towards the outside or vice versa)
- Location of the system fan (suction or pressure)
- Size (low, medium, or high gas flow quantity)

Of these four categories, the filter cleaning method is most commonly referenced. A brief description of the different cleaning methods employed on fabric filters is provided below.
4.5.1.1  Shaker Cleaning

In shaker baghouses, the direction of gas flow is maintained from inside-to-outside. Cleaning is accomplished by transferring energy through the bags suspended from a motor-driven hook or framework, causing oscillation. The shaking action may be either manual or motor operated (Aircon, 2017). Motion may be imparted to the bag in several ways; but, the general effect is to create a sine wave along the fabric. As the fabric moves outward from the bag centreline during portions of the wave action, accumulated dust on the surface moves with the fabric. When the fabric reaches the limit of its extension, the patches of dust have enough inertia to tear away from the fabric and descend to a hopper (US EPA 1998b).

Fabric filters with mechanical shaker cleaning can be used in many processes where dust is generated, can be collected, and ducted to a central location. Sonic horn enhancement of mechanical shaker cleaning is generally used for applications with dense particulate matters (US EPA 2003f).

A schematic diagram of shaker baghouse is presented in Figure 26.

![Figure 26 Typical shaker baghouse](Source: US EPA, 1998b)

4.5.1.2  Reverse-Air Cleaning

A reverse-air fabric filter blows air backwards through the bags from the clean-air (plenum) section of the unit. In this type of cleaning, gas flow to the bags is stopped in the compartment being cleaned and reverse (outside-in) air flow is directed through the bags. This gas flow in the opposite direction gently collapses the bags toward their centrelines, which causes the dust cake to detach from the fabric surface (US EPA 1998b).

The source of reverse air is generally a separate system fan capable of supplying clean, dry air for one or two compartments at a gas-to-cloth ratio as high or higher than that of the forward gas flow. Figure 27 illustrates a reverse-air cleaned baghouse (US EPA 1998b).
4.5.1.3 Pulse-jet Cleaning

The pulse-jet cleaning baghouse uses compressed air to force a burst of air down through the bag and expand it violently. As with shaker baghouses, the fabric reaches its extension limit and the dust separates from the bag. Air escaping through the bag carries the separated dust away from the fabric surface. In these types of units, filtering gas flows are opposite in direction (i.e. outside-in) when compared with shaker or reverse-air baghouses (US EPA, 1998b). A schematic diagram of shaker baghouse is presented in Figure 28.

4.5.2 Level of Air Pollution Control

The efficiency of any baghouse depends heavily on the dust loading conditions (Aircon, 2017). For a given combination of filter design and dust type, the effluent particle concentration from a fabric filter is nearly constant; whereas, the overall efficiency is more likely to vary with particulate loading (US EPA, 1998b).
Several factors determine fabric filter collection efficiency such as gas filtration velocity, particle characteristics, fabric characteristics, and cleaning mechanism. In general, collection efficiency increases with increasing filtration velocity and particle size.

### 4.5.3 Percentage of Air Pollutant Reduction

A properly designed and operated baghouse will generally have an extremely high PM collection efficiency of greater than 99.9%. Compared to other add-on technologies (e.g. cyclones), baghouses are particularly effective for collecting small particles. As an example, tests of baghouses on two utility boilers showed efficiencies of 99.8% for PM$_{10}$ and 99.6% to 99.9% for PM$_{2.5}$ (US EPA 1998b).

Current, commercially available fabric filters have design efficiencies between 99% and 99.9%; while, older ones from the 1980’s or 1990’s have operating efficiencies of 95% to 99.9% (US EPA, 2003g).

The efficiency of any baghouse depends much more on the dust-loading conditions. Laboratory tests performed on either 12 or 16 ounce single polyester bags usually result in an efficiency of 99.9% (by weight) when silica dust was used as the containment (Aircon, 2017).

### 4.5.4 Minimum, Average and Maximum Amount of CACs Emitted

Fabric filters or baghouses rely on a combination of filter design and cake deposit to achieve an effluent particle concentration that is nearly constant; whereas, the overall efficiency is more likely to vary with particulate loading. For this reason, fabric filters can be considered constant outlet devices rather than constant efficiency devices. Commercial filter suppliers often cite PM emission levels less than 0.002 grains scf$^{-1}$ (4.58 mg m$^{-3}$) are achievable, and in some instances, less than 0.001 grains scf$^{-1}$ (2.29 mg m$^{-3}$). In practice, PM emission levels can be considerably lower on average, depending on the design and application.

### 4.5.5 Minimum, Average and Maximum Amount of GHGs Emitted

Baghouses do not generate GHGs. Therefore, this section is not relevant to baghouses.

### 4.5.6 Trade-offs between Minimizing CACs and Controlling GHGs

Baghouses are designed to remove PM and do not generate GHGs. Therefore, there are no trade-offs expected between CACs reductions and GHG emissions from baghouses.

### 4.5.7 All Other Associated Emissions and Related Issues

When much of the pollutant loading consists of relatively large particles, mechanical collectors such as cyclones may be used in series to reduce the load on the fabric filter – especially at high inlet concentrations (US EPA, 2003f).
4.5.8 Associated Capital and Operating Costs

Costs for PM control using baghouses are driven by the waste stream volumetric flow rate and pollutant loading. In general, a small unit controlling a low pollutant loading will not be as cost effective as a large unit controlling a high pollutant loading. The estimated cost (expressed in 2002 USD) is presented below for a pollutant loading of 9 g m\(^{-3}\) and flow rates of 470 m\(^3\) s\(^{-1}\) to 1.0 m\(^3\) s\(^{-1}\) (US EPA, 2003f; US EPA, 2003g; US EPA, 2003h). It is estimated that for controlling more complex waste streams, the capital cost could increase by up to 40% and the operating and maintenance costs could increase by up to 5% than presented below.

- **Capital Cost:**
  - Pulse-Jet $13,000 to $55,000 per sm\(^3\) s\(^{-1}\)
  - Mechanical Shaker $17,000 to $153,000 per sm\(^3\) s\(^{-1}\) (Additional cost for Sonic Horn Enhancement $1,000 to $1,300 per sm\(^3\) s\(^{-1}\))
  - Reverse-Air Cleaned $19,000 to $180,000 per sm\(^3\) s\(^{-1}\) (Additional cost for Sonic Horn Enhancement $1,000 to $1,300 per sm\(^3\) s\(^{-1}\))

- **O & M Cost:**
  - Pulse-Jet $11,000 to $50,000 per sm\(^3\) s\(^{-1}\), annually
  - Mechanical Shaker $9,300 to $51,000 per sm\(^3\) s\(^{-1}\), annually
  - Reverse-Air Cleaned $14,000 to $58,000 per sm\(^3\) s\(^{-1}\), annually

- **Annualized Cost:**
  - Pulse-Jet $13,000 to $83,000 per sm\(^3\) s\(^{-1}\), annually
  - Mechanical Shaker $11,000 to $95,000 per sm\(^3\) s\(^{-1}\), annually
  - Reverse-Air Cleaned $17,000 to $106,000 per sm\(^3\) s\(^{-1}\), annually

- **Cost Effectiveness:**
  - Pulse-Jet $46 to $293 per metric ton
  - Mechanical Shaker $41 to $334 per sm\(^3\) s\(^{-1}\)
  - Reverse-Air Cleaned $58 to $372 per sm\(^3\) s\(^{-1}\)

4.6 Flares and Thermal Incinerators

Flares are control devices that destroy hydrocarbons (e.g. VOCs) or inorganic gases (e.g. ammonia) via combustion. Flares are designed to route these gases to a burner tip and to burn these gases in an open flame (i.e., in open air). They are used at chemical and fertilizer plants to dispose of intermediate process gases during start-up, shutdowns, and process upsets. At some plants with gaseous products (e.g. ethylene and ammonia), flares are connected on storage tanks and railcar loading areas to ensure that concentrated vapours are not released directly to atmosphere.

Thermal incinerators (or thermal oxidizers) are a second type of control technology that destroys hydrocarbons or inorganic gases via combustion. Some types of PM (e.g. PM from incomplete combustion, coke, and carbon residue) can be destroyed in the incinerator (US EPA, 2016a). Thermal incinerators are fundamental different from flares in that the gases are burned in a combustion chamber rather than an open flame. Thermal incinerators are often used at chemical and fertilizer plants to control waste streams from individual sources (e.g. main process vent at an EO plant, distilled grain dryer at an ethanol plant, etc.) or a number of minor vent sources (US EPA, 1986; Brady and Pratt, 2007).
4.6.1 Process Description

Flares and thermal incinerators are discussed in detail in Chapter 3.

As a safety device, flares are considered the best control option when the heating value of the emission stream cannot be recovered due to uncertain or intermittent flow during process upsets or emergencies. They are primarily used for burning flammable gas released via pressure relief valves during unplanned, over-pressuring of plant equipment. During plant start-ups and shutdowns, flares are also used for planned combustion of gases over relatively short periods of time while equipment is being brought into production or being taken off-line. They are designed and operated to handle large fluctuations in flow rate and VOC content.

Flares combust hydrocarbons and/or inorganic gases by means of a diffusion flame in open air (US EPA, 2000a). A diffusion flame has an inner core of waste gases, which is enveloped by a flame zone. Air diffuses toward the centre of the waste gas flow, which ignites with the gases on contact with the flame zone. This establishes a stable flame zone around the gas core above the burner tip (US EPA, 2000a). This inner waste gas core is also heated by diffusion of hot combustion products from the flame zone (US EPA, 2000a).

To achieve good combustion and smokeless burning, flares use an assist gas or pressure at the flare tip to educt and mix air with the waste gas (Bader et al., 2011). Flares are typically described by the method of assist, which include non-assisted, steam-assisted, air-assisted, or pressure-assisted flares.

Thermal incinerators (or thermal oxidizers) are another choice of combustion devices typically used to destroy hydrocarbons or inorganic gases by combusting them. The fundamental difference between flares and thermal incinerators is that the gases are burned in a combustion chamber, rather than an open flame. Thermal incinerators are preferable to flares when halogenated or sulphur-bearing compounds are present. Three main factors critical to achieve effective design and operation of a thermal oxidizer are temperature, residence time, and turbulence. Although they can accommodate minor flow fluctuations, thermal incinerators are not well suited to streams with highly variable flow because of reduced residence time and poor mixing during increased flow conditions.

Thermal incinerators are designed to raise the waste gas stream temperature to a desired reaction temperature and maintain the temperature for a given reaction time (referred to as residence time) to achieve the necessary destruction and removal efficiency (DRE) (US EPA, 2000b). For most VOC streams, thermal incinerators are designed to achieve a combustion temperature of at least 870°C for at least a 0.75 second residence time (US EPA, 2016a).

The basic type of thermal incinerator (often referred to as a direct flame incinerator) consists of a dilution air feed, a combustion chamber, and a stack. The dilution air feed is mixed with the waste gas stream prior to entering the combustion chamber. The stream then enters the combustion chamber and ignites in the direct flame. An auxiliary fuel source (e.g. natural gas) is used to sustain the flame while the waste gas stream enhances the burn. The combustion chamber, and a portion of the stack in some case, shapes the flow pathway such that the waste gas will achieve the necessary residence time at the reaction temperature. The combustion chamber is also designed to promote mixing.

Some types of thermal incinerators, including recuperative incinerators and regenerative thermal oxidizers, use thermal energy recovery techniques (e.g. preheater or ceramic beds) to improve the
thermal efficiency of the system and/or increase the DRE of the system. Similarly, some incinerators are equipped with catalyst beds to destroy certain VOCs at a lower temperature (i.e., 400°C), thus reducing the fuel requirements of the system (US EPA, 2016c).

4.6.2 Level of Air Pollution Control

Flares are typically designed to achieve a specified DRE level of combustible constituents in the waste gas stream. To achieve the highest possible DRE, the vent gas must be exposed to a high temperature flame for a relatively long time (i.e., long residence time). The major factors affecting these parameters, and thus the level of pollution control for a properly designed and operated flare, are vent gas flammability, auto-ignition temperature, heating value, density, and flame zone mixing (US EPA, 2000a). For example, a vent gas with a low heating value will produce a cooler flame (US EPA, 2000a). In general, chemical plants flare gases with high heating values (US EPA, 2015).

Thermal incinerators can achieve higher DRE than flares because they can maintain a higher temperature for a longer period since combustion occurs in an enclosed chamber. Direct flame thermal incinerators and recuperative incinerators that achieve the design specification of: 1) a combustion temperature of at least 870°C, and 2) at least a 0.75 second residence time can achieve a very high level of pollution control for VOCs. Thermal incinerators can also be used to control some types of PM including soot from incomplete combustion and coke particles from pyrolysis reactions.

4.6.3 Percentage of Air Pollutant Reduction

Flares should be capable of achieving a minimum DRE of 98% or greater for combustible constituents in the waste gas stream (US EPA, 2015). For properly operated flares, Texas Council on Environmental Quality (TCEQ; 2006) and TCEQ (2012) recommend using 98% DRE for C4 and greater VOCs, hydrogen sulphide, and hydrogen, and 99% DRE for C1 to C3 VOCs and ammonia to calculate maximum emission rates (e.g., maximum emission rate occurs when DRE is lowest).

Direct flame thermal incinerators and recuperative incinerators can achieve 98% to 99.99% DRE or greater for VOCs (US EPA, 2016a; US EPA, 2016b). RTO are typically limited to 95% to 99.5% DRE for VOCs (Banks Engineering, 2007). At chemical plants, US EPA (2016a) reports that thermal incinerators can control between 50% and 99.9% of PM10 emissions. Again, to achieve the highest possible DRE, the vent gas must be exposed to a high temperature flame for a relatively long time.

4.6.4 Minimum, Average and Maximum CACs Emitted

The information presented in this section is intended to provide a reasonable upper- and lower-bound and average quantity of CACs emitted; not the unqualified maximum and minimum quantity of CACs emitted, nor the actual mean quantity for this emission source across the industry.

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3 C3 compounds with elements other than carbon and hydrogen should use 98% DRE, with some exceptions that can still use 99% DRE, including methanol, ethanol, propanol, ethylene oxide, and propylene oxide.
The minimum, average, and maximum VOC emission levels post-combustion (e.g. after destruction and removal) is dependent on the inlet stream concentration. It is not possible to explicitly define minimum, average and maximum values for VOC emissions from flares and thermal incinerators.

Some thermal incinerators are designed to achieve 20 ppmV VOC in the exhaust (US EPA, 2016a). However, the ability to achieve this level still depends on the VOC concentration in the waste gas stream.

Similarly, the amount of SO2 emissions depends mostly on the amount of sulphur-bearing compounds in the waste gas stream. Again, it is not possible to explicitly define minimum, average and maximum values for SO2 emissions from flares and thermal incinerators.

US EPA (1983) reported NOX concentrations from steam- and air-assisted flares ranging from 0.50 to 8.16 ppm, and 2.20 ppm on average, which is low compared to other combustion sources However, the study cautions that these concentrations are subject to undefined dilutions of air and steam not normally encountered in other combustion sources. These concentrations translated to NOX emission rates ranging from 0.018 to 0.208 lb MMBtu\textsuperscript{-1} (8 to 89 g GJ\textsuperscript{-1}). US EPA (2015) presents a NOX emission factor of 0.068 lb MMBtu\textsuperscript{-1} (29 g GJ\textsuperscript{-1}), which approximately translates to the average value reported in the US EPA (1983) study. TCEQ (2012) reports NOX emission factors for different flare types and heat content in the waste gas stream as follows.

- Steam-assisted, high heat content: 0.0485 lb MMBtu\textsuperscript{-1} (21 g GJ\textsuperscript{-1})
- Steam-assisted, low heat content: 0.068 lb MMBtu\textsuperscript{-1} (29 g GJ\textsuperscript{-1})
- Air-assisted or unassisted, high heat content: 0.138 lb MMBtu\textsuperscript{-1} (59 g GJ\textsuperscript{-1})
- Air-assisted or unassisted, low heat content: 0.0641 lb MMBtu\textsuperscript{-1} (28 g GJ\textsuperscript{-1})

Similarly, TCEQ (2012) reports CO emission factors for the same flare types and heat contents as follows.

- Steam-assisted, high heat content: 0.3503 lb MMBtu\textsuperscript{-1} (151 g GJ\textsuperscript{-1})
- Steam-assisted, low heat content: 0.3465 lb MMBtu\textsuperscript{-1} (149 g GJ\textsuperscript{-1})
- Air-assisted or unassisted, high heat content: 0.2755 lb MMBtu\textsuperscript{-1} (118 g GJ\textsuperscript{-1})
- Air-assisted or unassisted, low heat content: 0.5496 lb MMBtu\textsuperscript{-1} (236 g GJ\textsuperscript{-1})

The US EPA (2015) reports a CO emission factor of 0.31 lb MMBtu\textsuperscript{-1} (133 g GJ\textsuperscript{-1}) representing both steam- and air-assisted flares for a variety of waste streams.

For thermal incinerators, the Bay Area Air Quality Management District (BAAQMD) in California specifies the reasonably achievable control level for NOX and CO to be 50 and 350 ppm, respectively, or 0.2 and 0.8 lb MMBtu\textsuperscript{-1} (86 and 344 g GJ\textsuperscript{-1}), respectively (BAAQMD, 2008).

NOX emissions are lower for an RTO than most other types of thermal oxidizer (Banks Engineering, 2007; US EPA, 2016c).

### 4.6.5 Minimum, Average and Maximum GHGs Emitted

The information presented in this section is intended to provide a reasonable upper- and lower-bound and average quantity of GHGs emitted: not the unqualified maximum and minimum quantity of GHGs emitted, nor the actual mean quantity for this emission source across the industry.
Flares and thermal incinerators are designed to convert HCs into CO₂ and water vapour. Therefore, these systems inherently generate significant quantities of GHGs.

The combustion efficiency of a flare or incinerator is the percentage of HC that is completely converted to CO₂ and water vapour. The DRE of a flare or incinerator is always greater than its combustion efficiency because the DRE includes the percentage of HC converted to other compounds and intermediates (e.g. CO, other HCs). It is generally estimated that a combustion efficiency of 96.5% is equivalent to a DRE of 98% for flares (US EPA, 2015).

Since most flares and incinerators achieve DRE greater than 98%, it is reasonable to assume that most systems achieve combustion efficiencies greater than 96.5%. This means a considerable quantity of HC is converted to GHGs, and any unconverted methane also contributes significant to the GHG quantity.

Clearly, the minimum, average, and maximum quantity of GHGs emitted are heavily dependent on the HC flow to the flare or thermal incinerator, and cannot be accurately enumerated.

### 4.6.6 Trade-offs between Minimizing CACs and Controlling GHGs

Flares and thermal incinerators are designed to control HCs by combusting them to form CO₂ and water. In the process, they will also produce NOₓ and possibly PM. The trade-off between minimizing CACs and controlling GHGs will depend on the waste stream being treated by the device. For example, ammonia combusts to nitrogen (N₂) and water vapour, as opposed to CO₂ and water vapour for HCs, so the trade-off between controlling a waste gas stream at an ammonia plant will be very different from an ethylene plant.

Additional natural gas must be used for lean waste gas streams where the net heating value of the waste gas is low (i.e., <300 Btu/scf), for example hydrogen streams (US EPA, 2000b). In these cases, the auxiliary fuel will be combusted and generate GHGs.

Recuperative incinerators and RTO can be used in place of direct flame incinerators to lower GHG emissions since less fuel will be burned. Likewise, incinerators equipped with catalyst beds can be used to reduce the fuel requirements of the system, if the waste gas stream allows.

It must be noted that flares and thermal incinerators should also be viewed as safety devices, needed to combust waste gases which cannot be: recovered or recycled at chemical and fertilizer plants; or vented directly to the atmosphere. In other words, they are a critical and mandatory component of most chemical and fertilizer plants.

### 4.6.7 All Other Associated Emissions and Related Issues

A list of major air emissions associated with flares and thermal incinerators is presented in Table 18. Other related issues with using flares are described below (US EPA, 2016d).
Noise

The turbulent mixing of gases, air, and steam at the flare tip produces a rumbling noise (ExxonMobil, 2017), similar to a large blower. The noise emissions from flares should be considered at the design stage to plan for appropriate siting, technology, and controls - especially in populated areas.

Smoke

If the amount and distribution of oxygen in the combustion zone is insufficient, larger molecules sent to flare can be cracked into carbon particles (US EPA, 2015). If these particles avoid further combustion, they cool down and form smoke or soot. Properly designed and operated flares with assist gas or pressure should be able to maintain smokeless combustion under most circumstances. For these flares, smoking tends to occur when there is an exceptionally sudden release of excess gases, such that the system does not respond immediately to supply additional assist gas or pressure (ExxonMobil, 2017). Unsaturated HC and highly branched HCs have a greater tendency to smoke as compared to saturated HC and unbranched HC (US EPA, 2015).

Heat Radiation

Flares generate a significant amount of radiant heat, such that the amount of radiation experienced at ground-level is an important consideration at the design stage in determining the flare’s stack height and siting to protect workers and equipment (Guigard et al., 2000).

Light

Flares also generate a notable amount of light that can be seen from far distances, especially at night, in some areas. The amount of light can be a major nuisance to nearby residence. They also cast an orange glow in the night sky, which can be concerning to the members of the public that might mistake the flare for a fire (ExxonMobil, 2017).

4.6.8 Associated Capital and Operating Costs

A general range of the capital cost for elevated flares and thermal incinerators is presented in Table 22.

<table>
<thead>
<tr>
<th>Control Device</th>
<th>Capital Cost (2002 USD per sm³/s)</th>
<th>Annual O &amp; M Cost (2002 USD per sm³/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elevated Flare</td>
<td>$27,000 to $4,000,000</td>
<td>$2,000 to $20,000</td>
</tr>
<tr>
<td>Direct Flame Incinerator</td>
<td>$53,000 to $190,000</td>
<td>$11,000 to $160,000</td>
</tr>
<tr>
<td>Recuperative Incinerator</td>
<td>$25,000 to $212,000</td>
<td>$10,000 to $53,000</td>
</tr>
<tr>
<td>Regenerative Thermal Oxidizer</td>
<td>$85,000 to $320,000</td>
<td>$8,500 to $21,000</td>
</tr>
</tbody>
</table>

(Sources: US EPA, 2016: Air Pollution Control Technology Fact Sheets, EPA-452/F-03-019; EPA-452/F-03-020; EPA-452/F-03-021; and EPA-452/F-03-022)
The costs in this table are a very general range and can vary depending on a number of factors including: waste gas flow rate and heating value, VOC concentration, and annual operating hours (US EPA, 2016c; US EPA, 2016d).

The decision on whether to use a flare or thermal incinerator should not be based on cost. Instead, flares should be used for waste gas streams with highly variable or intermittent flow, such as process upsets or start-ups and shutdowns. Thermal incinerators require more consistent flow rates in order to maintain the necessary residence time and proper mixing to achieve the stated DRE.

### 4.7 Example of Commercially Available Emission Reduction Alternatives

An example of emission control technologies investigated for a proposed methanol facility is provided in this section. This proposed facility will consist of two production lines, each with a daily production capacity of 5,000 metric tons of methanol. The Facility will process natural gas from a pipeline using a methane reforming process.

#### 4.7.1 Natural Gas-Fired Boilers

The boilers will combust natural gas and process off-gases to generate the heat needed to produce steam.

Table 23 presents main alternatives available to control emissions from natural gas boiler.

<table>
<thead>
<tr>
<th>Control Device(s)</th>
<th>Effluent NOX Concentration (ppm)</th>
<th>Emission Intensity (g/GJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NOX Alternatives</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LNBs, SCR, &amp; GCPs</td>
<td>4</td>
<td>2.2</td>
</tr>
<tr>
<td>LNBs &amp; GCPs</td>
<td>30</td>
<td>16</td>
</tr>
<tr>
<td>LNBs (old designs) with GCPs</td>
<td>40</td>
<td>22</td>
</tr>
<tr>
<td>Conventional Burners with SNCR &amp; GCPs</td>
<td>40</td>
<td>22</td>
</tr>
<tr>
<td>Conventional Burners with GCPs</td>
<td>80</td>
<td>43</td>
</tr>
<tr>
<td><strong>VOCs Alternatives</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation Catalyst and GCPs</td>
<td>6</td>
<td>1.1</td>
</tr>
<tr>
<td>GCPs</td>
<td>12</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>CO Alternatives</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation Catalyst and GCPs</td>
<td>5</td>
<td>1.6</td>
</tr>
<tr>
<td>GCPs</td>
<td>50</td>
<td>16</td>
</tr>
</tbody>
</table>

#### 4.7.2 Process Heaters

The heat created in the auto-thermal reformer (ATR) during the reforming process is used to heat the first step of the reforming process in the gas-heated reformer (GHR), which provides the partially-
reformed gases that react exothermically in the ATR. With the addition of natural gas, steam, and oxygen, this arrangement is essentially self-sustaining, but an external heat source is required to initiate the process. Each methanol production line will have a dedicated process heater to provide the heat needed during start-up.

Table 24 presents main alternatives available to control emissions from process heaters.

<table>
<thead>
<tr>
<th>Control Device(s)</th>
<th>Effluent NO&lt;sub&gt;x&lt;/sub&gt; Concentration (ppm)</th>
<th>Emission Intensity (g/GJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NO&lt;sub&gt;x&lt;/sub&gt; Alternatives</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LNBs, SCR, &amp; GCPs</td>
<td>5</td>
<td>2.2</td>
</tr>
<tr>
<td>LNBs &amp; GCPs</td>
<td>9</td>
<td>4.3</td>
</tr>
<tr>
<td>LNBs with GCPs</td>
<td>15</td>
<td>6.9</td>
</tr>
<tr>
<td>Conventional Burners with OTM &amp; GCPs</td>
<td>30</td>
<td>14</td>
</tr>
<tr>
<td>Conventional Burners with SNCR</td>
<td>42</td>
<td>19</td>
</tr>
<tr>
<td>Conventional Burners with GCPs</td>
<td>85</td>
<td>39</td>
</tr>
<tr>
<td><strong>VOCs Alternatives</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GCPs</td>
<td>14</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>CO Alternatives</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GCPs</td>
<td>5</td>
<td>1.4</td>
</tr>
</tbody>
</table>
5.0 Air Preheat

Air preheaters (APH) are heat exchanger devices used to transfer heat energy from the flue gas stream of combustion sources to new combustion air. APH are one of the most effective devices at improving the efficiency of a boiler or heater (Guerts International, 2016). In fact, heating combustion air can improve a boiler’s efficiency by about 1% for every 22°C increase in combustion air temperature (Sapkal et al., 2010).

For flue gas streams at 400°C, an APH can achieve a 10% to 12% improvement in thermal efficiency (Kamal Engineering, 2012).

It is worth noting that there have been few design changes over the years that improve the efficiency of APH (Dubil, 2014). Therefore, many of the numeric values discussed in this chapter should apply to older, existing units and newly installed units.

There are two basic types of air preheaters: recuperative and regenerative. Recuperative-type APH are shell and tube or shell and plate heat exchangers. Heat from the outgoing exhaust gases passed through the shell-side of the heat exchanger to transfer heat through the internal tubes or plates to the incoming combustion air. Recuperative-type APH are available in a wide variety of designs, flow capacities, and temperature ranges (United States Department of Energy, 2007). Air preheating with recuperative-type APH can be accomplished with counter-current, co-current, or cross-current designs to fit the specific installation (Guerts International, 2016).

Regenerative-type APH transfer heat from the flue gas into heating elements (e.g. plates) as it passes across them. The heating elements transfer the collected heat energy to the combustion air. This heat transfer can be accomplished by alternating flue gas and combustion air flow over the heating elements. In this case, there are two separate heating elements configured such that one element is heated by the flue gas while the other element transfers collected heat to the combustion air. After some time, the flow switches and heating elements roles are reversed. This regenerative technique is applied in regenerative thermal oxidizers (RTOs), which are discussed in Chapters 3 and 4.

Heaters can also be installed with two regenerative burners, with each having heating elements (called “regenerators”) connected directly to the burners. One burner is fired, while the other has flue gas passed over the regenerator (Southern California Gas Company, 2012). Again, the roles are reversed and the newly heat regenerator transfers heat to the combustion air at the burner. However, the most widely used type of regenerative APH is a rotating-plate (or rotary-) regenerative APH (Mallikarjuna et al., 2014). In this type of regenerative APH, the heating elements are angled plates arranged in a cylindrical shell called a rotor. The flue gas and combustion air ducting are connected to the rotor at opposite sides of the rotor. This ducting setup and plate arrangement creates two separate flow passages across the plates. A portion of the plates are exposed to the flue gas passage to collect heat. As the rotor slowly revolves, these newly heated plates move to the combustion air passage to transfer the heat to the air. The plates eventually return to the flue gas passage to collect more heat. The plate temperatures generally operate about halfway between the flue gas and air temperatures (Dubil, 2014).
5.1 Prevalence of Air Preheat Use

Air preheaters are used in both the chemical and fertilizer sectors. However, APH are not widely used on smaller gas-fired boilers (e.g. < 25,000 lb/hr steam capacity; US EPA, 2010); rather they are often installed in some of the main plant furnaces and heaters, such as pyrolysis furnaces and reformers. Of particular note, the configuration of reformers provides ample space in their long horizontal convection sections, which allows multiple streams to be preheated / superheated (e.g. feedstock, process air, steam). Combustion air is one of the preheat streams often incorporated into reformer designs to maximize thermal efficiency (European Commission, 2007; ThyssenKrupp Uhde, 2011; Guerts International, 2016). In fact, APH are utilized in several existing steam methane reformers in Canada.

It is less likely to incorporate APH in retrofit situations for reformers since the convection section in the original design wouldn’t likely have extra space available for the relatively large APH unit and the retrofit may demand other significant modifications to the reformer such as burner changes and new air ducting (Natural Resources Canada, 2012). That said, these additional difficulties do not preclude APH from being installed on retrofit reformers, as evident from a reformer upgrade project completed in 2015 at a methanol plant (Harker et al., 2016).

Newly designed ethylene plants (e.g. circa 2000) can incorporate APH units (NOVA Chemicals Corporation, 2002). There are also examples of APH being installed on retrofitted ethylene cracking furnaces as recently as 2012 / 2013 (NOVA Chemicals (Canada) Ltd., 2012).

Overall, it is clear from the above examples that APH is prevalent in the chemical and fertilizer industries. Moreover, APH is still a relevant energy reduction option for certain applications in newly designed chemical and fertilizer plants.

5.2 Effect of Air Preheat on Emissions

As mentioned previously, APH can achieve a 10% to 12% improvement in thermal efficiency for flue gas streams at 400°C. This efficiency directly translates to fuel savings for the unit. Thus, a comparable reduction in CO₂ emissions can be achieved through the use of APH.

The main processing equipment at some chemical and fertilizer plants have other upstream heat recovery units in the convection section, so the flue gas temperature at the APH unit might be lower than the example above (400°C). Therefore, the stated improvement in thermal efficiency and corresponding reduction in CO₂ emissions from installing APH is likely not achievable for these units.

Conversely, increasing the combustion air temperature through APH promotes the formation of thermal NOₓ. Preheating the combustion air from 21°C to 204°C increases NOₓ emissions by a factor of 1.4 (US EPA, 1993; European Commission, 2007). If the air is preheated to 316°C, the NOₓ emissions more than double (US EPA, 1993). In fact, it is this increase in NOₓ emissions that limits the application of APH in smaller boilers (US EPA, 2010).

Air preheaters can be installed with many of the NOₓ pollution control technologies to offset the increase in NOₓ emissions. It is overall environmental regulation driving compliance of all combustion units and associated equipment (i.e. APH) to meet more stringent NOₓ requirements. As a result, many
gas- and/or oil-fired LNB have been developed to incorporate the use of preheated ambient air (Baukal, 2012).

When new or retrofitted combustion equipment; such as pyrolysis furnaces, methane steam reformers, boilers and heaters, etc., are designed, they must ensure reliable operation under various circumstances and achievement of acceptable levels of air emissions whether APH is present or not. Its use is considered in the design and operation of a given combustion system (i.e. preheater installed on a boiler) to ensure minimal NOX emissions are generated to comply with all relevant air emission limits, standards and requirements. The challenge is to manage the combustion process and operational process of the entire combustion system in a manner that allows facilities to achieve these compliance goals efficiently.

It is also worth noting that radiant burners (e.g. burners with a fibrous ceramic burner at the tip) are not adversely affected by the elevated combustion air temperature from using APH (Alberta Research Council, 2007; Alzeta Corporation, 2017).

Carbon monoxide and hydrocarbon emissions can be reduced slightly by using APH since the higher air temperature promotes complete combustion.

### 5.3 Air Preheat Regulatory Requirements

At the time of this study, no regulatory requirements were found that recognize, directly affect, or give special consideration for air preheat use. This includes any special allowance or increase in limits of air emissions, such as NOX, to accommodate the additional emissions associated with the use of APR.
6.0 Fuel Types

Natural gas is the primary fuel used to operate major air emission sources at the vast majority of chemical and fertilizer plants. This chapter discusses the different fuel types used to supplement natural gas use and their impact on air emissions. The examination of alternative fuel choices other than natural gas, such as fuel oils and diesel fuel, is not included. Instead, the chapter focuses on gas streams recovered from downstream processes at a plant with sufficient heat content to be combusted in equipment burners as a supplementary fuel to natural gas.

6.1 Supplementary Fuels

6.1.1 Pyrolysis Furnace

At ethylene plants, there are multiple opportunities to recover gases that were not reacted / cracked in the pyrolysis furnace. Most of these gases are recovered and recycled to the upstream feedstock stream or purified and sold as products. In cases where it is too costly to further separate the recovered gas into useable products, the gas mixture can instead be recycled to the pyrolysis furnace burners to supplement fuel use. Below presents a simple block diagram of the ethylene production process and opportunities in the process to recycle waste streams for use as a supplementary fuel source for the pyrolysis furnaces.

Figure 29 Block diagram of an ethylene plant and supplementary fuel source opportunities from recycled waste streams.

At the end of the compressor and condensate section at the ethylene plant, a hydrogen- and methane-rich stream can be isolated from main process stream (ERM, 2014). Most of the hydrogen can be recovered from this off-gas stream; but, some of the hydrogen, methane, and other trace hydrocarbons cannot feasibly be separated into useable products. This waste stream, referred to as tail gas, contains approximately 75% hydrogen, 24% methane, other trace hydrocarbons, CO, CO2, and inerts (ERM, 2014). It has a sufficient heating value (e.g. 523 Btu scf⁻¹) to be recycled and blended with natural gas to fire the pyrolysis furnace burners (ERM, 2014).

Similarly, in the hydrocarbon separation section, the overhead stream from the demethanizer contains hydrogen, methane, and some C2 and C3 fractions. Almost all of the C2 and C3 fractions and a majority of the hydrogen can be separated from methane using multiple refrigeration / distillation units. These separated streams can be reused and sold as products. However, the separation process will inevitably generate an off-gas stream, comprised mostly of hydrogen and methane (Yan, 2000). While it is too costly to further separate this off-gas stream, the stream has high enough heat content such that it can be used as a fuel gas in the pyrolysis furnace burners (Yan, 2000; BASF, 2011).
These are a few examples of recycle streams at ethylene plants that can be used to supplement natural gas use. It is possible that other off-gas streams in the ethylene production process can also be used as supplementary fuel for the burners.

Overall, the use of supplementary fuels in pyrolysis furnaces is a fairly common practice, given that there are multiple opportunities to utilize the off-gas streams downstream of processing units at ethylene plants. Of eight companies reporting primary fuel type(s) for their pyrolysis furnaces to the US EPA’s RACT/BACT/LAER Clearinghouse, six companies (or 75%) indicated they used process off-gas to supplement their natural gas use in the pyrolysis furnaces (US EPA, 2017).

### 6.1.2 Steam Methane Reformer

At hydrogen plants using an SMR, impurities in the hydrogen stream are removed in the pressure swing adsorption (PSA) unit to produce a high purity hydrogen product (99.9% or higher hydrogen content) (Rostrup-Nielsen and Rostrup-Nielsen, 2002). The off-gas stream from the PSA unit, referred to as PSA off-gas or PSA gas, contains unreacted methane, some unrecovered hydrogen, and other trace constituents. This stream is typically mixed with natural gas for use in the SMR burners or alternatively can be recycled as SMR feedstock (Baukal, 2012; Rostrup-Nielsen and Rostrup-Nielsen, 2002).

At ammonia plants, natural gas use can be reduced by firing burners in the SMR with a purge gas collected from the cooling and condensation stage after the ammonia converter (a.k.a. ammonia synthesis loop) (Linde, 2017). In the ammonia synthesis loop, the reaction by-products (i.e., other than the primary ammonia reaction) and inerts accumulate and adversely affect the ammonia production by reducing the reactants partial pressures and putting a greater load on the loop (Ruddock et al, 2003). They must, therefore, be continuously purged from the system to maintain concentrations within set limits. This purge stream typically contains 60% hydrogen, 20% nitrogen, 10% methane, 5% argon, and 4% ammonia in varying concentrations, depending on the ammonia plant design and operation (Linde, 2017). The purge gas is typically mixed with the main fuel gas (e.g. natural gas) and supplied to the burners in the SMR (Baukal, 2012). However, it can be economical to first recover the hydrogen, ammonia, and inerts (Linde, 2017). This is accomplished using a purge gas recovery system, which consists of separate ammonia and hydrogen recovery units. Ammonia can be recovered using a water wash system, while hydrogen can be separated in a coldbox or membrane unit and recycled upstream of the ammonia converter (Membrane Technology and Research, Inc., 2016; Linde, 2017). Inerts are separated from the remaining fuel gas, which is mostly methane, in a series of rectification columns (Linde, 2017). The fuel gas is then sent to the burners in the SMR.

Like ammonia plants, methanol plants produce several other hydrocarbon by-products at the same time as methanol in the synthesis loop, which are purged from the loop (US Methanol Corp., 2016). Again, these by-products are purged to prevent accumulation in the loop and adversely affecting methanol production by reducing the reactants partial pressures and putting a greater load on the loop. The purge gas is rich in hydrogen (e.g. 67 mole percent), which can be used as a fuel in the SMR burners (Celanese, 2013; Baukal, 2012; US Methanol Corp., 2016).

Of 27 companies reporting primary fuel type(s) for their steam methane reformers to the US EPA’s RACT/BACT/LAER Clearinghouse, eight companies (3 hydrogen plants, 3 ammonia plants, and 2 methanol plants), or 30%, indicated they used process off-gas to supplement their natural gas use in the pyrolysis furnaces (US EPA, 2017).
6.1.3 **Boilers and Heaters**

The off-gas streams from ethylene, methanol, ammonia, and hydrogen plants can be used to supplement natural gas use in burners for steam boilers and heaters instead of the pyrolysis furnace and SMR (Ramboll Environ, 2016) – albeit it is not as common a practice. Purge gas streams at other chemical and fertilizer plants can also be recovered and burned in boilers and process heaters / furnaces. For example, at polyethylene plants, the PE resins leaving the reactor contain un-reacted hydrocarbons and by-products, which are purged in the finishing stages using nitrogen. The nitrogen can be removed, and the purge gas can be burned in process heaters and/or boilers (Membrane Technology and Research Inc., 2017).

6.1.4 **Flares and Thermal Incinerators**

Ramboll Environ is not aware of specific examples where other fuels from the chemical or fertilizer plant processes were used to supplement natural gas use for flares and thermal incinerators.

6.2 **Effect of Fuel Type on Emissions**

The use of off-gas streams in burners should not have a significant impact on the emission intensity of CACs, especially if blended with natural gas. One notable exception is firing burners with the purge gas stream from ammonia plants if the ammonia is not recovered prior to use in the burners. Ammonia converts to NO\textsubscript{X} emissions through combustion, and therefore trace amounts of ammonia can increase NO\textsubscript{X} emissions (Baukal, 2012). Burner vendors report that 0.2% ammonia by volume in the purge gas stream will contribute to over 80 ppmv, to the burner outlet NO\textsubscript{X} concentration (Hodge and Popovici, 1994). This issue can be mostly alleviated by installing a purge gas recovery system to reduce the ammonia content prior to firing the gas in the burners.

Furthermore, utilizing off-gas streams as fuel for combustion sources does not prohibit the use of burner technologies that inhibit the formation of NO\textsubscript{X}.

Off-gas streams with high hydrogen content can actually reduce the GHG emission intensity relative to natural gas since hydrogen does not contain carbon atoms (BASF, 2011). Celanese (2013) calculated the GHG emission intensity from burning purge gas (with 67 mole percent hydrogen) in an SMR at a methanol plant to be 30% of the natural gas burning emission intensity (i.e., 70% reduction).
7.0 Jurisdictional Review of Air Emissions Requirements

A jurisdictional review was completed to identify and discuss the air emission requirements associated with the chemical and fertilizer sector in leading jurisdictions in Canada, the United States and Europe. The jurisdictional review focused on leading jurisdictions with well-developed air quality regulatory programs that are currently used to encourage and/or enforce evolving technologies at chemical and fertilizer plants.

7.1 Canadian Provinces

7.1.1 British Columbia

The Environmental Management Act (EMA) provides the legal framework for the regulation of industrial air emissions in the province of British Columbia. Under the EMA a number of regulations, amendments and codes of practice have been implemented to balance the regulatory burden with the expected level of risk posed by industrial activities. This regulatory efficiency is accomplished by having simple or minimal requirements for lower-risk activities and only requiring comprehensive assessments when justified by the potential level of risk. For the purposes of discharge authorizations, operations are classified as high, medium or low risk and are subject to the following requirements.

- High-risk operations, or those where development of a code of practice is impractical, require a permit or approval to authorize their discharges. A Technical Assessment Report must be prepared to support the permit application.
- Medium-risk operations must register under their specific code of practice or regulation, if required by that code or regulation. If a code of practice or regulation has not been developed, a permit or approval is required.
- Low-risk operations do not require formal authorization to discharge waste. However, the discharges must not cause pollution or present a risk to public health. “Pollution” is defined by the EMA as “the presence in the environment of substances or contaminants that substantially alter or impair the usefulness of the environment”.

The Waste Discharge Regulation B.C. Reg. 320/2004 (WDR) has a central role in the regulation of industrial air emissions. Schedules 1 and 2 of the Waste Discharge Regulation provide a listing of industries and activities that are considered “high” and “medium” risk operations respectively. Schedule 1 lists high-risk operations that include chemical and chemical products industry, oil and natural gas industry, and municipal solid waste management among several other industrial activities. Schedule 2 lists medium-risk operations such as the asphalt plant industry, petroleum storage, and wood processing industry. Activities not explicitly identified in Schedules 1 and 2 are considered “low risk” and do not require approval, provided that they do not “cause pollution” as per 6(4) of the EMA.

Schedule 1 of the WDR encompasses both the chemical and fertilizer sectors, as “chemical and chemical products industry” is broadly defined to mean: “…establishments, except home-based businesses, educational facilities and establishments of hobbyists or artisans, engaged in manufacturing industrial organic or inorganic chemicals, fertilizers, pesticides, plastics, synthetic resins or moulding compounds, and includes, but is not limited to, establishments manufacturing food supplements, vitamins or pharmaceuticals, except pharmaceuticals referred to in the definition of "biotechnology industry"; (B.C. Re. 320/2004)”
No specific regulatory requirements for the chemical or fertilizer sector were identified in the WDR. Instead, a permit/approval application, accompanied by a Technical Assessment Report, would be required for chemical or fertilizer production facilities as they are Schedule 1 activities. The expectations for the Technical Assessment Report are outlined in the guidance document “Technical Assessment” and include the following:

- Preparation by a qualified professional
- Description of phases of project including site preparation and construction; site operations; and site closure.
- Identification of non-product outputs (i.e. discharges) to the environment – “Air Contaminants – including those listed in the application or that are currently authorized, spills, fugitive emissions from all processes (including cooling), emissions from ponds and yards.”
- Assessment of discharges including potential impacts to humans and other receptors by comparison of predicted ambient environmental quality to established provincial or federal ambient environmental quality guidelines. (Technical Assessment, British Columbia Ministry of Environment (BC MOE), April 2015)

For air discharges, a Technical Assessment would involve ambient air dispersion modelling. The British Columbia Air Quality Dispersion Modelling Guideline (BC MOE, 2015) outlines the requirements for dispersion modelling assessments that accompany approval applications for higher-risk sources that include the chemical and fertilizer sectors. A “Level 3” (i.e. Comprehensive) air dispersion modelling assessment is required for these sources using either the AERMOD or CALPUFF dispersion models. The guideline provides factors to consider in the selection of model. It also outlines considerations regarding the uncertainty of fugitive emissions including approaches for reporting and interpreting modelling results for these sources. When developing an air dispersion modelling plan for a particular application, consultation with BC MOE is recommended to obtain input and initial feedback from the regulator on items such as the selection of an appropriate dispersion model and treatment of fugitive emissions. The consultation will also help expedite the approval of a modelling plan.

A Level 3 Assessment must include cumulative effects through a consideration of background concentrations. The guideline suggests acceptable approaches for the purposes of developing appropriate background concentrations that include:

- A network of long-term ambient air monitoring stations near the source under study;
- Long-term ambient air monitoring at a different location that is adequately representative; and
- Modelled background.

The BC MOE handles permitting throughout the province with the exception of the Lower Fraser Valley Air Zone which has been delegated to Metro Vancouver by the EMA. The requirements from Metro Vancouver may differ from the BC MOE as specific bylaws and rules can be developed by Metro Vancouver. Guidance from Metro Vancouver states that certain types of operations may not even require a permit and would be authorized instead under an emission regulation. Metro Vancouver can assist applicants with this determination and suggests consultation at the outset of any proposed project. Similar to the requirements for BC, no specific regulations were found targeting the chemical and fertilizer sector directly. A permit application including a technical assessment and refined air dispersion modelling assessment would likely be required analogous to how facilities in this sector, which would fall into Schedule 1, would be handled by the BC MOE. The Boilers and Process Heaters Emission Regulation Bylaw No. 1087, 2008 and Amending Bylaw No. 1190, 2013 may be relevant for
sources at a chemical or fertilizer facility, applying to boilers or process heaters up to 50 MW. The consolidated requirements include provisions regarding dispersion modelling, emission testing, emission limits and a fee structure. Emission limits and monitoring requirements are provided in the following table.

<table>
<thead>
<tr>
<th>Equipment/Process</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>New/modified boilers or process heaters fuelled by natural gas or propane</td>
<td>Concentration in flue gas: Nitrogen oxides ≤ 60 mg/m³</td>
</tr>
<tr>
<td>Boilers or process heaters fuelled by Biomass, where Facility Capacity &gt;3MW</td>
<td>Concentration in flue gas: Filterable particulate matter ≤ 10 mg/m³ Carbon Monoxide ≤ 250 ppmv Total Volatile Organic Compounds ≤ 20 mg/m³ Opacity ≤ 5% Continuous Emission Monitoring System (CEMS) required for carbon monoxide; oxygen; and opacity. Dispersion modelling for nitrogen oxides, PM₁₀, and PM₂.₅ (1h /24h and annual averaging time)</td>
</tr>
<tr>
<td>Boilers or process heaters fuelled by Biomass, where Facility Capacity ≤ 3MW</td>
<td>Concentration in flue gas: Filterable particulate matter ≤ 18 mg/m³ Carbon Monoxide ≤ 250 ppmv Total Volatile Organic Compounds ≤ 20 mg/m³ Opacity ≤ 5% CEMS required for oxygen; and carbon monoxide (if Facility Capacity &gt; 1MW) Dispersion modelling for nitrogen oxides, PM₁₀, and PM₂.₅ (1h/ 24h averaging time)</td>
</tr>
<tr>
<td>Use of fuel oil as standby fuel</td>
<td>Hours of operation ≤ 350 hrs per calendar year Sulphur content not to exceed 15 mg/kg</td>
</tr>
</tbody>
</table>

Notes:
- For natural gas or propane, concentrations are referenced at 3% oxygen content in stack gas corrected to dry conditions at 20°C and 101.325 kilopascals.
- For biomass, concentrations are referenced at 8% oxygen content in stack gas corrected to dry conditions at 20°C and 101.325 kilopascals

In summary, no specific regulations or codes of practice were identified for the chemical or fertilizer sector in British Columbia. These facilities would require an individual permit or authorization of discharges for air emissions, which would only be issued after a comprehensive air dispersion modelling assessment.

### 7.1.2 Ontario

The Ontario Environmental Protection Act (EPA) provides the regulatory framework for the regulation of air emissions from industrial sources, including those in the chemical and fertilizer sectors.
Regulation of air quality in Ontario is administered by the Ministry of the Environment and Climate Change (MOECC). Regulations, standards and guidelines under the EPA describe the requirements that must be met by various industries in Ontario. Specific to the petrochemical sector, the Petrochemical Industry Standard provides requirements for major sources of benzene and 1,3-butadiene emissions within this sector. Emissions of all other compounds in the petrochemical sector and all emissions in the chemical and fertilizer sectors must comply with regulations broadly applicable to industrial sources in Ontario. Regulations or guidelines that may be applicable to the chemical and fertilizer sector are discussed below.

**Ontario Regulation 419/05 – Local Air Quality**

O. Reg. 419/05, Air Pollution – Local Air Quality was introduced on November 30, 2005, and replaced Ontario Regulation 346, R.R.O. 1990, “General - Air Pollution”. In Ontario, chemical manufacturing facilities must have an Environmental Compliance Approval (ECA; formerly Certificate of Approval or CofA) for sources of air emissions. The ECA application requirements, including the methodology to assess the air impacts of the proposed new source(s), and air standards, are largely specified in Ontario Regulation 419/05 (O. Reg. 419/05) and are supplemented by additional guidance documents. ECAs are issued by the MOECC following a detailed technical review by an MOECC Engineer of the air dispersion modelling assessment, as documented in the Emission Summary and Dispersion Modelling (ESDM) report that accompanies an ECA application.

A new general manufacturing registry (O. Reg. 1/17) has been introduced early in 2017 by the MOECC, which eliminates the requirement for obtaining an ECA for lower-risk sectors. As opposed to defining lower-risk sectors, O. Reg. 1/17 identifies specific facility types and activities by NAICS code which are considered higher risk and ineligible for the registry due to potential air, noise and/or odour impacts. The chemical manufacturing sector (NAICS 325) falls into this category. Therefore, under Section 9 of the Ontario Environmental Protection Act, all new or modified sources at facilities in the chemical and fertilizer sectors are still required to obtain an ECA covering the sources prior to construction or operation. If the facility has an ECA with Limited Operational Flexibility (LOF), a new ECA may not be required because modifications may be covered under the existing approval. This will only be considered if the facility can demonstrate compliance with the air standards through dispersion modelling and that records/documentation are updated in accordance with the ECA with LOF. Certain small sources at a facility may be considered negligible, in accordance with MOECC guidance, which may allow them to be excluded from the air dispersion modelling assessment.

O. Reg. 419/05 includes very prescriptive mandatory requirements that must be addressed in applications for air approvals (permits). This permitting program includes a requirement for air dispersion modelling to predict concentrations at points of impingement (POI). A POI is typically defined as a ground level location at or beyond the property line of the facility. A POI may also be located on or within a facility’s property if there is a child care facility present, or the facility itself is a healthcare facility, a senior citizens’ residence/long-term care facility or an educational facility. Certain elevated receptors may also be considered a POI, such as openable windows or air intakes on sufficiently nearby buildings at a neighbouring property. Maximum predicted concentrations at POI are compared to Air Quality Standards or other criteria. Most of the standards are based on Ambient Air Quality Criteria (AAQC); however, they are subject to more rigorous requirements than AAQCs. Almost all of the Schedule 3 Standards are the same as the AAQCs, which are developed through the MOECC’s standard setting process. In addition to the provisions provided directly within O. Reg. 419/05, the MOECC also has issued Guidance for Preparing an Emission Summary and Dispersion Modelling (ESDM) Report (Guideline A-10), and an Air Dispersion Modelling Guideline for Ontario.
(ADGMO) also referred to as Guideline A-11 that serve to clarify expectations of the technical evaluations to support ECA applications.

Air dispersion modelling assessments, as per O.Reg.419/05 and associated guidance, consider air quality impacts from the proponent’s facility only. They do not specifically account for background ambient air concentrations nor do they consider cumulative impacts through approaches commonly used in other jurisdictions, such as the inclusion of significant neighbouring sources emitting common contaminants in the dispersion model. Modelling using non-default options such NO to NO₂ conversion algorithms is also not common in Ontario. Air Standards in Ontario are considered “effects-based” standards that are developed without consideration of technical or economic issues and are revised from time to time. Ontario standards can be more stringent than standards in other provinces where cumulative effects are prescriptively evaluated and/or technical and economic considerations factored into the standard-setting process. This is especially evident with some recently implemented standards for air toxics. For instance the new standard for benzene in Ontario is an annual average concentration of 0.45 µg m⁻³, a level that may be below some urban background concentrations.

Several years ago, as a result of an appeal of an approval, Ontario’s Environmental Review Tribunal (ERT) found that the MOECC must consider cumulative effects before issuing an approval. The MOECC has stated that they are in the process of developing a framework for assessing cumulative effects; but, this has not yet been released in any form.

Routinely, the MOECC does not explicitly require a proponent to address cumulative effects in a permit application. The MOECC has stated that they “consider” cumulative effects on every approval; although, the overall approval process and O. Reg. 419/05 are reliant on the assumption that the “effects-based” air standards in Ontario are, in most circumstances, sufficiently conservative to be protective. However, in a few cases where public comment on applications has demanded it, typically where there is already a significant industrial presence, the MOECC has required the proponent to prepare and submit an assessment of cumulative effects focused on specific contaminants.

All compounds emitted from the facility need to be considered in ECA applications. This requirement means that the ground level concentrations for compounds, for which no standard or assessment value has been published by the MOECC, still need to be modelled. For chemical or fertilizer facilities, this modelling would most likely be completed using the AERMOD model. The MOECC would then evaluate whether the concentration of these compounds (i.e. those without a standard or assessment value) is acceptable with input from Ministry scientists/toxicologists. If a refined air dispersion modelling assessment predicts POI concentrations resulting from a facility’s emissions are above the Schedule 3 Standards, a facility can choose to either abate emissions if feasible in the short term, or has the following two alternative compliance options available.

1. Request a site-specific standard (SSS)
2. Register under a sector/equipment-based technical standard (if available)

These alternative compliance options are discussed in further detail below.

O.Reg. 419/05 Alternative Compliance Option #1 – Site Specific Standard (SSS)

The SSS process generally results in the application of Best Available Technology at industrial emission sources that specifically contribute to a facility’s inability to meet one or more provincial air quality guidelines or standards. The MOECC has the authority to grant a facility with a SSS for a
contaminant that is less stringent than the corresponding O. Reg. 419/05 standard which could not be achieved – allowing the facility to continue to operate. However, a SSS is only issued after a detailed technical assessment of the documentation provided by the proponent requesting a SSS. The proponent is required to complete a technology benchmarking report and submit a plan outlining the implementation of technically and economically feasible technologies for emission reduction. The technologies or abatement strategies are specifically chosen to reduce POI concentrations (i.e. typically ground-level) of target contaminants. Inherent in the requirements of the regulation is the guiding principle of continuous improvement. If a facility is unable to meet air quality standards, even after implementing technically feasible measures to reduce emissions of certain pollutants, it will need to revisit the plans on a regular basis (typically every 5 or 10 years) to reassess feasibility of emission abatement actions.

In assessing what constitutes Best Available Technology for Ontario, a structured evaluation of control measures documented in a Technology Benchmarking Report is implemented in accordance with the Guideline for the Implementation of Air Standards in Ontario (GIASO) and other MOECC-issued guidance. Technologies must firstly be evaluated for technical feasibility and effectiveness in reducing emissions, without the consideration of economic arguments. Control strategies involving a combination of material substitution, process or work practice changes, and add-on controls need to be considered as well. In general, the most effective control strategy that is technically feasible needs to be included in the abatement plan that is prepared by a facility. However, the MOECC will also consider the cost effectiveness of solutions (i.e. cost per tonne reduction or Total Resource Effectiveness) and may allow facilities to delay actions on this basis. If a reapplication for a new SSS is necessary as the standard cannot be met when the original SSS expires, previous conclusions with respect to technical feasibility and/or cost effectiveness would need to be reassessed, typically every 5 to 10 years.

In Ontario, industrial facilities that are requesting a SSS are also required to host a public meeting. Summary documents of the meetings must be posted on a company’s website. Continued use of air dispersion modelling as an assessment and compliance tool is required for all compounds at facilities with one or more SSSs. Any facility, regardless of sector, is eligible to apply for a SSS. As a result, this process may be applicable to the chemical and fertilizer sectors.

O.Reg. 419/05 Alternative Compliance Option #2 – Technical Standard

O. Reg. 419/05 allows sectors in which more than one facility is unable to meet the “effects-based” air quality standards to make a request to the MOECC for a Technical Standard to be developed. Technical Standards are issued after an extensive consultation process that includes significant technology benchmarking; along with, a review and evaluation of the major air emission sources that contribute to facilities in a given sector being unable to achieve an air quality standard. Technical Standards can be sector and contaminant specific providing broadly applicable requirements for specific sources that will reduce and control emissions in accordance with best practices. Emissions of specific contaminants from sources or equipment covered by an applicable technical standard are exempt from air dispersion modelling requirements. Instead, compliance is based on meeting the requirements of the technical standard which mandate implementation of technology-based solutions and/or best practices to manage emissions. Once a technical standard is published, eligible facilities are able to register under it.

Existing technical standards are currently consolidated in the MOECC publication “Technical Standards to Manage Air Pollution Version 5 – July 27, 2016”. A technical (industry) standard for the
Petrochemical sector was added to this version of the consolidated publication. The Petrochemical Industry Standard applies to facilities with NAICS code 325110 (Petrochemical Manufacturing) and covers sources of benzene and 1,3-butadiene. The sector had identified that more than one facility would not be able to meet the stringent new air quality standards for these contaminants which came into effect in July of 2016, and initiated the development of a technical standard well in advance of this phase-in date. The Petrochemical Industry Standard includes general performance requirements of air pollution control devices and flares; addresses air emissions from industrial sewage, product loading, and storage vessels; and outlines leak detection and repair (LDAR) programs, and ambient air monitoring requirements.

Guideline A-9: NO\textsubscript{X} Emissions from Boilers and Heaters

Guideline A-9 applies to new and modified fossil-fuel fired boilers and heaters which have a fuel energy input of greater than 10 million Btu hr\textsuperscript{-1}. Limits are specified in terms of grams of NO\textsubscript{X} emitted per gigajoule of fuel energy consumed. It also requires the submission of a statement signed by a licenced Professional Engineer in Ontario stating compliance with the limits.

The Guideline A-9 is the product of how the MOECC is interpreting and applying the CCME Guideline, “National Emission Guideline for Commercial/Industrial Boilers and Heaters, approved by the Canadian Council of Ministers of the Environment in March, 1998”. Approvals/permits (i.e. ECAs, formerly CofAs) are issued once the MOECC review engineer is satisfied that Guideline A-9 will be met by relevant sources.

The limits in grams of NO\textsubscript{X} (as NO\textsubscript{2}) per GJ of heat input for applicable fuels are shown in the table taken from the guideline. The guideline also provides the limits in ppm in flue gas at specified conditions. There are no ongoing source testing and/or CEMS requirements in Guideline A-9.

<table>
<thead>
<tr>
<th>Capacity</th>
<th>NO\textsubscript{X} Emission Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gaseous Fuel</td>
</tr>
<tr>
<td>10.5 - 105 GJ/h</td>
<td>26 g/GJ</td>
</tr>
<tr>
<td>(10 - 100 MMBtu/h)</td>
<td></td>
</tr>
<tr>
<td>&gt;105 GJ/h</td>
<td>40 g/GJ</td>
</tr>
<tr>
<td>(&gt;100 MMBtu/h)</td>
<td></td>
</tr>
</tbody>
</table>

O. Reg. 194/05 Industry Emissions – Nitrogen Oxides and Sulphur Dioxide

The regulation defines a framework for capping emissions of sulphur dioxide and nitrogen oxides for cement, non-ferrous smelting, petroleum, carbon black, flat glass, pulp and paper, and iron and steel sectors. It defines allowances and reduction credits that are available for trade. The basis for these targets is established by Ontario’s Industry Emissions Reduction Plan. Facilities subject to this
regulation are still subject to O.Reg. 419/05 for NO\textsubscript{X} and SO\textsubscript{2} that require local ground-level air quality impacts be assessed and reduced if unacceptable.

**R.R.O. 1990, Reg. 350 Lambton Industry Meteorological Alert**

This regulation applies the bubble concept to an area of high emissions intensity using an ambient monitoring network called the “Lambton Industry Meteorological Alert System” which restricts operations of facilities when the concentration of sulphur dioxide reaches 0.07 parts per million parts in air. During an Alert, no person shall cause or permit the emission of sulphur dioxide from a source of contaminant so that its concentration at a point of impingement exceeds 415 micrograms of sulphur dioxide per cubic metre of air, half hour average.

**7.1.3 Quebec**

Quebec has an *Environmental Quality Act* under which regulations targeting industrial air emission sources exist including:

- Q-2, r.4.1 Clean Air Regulation
- Q-2, r.5 Regulation Respecting Industrial Depollution Attestations (Regulation Q-2 r.5 “Règlement sur les attestations d'assainissement en milieu industriel”)
- Q-2, r.15 Regulation Respecting Mandatory Reporting of Certain Emissions of Contaminants into the Atmosphere

The Clean Air Regulation includes fugitive particle emission standards, emission opacity requirements, VOC emission standards, fuel sulphur content limits, emission limits from combustion equipment (i.e. boilers/process heaters) for PM and NO\textsubscript{X} (see following table), and air quality standards (Schedule K). It also provides direction on periodic source testing requirements for specific source types.
<table>
<thead>
<tr>
<th>Equipment/Process</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>New fuel burning equipment with a rated capacity from 3 to 30 MW</td>
<td><strong>Nitrogen Oxide Emission Limit (g GJ⁻¹ of fuel input):</strong>&lt;br&gt;26 g GJ⁻¹ for gas&lt;br&gt;40 g GJ⁻¹ for light fuel oil&lt;br&gt;90 g GJ⁻¹ for heavy fuel oil (nitrogen content ≤0.35%)&lt;br&gt;110 g GJ⁻¹ for heavy fuel oil (nitrogen content &gt;0.35%)</td>
</tr>
<tr>
<td>New fuel burning equipment with a rated capacity greater than 30 MW</td>
<td><strong>Nitrogen Oxide Emission Limit (g GJ⁻¹ of fuel input):</strong>&lt;br&gt;40 g GJ⁻¹ for gas&lt;br&gt;50 g GJ⁻¹ for light fuel oil&lt;br&gt;90 g GJ⁻¹ for heavy fuel oil (nitrogen content ≤0.35%)&lt;br&gt;125 g GJ⁻¹ for heavy fuel oil (nitrogen content &gt;0.35%)</td>
</tr>
<tr>
<td>Existing fuel burning equipment put into operation after Nov 14, 1979 with a rated capacity between 15 and 70 MW</td>
<td><strong>Nitrogen Oxide Emission Limit (g GJ⁻¹ of fuel input):</strong>&lt;br&gt;80 g GJ⁻¹ for gas&lt;br&gt;175 g GJ⁻¹ for light or heavy fuel oil</td>
</tr>
<tr>
<td>Existing fuel burning equipment put into operation after Nov 14, 1979 with a rated capacity greater than 70 MW</td>
<td><strong>Nitrogen Oxide Emission Limit (g GJ⁻¹ of fuel input):</strong>&lt;br&gt;110 g GJ⁻¹ for gas&lt;br&gt;135 g GJ⁻¹ for light or heavy fuel oil</td>
</tr>
<tr>
<td>Fuel burning equipment with a rated capacity from 3 to 15 MW and fuelled by light or heavy fuel oil</td>
<td><strong>Particles Emission Limit (g GJ⁻¹ of fuel input):</strong>&lt;br&gt;85 g GJ⁻¹ if put into operation before Nov 15, 1979&lt;br&gt;60 g GJ⁻¹ if put into operation after Nov 14, 1979</td>
</tr>
<tr>
<td>Fuel burning equipment with a rated capacity greater than 15 MW and fuelled by light or heavy fuel oil</td>
<td><strong>Particles Emission Limit (g GJ⁻¹ of fuel input):</strong>&lt;br&gt;60 g GJ⁻¹ if put into operation before Nov 15, 1979&lt;br&gt;45 g GJ⁻¹ if put into operation after Nov 14, 1979</td>
</tr>
</tbody>
</table>

Some specific requirements for the chemical and fertilizer sectors found in the Clean Air Regulation are as follows:

- Fertilizer production or mixing plants must not emit particles into the atmosphere in a concentration greater than 30 mg Rm⁻³ of dry gas for each emission point;
- Particle emissions from the transfer, fall or handling of materials including … fertilizers… must not be visible more than 2 metres from the emission point;
- A petrochemical or organic chemical plant having production greater than 250 million litres per year must implement a plan to detect and repair any volatile organic compound leak causing a concentration in the atmosphere in excess of 10,000 ppm, or any butadiene or benzene leak causing a concentration in the atmosphere in excess of 1,000 ppm;
- For flares at petrochemical plants with steam injection, the steam/gas ratio must be regulated automatically; and
- Equipment-specific requirements for large tanks (>75 m³).
Under the *Environmental Quality Act*, industrial sources of air emissions are required to hold a certificate of authorization: “No one may erect or alter a structure, undertake to operate an industry, carry on an activity or use an industrial process or increase the production of any goods or services if it seems likely that this will result in an emission, deposit, issuance or discharge of contaminants into the environment or a change in the quality of the environment, unless he first obtains from the minister a certificate of authorization.(Q-2, s.22, as of Nov 2016)”

To obtain a certificate of authorization, a proponent needs to demonstrate that the requirements of the Clean Air Regulation will be met, including the Air Quality Standards given in Schedule K demonstrated through air dispersion modelling. Modelling guidance from Quebec requires that AERMOD or other recognized model (i.e. Screen, CALPUFF) be used and background concentrations be accounted for. In demonstrating compliance with the NO₂ standard, NO to NO₂ conversion can be considered as well.

The City of Montreal regulates sources situated within its boundaries in accordance with “Règlement 90”. The provincial Clean Air Regulation does not apply to sources covered by the bylaws of the city. The bylaw includes limits on sulphur content in fuels, and requires estimation of emissions and comparison to air quality limits using a prescribed calculation; as well as, implementation of leak detection and repair programs at petrochemical and organic chemical plants.

### Saskatchewan

The *Environmental Management and Protection Act* (2010) and the General Regulations Saskatchewan Environmental Code (the Code) regulate air emissions from industrial sources. While no specific regulations for the fertilizer or chemical sectors were identified, the general regulations, in the aforementioned Act and Code, are broad enough to cover these sectors.

The Environmental Code covers industrial air emissions in the E.1.2 Industrial Source (Air Quality) Chapter. Under the new regulations and the Environmental Code, industrial facilities, which would include chemical and fertilizer plants, are required submit an environmental protection plan (EPP) instead of obtaining a permit. Existing permits, covering present operations at an industrial facility, issued prior to 2010 under previous regulations such as the *Clean Air Act* remain in force until Jan 1, 2020, unless they expire sooner, at which time the facility would need to have fully transitioned to operating in accordance with an accepted environmental protection plan. This phased-in transition applies only to sources as they were previously permitted; new industrial sources will now require an EPP instead of applying for a permit. The regulation identifies “results-based objective” of limiting the probability of an unacceptable adverse effect. The EPP must be signed by a “qualified person” who is of the opinion that the methods and components in the EPP will satisfy the results-based objective, including taking reasonable measures to:

- Site an industrial source facility in an acceptable location;
- Ensure that the ambient air quality standards found in Table 20 of the Saskatchewan Environmental Quality Standard (SEQD) are met. Standards exist for total suspended particulate, PM₁₀, PM₂.₅, potash, SO₂, CO, NO₂ and H₂S;
- Ensure that the applicable sector-specific emission limit standards found in Table 21 of the SEQD are met;

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4 [http://ville.montreal.qc.ca/portal/page?_pageid=7237,75191583&_dad=portal&_schema=PORTAL](http://ville.montreal.qc.ca/portal/page?_pageid=7237,75191583&_dad=portal&_schema=PORTAL)

• Calculate or measure annual air contaminant emissions;
• Minimize the effects on the environment of air contaminants (water quality, ecology);
• Minimize the release of fugitive air contaminants from industrial source facilities; and
• Include components on monitoring, recording and reporting.

In general, the provisions in the EPP, including monitoring requirements, will be developed by industry/environmental professionals and the ‘qualified person’ will provide a signed statement regarding their adequacy for achieving the results-based objectives. Prescriptive monitoring requirements, in relation to source testing and application of CEMS at certain facility/source types, do not exist. Currently there is only one sector-specific emission limit in Table 21 of the SECD that applies to potash mining and is therefore relevant to the fertilizer industry. It reads: “No person shall cause or allow the discharge of particulate matter into the ambient air from the product drying process of a new plant in a concentration exceeding 0.57 grams per dry standard cubic meter.”

7.2 United States

7.2.1 U.S. Environmental Protection Agency

The United States Environmental Protection Agency (US EPA) is the main federal environmental regulatory agency in the United States (U.S.). US EPA performs scientific research regarding environmental impacts to various media, and plays a major role in developing U.S. policy and adopting environmental regulations. US EPA delegates some of its authority to State agencies, who then implement federal programs in addition to their own State programs. Individual States have the ability to implement environmental regulatory tools and provisions that are more stringent than the Federal requirements; but, never ones that are less strict than the national obligations.

The primary statute regulating air quality in the U.S. is the Clean Air Act (CAA), which was originally adopted in 1970 and most recently amended in 1990. The CAA contains mandates for US EPA in its regulation of air quality, by specifying pollutants to be regulated, as well as the types of regulations that US EPA should develop for industrial, commercial and residential sources of air pollution.

US EPA adopts National Ambient Air Quality Standards (NAAQS) for criteria pollutants specified by the CAA. These criteria pollutants are PM$_{2.5}$, PM$_{10}$, SO$_2$, NO$_2$, ozone, CO and lead. Precursors to criteria pollutant formation are also regulated under U.S. criteria pollutant programs. These include VOC and NO$_X$, which are treated as precursors to ozone, and SO$_X$ and NO$_X$ (and in some cases, VOC and NH$_3$), which are treated as precursors to PM$_{2.5}$. Based on ambient air monitoring data, areas within a state are designated as either nonattainment, attainment or unclassifiable for each criteria pollutant. Attainment areas are those areas where the levels of criteria pollutants meet or are below the NAAQS. Nonattainment areas are those areas where the criteria pollutant levels exceed a given NAAQS, or that contribute to exceedances in a nearby area that does not meet a NAAQS. Unclassifiable areas are those that cannot be classified on the basis of available information. For regulatory purposes, unclassifiable areas are treated as attainment areas.

A State Implementation Plan (SIP) is the federally approved and enforceable plan by which each state in the U.S. identifies how it will attain and/or maintain compliance with the NAAQS. The SIP would typically include rules, emissions inventories, ambient monitoring data, control strategies and goals, and modelling results. Each item in the SIP must be adopted by a state after public notice and
comment, then submitted to US EPA for approval, and finally approved into the SIP by US EPA after public notice and comment.

Section 172 of the Federal CAA, entitled “Nonattainment Plan Provisions,” specifies SIP content with respect to attaining the NAAQS in nonattainment areas. SIP requirements for nonattainment areas include:

- Submitting an approval plan within three years of an area being designated a nonattainment area, including modelling that demonstrates attainment after implementation of the proposed control strategy;
- Providing for the implementation of reasonably available control technologies (“RACT”);
- Compiling a comprehensive emissions inventory for all relevant pollutants;
- Implementing New Source Review (“NSR”) for nonattainment pollutants for all new or modified stationary sources that mandates use of control technologies that meet LAER and requires sufficient emission offsets from other sources in the area to ensure reasonable progress towards attainment of NAAQS; and
- Providing for the implementation of contingency measures in the event that the area fails to make reasonable progress or meet its attainment deadline.

For a nonattainment area to be re-designated as an attainment area, a revised SIP must be submitted and approved. This re-designation would only occur after actual ambient monitoring data has demonstrated that attainment of the NAAQS has been achieved. Further, under Section 175 of the CAA, such re-designation is contingent on providing for the maintenance of NAAQS compliance for at least 10 years after the re-designation and must include measures to ensure such maintenance.

### 7.2.2 Air Permits - New Source Review

New Source Review (NSR) is a permit requirement for new or modified facilities, and is therefore also referred to as construction or preconstruction permitting. This regulation is primarily applicable to the pollutants listed under NAAQS and can apply to other regulated air pollutants, but NSR does not apply to HAPs. HAPs are federally regulated by the National Emission Standards for Hazardous Air Pollutants (NESHAPs), which is discussed in Section 7.2.4.

Since 2010, Greenhouse Gas (GHG) emissions are also regulated under the NSR program. Based on a decision from the United States Supreme Court challenging the regulation of GHG emissions under this program, GHG permit review is required only for sources that trigger major source NSR for at least one other pollutant. Sources are termed “major sources” if their actual or potential emissions meet or exceed a threshold value (e.g. 10 and 100 short tons per year for HAPs and other air pollutants, respectively).

The basic requirement for an NSR program is defined under Title I, Parts C and D of the CAA 1990 amendments. The issuing authority for NSR permits in most cases is either the state, local, or Indian Tribal government. However, the US EPA can issue NSR permits when a state or local program has not been approved to do so. If states can demonstrate that their program is as stringent as, or more stringent than US EPA's requirements, then a separate program by local and/or state governments may be developed, which can then be approved into the SIP for that state. In some cases, state or local governments may accept delegation of US EPA's NSR program and are referred to as "delegated states."
The NSR permitting requirements may be categorized into three classes:

1. Prevention of Significant Deterioration (PSD): PSD applies to new major sources as well as existing sources making a major modification of a pollutant, for which the area is designated attainment;
2. Nonattainment NSR permits (NNSR): NNSR applies to new major sources and existing sources making a major modification of a pollutant for which the area is designated nonattainment; and
3. Minor source permits.

PSD applies to new major sources, and major modifications at existing sources, of a pollutant for which the area is designated as attainment or unclassifiable with the NAAQS. PSD can also be required for increases in emissions of other regulated pollutants for which a NAAQS has not been developed – with the exception of HAPs. Overall, PSD requires: the installation of the Best Available Control Technology (BACT); an air quality analysis; an additional impacts analysis; and public involvement. Each element is further explained below.

- BACT is the maximum degree of emission control that has been achieved in practice and is considered feasible.

Section 169(3) of the federal CAA defines BACT as follows.

The term "best available control technology" means an emission limitation based on the maximum degree of reduction of each pollutant subject to regulation under this Act emitted from or which results from any major emitting facility, which the permitting authority, on a case-by-case basis, taking into account energy, environmental, and economic impacts and other costs, determines is achievable for such facility through application of production processes and available methods, systems, and techniques, including fuel cleaning, clean fuels, or treatment or innovative fuel combustion techniques for control of each pollutant. In no event shall application of “best available control technology” result in emissions of any pollutant which will exceed the emissions allowed by any applicable standard established pursuant to section 111 or 112 of this Act. Emissions from any source utilizing clean fuels, or any other means, to comply with this paragraph shall not be allowed to increase above levels that would have been required under this paragraph as it existed prior to enactment of the federal Clean Air Act Amendment so 1990.

As identified above, the feasibility of BACT is a case-by-case decision that considers energy, environmental, and economic impact. BACT encompasses several different aspects that include; but, are not limited to: design, equipment, work practice, or operational standard that can require add-on control equipment or modification of the production processes or methods. BACT is most commonly determined to be an emission rate, or in some cases, a pollution control efficiency. Ultimately, the BACT determination will allow the reviewing agency to assign emission limits that reflect the degree of BACT emissions control applied to an industrial site.

- The air quality analysis is the demonstration that emissions from a proposed new source or major modification of an existing source will not cause or contribute to a violation of any applicable NAAQS or PSD increment. The PSD increment is the amount of pollution an area is allowed to increase above a baseline concentration established for that area. It sets a cap on the
allowable emissions increase thus preventing the air pollutant concentrations in clean areas from increasing up to the levels set by the NAAQS. Generally, an air quality analysis involves the use of both ambient air monitoring data, and air quality dispersion modelling results. The dispersion modelling may include predictions resulting from the proposed project and emissions from nearby sources. Class I areas are areas of special national or regional natural, scenic, recreational, or historic value for which the PSD regulations provide special protection (e.g. National Parks and National Wilderness Areas).

- The additional impacts analysis assesses the impacts on soils, vegetation, and visibility caused by any increase in air emissions of any regulated pollutant from the source or modification under review, and from associated growth. Associated growth is industrial, commercial, and residential growth that may occur in the area due to the source.

- Public involvement with the NSR can occur in one of the following three ways.
  1. Public comment on NSR permits.
  2. Public comment on proposed US EPA NSR regulations and actions to approve state and local agency’s NSR regulations.
  3. Public can bring enforcement actions against sources that are not complying with their permits.

Nonattainment NSR applies to new major sources or major modifications at existing sources of a pollutant for which the area the source is located in is not in attainment with the NAAQS. All nonattainment NSR programs require: the installation of the lowest achievable emission rate (LAER) technology; emission offsets; and an opportunity for public involvement. Each element is explained further below.

- As defined in Section 171(3) of the federal CAA, LAER means for any source, that rate of emissions which reflects –
  (a) the most stringent emission limitation which is contained in the implementation plan of any State for such class or category of source, unless the owner or operator of the proposed source demonstrates that such limitations are not achievable, or
  (b) the most stringent emission limitation which is achieved in practice by such class or category of sources, whichever is more stringent.

In no event shall the application of this term permit a proposed new or modified source to emit any pollutant in excess of the amount allowable under applicable new source standards of performance.

The emissions may result from a combination of emissions-limiting measures such as a change in the raw material processed, a process modification, or add-on controls.

Similar to BACT, LAER is typically defined as an emission rate, or in some cases, a pollution control efficiency. Ultimately, the LAER will be used by the reviewing agency to assign emission limits that reflect LAER emissions control applied to an industrial site.

By definition, BACT is less stringent than LAER and allows for consideration of energy, environmental and economic impacts; along with evaluation of alternative production processes, available methods, systems and techniques on a case-by-case basis. LAER, on the other hand, is more uniform for a given class or category of air emission source leaving little
latitude as to what is achieved in practice. As a result, highly similar sources can have different 
BACT requirements; but, typically do not have different LAER requirements.

- Emission offsets are emission reductions that have been obtained from other sources within a 
nonattainment area, often in the form of Emission Reduction Credits (ERCs). The requirement 
to obtain offsets allows a nonattainment area to move towards attainment of the NAAQS while 
still allowing some industrial growth. Buying and selling of ERCs is typically overseen by the 
State or local air permit agency. Emission offsets must be obtained to at least offset the 
emissions increase from the new source or modification, and provide a net air quality benefit. 
So, often a source will be required to purchase a quantity of offsets or ERCs that is greater than 
the amount of proposed new emissions.

- The opportunities for public involvement with Nonattainment NSR are similar to those listed 
above in the summary of the PSD program.

Minor Source Permitting are for stationary sources that do not require PSD or nonattainment NSR 
permits. The purpose of a minor NSR permit program is to allow industrial source growth without 
interfering with attainment or maintenance of a NAAQS or violating the control strategy in 
nonattainment areas. The types of requirements included in minor NSR permits vary dramatically by 
State. For sources with emissions close to the levels specified for major source or major modifications, 
minor NSR permits can contain conditions that limit emissions to avoid PSD or nonattainment NSR. 
These permits are often called “synthetic minor” permits.

### 7.2.3 New Source Performance Standards (NSPS)

Section 111 of the *Clean Air Act* authorizes the US EPA to develop technology based standards which 
apply to specific categories of stationary sources. These standards are referred to as New Source 
Performance Standards (NSPS) and are found in 40 C.F.R. Part 60. The NSPS are federally imposed 
and enforced standards that apply to new, modified and reconstructed facilities in specific source 
categories, including the chemical and fertilizer industry. NSPS rules may also apply to common types 
of equipment found at a variety of industrial source categories, including boilers, engines, and tanks. 
The NSPS are developed and implemented by US EPA and are delegated to the States. However, even 
when delegated to the States, US EPA retains the authority to implement and enforce the NSPS.

NSPS rules commonly contain emission limits and operational requirements, as well as monitoring, 
recordkeeping and reporting. Sources subject to an NSPS must submit an initial notification of 
applicability and a proposed compliance approach to US EPA and the State agency overseeing a 
particular standard. Initial source testing is commonly required within 180 days of initial start-up to 
demonstrate compliance with NSPS emission limits. NSPS limits also serve as a minimum requirement 
for any case-by-case BACT or LAER determination under the NSR permit program.

Below is a discussion of some of the applicable NSPS to the chemical and fertilizer sectors.

#### 7.2.3.1 Chemical Sector NSPS

**Synthetic Organic Chemical Manufacturing Industry NSPS (40 C.F.R. Part 60, Subparts VV, 
VVa, III, NNN and RRR)**
The Synthetic Organic Chemical Manufacturing Industry (SOCMI) NSPS apply to equipment used to produce as a product, co-product, by-product, or intermediate any organic compounds listed in these NSPS rules. Listed product compounds include ethanol, ethylene glycol, ethylene, ethylene oxide, and methanol. The following is a list of equipment regulated under these NSPS standards:

- Subpart VV: Equipment built or modified between January 5, 1981 and November 7, 2006
- Subpart VVa: Equipment built or modified on or after November 7, 2006
- Subpart III: Air oxidation reactors built or modified after October 21, 1983;
- Subpart NNN: Distillation units built or modified after December 30, 1983;
- Subpart RRR: Reactor processes built or modified after June 29, 1990

The emissions standards and associated monitoring, recordkeeping and reporting are similar for air oxidation reactors, distillation units, and reactor processes. In each case, limits apply to operations with or without recovery streams. Each NSPS also provides the same three compliance options:

- Reduce overall VOC emissions by 98% or achieve a control device outlet concentration of 20 ppmv @ 3% oxygen;
- Combust emissions in a flare that meets specified design requirements; or
- Maintain a Total Resource Effectiveness (TRE) index value greater than 1.0 without use of VOC emission control devices (where TRE is a measure of the supplemental total resource requirement per unit reduction of Total Organic Compound (TOC) associated with an individual air oxidation vent stream, based on vent stream flow rate, emission rate of TOC, net heating value, and corrosion properties).

Continuous parametric monitoring is required for control devices and is used to demonstrate with these limits, such as flares, incinerators or other combustion devices (e.g., boilers). These requirements are provided in:

- 40 CFR 63.987 - Flare requirements; and
- 40 CFR 63.988 - Incinerators, boilers, and process heaters.

Subparts VV and VVa contain requirements for equipment leaks. Subpart VV applies to equipment built or modified between January 5, 1981 and November 7, 2006, and Subpart VVa applies to equipment built or modified on or after November 7, 2006. These NSPS contain leak requirements for pumps, compressors and components at SOCMI facilities. Facilities are required to implement Leak Detection and Repair (LDAR) programs designed to identify VOC leaks and perform repairs within specified periods.

**Polymer Manufacturing Industry NSPS (40 C.F.R. Part 60, Subpart DDD)**

The provisions of this subpart apply to affected facilities involved in the manufacture of listed polymers, including polyethylene. Facilities built or modified after September 30, 1987 may be subject to this subpart. All equipment used in the manufacture of polyethylene are regulated under this subpart, beginning with raw materials preparation and ending with product storage, and cover all emissions from such equipment. Control of VOC emissions is required for equipment with emissions above listed threshold values, which are specific to individual processes and polymers. Separate thresholds exist for high-density vs. low-density polyethylene, and depend on the manufacturing process type (e.g., liquid phase solution or liquid phase slurry process). Processes requiring control must achieve a VOC control efficiency of 98%, unless the outlet VOC concentration in the exhaust of a control device is reduced below 20 ppmv. Combustion of captured process VOC emissions by a boiler or flare is also allowed as a compliance option.
Equipment leaks from processes subject to this NSPS standard are subject to the requirements of 40 C.F.R. Part 60, Subpart VV (described above), which is incorporated by reference.

7.2.3.2 Fertilizer Sector NSPS

Nitric Acid Plant NSPS (40 C.F.R. Part 60, Subparts G and Ga)

The NSPS for Nitric Acid Plants were initially promulgated in 1971 under Subpart G. Regulated plants include those producing weak nitric acid (30% to 70% in strength) by either the pressure or atmospheric pressure process. The NSPS was reviewed and the standard was updated on August 14, 2012 under Subpart Ga. The updated NSPS regulates NOX emissions and opacity from new, modified or reconstructed Nitric Acid Production Units.

Under Subpart G, emissions from any Nitric Acid Production Unit built between listed dates in 1971 and 2011 are limited to:

- NOX limit (expressed as NO2): 1.5 kg per metric ton of acid produced (3.0 lb ton⁻¹), the production being expressed as 100% nitric acid; and
- Visible emissions are limited to 10% opacity.

Under Subpart Ga, emissions from any Nitric Acid Production Unit built after October 14, 2011 are subject to the following:

- NOX limit (expressed as NO2): 0.50 lb ton⁻¹ (0.25 kg tonne⁻¹) of nitric acid produced, as a 30-day emission rate; the production being expressed as 100% nitric acid;
- Facilities subject to this standard are required to install a Continuous Emission Monitoring System (CEMS) to monitor NOX emissions; and
- The standard also contains affirmative defence provisions for emission limits exceedances that occur during periods of malfunction.

7.2.3.3 Other NSPS relevant to the chemical and fertilizer sector

Boiler NSPS (40 C.F.R. Part 60, Subparts D, Da, Db, and Dc)

The four boiler NSPS contain requirements for boilers that are built or modified after the applicability date listed in the rule. These standards contain requirements for units rated 10 MMBtu hr⁻¹ to 100 MMBtu hr⁻¹ built or modified after June 9, 1989 (Subpart Dc), units rated 100 MMBtu hr⁻¹ to 250 MMBtu hr⁻¹ built or modified after June 19, 1984 (Db), and units rated greater than 250 MMBtu hr⁻¹ built or modified after December 22, 1976 and September 18, 1978 (Subparts D and Da, respectively). These standards contain NOX, SO2 and PM emission limits for specific fuels, as well as monitoring, recordkeeping and reporting provisions.

There are multiple limits for each pollutant depending on date of construction / modification. Readers should refer to the applicable Boiler NSPS Subpart for specific details on limits.
Tank NSPS (40 C.F.R. Part 60, Subparts K, Ka and Kb)

The NSPS for tanks contain VOC control requirements for tanks built or modified after the rule applicability dates, starting on June 11, 1973 (Subpart K), and for tanks with capacity larger than 75 m$^3$ (about 20,000 gallons). The rule contains exemptions for stored liquids with low vapour pressure. Control options include the use of a floating roof, fixed roof tank with specified design seals, or implementation of vapour recovery.

7.2.4 National Emissions Standards for Hazardous Air Pollutants (NESHAPs)

National Emissions Standards for Hazardous Air Pollutants (NESHAPs) are federal regulations that apply to HAPs. The NESHAP program was developed in 1977, and currently lists 187 pollutants as HAPs. The CAA requires the US EPA to regulate emissions of HAPs from a published list of industrial source categories. These standards are authorized by Section 112 of the CAA and the regulations are published in 40 C.F.R. Parts 61 and 63. Section 112d states that the US EPA must promulgate regulations establishing emission standards (NESHAPs) for each category or subcategory of major sources and area sources of HAPs (Section 112c). The US EPA is also required to perform a Residual Risk Analysis for each NESHAP to ensure that controlled emissions after implementation of a NESHAP will not result in unacceptable risks.

Prior to the 1990 CAA amendments, the US EPA regulated HAPs emissions by adopting regulations that were pollutant-specific. Each of the NESHAPs adopted prior to 1990 covered a single pollutant (e.g., benzene) or category of pollutants (e.g., radionuclides), and contained emission limits based on estimated health risks. These NESHAPs also contained monitoring, recordkeeping and reporting requirements, as appropriated. There are 22 pollutant-specific NESHAPs. While these standards remain in effect, the US EPA has discontinued the adoption of new pollutant-specific NESHAPs.

The 1990 CAA amendments required that the US EPA develop regulations for individual source categories. These categories can be defined to be either equipment found at a variety of facilities (e.g., boilers or engines) or as a type of facility (e.g., oil refineries). The post-1990 NESHAPs are control technology based standards, as opposed to risk-based standards developed prior to 1990. Sources are considered to be a “major source” of HAPs if:

- any single HAP emission is greater than 10 short tons per year, or
- the total HAP emissions for a facility are greater than 25 short tons per year.

Non-major sources of HAPs are referred to as area sources. For post-1990 standards, the US EPA determines an emission rate or level of control determined to be the Maximum Achievable Control Technology (MACT). In determining MACT, the US EPA selects the level of control achieved by the top-performing 12% of sources (or the average of the best-performing 5 sources, for categories with fewer than 30 sources). Less stringent standards, which are known as generally available control technology (GACT), are allowed at the Administrator's discretion for area sources. To date, the US EPA has adopted over 100 MACT and GACT NESHAPs, with new rules pending or proposed.

Sources subject to NESHAPs are commonly required to perform monitoring, recordkeeping and reporting as required by each standard, as well as quarterly reporting of excess emissions. Sources subject to NESHAPs are also typically required to develop a Start-up, Shutdown and Malfunction (SSM) plan describing actions for minimizing HAPs emissions during these periods.
The US EPA goal is to have a MACT standard that applies to all sources. The second round of MACT development is to assess human health impacts of standards or “residual risk”. The residual risk program includes consideration of aggregate sources within an airshed; as well as, cumulative effects for a regulated source category.

7.2.4.1 Chemical Sector NESHAPs

**Synthetic Organic Chemical Manufacturing Industry NESHAPs (40 C.F.R. Part 63, Subparts F, G, H, and I)**

The SOCMI is defined as industrial facilities that manufacture as a primary product one or more of the organic compounds listed in Table 1 to Subpart F. Sources are also regulated if they use as a reactant or manufacture as a product, or co-product, one or more of the organic compounds listed in Table 2 to Subpart F. Tables 1 and 2 both include ethylene glycol, ethylene oxide and methanol.

The NESHAP rules for the SOCMI sector consist of four subparts found in 40 C.F.R. part 63, namely Subparts F, G, H and I. Subpart F provides the applicability criteria for SOCMI sources, requires that owners and operators of SOCMI sources comply with subparts G and H, and specifies general recordkeeping and reporting requirements. Subpart F also clarifies how processes should be classified into the categories specified in the rule (e.g., clarification concerning the boundary between process units subject to different emissions or work practice standards).

The specific control, monitoring, reporting, and recordkeeping requirements are stated in Subpart G for process vents, storage vessels, transfer racks, and wastewater streams. For many sources, this subpart references emissions standards and work practices in the SOCMI NSPS, including NSPS Subpart III (Air oxidation reactors), NSPS Subpart NNN (Distillation units) and NSPS Subpart RRR (Reactor processes). Specific requirements and compliance deadlines are described for five different groups: Group I to V, depending on the nature of the chemical being produced. Ethylene glycol and ethylene oxide are listed as Group I compounds, and methanol is listed as a Group IV compound.

Subpart H contains requirements for equipment leak detection and repair. Subpart I provides the applicability criteria for the non-SOCMI processes subject to the negotiated regulation for equipment leaks, and requires owners and operators to comply with Subpart H.

**Equipment Leak NESHAPs (40 C.F.R. Part 63, Subparts TT and UU)**

The provisions of these subparts apply to the control of emissions from equipment leaks for which another subpart references the use of this subpart, such as Subpart YY (Generic NESHAP) or Subpart FFFF (MON NESHAP). The standards specify leak detection and repair requirements for equipment and components depending on several factors, including frequency of use, leak detection history and the nature of liquids stored (i.e., light vs. heavy liquids). Subpart TT contains control level 1 requirements, while Subpart UU contains control level 2 requirements. Control level 2 requirements are significantly more stringent than level 1. For example, under level 1 a leak is defined as a measured VOC concentration of 10,000 ppmv, while under level 2 the leak value is set at 500 ppmv. Level 2 requirements also contain a provision for development of a quality improvement program for chronic leak incidents.
Storage Vessel (Tank) NESHAP (40 C.F.R. Part 63, Subpart WW)

The provisions of this subpart apply to the control of HAPs emissions from storage vessels for which another subpart references the use of this subpart. This subpart is considered to mandate the control level 2 requirements for storage tanks. Tanks subject to this subpart must be equipped with an internal or external floating roof, designed and operated with the appropriate decks, shoes and seals specified by the rule. The rule also contains inspection and repair requirements.

Heat Exchange Systems and Waste Operations (Ethylene Manufacturing Process Units) NESHAP (40 C.F.R. Part 63, Subpart XX)

This subpart establishes requirements for controlling HAPs emissions from heat exchange systems and waste streams at new and existing ethylene production units. The standard requires cooling water leak detection and repair, according to the frequency specified by the rule. Less frequent monitoring is allowed when no leaks are detected. Leaks must be repaired as soon as practical but not later than 45 calendar days after detection. This subpart also incorporates by reference portions of the Benzene Waste Operations NESHAP in 40 C.F.R. 61, Subpart FF, which includes requirements for continuous butadiene waste streams and waste streams that contain benzene.

Generic NESHAP (40 C.F.R. Part 63, Subpart YY)

This standard applies to several types of chemical production facilities, including ethylene production plants. These have been combined into one NESHAP since they share common equipment, such as storage vessels, process vents, transfer racks, equipment leaks, and wastewater streams. Under this standard, HAPs emissions from process vents at ethylene production plants must be controlled by 98%, unless the outlet VOC concentration in the exhaust of a control device is reduced below 20 ppmv. For other listed equipment, this subpart references other subparts described in this report, including Subpart UU (Equipment Leaks), Subpart WW (Tanks) and Subpart XX (Heat Exchange and Waste Systems).

Organic Liquids Distribution NESHAP (40 C.F.R. Part 63, Subpart EEEE)

This subpart applies to storage tanks, transfer racks and components used for the storage and transfer of organic liquids listed in Table 1 of Subpart EEEE. This table lists ethylene glycol, ethylene oxide and methanol as regulated organic liquids. Larger tanks and transfer racks with high throughput are required to control organic HAPs emissions when processing/storing organic liquids with a true vapour pressure that is greater than or equal to 27.6 kilopascals (4.0 psia). Equipment requiring control must achieve a VOC reduction of 95% control or an exhaust concentration that is less than or equal to 20 ppmv (at 3% oxygen). Compliance with the work practice standards of other subparts is also listed as a compliance option, including Subparts H, TT or UU (Equipment Leaks) or Subpart WW (Tanks).

Miscellaneous Organic Chemical Manufacturing NESHAP (40 C.F.R. Part 63, Subpart FFFF)

The “Miscellaneous Organic Chemical Manufacturing” source category covers source categories related to miscellaneous chemical production, including polymers and resins. Chlorinated paraffin production, rubber chemical production, polyester resin production and alkyd resin production are some examples of processes that are covered by this rule. This category is commonly referred to as the “MON” sector, which is an abbreviation of “Miscellaneous Organic NESHAP.”
The MON NESHAP establishes emission limits and work practice standards for new and existing miscellaneous organic chemical manufacturing process units, wastewater treatment and conveyance systems, transfer operations, and associated ancillary equipment. The HAPs emitted from MON manufacturing facilities include toluene, methanol, xylene, hydrogen chloride, and methylene chloride.

Elements of this subpart include:

- Regulation of miscellaneous organic chemical manufacturing process units (MCPU) that are located at, or are a part of, a major source of HAPs;
- MCPUs are defined as all equipment which collectively functions to produce a product or isolated intermediate that is listed in 1987 version of Standard Industrial Classification (SIC) code 282, 283, 284, 285, 286, 287, 289, or 386, or the 1997 version of North American Industry Classification System (NAICS) code 325. These lists include ethanol production;
- Emission Limits and Work Practice Standards for:
  - Batch Process Vents
  - Continuous Process Vents
  - Storage Tanks
  - Transfer Racks
  - Equipment Leaks
  - Wastewater Streams
- Depending on the size and nature of the operation, this NESHAP requires capture and control of organic, metallic, and/or halogenated HAPs emissions to achieve either 95% to 98% destruction (requirements specific to a process unit) or a control device outlet concentration below specified values (e.g., 20 ppmv VOC).

7.2.4.2 Other NESHAPs relevant to the chemical and fertilizer sector

**Boiler NESHAP (40 C.F.R. Part 63, Subparts DDDDD and JJJJJJ)**

The Boiler NESHAP standards respectively regulate HAPs emissions from boilers located at major sources of HAPs (Subpart DDDDD) and area sources of HAPs (Subpart JJJJJJ). These standards were primarily adopted to regulate emissions from boilers firing solid and liquid fuels, since HAPs emissions from the combustion of these fuels is significantly larger as compared to firing natural gas. These NESHAP contain control requirements for mercury and hydrogen chloride (HCl), as well as a list of other related organic, metallic and halogenated HAPs.

For natural gas fired units, such as those used most commonly in the chemical and fertilizer sector, requirements are more minimal. These units are subject to CO emission limits (regulated as a surrogate pollutant for organic HAPs emissions, primarily for coal fired boilers), as well as a one-time energy assessment and annual tune-ups.

7.3 U.S. States

Facilities located in the U.S. are subject to Federal air quality regulations, in addition to regulations adopted by the State or local agency in the jurisdiction where they are located. Many U.S. States adopt programs similar in design to those mandated by Federal law; while others (such as California) adopt requirements significantly more stringent than Federal law. More stringent regulations may be adopted
in response to more significant air quality problems, such as nonattainment of a NAAQS, or may also be designed to proactively prevent such problems from occurring.

The following is a discussion of air quality regulations in selected U.S. states. The examination considers both air permitting requirements and those obligations that are unique to the chemical and fertilizer sectors.

### 7.3.1 California

In California, air emissions from industrial sources are regulated by 35 different Air Pollution Control Districts. The boundaries of some of these Districts correspond to county boundaries, although air quality around large metropolitan areas such as San Francisco and Los Angeles is regulated by Districts spanning multiple counties. California is known to be among the most stringent States in terms of adoption of environmental laws and regulations. For example, control requirements such as BACT are required for all permitted sources in the larger Districts, while this requirement is limited to major sources under regulations adopted by US EPA and many other States. California’s requirements related to Toxic Air Contaminants (TACs) are also fairly stringent. The list of TACs regulated by California contains over 500 compounds (compared to 187 regulated as Federal HAPs) and proposed increases in TAC emissions are often subject to a human health risk assessment, requiring dispersion modelling and exposure calculations.

The rules applicable to the chemical and fertilizer sector in selected Districts are as follows:

#### 7.3.1.1 Bay Area Air Quality Management District (BAAQMD)

- **Regulation 8, Rule 5 (Storage of Organic Liquids):** requirements for tanks as small as 264 gallons, with requirements ranging from use of a submerged fill pipe to floating roofs, or pressure tanks for high vapour pressure liquids
- **Regulation 8, Rule 18 (Equipment Leaks):** LDAR requirements for large chemical plants (defined as those with 100+ valves)
- **Regulation 8, Rule 22 (Valves and Flanges at Chemical Plants):** LDAR requirements for small chemical plants (those with <100 valves)
- **Regulation 8, Rule 28 (Episodic Releases From Pressure Relief Devices):** limitations on use of pressure release valves and reporting requirements for release incidents
- **Regulation 9, Rule 7 (Boiler and Process Heaters):** NO\textsubscript{X} limits on boilers with heat rating >2.5 MMBtu hr\textsuperscript{-1} range from 5 to 30 ppmv @ 3% oxygen, depending on size and fuel type. The final emission limits as stated in Regulation 9, Rule 7 are found in Table 25 below.
Table 25  NO\textsubscript{X} and CO emission limits for the Bay Area Air Management District (BAAQMD)

<table>
<thead>
<tr>
<th>Emission Limit</th>
<th>Rated Heat Input (million BTU hr(^{-1}))</th>
<th>Fuel</th>
<th>NO\textsubscript{X} Limit (ppmv, dry at 3% oxygen)</th>
<th>CO Limit (ppmv, dry at 3% oxygen)</th>
</tr>
</thead>
<tbody>
<tr>
<td>307.1</td>
<td>&gt;2 to 5</td>
<td>Gaseous, except landfill or digester gas</td>
<td>30</td>
<td>400</td>
</tr>
<tr>
<td>307.2</td>
<td>&gt;5 to &lt;10</td>
<td>Gaseous, except landfill or digester gas</td>
<td>15</td>
<td>400</td>
</tr>
<tr>
<td>307.3</td>
<td>10 to &lt;20</td>
<td>Gaseous, except landfill or digester gas</td>
<td>15</td>
<td>400</td>
</tr>
<tr>
<td>307.4</td>
<td>20 or more, load-following unit</td>
<td>Gaseous, except landfill or digester gas</td>
<td>15</td>
<td>400</td>
</tr>
<tr>
<td>307.5</td>
<td>20 to &lt;75</td>
<td>Gaseous, except landfill or digester gas</td>
<td>9</td>
<td>400</td>
</tr>
<tr>
<td>307.6</td>
<td>75 or more</td>
<td>Gaseous, except landfill or digester gas</td>
<td>5</td>
<td>400</td>
</tr>
<tr>
<td>307.7</td>
<td>1 or more</td>
<td>Landfill or digester gas</td>
<td>30</td>
<td>400</td>
</tr>
<tr>
<td>307.8</td>
<td>1 or more</td>
<td>Non-gaseous</td>
<td>40</td>
<td>400</td>
</tr>
<tr>
<td>307.9</td>
<td>1 or more</td>
<td>Multiple fuels</td>
<td>Heat-input weighted average limit</td>
<td>400</td>
</tr>
</tbody>
</table>

7.3.1.2  San Joaquin Valley Air Pollution Control District (SJVAPCD)
- Rule 4455 (Components): LDAR requirements for chemical plants
- Rule 4623 (Storage of Organic Liquids): requirements for tanks 1,100 gallons in size, with requirements to use either floating roofs, or pressure tanks for high vapour pressure liquids
- Rules 4304 through 4308 (Boilers): requirements for boilers and process heaters as small as 0.075 MMBtu hr\(^{-1}\), with NO\textsubscript{X} limits ranging from 5 to 30 ppmv @ 3% oxygen, depending on size and fuel type. Some of the rules also identify CO limits for some boilers and process heaters.

7.3.1.3  South Coast Air Quality Management District (SCAQMD)
- Rule 1149 (Storage Tank Cleaning): requirements for cleaning and degassing of storage tanks and associated VOC liquid pipelines
- Rule 1173 (Components): LDAR requirements for chemical plants
- Rules 1146, 1146.1 and 1146.2 (Boilers): requirements for boilers and process heaters of all sizes and fuel types, with NO\textsubscript{X} limits ranging from 5 to 30 ppmv @ 3% oxygen

7.3.2  Illinois

Air quality in the State of Illinois is regulated by the Illinois Environmental Protection Agency (IEPA) which issues air permits and regulations for industrial emissions sources.

Illinois operates federally required stationary source permitting programs. There is no specific requirements for the chemical and fertilizer sector that are different than federal programs.
The rules applicable to the chemical and fertilizer sector are found in 35 I.A.C. Part 215, which contains sections for various sources of VOC emissions, including the following:

- Subpart B (Storage and Loading);
- Subpart Q (Leaks from SOCMI sources); and
- Subpart RR (Miscellaneous Organic Chemical Manufacturing) – focusing on the air emissions of volatile organic material.

### 7.3.3 Louisiana

Air quality in the State of Louisiana is regulated by the Louisiana Department of Environmental Quality (LDEQ) which issues air permits and regulations for industrial emissions sources.

Louisiana operates federally required stationary source permitting programs. There is no specific requirements for the chemical and fertilizer sector that are different than the federal programs that are in place.

The rules applicable to the chemical and fertilizer sector are found in Title 33 of the Louisiana Environmental Regulatory Code. This includes the following sections:

- Chapter 21(A): Tank and LDAR requirements for organic liquids;
- Chapter 21(J): Limits for SOCMI facilities. The provisions of this Subchapter apply to any vent stream discharging to the atmosphere and originating from a process unit in which a reactor process or distillation operation is located; and
- Chapter 23(D): Nitric Acid Plants. The purpose of this Subchapter is to limit the quantity of atmospheric emissions from nitric acid plants. This Subchapter is applicable to all nitric acid production units not subject to NSPS in the state.

### 7.3.4 New Jersey

Air quality in the State of New Jersey is regulated by the New Jersey Department of Environmental Protection (NDEP) which issues air permits and regulations for industrial emissions sources.

New Jersey operates federally required stationary source permitting programs. There is no specific requirements for the chemical and fertilizer sector that are different than federal programs.

The rules applicable to the chemical and fertilizer sector are found in New Jersey Administrative Code (NJAC) 7:27-16 (Control and Prohibition of Air Pollution by Volatile Organic Compounds). This includes the following sections:

- Section 7:27-16.2 (Storage tanks);
- Section 7:27-16.8 (Boilers); and
- Section 7:27-16.18 (Leak detection and repair).
7.3.5  **North Carolina**

Air quality in the State of North Carolina is regulated by the North Carolina Department of Environmental Quality (NCDEQ) which issues air permits and regulations for industrial emissions sources.

North Carolina operates federally required stationary source permitting programs. There are no specific requirements for the chemical and fertilizer sector that are different than federal programs.

The rules applicable to the chemical and fertilizer sector are found in the North Carolina Administrative Code. This includes the following sections:

- 15A NCAC 02D .0943 (Synthetic Organic Chemical and Polymer Manufacturing);
- 15A NCAC 02D .0944 (Manufacture of Polyethylene: Polypropylene and Polystyrene);
- 15A NCAC 02D .0949 (Storage of Organic Compounds); and
- 15A NCAC 02D .1407 (Boilers and Process Heaters).

7.3.6  **Ohio**

Air quality from sources located in the State of Ohio is regulated by the Ohio Environmental Protection Agency (Ohio EPA) which issues air permits and regulations for industrial emissions sources.

Ohio operates federally required stationary source permitting programs. There are no specific requirements for the chemical and fertilizer sector that are different than federal programs.

The rules applicable to the chemical and fertilizer sector are found in Chapter 3745 of the Ohio Administrative Code (OAC). This includes the following sections:

- Chapter 3745-21-13 (Reactors and distillation units at SOCMI plants); and
- Chapter 3745-21-21 (Storage tanks).

7.3.7  **Pennsylvania**

Air quality in the State of Pennsylvania is regulated by the Pennsylvania Department of Environmental Protection (PADEP) which issues air permits and regulations for industrial emissions sources.

Pennsylvania operates federally required stationary source permitting programs. There are no specific requirements for the chemical and fertilizer sector that are different than federal programs.

The rules applicable to the chemical and fertilizer sector are found in Pennsylvania Code, Chapter 129. This includes the following sections:

- 129.11. Nitric acid plants;
- 129.56. Storage tanks greater than 40,000 gallons capacity containing VOCs;
- 129.57. Storage tanks less than or equal to 40,000 gallons capacity containing VOCs;
- 129.65. Ethylene production plants;
- 129.71. Synthetic organic chemical and polymer manufacturing—fugitive sources; and
- 129.201. Boilers.
7.3.8 South Carolina

Air quality in the State of South Carolina is regulated by the South Carolina Department of Health and Environmental Control (DHEC) which issues air permits and regulations for industrial emissions sources.

South Carolina operates federally required stationary source permitting programs. There are no specific requirements for the chemical and fertilizer sector that are different than federal programs.

The rules applicable to the chemical and fertilizer sector are found in S.C. Regulation 61. This regulation contains generic rules that apply to all industrial facilities, but South Carolina DHEC has not adopted specific rules covering the chemical and fertilizer sector, or processes and equipment associated with this sector. Emission limits and operational requirements for individual sources would therefore typically be determined on a case-by-case basis during the issuance of an air permit prior to initial construction.

7.3.9 Texas

Air quality in the State of Texas is regulated by the Texas Council on Environmental Quality (TCEQ) which issues air permits and regulations for industrial emissions sources.

Texas operates federally required stationary source permitting programs. There are no specific requirements for the chemical and fertilizer sector that are different than federal programs.

While the TCEQ is responsible for managing air quality throughout Texas, local organizations are actively involved in dealing with more local air quality issues related to non-attainment. These organizations include Councils of Governments (COGs; which are voluntary regional planning organizations), stakeholder groups such as Northeast Texas Air Care (which includes representatives from local governments, industries and environmental groups) and metropolitan planning organizations (MPOs).

The rules applicable to the chemical and fertilizer sector are found in Texas Administrative Code (TAC), Title 30, Chapter 100 through 121. This includes the following rules:

- 30 TAC 106: Permits by Rule, for smaller sources of emissions not requiring preconstruction approval;
- 30 TAC 115(B)(1): Storage tank requirements four sources located in areas currently or anticipated to become ozone nonattainment areas;
- 30 TAC 115(B)(2): VOC limits on SOCMI operations;
- 30 TAC 115(H): VOC limits on highly-reactive VOCs, including ethylene; and
- 30 TAC 117: Control of NOX emissions from sources located in ozone nonattainment areas (Beaumont-Port Arthur, Houston-Galveston-Brazoria, and Dallas-Fort Worth).

7.4 Europe Union

7.4.1 European Union and Member States
At the core of the European Union (EU) are the Member States — the 28 states that belong to the Union — and their citizens. The unique feature of the EU is that, although these are all sovereign, independent states, they have pooled some of their ‘sovereignty’ in order to gain strength and the benefits of size. In practice, pooling sovereignty means that the Member States (MS) delegate some of their decision-making powers to the shared institutions they have created, so that decisions on specific matters of joint interest can be made democratically at European level. The EU, thus, sits between the fully federal system found in the United States and the loose, intergovernmental cooperation system seen in the United Nations.

![European Union and Member States (2016)](image)

Decision-making at EU level involves various European institutions, in particular the European Commission, which represents the interests of the EU as a whole. It implements the laws with the Member States. With regard to environmental policy, the decision-making competences are shared between the EU and the Member States. This means that if legislation is passed at EU level, then these laws have priority. However, if no legislation is adopted at EU level, then the individual Member States may legislate at national level. The Directorate-General for Environment (DG Environment) is the European Commission department responsible for EU policy on the environment. DG Environment aims to protect, preserve and improve the environment for present and future generations, proposing and implementing policies that ensure a high level of environmental protection and preserving the quality of life of EU citizens. It also makes sure that Member States apply EU environmental law correctly and it represents the EU in environmental matters at international meetings.
7.4.2 Legislation Framework concerning Air Quality and Emissions

EU air quality legislation relies on several tens of directives and decisions. The most important of these documents is the Directive 2008/50/EC (known as Air Quality Directive) and its four Daughter Directives on ambient air quality and cleaner air for Europe (entered into force on 11 June 2008).

The two main ambient air quality emission directives in the EU are as follows.

1. Directive 2001/81/EC of the European Parliament and the Council on National Emission Ceilings for certain pollutants (NEC Directive): sets the upper limits for each Member State for the total emissions in 2010 of the four pollutants responsible for acidification, eutrophication and ground-level ozone pollution (SO2, NOX, VOCs and ammonia), but leaves it largely to the Member States to decide which measures – on top of Community legislation for specific source categories - to take in order to comply.

2. Directive 2010/75/EU on Industrial Emissions (IED): sets out the main principles for the permitting and control of installations based on an integrated approach and the application of best available techniques (BAT). BAT is defined using an exchange of information with experts from Member States, industry and environmental organizations.

On January 7th 2014, the IED repealed and replaced the following directives:
- Directive 2008/1/EC on integrated pollution prevention and control (IPPC),
- Directive 2000/76/EC on waste incineration,
- Directive 1999/13/EC on activities using organic solvents, and

Note that this IED directive is completed by several sectorial directives.

The IED aims to achieve a high level of protection of human health and the environment taken as a whole by reducing harmful industrial emissions across the EU, in particular through better application of BAT. This directive is further described in the next section.

7.4.3 Integrated Industrial Emissions Directive (IED)

Directive 2010/75/EU on industrial emissions focuses on the largest industrial, agricultural, and waste treatment installations. The directive includes methodologies and reference documents for use of “best available techniques”, to be applied across all members of the EU in an attempt to limit imbalances in the Union regarding levels of air emissions emitted from industrial activities. Reference documents are available regarding what the options are for best available techniques. (Recital 13). This approach applies across the EU to all the industrial sectors listed in the directive, regardless of air quality. The emission levels are determined by BAT, and there may be additional limitations required by air quality plans, depending on the receiving environment; for example, the requirement to reduce industrial production or activity during high pollution events.

In Europe, the guidance and procedures for emission control technology selection applies regardless of whether the status of the air quality in a given area, where the industrial source is located, is classified as attainment or non-attainment. According to Article 14 of the IED, BAT conclusions shall be the reference, or minimum, when setting the permit conditions to new and existing installations covered by
the Directive\textsuperscript{6}. According to article 15 of the IED, emission limit values and the equivalent parameters and technical measures in permits shall be based on the best available techniques, without prescribing the use of any technique or specific technology.

Best Available Techniques Not Entailing Excessive Cost (BATNEEC; also more simply referred to as Best Available Technology or BAT) is the primary emission standard requirement for sources in Member States. BATNEEC seeks to strike a balance between using state-of-the-art techniques (including technologies) to minimize emissions, and the cost of doing so. The IED, 2010/75/EC, provides the determination of Best Available Techniques (BAT) references through exchange information between MS, industries, Non-Governmental Organizations and the European Commission. The definition of BAT and the BAT-associated environmental performance at EU level is determined through an exchange of information between the European Commission, the Member States, industry, and non-governmental environmental organizations. Please note: the Commission organizes an exchange of information with experts from Member States, industry and environmental organizations. This work is co-ordinated by the European IPPC Bureau of the Institute for Prospective Technology Studies at the EU Joint Research Centre in Seville (Spain). This process results in BAT Reference Documents (BREFs) containing the BAT conclusions, which are adopted by the Commission as Implementing Decisions\textsuperscript{7}.

The BREF documents including the BAT are publically available on the EU website. For a given industrial sector, a BREF document provides:

- A review of technical and economical state-of-the art techniques;
- An inventory of available technologies;
- An emissions and consumption inventory\textsuperscript{8};
- A choice of what technique is the best available among others; and
- A description of emergent techniques.

For each specific industrial sector and for all of the EU zones, a BREF lists the reference documents that have been drawn (or are planned to be drawn) as part of the exchange of information carried out in the framework of Article 13(1) of the IED, 2010/75/EU. It contains the Best Available Techniques (BAT) reference documents that have been adopted under both the IPPC Directive (2008/1/EC) and the IED. BREFs adopted under the IED provide "BAT conclusions", which correspond to the parts of BAT reference document laying down the conclusions on best available techniques, their description, information to assess their applicability, the emission levels associated with the best available techniques, associated monitoring, associated consumption levels and, where appropriate, relevant site remediation measures.

Several BREFs focus on industrial sectors with potential area and/or fugitive emissions, including:

- Common Waste Water and Waste Gas Treatment/ Management Systems in the Chemical Sector;
- Waste Treatment;
- Emissions from Storage; and
- Iron and Steel Production (including open stockyards).

\textsuperscript{6} BAT conclusions are the final evaluations of Best Available Techniques and form part of every BAT Reference Document (BREF).

\textsuperscript{7} Implementing Decisions lay down rules concerning guidance on the collection of data and on the drawing up of BAT reference documents and on their quality assurance referred to in IED 2010/75/EU

\textsuperscript{8} A consumption inventory refers to materials consumed in the production process. For example, urea production consumes ammonia, carbon dioxide, cooling water, steam, and electrical power.
All these documents include BAT for limiting atmospheric emissions.

Related to the BAT conclusions, Best Available Techniques Associated Emission Levels (or BAT-AEL) give a range of emission levels obtained under normal operating conditions using the best available techniques (or a combination of BAT). BAT-AEL are generally expressed in mg Nm\(^{-3}\) for each source.

For new installations in the EU, the provisions of the IED apply from 7 January 2013. For setting permit conditions, all relevant BAT conclusions adopted in accordance with Article 13 and published before the permit is issued shall be applied for the purpose of Articles 14, 15 and 16 of the IED and the installation shall immediately comply with these conditions. Around 50,000 installations undertaking the industrial activities listed in Annex I of the IED are required to operate in accordance with a permit (granted by the authorities in the Member States). This permit should contain conditions set in accordance with the principles and provisions of the IED.

Recently, a proposal (COM/2013/0919) has been submitted to introduce provisions on emission limit values and monitoring requirements for Small and Medium-sized Enterprises (SMEs)\(^9\). This proposal is the result of Stakeholder and Public consultations highlighting “failure to limit pollution from significant point sources or from products” originating from SMEs, in which most of the medium combustion plants are operated. On November 10th 2015, the Council adopted a new directive to limit the emissions from combustion plants of medium size. These new rules are part of the clean air legislative package, which aims at improving air quality in the EU. This new directive sets emission limit values for certain pollutants, namely \(\text{SO}_2\), \(\text{NO}_x\) and dust. These limits will be applied for new and existing combustion plants of medium size (between 1 and 50 MW).

### 7.4.4 Air Emission Control Applied to Chemical and Fertilizer Sector

The following sections identify the BAT and BAT-AEL in the BREF documents applicable to the chemical and fertilizer sectors in the EU.

#### 7.4.4.1 CWW: Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector

The Best available technique Conclusions (BAT-Conclusions) of this document has been published. The BAT techniques are:

- In order to facilitate the recovery of compounds and the reduction of emissions to air, BAT is to enclose the emission sources and to treat the emissions, where possible;
- In order to reduce emissions to air, BAT is to use an integrated waste gas management and treatment strategy that includes process-integrated and waste gas treatment techniques;
- In order to prevent emissions to air from flares, BAT is to use flaring only for safety reasons or non-routine operational conditions (e.g. start-ups, shutdowns);
- In order to prevent or, where that is not practicable, to reduce diffuse VOC emissions to air, BAT is to use a combination of the techniques given below:
  - Limit the number of potential emission sources,
  - Maximize process-inherent containment features,

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\(^9\) The main factors determining a SME are head count (<250) and either turnover (≤ 50 million €) or balance sheet total (≤ 50 million €)
Select high-integrity equipment,
Facilitate maintenance activities by ensuring access to potentially leaky equipment,
Ensure well-defined and comprehensive procedures for plant/equipment construction and assembly. This includes using the designed gasket stress for flanged joint assembly,
Ensure robust plant/equipment commissioning and handover procedures in line with the design requirements,
Ensure good maintenance and timely replacement of equipment, and
Use a risk-based leak detection and repair (LDAR) program;

As far as it is reasonable, prevent diffuse VOC emissions, collect them at source, and treat them.

There are no BAT-AEL (i.e. emission limit values) defined in this document.

7.4.4.2 LVOC: Large Volume Organic Chemical Industry

This BREF document targets the following plants:
- Lower olefins (cracking process);
- Aromatics (benzene, toluene, xylene aromatics);
- Oxygenated compounds (ethylene oxide & ethylene glycols, formaldehyde);
- Nitrogenated compounds (acrylonitrile, toluene diisocyanate);
- Halogenated compounds (ethylene dichloride & vinyl chloride monomer); and
- Organo-metallic compounds.

The relevant BAT techniques to this study are:
- The BAT process route for ethylene oxide (EO) is the direct oxidation of ethylene by pure oxygen (due to the lower ethylene consumption and lower off-gas production);
- The BAT process route for ethylene glycol (EG) is based on the hydrolysis of EO (with reaction conditions to maximize production of the desired glycol(s) and minimize energy consumption); and
- Almost all the organic air emissions from EO/EG plants can be prevented, re-used, recycled or combusted, in the following manner:
  - Carbon dioxide is produced as a by-product during the manufacture of EO and has to be removed from the system to prevent build up. The formation of carbon dioxide can be minimized through the development of EO catalysts and/or selling the carbon dioxide as a commercial by-product (only where suitable outlets for the treated stream exist).

Due to its toxic and carcinogenic nature, threshold limit values for EO in ambient air are very low (in the order of 1 ppm). For occupational health reasons, extensive measures have been taken by the industry to prevent EO releases, including fugitives, or to detect them at an early stage, such that remedial measures can be taken promptly. The specific techniques to minimize fugitive emissions may include:
- careful material selection for seals, O-rings, gaskets, etc. in EO duty;
- use of double seals or tandem seals on pumps in EO duty or use of canned or magnetic drive pumps;
- installation of sensitive EO detection systems for continuous monitoring of ambient air quality (these systems also detect ethylene);
• application of metal strips around flanges with a vent pipe sticking out of the insulation that is monitored for EO release on a regular basis; and  
• monitoring of EO plant personnel for EO exposure (since exposure means emission).

There are BAT-AEL defined for a variety of substances emitted from large volume organic chemical industry, such as PM, SO2 and acid gases, NOX, NH3 and amines, and H2S. Some BAT-AEL distinguish between different control techniques (for example, PM emission levels for ESP, fabric filters, and cyclones). A summary of these BAT-AEL are presented in Table 26 below.

Table 26  BAT-AEL for large volume organic chemical industry

<table>
<thead>
<tr>
<th>Substance</th>
<th>Average emission level from point sources</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Particulates</td>
<td>• Cyclone : Up to 95% reduction</td>
</tr>
<tr>
<td></td>
<td>• Electrostatic precipitator : 5-15 mg Nm⁻³ (99% reduction)</td>
</tr>
<tr>
<td></td>
<td>• Fabric filter: &lt; 5 mg Nm⁻³</td>
</tr>
<tr>
<td></td>
<td>• Two stage dust filter: 1 mg Nm⁻³</td>
</tr>
<tr>
<td></td>
<td>• Ceramic filter: &lt; 1 mg Nm⁻³</td>
</tr>
<tr>
<td></td>
<td>• Absolute Filter: &lt; 0.1 mg Nm⁻³</td>
</tr>
<tr>
<td></td>
<td>• HEAF Filter: up to 99% reduction</td>
</tr>
<tr>
<td></td>
<td>• Mist Filter: up to 99% reduction</td>
</tr>
<tr>
<td>Sulphur dioxide and acid gases</td>
<td>• Wet limestone scrubbing: 90-97% reduction SO₂ &lt; 50 mg Nm⁻³</td>
</tr>
<tr>
<td></td>
<td>• Scrubbers: HCl &lt; 10 mg Nm⁻³ and HBr &lt; 5 mg Nm⁻³</td>
</tr>
<tr>
<td></td>
<td>• Semi dry sorbent injection: SO₂ &lt; 100 mg Nm⁻³, HCl &lt; 10-20 mg Nm⁻³ and HF &lt; 1-5 mg Nm⁻³</td>
</tr>
<tr>
<td>Nitrogen oxides</td>
<td>• SNCR: 50-80% NOₓ reduction</td>
</tr>
<tr>
<td></td>
<td>• SCR: 85-95% reduction – NOₓ &lt; 50 mg m⁻³ and ammonia &lt; 5 mg m⁻³</td>
</tr>
<tr>
<td>Dioxins</td>
<td>&lt; 0.1 ng Toxic Equivalent (TEQ) Nm⁻³ (primary measures + adsorption 3-bed catalyst)</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.05 mg Nm⁻³ (adsorption)</td>
</tr>
<tr>
<td>Ammonia and amines</td>
<td>&lt; 1-10 mg Nm⁻³ (scrubber)</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>1-5 mg Nm⁻³ (absorption)</td>
</tr>
</tbody>
</table>

7.4.4.3 OFC: Manufacture of Organic Fine Chemicals

This BREF document targets the following plants:
• Dyes and pigments;  
• Plant health products and biocides;  
• Pharmaceutical products (chemical and biological processes); and  
• Explosives.

The BAT techniques are:
• Emission profiles should be recorded instead of levels derived from short sampling periods;
- Emission data should be related to the operations responsible:
  - For emissions to air, BAT is to monitor the emission profile which reflects the operational mode of the production process;
  - In the case of a non-oxidative abatement/recovery system, BAT is to apply a continuous monitoring system (e.g. Flame Ionization Detector, FID), where exhaust gases from various processes are treated in a central recovery/abatement system;
  - BAT is to individually monitor substances with ecotoxicological potential if such substances are released;
- BAT is to assess the individual exhaust gas volume flows from process equipment to recovery/abatement systems;
- BAT is to re-use solvents as far as purity requirements (e.g. requirements according to current good manufacturing practice). Methanol recovery is often not economically viable due to the low market price; and
- BAT is to contain and enclose sources and to close any openings in order to minimize uncontrolled emissions.

One or a combination of techniques can be applied as a recovery/abatement system for a whole site, an individual production building, or an individual process. This depends on the particular situation and affects the number of point sources.

There are BAT-AEL defined for a variety of substances emitted from facilities involved in the manufacture of organic fine chemicals, such as total organic compounds (TOC), NOx, NH3, and SOx. Some BAT-AEL distinguish between different control techniques (for example, TOC emission levels for thermal oxidation and non-oxidative recovery). A summary of these BAT-AEL are presented in Table 27 below.

### Table 27  BAT-AEL for manufacture of organic fine chemicals

<table>
<thead>
<tr>
<th>Substance</th>
<th>Average emission level from point sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total organic carbon</td>
<td>20 mg Nm⁻³ (Non oxidative recovery/abatement techniques)</td>
</tr>
<tr>
<td></td>
<td>&lt; 5 mg Nm⁻³ (thermal oxidation/incineration or catalytic oxidation)</td>
</tr>
<tr>
<td>NOx</td>
<td>13 – 50 mg Nm⁻³ (Thermal oxidation/incineration or catalytic oxidation)</td>
</tr>
<tr>
<td></td>
<td>25-150 mg Nm⁻³ (Thermal oxidation/incineration, catalytic oxidation, input of nitrogenous organic compounds)</td>
</tr>
<tr>
<td></td>
<td>7-220 mg Nm⁻³ (Chemical production processes, e.g. nitration, recovery of spent acids)</td>
</tr>
<tr>
<td>HCl</td>
<td>0.2 - 7.5 mg Nm⁻³</td>
</tr>
<tr>
<td>Cl₂</td>
<td>0.1 - 1 mg Nm⁻³</td>
</tr>
<tr>
<td>HBr</td>
<td>&lt; 1 mg Nm⁻³</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.1 - 10 mg Nm⁻³</td>
</tr>
<tr>
<td></td>
<td>&lt; 2mg Nm⁻³ (from Selective catalytic reduction or Selective non-catalytic reduction)</td>
</tr>
<tr>
<td>SOx</td>
<td>1 - 15 mg Nm⁻³</td>
</tr>
<tr>
<td>Cyanides as HCN</td>
<td>1 mg Nm⁻³</td>
</tr>
</tbody>
</table>
The list of products covered under the “Production of Polymers” (POL) reference document is not explicitly defined but includes polyolefins, polystyrene, polyvinyl chloride, unsaturated polyesters, emulsion polymerized styrene butadiene rubbers, solution polymerized rubbers containing butadiene, polyamides, polyethylene terephthalate fibres and viscose fibres.

BAT techniques for polyethylene are:
- To recover monomers from reciprocating compressors in LDPE processes to:
  - recycle them back to the process; and/or
  - send them to a thermal oxidizer.
- To collect off-gases from the extruders. Off-gases from the extruding section (extruder rear seal) in LDPE production are rich in VOC. By sucking off the fumes from the extrusion section, the emission of monomers is reduced;
- To reduce the emissions from finishing and storage sections by treatment of purge air; and
- To operate the reactor at the highest possible polymer concentration. By increasing the concentration of the polymer in the reactor, the overall energy efficiency of the production process is optimized to use closed-loop cooling systems.

As presented in Table 28 below, there are BAT-AEL defined for VOCs and dust, which are specific to the type of PE production, such as LDPE, LDPE copolymer, HDPE, LLDPE.

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>VOC (g t⁻¹)</th>
<th>Dust (g t⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low density polyethylene (LDPE)</td>
<td>New plant: 700 – 1,100</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Existing plant: 1,100 – 2,100</td>
<td></td>
</tr>
<tr>
<td>LDPE copolymers</td>
<td>2,000</td>
<td>20</td>
</tr>
<tr>
<td>High density polyethylene (HDPE)</td>
<td>New plant: 300 – 500</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>Existing plant: 500 – 1,800</td>
<td></td>
</tr>
<tr>
<td>Linear low density polyethylene (LLDPE)</td>
<td>New plant: 200 – 500</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Existing plant: 500 - 700</td>
<td></td>
</tr>
</tbody>
</table>

7.4.4.5 LVIC-AAF: Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilizers

This document targets the following plants:
- Ammonia, hydrogen fluoride;
- Hydrofluoric acid, phosphoric acid, nitric acid, sulphuric acid, oleum; and
- Phosphorus-, nitrogen- or potassium-based fertilizers (simple or compound fertilizers).

**Ammonia Plants**

For new ammonia installations, BAT is to apply conventional reforming, reduced primary reforming or heat exchange auto thermal reforming. In order to achieve the NOX concentration emission levels (see below for details), techniques such as SNCR at the primary reformer (if the furnace allows the required temperature and retention time windows), low NOX burners, ammonia removal from purge and flash
gases, or low temperature desulphurization for auto thermal heat exchange reforming, should be applied.

BAT for new ammonia installations includes:
- Advanced conventional reforming processes and processes with reduced primary reforming:
  - 90-230 mg Nm\(^{-3}\) NO\(_X\) emission as NO\(_2\).
- Heat exchange auto-thermal reforming:
  - Process air heater: 80 mg Nm\(^{-3}\) NO\(_X\) emission as NO\(_2\); and
  - Auxiliary boiler: 20 mg Nm\(^{-3}\) NO\(_X\) emission as NO\(_2\).

No direct correlation between concentration levels and emission factors could be established. However, emission factors of 0.29 – 0.32 kg ton\(^{-1}\) NH\(_3\) are seen as a benchmark for conventional reforming processes and processes with reduced primary reforming. For heat exchange auto-thermal reforming, an emission factor of 0.175 kg ton\(^{-1}\) NH\(_3\) is seen as a benchmark.

**Urea Plants**

There are no BAT specified for the urea synthesis and concentration process. These are, however, specific BAT for improving the environmental performance of the finishing section of a urea plant. Examples of these BAT include:
- applying plate bank product cooling,
- redirecting urea fines to the concentrated urea solution,
- selecting proper size of screens and mills, e.g. roller or chain mills,
- applying surge hoppers for granulation recycle control, or
- applying product size distribution measurement and control.

BAT is to treat all exhaust gases from the wet sections by scrubbing, taking into account the lower explosion limit and to recycle the resulting ammonia solutions to the process.

BAT is to reduce ammonia and dust emissions from prilling or granulation, e.g. by scrubbing or optimising the operation conditions of prilling towers, and to re-use scrubber liquids on-site. If the scrubbing liquid can be re-used, then preferably by acidic scrubbing, if not, by water scrubbing. In optimising the emission levels to the values mentioned above even with water scrubbing.

Untreated emission levels from urea finishing were reported at 70 to 140 mg Nm\(^{-3}\) and 60 to 130 mg Nm\(^{-3}\) for ammonia and dust, respectively. Achievable emission levels from scrubbing devices installed at this stage of urea production were reported in the range of:
- Ammonia: 3 to 30 mg Nm\(^{-3}\); and
- Dust: 15 to 55 mg Nm\(^{-3}\).

**Nitric Acid Plants**

BAT is to reduce emissions during start-up and shutdown conditions.

BAT is to reduce emissions of N\(_2\)O by applying a combination of the following techniques:
- Optimizing the filtration of raw materials;
- Optimizing the mixing of raw materials;
- Optimizing the gas distribution over the catalyst;
• Monitoring catalyst performance and adjusting the campaign length;
• Optimization of the NH₃:air ratio;
• Optimizing the pressure and temperature of the oxidation step;
• N₂O decomposition by extension of the reactor chamber in new plants; and
• Catalytic N₂O decomposition in the reactor chamber combined NOₓ and N₂O abatement in tail gases.

BAT is to reduce emissions of NOₓ by applying one or a combination of the following techniques:
• Optimisation of the absorption stage;
• Combined NOₓ and N₂O abatement in tail gases; and/or
• SCR.

BAT is addition of H₂O₂ to the last absorption stage. This addition increases the absorption efficiency, resulting in greater nitric acid formation and ultimately, fewer NOₓ emissions to air.

BAT-AEL for nitric acid plants are:
• For new nitric acid plants:
  o N₂O emission level: 0.12 - 0.6 kg t⁻¹ 100% HNO₃ (20 - 100 ppmv)
  o NOₓ emission level, as NO₂: 5 – 75 ppmv
• For existing nitric acid plants:
  o N₂O emission level: 0.12 - 1.85 kg t⁻¹ 100% HNO₃ (20 - 300 ppmv)
  o NOₓ emission level as NO₂: 5 – 90 ppmv (up to 150 ppmv, where safety aspects due to deposits of ammonium nitrate restrict the effect of SCR or with addition of H₂O₂ instead of applying SCR).

7.5 European Member States

7.5.1 Belgium

Belgian environmental regulations are defined on a regional level for Flanders, Wallonia, and Brussels, respectively. As the Brussels region does not have much industry relative to the other regions, this section focuses on the regions of Flanders and Wallonia.

7.5.1.1 General FrameworkRelated to Air Emissions/Air Quality Regulations

Flanders

The regulation regarding the environmental permit for the Flanders region is defined by the Flemish decree of June 28, 1985 and the practical implementation through the Flemish regulation called VLAREM I, II and III (or ‘Vlaams reglement inzake milieuvergunning’; BS February 6th, 1991). These regulations are organized as follows:
• VLAREM I includes all definitions, subdivisions for activities and procedures;
• VLAREM II defines the general and sectoral conditions for all permitted installations/activities and the environmental quality standards; and
• VLAREM III defines additional and sectoral conditions for installations with a potentially high impact on the environment (ref. EU IPPC/IED directive) based on the best available techniques (BAT, BREF).
VLAREM is the reference document for an environmental permit application in Flanders. An environmental permit application for activities and installations listed in VLAREM is to be submitted to the local city or commune and is evaluated on a provincial level. The province will request advice from the Agency for the Environment, Nature and Energy (LNE Vlaanderen) regarding the environmental impacts including air emissions of the requested activities. This Agency is also responsible for the verification of company compliance with the environmental regulation by combining preventive methods (e.g. inspections) with repressive methods (e.g. sanctions).

The VLAREM legislation includes air emissions and air quality regulations.

Wallonia

The general framework related to Air emissions and Air quality regulations in the Walloon region of Belgium is mainly defined by the Law of December 28th 1964, related to the reduction of atmospheric pollution.

This law states that the government of the Walloon region has the power to take all appropriate measures to prevent or fight atmospheric pollution, including:

- Forbidding certain types of pollution and techniques that may create pollution, and ruling over the techniques that aim at reducing and preventing atmospheric pollution;
- Giving approval for the experts in charge of installing, maintaining, controlling and inspecting devices defined by the government;
- Giving approval for the experts in charge of monitoring the ambient air quality;
- Deciding of objectives to follow for the ambient air quality; and
- Defining special protection areas where some types of pollution can be limited or forbidden.

This law is enforced through a number of Acts. For air emissions related to the industry sector, the requirements have been integrated in the permitting legislation discussed in Section 7.5.1.2.

The Walloon Air and Climate Agency (AwAC) is the official agency in charge of managing air, climate and stratospheric ozone quality policy. The Environmental Inspection Agency or Department of Police and Controls (DPC) is in charge of verifying that the applicable environmental regulation is complied with, notably by the industry sector. This mission is achieved by combining preventive methods (e.g. inspections) with repressive methods (e.g. sanctions). Its scope of action includes the compliance with air emissions and air quality regulation. A non-compliance with the regulation related to air emissions / air quality represents a Category 3 offense in the Walloon region, which can lead to administrative fines up to 10,000 €.

7.5.1.2 Requirements Concerning Industrial Air Emissions

Flanders

European directives regarding air emissions (a.o. 2004/107/EG, 2008/50/EG, IPPC: 96/61/EG, IED: 2010/75/EU) have been transposed into local regulation for the Flanders region (VLAREM I, II and III). Air emission regulation is specifically defined by the following items in VLAREM II:

- Article 1.1.2 sub: definitions of air pollution (definities luchtverontreiniging);
- Division 2.5.2: regulator tasks (beleidstaken); and
Appendix 2.5.3: monitoring and management of air quality (Beoordeling en beheer van luchtkwaliteit).

VLAREM II defines sector specific requirements, which can include air emission restrictions. As an example for the chemical sector: the production of caprolactam, or \((\text{CH}_2)_5\text{C(O)NH}\) (according to the Raschig method), which is a precursor to the synthetic polymer Nylon 6 imposes a maximum NO\(_2\) emission limit of 15 kg NO\(_X\) per ton of caprolactam produced. VLAREM III defines additional and sectoral conditions for installations with a potentially high impact on the environment (ref. EU IPPC/IED directive) based on the best available techniques (BAT, BREF).

The chemical and fertilizer installations for which a BREF is available include:
- Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers Industries (2007);
- Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (BATC 2016);
- Large Volume Organic Chemical Industry (2003);
- Manufacture of Large Organic Fine Chemicals (2006); and
- Production of Inorganic Specialty Chemicals (2007).

Companies that operate installations and activities which are listed in VLAREM must apply for an environmental permit. These are integrated permits which contain provisions for air emissions, water, waste, soil and groundwater protection, and hazardous materials storage. As mentioned above, permit applications are evaluated on a provincial or local level. When an environmental permit is issued, specific conditions may be applied regarding air emissions not listed in VLAREM. This enables the local regulator to impose more stringent requirements than those listed in VLAREM (transposed European Directives) based on specific local conditions and potential impacts on the environment.

Wallonia

The IED (2010/75/EU) has been entirely transposed in the Walloon legislation and has been in effect since February 18th, 2014. Subsequently, all requirements from this directive are applicable and must be complied with in the Walloon region.

Any installation within the scope of the IED will have the corresponding Best Available Techniques (BAT) covered as specific conditions in its environmental permit.

In addition to the conditions stated in the environmental permit, some laws in the Walloon region impose conditions specific to some sectors. The existing sector conditions that may be related to the chemical and fertilizer sectors include:
- Installations or activities consuming solvents;
- Installations having an activity leading to the emission of greenhouse gases;
- Installations producing titanium dioxide; and
- Combustion installations.

The chemical and fertilizer installations for which a BREF is available include:
- Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers Industries (2007);
- Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (BATC 2016);
- Large Volume Organic Chemical Industry (2003);
Companies that operate installations and activities which are listed by the Walloon region must apply for an environmental permit. These permits are integrated permits and contain provisions for water, waste, soil and groundwater protection, hazardous materials storage, as well as air emissions. In addition to general and sector operating conditions that may be applicable to the installation or activity, the Competent Authority may require additional specific conditions. These operating conditions can be related to the air emissions of the installation or activity and may require to comply with specific limits for airborne components or to install mitigation measures related to air emissions.

If the installation is within the scope of the IED, the specific conditions will be defined based on the corresponding BAT conditions and requirements. However, a derogation of the BAT conditions can be granted, but only for a limited period of time during which the installation must take the necessary measures to get into compliance with the BAT conditions. The date of revision of the permit will be based on the revision of the corresponding BREF.

If the installation is outside of the scope of the IED, the specific conditions will be defined solely based on the advice of the AwAC.

### 7.5.2 France

#### 7.5.2.1 Air Quality Legislation Framework

Air quality management in France is based on French law set out in the 96-1236 Legislation on Air and the Rational Use of Energy (LAURE), published on December 30th 1996, and codified in the Code of Environment. The legislative provisions and regulations related to air quality appear in articles L220-1 to L228-3 and R221-1 to D228-1. In addition, the French regulation 2015-992 dedicated to the energy transition for a green growth (LTECV) provides provisions, for example the national atmospheric pollutant emissions reduction plan (PREPA).

As of early 2015, 36 zones (including areas with exceedances of Air Quality (AQ) Limit Values (LV) and agglomerations greater than 250,000 inhabitants) covering 47% of the French population were required to develop a Protection Plan of Atmosphere (PPA). The procedure for developing PPAs is provided in the Code of Environment (articles L222-4 to L222-7 and R222-13 to R222 36). The PPA defines objectives and measures required by the legislation or public / stakeholders in order to lower the concentration of pollutants to a level below the thresholds set at European or French levels in areas where exceedances exist or could be possible. Of note, with regards to one of these pollutants, PM$_{10}$, several agglomerations are currently not compliant with the standards (15 areas since 2005).

The objectives and measures in the PPA are defined for each zone, depending on the local sources and the local context. For example, the PPA can define emission reduction for industrial sector.

#### 7.5.2.2 Regulation of Industrial Emissions

**Transposition of the IED in France**
France is subject to the European Directive on Industrial Emissions (IED) 2010/75/EU. The general transposition of the IED into national law was introduced into the Code of the Environment (Section 8 in Title V of Chapter I of Book V) on May 2nd, 2013.

Consequently, BAT and BREFs conclusions apply across the French territories. Therefore, when BAT conclusions are published for a particular sector, facilities in the sector generally have one year to provide a cost / benefit analysis (and if necessary ask for a derogation to the local authorities), and between 3 and 5 years to comply with the BAT-AEL.

**Permitting Process**

At the national level, any industrial (or agricultural) operation likely to generate risks or cause pollution or nuisance is defined as a Classified Installation (Facility) for the Protection of Environment (ICPE). Activities under the classified facilities legislation are listed in a nomenclature and are required to obtain a permit, registration or declaration system, depending on the significance of the risks or inconvenience that may be caused.

In the case of a new industrial facility / activity, or a significant modification of the activities at an existing facility, the operator shall report:

- A new activity within the scope of the nomenclature of classified installations;
- An increase in storage or production volumes;
- The transfer of a production line or storage area within the facility (likely to result in a change in noise level, change in risk areas);
- A change in storage conditions (for example, accident scenarios can be modified by switching from underground to overhead storage conditions);
- An extension of operating periods (likely to affect noise, traffic, exposure time); and
- A change in raw materials or processes making it necessary to review associated risks.

In this case, the installation shall renew their environmental permit and declaration procedure. Note that there is no expiry date for permits. Throughout the lifecycle of the facility, the operator can implement changes in their activity so long as they provide sufficient information according to the level of change, as follows:

- Non-significant changes: the operator must simply notify the Inspectorate;
- Significant changes, resulting in no significant hazards or inconvenience: the operator is required to notify the Inspectorate of classified facilities; or
- Significant changes, likely to result in significant hazards and annoyances: the operator is required to submit a permit application in accordance with the Code of Environment.

These changes must be presented to the Council Department of the Environment and Health and Technology Risks (CODERST). Additional requirements are defined to account for these changes. For example, as noted above, significant changes likely to result in significant hazards and annoyances will require a permit application in accordance with the Code of Environment. In this case, Health Risk Assessment (HRA, or ERS in French) and “Interpretation de l’Etat des Milieux” (IEM) reports may also be required.

An environmental impact assessment (through an Impact Study) is necessary for new facilities requiring an environmental permit and for existing facilities which are not compliant with IED requirements.
The Impact Study must present an analysis of the direct and indirect, temporary and permanent effects of the activities on health and the environment, and the measures considered by the applicant to eliminate, limit and if possible compensate for the nuisance of the installation as well as an estimate of associated expenses. The Impact Study must include:

- An air dispersion modelling study to assess the health risks from the operating permit upgrade (based on Article 4, circa August 9th 2013, on the approach to prevention and management of health risks of classified installations subject to authorization);
- The comparison of the projected installation to the Best Available Technologies (BAT). Note that if BAT conclusions have not been published, the associated emission levels and techniques in this document are considered as best technologies but not as regulatory values or techniques; and
- An IED Baseline Report. The aim of this report is primarily to assess the soil quality at the start of the renewal of the permit of an industrial activity to establish its initial state. The goal is to provide a basis for comparison upon definitive closure of the activity, in order to make objective decision on the application of the “polluter pays principle”.

The HRA focuses on the identification, description and quantification of the local population’s health risks resulting from exposure to pollution. Moreover, since the August 9th 2013 Article was published, an integrated approach is required by the authorities, such that the HRA must be accompanied with an Environmental Condition Assessment (Interpretation de l’Etat des Milieux, IEM), which includes all media (air, water, soils). This IEM shall consider environmental measurements to establish baseline / background levels and the potential cumulative impacts resulting from activity, in order to determine:

- If past and current emissions (for existing facilities) contribute to an environmental degradation; and
- If the actual degradation is compatible with the uses of the environment (typically by local population: housing, local production of vegetables, etc.), including current and future industrial activities. If this is not the case, suitable actions must be undertaken by the operator, based on more efficient control technology or alternative process.

Within the HRA, two risk indicators are used and compared to references (i.e. ratio to reference concentrations or toxicological values): Risk index (RI) for threshold effects and Excess of Individual Risk (EIR) for non-threshold effects (i.e. carcinogenic effects). All the media affected by atmospheric emissions are considered, generally air, soil and vegetation.

Through the coupled IEM study, a matrix is used in order to assess the impact of the industrial activity on local population and provide additional measures in case of vulnerability.

<table>
<thead>
<tr>
<th>Table 29</th>
<th>Health risk assessment process</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Comparison to Standards</strong></td>
<td><strong>Range in the risk management</strong></td>
</tr>
<tr>
<td>C &lt; C_{reference}</td>
<td>RI&lt; 0.2 EIR&lt;10^{-6}</td>
</tr>
<tr>
<td>C &lt; C_{reference} (with a potential future update)</td>
<td>RI between 0.2 and 5 EIR between 10^{-5} et 10^{-6}</td>
</tr>
<tr>
<td>C &gt; C_{reference}</td>
<td>RI&gt; 5 EIR&gt;10^{-4}</td>
</tr>
</tbody>
</table>
Local authorities generally require the applicant to prepare a cost / benefit analysis when control measures are required and to evaluate the feasibility of these measures. A quantitative impact assessment (using dispersion modeling) is required for IED facilities.

As indicated in the French legislation (Code of Environment), a cumulative impact assessment shall be considered in order to assess potential health effect on exposed population for a specific project with others known projects, which:

- were subject to an environmental permit authorization and a public survey; and
- were subject to an impact assessment study including the public conclusion of the administrative authority.

Cumulative impact, in term of multi-pollutant concentrations resulting from one installation, must be considered as well. For the cumulative impact assessment, a modelling approach can be used that incorporates all sources and baseline datasets.

**French ICPE Regimes and Emission Limit Values**

Depending on their nature and capacities, industrial activities are subject to the following main permit regimes:

- Non classified (NC): All the activities of the facility are below the classification thresholds of the relevant rubrics (see below for details), thus the facility is not a classified installation. It comes under the mayor’s authority;
- Declaration (D): The facility performing activities within the thresholds for declaration must issue a declaration to the Prefect before start-up. The risk is then deemed acceptable, provided that the facility complies with standard national operational requirements, called “standard orders”;
- Declaration with monitoring (DC): The facility performing activities within the thresholds for “declaration with monitoring” must issue a declaration to the Prefect before start-up and is also subject to periodic monitoring (Environmental code, regulatory section, title V articles R. 512-56 to R. 512-66 and R. 514-5) carried out by an organization approved by the Ministry for Ecology, Sustainable Development and Spatial Planning;
- Registration (E): The facility performing activities exceeding the thresholds for registration must submit an application for a permit before start-up. The Prefect may authorize or refuse the operation. If authorized, a permit in the form of a site-specific “Registration Prefectoral” order is issued;
- Authorization (A): The facility performing activities exceeding the thresholds for authorization must submit an application for a permit before start-up, demonstrating an acceptable level of risk. The Prefect may authorize or refuse the operation. If authorized, a permit in the form of a site-specific “Authorization Prefectoral” order is issued. The requirements of the operating permit are based on the Ministerial Order of February 2nd, 1998;
- Authorization with public utility (link to Seveso regulation): Roughly corresponding with the Seveso upper tier sites as defined by the Seveso II and Seveso III European directive, these installations present technological risks; the approach is the same as with the permit, but public easements are added in order to prevent third parties from settling near these high-risk activities; and
- Authorization (IED): Roughly corresponding with the Industrial Emissions Directive (IED), these installations present environmental risks; the approach is the same as with the permit, but
comparison with Best Available Technologies (BAT) are added in order to reduce environmental emission. The requirements of the operating permit are based on the BAT-AEL.

The ICPE regulation is based on an integrated approach; specifically one operating permit (Arrêté Préfectoral d’Autorisation d’Exploiter), which covers all aspects of environmental impacts (air, water, ground, noise, etc.) as well as industrial risks and public health.

The rubrics for classified installations are divided into four sections:

- Rubrics 1XXX: Substances (e.g., toxic, flammable, radioactive substances, etc.);
- Rubrics 2XXX: Activities (e.g., food processing activities, wood, waste, etc.);
- Rubrics 3XXX: IED activities; and
- Rubrics 4XXX: Seveso III substances.

Table 30 below presents the ICPE regimes of chemical plants.

<table>
<thead>
<tr>
<th>Plant</th>
<th>ICPE Item</th>
<th>Related regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacture of fertilizer</td>
<td>2170</td>
<td>Production &lt; 10 t d⁻¹ → Declaration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Production &gt; 10 t d⁻¹ → Authorization</td>
</tr>
<tr>
<td></td>
<td>3430</td>
<td>-</td>
</tr>
<tr>
<td>Ethanol plants</td>
<td>4330/4331 (Flammable liquids)</td>
<td>Total quantity : ≥1000 t → Authorization</td>
</tr>
<tr>
<td>Ethylene glycol plants</td>
<td></td>
<td>Total quantity : between 100 and 1000 t → Registration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total quantity : &lt;100 t → Declaration</td>
</tr>
<tr>
<td>Ethylene oxide plants</td>
<td>4720</td>
<td>Total quantity : ≥5 t → Authorization</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total quantity : between 500 kg and 5 t → Declaration</td>
</tr>
<tr>
<td>Ethylene plants</td>
<td>4718</td>
<td>Total quantity : ≥50 t → Authorization</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total quantity : between 6 t and 50 t → Declaration</td>
</tr>
<tr>
<td>Methanol plants</td>
<td>4722</td>
<td>Total quantity : ≥500 t → Authorization</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total quantity : between 50 t and 500 t → Declaration</td>
</tr>
<tr>
<td>Polyethylene plants</td>
<td>2661/2662</td>
<td>Production: ≥70 t d⁻¹ → Authorization</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Production: between 10 and 70 t d⁻¹ → Registration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Production: between 1 and 10 t d⁻¹ → Declaration</td>
</tr>
<tr>
<td>Stand-alone hydrogen production plants</td>
<td>4715 (Hydrogen)</td>
<td>Total quantity : ≥1 t → Authorization</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total quantity : between 100 kg and 1 t → Declaration</td>
</tr>
<tr>
<td>Ammonia plants</td>
<td>4735</td>
<td>Total quantity : ≥1.5 t → Authorization</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total quantity : between 150 kg and 1.5 t → Declaration</td>
</tr>
</tbody>
</table>
The applicable emission limit values are based on:
  - BAT and BAT-AEL for IED plants (see Europe Chapter);
  - Ministerial order of February 2\textsuperscript{nd}, 1998 for Authorization plants (presented below) ; and
  - Standard orders for Declaration plants (presented in the subsequent section).

7.5.2.3 General emission limit values for plants under authorization regime

If the facility is classified under the Authorization regime, emission limit values are based on the prescriptions issued from the ministerial order dated February 2\textsuperscript{nd}, 1998. Table 31 below presents the air emission requirements.
<table>
<thead>
<tr>
<th>Substance</th>
<th>Emission limit values</th>
</tr>
</thead>
</table>
| Dust (PM)                                     | 100 mg m\(^{-3}\) if the mass flowrate is below or equivalent to 1 kg h\(^{-1}\)  
40 mg m\(^{-3}\) if the mass flowrate is greater than 1 kg h\(^{-1}\). |
| Sulphur dioxide (SO\(_2\))                    | 300 mg m\(^{-3}\) if the mass flowrate is greater than 25 kg h\(^{-1}\).                                                                       |
| Nitrogen oxide (without N\(_2\)O)             | 500 mg m\(^{-3}\) if the mass flowrate is greater than 25 kg h\(^{-1}\).                                                                       |
| Hydrogen chloride (HCl)                       | 50 mg m\(^{-3}\) if the mass flowrate is greater than 1 kg h\(^{-1}\).                                                                       |
| Hydrogen fluoride (HF)                        | 5 mg m\(^{-3}\) if the mass flowrate is greater than 500 g h\(^{-1}\). In case of manufacture of phosphoric acid, phosphorus and phosphate fertilizers, the values are increased to 10 mg m\(^{-3}\). |
| VOCs                                          | 110 mg m\(^{-3}\) if the total mass flowrate (equivalent C) is greater than 2 kg h\(^{-1}\). In case of utilization of an oxidizer, this value is reduced to 20 mg m\(^{-3}\) or 50 mg m\(^{-3}\) if depuration yield is greater than 98%.  
For specific VOCs (listed in Appendix III of the ministerial order) the limit value is 20 mg m\(^{-3}\) if the mass flowrate is greater than 0.1 kg h\(^{-1}\).  
For carcinogen VOCs (with specific hazard statement: H340, 350, 350i, 360D or 360f) the limit value is 2 mg m\(^{-3}\) if the mass flowrate is greater than 10 g h\(^{-1}\).  
For halogen VOCs (with specific hazard statement : H341 or 351) the limit value is 20 mg m\(^{-3}\) if the mass flowrate is greater than 100 g h\(^{-1}\). |
| Cadmium, mercury and thallium                 | 0.05 mg m\(^{-3}\) for each metal (and no greater than 0.1 mg m\(^{-3}\) for the sum) if the total mass flowrate is greater than 1 g h\(^{-1}\). |
| Arsenic, selenium and tellurium               | 1 mg m\(^{-3}\) for the sum if the total mass flowrate is greater than 5 g h\(^{-1}\).                                                            |
| Lead                                          | 1 mg m\(^{-3}\) for the sum if the total mass flowrate is greater than 10 g h\(^{-1}\).                                                          |
| Antimony, chromium, cobalt, copper, tin, manganese, nickel, vanadium and zinc | 5 mg m\(^{-3}\) for the sum if the total mass flowrate is greater than 25 g h\(^{-1}\). In case of manufacture of zinc monoxide (ZnO) an manganese dioxide (MnO\(_2\)), the limit value is increased to 10 mg m\(^{-3}\) respectively for zinc and manganese. |
| Phosgene or phosgene                          | 1 mg m\(^{-3}\) for the sum if the total mass flowrate is greater than 10 g h\(^{-1}\).                                                            |
| Cyanuric acid (expressed in HCN), bromine (expressed in HBr), chlorine (expressed in HCl) and hydrogen sulphide (H\(_2\)S) | 5 mg m\(^{-3}\) for each substance if the mass flowrate is greater than 50 g h\(^{-1}\). |
| Ammonia                                       | 50 mg m\(^{-3}\) if the mass flowrate is greater than 100 g h\(^{-1}\).                                                                      |
| Asbestos                                      | 0.1 mg m\(^{-3}\) if the used quantity is greater than 100 kg y\(^{-1}\) and 0.5 mg m\(^{-3}\) for the total dust.  |
| Other fibers                                  | 1 mg m\(^{-3}\) if the used quantity is greater than 100 kg y\(^{-1}\) and 50 mg m\(^{-3}\) for the total dust.  |
| Carcinogen substances                         | Specific limit values are defined by permit given by local authorities (Prefecture).                                                             |
7.5.2.4 Specific prescriptions for chemical and fertilizer plants under declaration regime

In addition to the French ministerial order, some plants of the chemical and fertilizer sector are also covered by specific items under the ICPE legislation.

For these items, there are specific emissions limits values defined in standard national operational requirements, called “standard orders”. These orders are usually used for facility under the declaration regime. A summary of these specific air emission requirements is presented Table 32 below.
### Table 32 Specific emission limit values associated with the chemical and fertilizer sector

<table>
<thead>
<tr>
<th>Plant</th>
<th>ICPE Item</th>
<th>Specific emission limit values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene plants</td>
<td>4718</td>
<td>No specific emission limit value.</td>
</tr>
<tr>
<td>Polyethylene plants</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ethylene oxide plants</td>
<td>4720</td>
<td>Any arrangement, with the exception of sterilizers, will be taken to avoid the release of ethylene and/or propylene oxides into the atmosphere. In the case of sterilizers, every effort will be made to limit the emission of ethylene and/or propylene oxides to 1 ppm in the working environment.</td>
</tr>
<tr>
<td>Ethylene glycol plants</td>
<td>4330/4331</td>
<td>Dust:</td>
</tr>
<tr>
<td>Ethanol plants (Flammable liquids)</td>
<td>4722</td>
<td>• 150 mg m$^3$ if the mass flowrate is below or equivalent to 1 kg h$^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• 100 mg m$^3$ if the mass flowrate is greater than 1 kg h$^{-1}$.</td>
</tr>
<tr>
<td>Methanol plants</td>
<td>4722</td>
<td>Dust:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• 150 mg m$^3$ if the mass flowrate is below or equivalent to 1 kg h$^{-1}$.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• 100 mg m$^3$ if the mass flowrate is greater than 1 kg h$^{-1}$.</td>
</tr>
<tr>
<td>Stand-alone hydrogen production plants</td>
<td>4715</td>
<td>Liquid hydrogen:</td>
</tr>
<tr>
<td></td>
<td>(Hydrogen)</td>
<td>• Valves, venting or venting devices must be connected to a chimney inside the fence without accidental obstruction.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• The chimney must be equipped with an easily operable flame extinguishing system (e.g. a nitrogen injection system or equivalent).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• In addition, it must open in such a way that there is no obstacle or equipment (building, power line, etc.) in the upper part in an area delimited by a half-sphere with a radius of 20 meters and center the point located 3 meters below the exit of the chimney.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gas hydrogen:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• All venting of hydrogen must be carried out in the open air and, in any case, in a place and at a height sufficient to present no risk.</td>
</tr>
<tr>
<td>Ammonia plants</td>
<td>4735</td>
<td>No specific emission limit value.</td>
</tr>
<tr>
<td>Ammonium nitrate plants</td>
<td>4702 or 4703</td>
<td>No specific emission limit value.</td>
</tr>
</tbody>
</table>

Note that VOC emission limit values are defined in the ministerial order of February 2$^{nd}$, 1998 and are applicable to these plants.
7.5.3 Germany

7.5.3.1 General framework related to air emissions/air quality regulations

The German government bases air pollution control on four strategies:

- Establishing environmental quality standards;
- Emission reduction requirements according to the best available technology;
- Product regulations; and
- Developing air emission ceilings.

Industrial Emissions

European air quality regulations, for example stipulated within the European IED, 2010/75/EU, and the Directive on ambient air quality and cleaner air (2008/50/EC) are transposed into German law mainly by the Federal Immission Control Act (BImSchG) and its implemented ordinances and administrative regulations (refer to Section 7.5.3.2 below).

Air Quality Plans

The responsibility to meet air quality levels enables regional and local competent authorities to set up air quality plans containing various measures to improve air quality. To date, more than 150 air quality plans have been enforced. An example for measures are the definition of Low Emission Zones, in which vehicles without low emission standards are excluded from areas within the zone, in particular when concentrations of specific air pollutants (mainly PM and NO2) are high. Details are regulated in 11th Federal Immission Control Ordinance.

Industrial emissions have to be included and accounted for in these air quality plans. However, immediate measures to improve air quality where threshold values are exceeded do not apply to industrial activities in the current legislation.

7.5.3.2 Requirements concerning industrial emissions

The Federal Immission Control Act (BImSchG) and its implemented ordinances and administrative regulations regulate industrial emissions in Germany. Air quality in context of the BImSchG includes air pollution, noise, vibration and similar phenomena.

In addition, there are also provisions on air quality at the German federal states level.

Furthermore, the Technical Instructions on Air Quality Control (“TA Luft”) establishes emission limit values for relevant air pollutants, such as total dust, metals, inorganic gases (e.g. ammonia), SOX, NOX, and specific VOCs, from installations in order to protect citizens as well as the environment from unacceptable high pollutant emissions by these provisions.

The Federal Immission Control Act and the Technical Instructions on Noise Abatement (“TA Lärm”) are German instruments for protecting the population from noise and from commercial activities. Threshold values are defined therein, and are included in operating permits for facilities where appropriate. Noise contingency plans are developed for larger industrial or commercial parts. These
plans define noise limits (differentiated between day- and night-time) for each plant / planned area for industrial or commercial use.

In accordance with this legislation, licenses for the operation of industrial or commercial installations are only issued if there are no adverse effects on the environment due to noise.

Emissions need to be declared according to 11th Federal Immission Control Ordinance. The reporting period is every 4 years. The declaration must include, but is not limited to, information on the number and type of emission sources, the emission relevant processes and the throughput of substances. The focus is on data related to emissions into the atmosphere that were produced during the reporting period. Note that passive or diffuse emissions such as breathing losses from fuel tanks, fugitive dust from waste dumps or traffic routes, or during the transfer of raw materials and additives shall also be included.

7.5.3.3 Specific requirements for chemical and fertilizer sectors

**Emission Limit Values**

The air emission limit values presented in this section are based on Technical Instructions on Air Quality Control and apply to all facilities in Germany that require a permit for operation.

The limit values are categorized into immission and emission limit values. The immission part contains regulations to protect human health, animals, plants, waters, soils, atmosphere, as well as cultural and tangible assets, from unacceptable high pollution levels. Immissions are reported either as mass concentrations (mass of air pollutant per unit volume of air), or as deposition (mass of pollutant per unit area of ground per unit time), which is a German specificity in Europe (generally only air concentrations are regulated).

Emissions are grouped into dusty, organic and inorganic sections. Substance-specific air emission limit values are often categorized in emission classes. The smaller the class number, the more stringent the limit value.

Emission limit values are defined in Technical Instructions on Air Quality Control, section 5.2. Emission limit values for total dust and inorganic constituents in dust are presented in Table 33 and Table 34, respectively.

**Table 33 Germany’s emissions limit values for dusty substances**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Mass volume</th>
<th>Mass concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total dust, including PM</td>
<td>0.20 kg h⁻¹</td>
<td>20 mg m⁻³</td>
</tr>
</tbody>
</table>

Note that mass concentration shall not exceed 0.15 g m⁻³, even if the limit value for mass volume of 0.20 kg h⁻¹ is met.
### Table 34  Germany’s emissions limit values for dusty inorganic substances

<table>
<thead>
<tr>
<th>Class</th>
<th>Substance</th>
<th>Mass volume</th>
<th>Mass concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Mercury and its compounds</td>
<td>0.25 g h(^{-1})</td>
<td>0.05 mg m(^{-3})</td>
</tr>
<tr>
<td></td>
<td>Thallium and its compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>Lead and its compounds</td>
<td>2.5 g h(^{-1})</td>
<td>0.5 mg m(^{-3})</td>
</tr>
<tr>
<td></td>
<td>Cobalt and its compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nickel and its compounds</td>
<td>2.5 g h(^{-1})</td>
<td>0.5 mg m(^{-3})</td>
</tr>
<tr>
<td></td>
<td>Selenium and its compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tellurium and its compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>Antimony and its compounds</td>
<td>5 g h(^{-1})</td>
<td>1 mg m(^{-3})</td>
</tr>
<tr>
<td></td>
<td>Chromium and its compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cyanide, easily soluble</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fluoride, easily soluble</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Copper and its compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Manganese and its compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vanadium and its compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tin and its compounds</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Inorganic substances not listed in this document but meet at least one of the criteria below are categorized as class III substances.
- Suspected to be carcinogenic or mutagenic (categories K3 or M3, R 40), and/or
- Suspected to be toxic to reproduction (categories RE3 or RF3, R62 or R63).

There are also air emission limits for storage, handling, transport or loading operations relate to solid inorganic matter (section 5.2.2 class I and II), solid organic matter (section 5.2.5 class I) or solid matter related to carcinogenic, mutagenic or toxic to reproduction (section 5.2.7). These limits are defined in sections 5.2.3.2 to 5.2.3.5 and apply to the fine fraction of solid matter (<5 mm when sieved as dry mass). Emission limit values for inorganic and organic substances are presented in Table 35 and Table 36, respectively.
### Table 35  
**Germany’s emissions limit values for gaseous inorganic substances**

<table>
<thead>
<tr>
<th>Class</th>
<th>Substance</th>
<th>Mass volume</th>
<th>Mass concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Arsine</td>
<td>2.5 g h⁻¹</td>
<td>0.5 mg m⁻³</td>
</tr>
<tr>
<td></td>
<td>Chloric cyan</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phosgene</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrogen phosphoride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>Bromine (hydrogen bromine)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chlorine</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrocyanic acid</td>
<td>15 g h⁻¹</td>
<td>3 mg m⁻³</td>
</tr>
<tr>
<td></td>
<td>Fluorine (hydrofluoric acid)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrogen sulphide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>Ammonia</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gaseous inorganic chlorine compounds (if not included in Class I or II)</td>
<td>0.15 kg h⁻¹</td>
<td>30 mg m⁻³</td>
</tr>
<tr>
<td>IV</td>
<td>Sulphuric oxides SO₂ &amp; SO₃ (as sulphuric dioxide)</td>
<td>1.8 kg h⁻¹</td>
<td>0.35 g m⁻³</td>
</tr>
<tr>
<td></td>
<td>Nitrogen oxide: nitrogen monoxide, nitrogen dioxide</td>
<td>1.8 kg h⁻¹</td>
<td>0.35 g m⁻³</td>
</tr>
</tbody>
</table>

Note that exhaust gas from thermal or catalytic afterburners nitrogen monoxide and nitrogen dioxide is limited to 0.10 mg m⁻³. Simultaneously, CO emissions shall not exceed 0.10 mg m⁻³.
### Table 36: Germany’s emissions limit values for gaseous organic substances

<table>
<thead>
<tr>
<th>Class</th>
<th>Substance</th>
<th>Mass volume</th>
<th>Mass concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>—</td>
<td>Organic substance in exhaust gas (excluding dusty organic substances)</td>
<td>0.50 kg h⁻¹</td>
<td>50 mg m⁻³</td>
</tr>
<tr>
<td>—</td>
<td>Organic substance in exhaust gas: Exemption for old facilities with an annual mass volume of organic substances with less than 1.5 Mg/a. Operating hours with mass volume &gt; 0.5 kg h⁻¹ &lt; 1.5 kg h⁻¹ should be less than 8 operating hours per day.</td>
<td>1.5 kg h⁻¹</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>Complete list of substances listed in Appendix 4</td>
<td>0.10 kg h⁻¹</td>
<td>20 mg m⁻³</td>
</tr>
<tr>
<td>II</td>
<td>1-Bromine-3-chloropropene</td>
<td>0.50 kg h⁻¹</td>
<td>0.10 g m⁻³</td>
</tr>
<tr>
<td></td>
<td>1,1-Dichloroethane</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,2-Dichloroethylene, cis and trans</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methylformiate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nitroethane</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nitromethane</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Octamethylcyclotetrasiloxane</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,1,1-Trichloroethane</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,3,5-Trioxane</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note that old facilities with an annual mass volume of organic substances with up to 1.5 Mg a⁻¹ (listed as total C) have a limit value for “total C” of 1.5 kg h⁻¹. The number of operating hours with mass volumes between 0.5 – 1.5 kg h⁻¹ shall be less than 8 operating hours per day.

If substances of more than one class are present, emission limits of class II shall not be exceeded in the exhaust gas for combined substances of class I and class II.

Organic substances as well as secondary products of organic substances meeting at least one of the criteria below are categorized as class I substances:

- Suspected to be carcinogenic or mutagenic (categories K3 or M3, R 40);
- Suspected to be toxic to reproduction (categories RE3 or RF3, R62 or R63);
- Limit value at the workplace is lower than 25 mg m⁻³;
- Toxic or very toxic;
- May cause irreversible damage;
- May cause sensitization when inhaled;
- Have high odour intensity; and
- Slowly degradable and highly accumulative.

Section 5.2 (general requirements to emission limits) or Section 5.4 (special provisions for certain types of installations) do not contain any provisions regarding emission reduction. BAT Reference documents, or the VDI/DIN Air Pollution Prevention Manual, shall be used to determine the appropriate emission reduction technology on a case-by-case basis.
Specific Permitting Process

The permitting process in Germany is regulated in the Federal Immission Control Act. Permits are granted with the condition that the air emissions associated with facility construction and operation will not lead to harmful human and environmental effects.

Air quality modelling is an important part of the permitting process in order to prove compliance with applicable regulation. German modelling requirements are specified in Annex 3 of Technical Instructions on Air Quality Control. The software AUSTAL2000 has been developed to align with these requirements. AUSTAL2000 is well-known to authorities and widely used for permitting purposes in Germany. Deposition is modelled with AUSTAL2000 and may eventually be supported with data from in situ measurements for the permitting process.

For new plants, a baseline report must be prepared and submitted to the appropriate authority. The baseline report analyzes the existing environmental conditions in the area. When a facility closes, the original environmental conditions have to be restored.

Changes at existing facilities can also be subject to permitting. Minor changes require notification to the authority, whereas major changes require a permit that could involve a public hearing component. The latter applies if the changes being made to the facility have significant negative effects on the assets of protection aforementioned. Additional air emissions are always subject to permitting.

For some new plants and major changes within an existing plant, the development of an Environmental Impact Assessment (EIA) is mandatory. Contents of the EIA are regulated in the German Act on Environmental Impact Annex 1, column 1 and 2. For these mandatory EIAs, public involvement is a component of the permitting process (reference to §10 BImSchG).

If the facility modification is characterized as category “A” or “S” in column 2 of the Act on Environmental Impact (and the original EIA did not reveal significant negative effects on human health and the environment), then the facility does not have to conduct a completely new EIA. A facility modification is considered to be non-significant if: 1) emission quantities are considered to be low; 2) the existing load of immission is low; or 3) the additional load of immission is irrelevant.

During the permitting process, the most relevant provisions related to air emissions are:

- immission values for the protection of human health, for the protection against significant nuisances or significant disadvantages, and the protection against harmful environmental effects due to deposition;
- requirements to determine the existing, additional and total load;
- established criteria to compare and evaluate immissions against immission values; and
- requirements for the implementation of a special-case examination.

For the permitting process, the determination and evaluation of immission parameter (most importantly, the existing load, additional load and total load of immissions) is formalized and defined in sections 4.6 and 4.8 of Technical Instructions on Air Quality Control. Section 4.8 regulates the procedures for special cases and when immission values have not been defined.
In summary, it is mandatory to investigate if and to which extend immissions / deposition adversely affect the current or future use of the area. This is of particular importance, if sensitive areas such as playgrounds and residential areas are located nearby.

A permit can be granted even if immission values are exceeded, provided that the indicator for the additional load caused by emissions from the installation does not exceed 3.0% of the annual immission value in the area of assessment for the particular pollutant. In this case, environmental protection is achieved by imposing conditions that require either:

- further measures for clean air maintenance, including, in particular, measures which reach beyond the state of the art techniques, are carried out; or
- no later than 12 months after the installation has been put into operation, rehabilitation measures (dismantling, closing down, alteration) or other measures to achieve compliance with the immission values are carried out at existing installations of the applicant or third parties.

Plants and facilities that are subject to the permitting requirements are listed in the 4th Ordinance of the Federal Immission Control Act (Ordinance on Facilities and attendant Facilities Requiring Authorization; 4. BImSchV). Therein, a classification-based procedure is used to differentiate between Column 1 (larger size) and Column 2 (smaller size) installations depending on their capacity or size.

Section 4 of the BImSchV relates to “Chemical products, pharmaceuticals, mineral oil refining and further processing” and thus covers both, chemical plants and fertilizer plants relevant to this investigation. In particular, number 4.1 in this section is applicable to all chemical and fertilizer plants that are all listed in Column 1 (referred to as “Installations for the production of substances or groups of substances by chemical transformation on industrial scale…”). Subsections relevant to this study are presented in Table 37.
<table>
<thead>
<tr>
<th>Chemical plants</th>
<th># in Annex of 4.BImSchV</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>4.1b</td>
<td>for the production of oxygen-containing hydrocarbons, such as alcohols, aldehydes, ketones, carboxylic acids, esters, acetates, ethers, peroxides, epoxides.</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>4.1b</td>
<td>for the production of oxygen-containing hydrocarbons, such as alcohols, aldehydes, ketones, carboxylic acids, esters, acetates, ethers, peroxides, epoxides.</td>
</tr>
<tr>
<td>Ethylene oxide</td>
<td>4.1b</td>
<td>for the production of oxygen-containing hydrocarbons, such as alcohols, aldehydes, ketones, carboxylic acids, esters, acetates, ethers, peroxides, epoxides.</td>
</tr>
<tr>
<td>Methanol</td>
<td>4.1b</td>
<td>for the production of oxygen-containing hydrocarbons, such as alcohols, aldehydes, ketones, carboxylic acids, esters, acetates, ethers, peroxides, epoxides.</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>4.1a or 4.1h</td>
<td>for the production of hydrocarbons (linear or cyclic, saturated or unsaturated, aliphatic or aromatic). for the production of basic plastic materials (synthetic resins, polymers, man-made fibres, fibres on basis of cellulose).</td>
</tr>
<tr>
<td>Stand-alone hydrogen production plants</td>
<td>4.1l</td>
<td>for the production of gases, such as ammonia, chlorine and hydrogen chloride, fluorine and hydrogen fluoride, carbon oxides, hydrogen, sulphur dioxide, phosgene.</td>
</tr>
<tr>
<td>Fertilizer plants</td>
<td>Generally 4.1q</td>
<td>for the production of phosphorous-, nitrogen- or potassium-based fertilizers (simple or compound fertilizers).</td>
</tr>
<tr>
<td>Ammonia</td>
<td>4.1q</td>
<td>for the production of phosphorous-, nitrogen- or potassium-based fertilizers (simple or compound fertilizers).</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>4.1q</td>
<td>for the production of phosphorous-, nitrogen- or potassium-based fertilizers (simple or compound fertilizers).</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>4.1m or 4.1q</td>
<td>for the production of acids, such as chromic acid, hydrofluoric acid, phosphoric acid, hydrofluoric acid, phosphoric acid, nitric acid, hydrochloric acid, sulphuric acid, aloesum, sulphurous acids. for the production of phosphorous-, nitrogen- or potassium-based fertilizers (simple or compound fertilizers).</td>
</tr>
<tr>
<td>Urea</td>
<td>4.1q</td>
<td>for the production of phosphorous-, nitrogen- or potassium-based fertilizers (simple or compound fertilizers).</td>
</tr>
</tbody>
</table>

Note that if an installation can be classified into more than one of the installation categories listed in this Annex, the more specific category of installation shall apply.
The 12th Ordinance of the Federal Immission Control Act (Hazardous Incident Ordinance) transposes the European Directive 96/82/EC on the control of major accidents involving dangerous substances. Depending on the amount of hazardous substances produced, handled and stored on-site, a facility may fall under the basic or extended obligations of the Hazardous Incident Ordinance.

Chemical companies, to which this Ordinance applies, are obliged to inform the public about the risks of the plant and appropriate emergency behaviour by providing hazardous incident information.

Some further details / exceptions related to air emission limit values are regulated in Technical Instructions on Air Quality Control, section 5.4.4. This section relates to “chemical products, pharmaceuticals, mineral oil refinement and further processing”, and covers:

- Section 5.4.4.1h.5 refers to the “production of polyethylene by high pressure polymerization”. For old facilities, the mass concentration in exhaust of granulate decarburization is limited to 80 mg m\(^{-3}\) (total C). Limit values for organic substances of class I and II in section 5.2.5 do not apply.
- Section 5.4.4.1m.1 refers to “production of sulphuric acid”. The limit value for nitrogen oxide is set at 0.20 g m\(^{-3}\) in mass concentration of exhaust gas (listed as Nitrogen dioxide). The limit value for Nitrous oxide is set at 0.80 g m\(^{-3}\) in mass concentration of exhaust gas.
- Section 5.4.4.1m.2 refers to “production of SO\(_2\), SO\(_3\), sulphuric acid, and oleum”. The generation of aerosols of sulphuric acid has to be minimized as far as possible when handling with sulphuric acid or oleum.
- Section 5.4.4.1q refers to the “production of phosphorus- nitogenic- or potassium containing fertilizers”. Old facilities have to meet the following limit values at relevant operation units for the parameters:
  - Total dust: 50 mg m\(^{-3}\) in mass concentration in exhaust of prilling, granulation, drying;
  - Ammonia: 60 mg m\(^{-3}\) in mass concentration in exhaust of prilling; and
  - Ammonia: 50 mg m\(^{-3}\) in mass concentration in exhaust from granulation and drying.

The requirements within the 31st Federal Immission Control Ordinance (German Solvent Ordinance) may also be applicable. Therein, air emission limit values are regulated to constrain emissions from volatile organic compounds when using organic solvents. Annex 1 and 2 list types of facilities and operations using solvents accordingly, which fall under this ordinance.

Other Specificities to be highlighted

The Technical Instructions on Air Quality Control is currently being revised. A new version is expected by mid-2017, and more than 50,000 facilities will be affected by the amendments. A revision of certain parts including section 5.2 related to “general requirements to limit emission” is currently in discussion. One example of future changes may be related to tighter limit values of dust emission for certain industries.

There may be two future regulations applicable to certain industrial sectors for which BAT are currently available: BAT as well as the revised Technical Instructions on Air Quality Control.
7.5.4 Italy

7.5.4.1 Regulatory Framework

According to Italian regulations, a permit is required for any industrial source of air emissions (both minor or significant sources; regardless of whether the source is located in a NAA).

For major projects, a full EIA or IPPC permit is required. Major projects are defined as those listed in:
- Annexes I and item 2 in Annex 2 of the EU’s EIA Directive, 2011/92/EU; and
- Annex I of the EU’s IED, 2010/75/EU.

For minor sources, a permit issued by local authorities is required.

Permits must be periodically renewed – the renewal period is differentiated for particular type(s) of sources. The location of the site within a NAA does not modify the permitting procedure.

Facilities and production units related to the chemical and fertilizer sectors are authorized under the umbrella of the IPPC regulation, implemented in Italy by the D.Lgs 152/06, as amended. Applicable limits are:
- When applicable, the limits set forth by the EU IED, implemented by a recent modification the abovementioned D.Lgs 152/06 (D.Lgs. 46/2014, issued March 2014); and
- Otherwise, Section V of the D.Lgs 152/06.

Section V of D.Lgs 152 was initially issued in 1988, then slightly modified and included in the original version of D.Lgs 152, issued in 2006. In order to avoid different and less restrictive requirements for new facilities in comparison with older ones, limits indicated in Section V of the D.Lgs 152 cannot be exceeded, even in the case where IED sets less stringent limits (art. 29-sexies of the D.Lgs. 152 as modified in March 2014).

7.5.4.2 Section V of D.Lgs 152/06

Section V of D.Lgs 152 sets:
- Specific air emission limits for identified production activities; and
- Generic air emission limits that are applicable to all activities, when specific emission limits are not defined.

Specific Limits

Specific limits are not defined for any of the chemical plants discussed in this study.

Of note though, the VOC emission limit for terephthalic acid and dimethyl terephthalate production units at polymers and polyesters facilities with an overall emission of VOC exceeding 3 kg h\(^{-1}\) is 350 mg C Nm\(^{-3}\) for individual process units.

Conversely, there are specific limits that affect process units at certain fertilizer plants including ammonia plants, ammonium nitrate plants, nitric acid plants, and urea plants. More specifically, these emission limits apply to process units involved in the production, granulation, and/or drying of...
phosphorus, nitrogenous and potassic fertilizers (point 30 Part III Annex I Part V D.Lgs. 152/06). These emission limits include:

- Total Particulate Matter: 75 mg Nm$^{-3}$; 100 to 150 mg Nm$^{-3}$ for prill plant or fluid beds;
- Ammonia: 200 mg Nm$^{-3}$ for prill plant or fluid beds.

Emission limits from combustion units with a capacity up to 50 Megawatts Thermal (MWth) fed by gaseous fuels are reported in Table 38 below.

**Table 38** Italy’s emission limits for PM, NO$_X$, SO$_2$, applicable to combustion units with a capacity up to 50 MWth fed by gaseous fuels

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Limit Value (and note)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM</td>
<td>5 mg Nm$^{-3}$ (The emission value is assumed respected (without need of monitoring) in unit fed with natural gas or Liquefied Petroleum Gas.)</td>
</tr>
<tr>
<td>NO$_X$</td>
<td>350 mg Nm$^{-3}$ (If the fuel is a process gas that contains nitrogen, the emission limit does not apply; emissions have to be controlled, in accordance to the specific permit to be issued by competent authority.)</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>35 mg Nm$^{-3}$ (The emission value is assumed respected (without need of monitoring) in unit fed with natural gas or Liquefied Petroleum Gas.)</td>
</tr>
</tbody>
</table>

**Generic Limits**

Although not specific to chemical and fertilizer plants, all production units must meet generic limits. These emission limits are regulated according to their hazard characteristics. Pollutants are divided into five main groups, and then, for each group, different limits are set for different classes of hazard. Table 39 presents the generic emission limits for each pollutant group and hazard class.
### Table 39  Italy’s generic emission limits for all production units

<table>
<thead>
<tr>
<th>Pollutant Group</th>
<th>Hazard Class*</th>
<th>Limit Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substances classified carcinogenic or toxic to reproduction or mutagenic</td>
<td>Class I</td>
<td>0.1 mg Nm$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Class II</td>
<td>1 mg Nm$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Class III</td>
<td>5 mg Nm$^{-3}$</td>
</tr>
<tr>
<td>Substances that can be accumulated or with high toxicity</td>
<td>Class I</td>
<td>0.01 mg Nm$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Class II</td>
<td>0.5 mg Nm$^{-3}$</td>
</tr>
<tr>
<td>Inorganic substances which occur mainly as particulate matters</td>
<td>Class I</td>
<td>0.2 mg Nm$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Class II</td>
<td>1 mg Nm$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Class III</td>
<td>5 mg Nm$^{-3}$</td>
</tr>
<tr>
<td>Inorganic substances which occur mainly as gas or vapour</td>
<td>Class I</td>
<td>1 mg Nm$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Class II</td>
<td>5 mg Nm$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Class III</td>
<td>30 mg Nm$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Class IV</td>
<td>250 mg Nm$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Class V</td>
<td>500 mg Nm$^{-3}$</td>
</tr>
<tr>
<td>Organic compounds as gases, vapours or dust particulate matters</td>
<td>Class I</td>
<td>5 mg Nm$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Class II</td>
<td>20 mg Nm$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Class III</td>
<td>150 mg Nm$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Class IV</td>
<td>300 mg Nm$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Class V</td>
<td>600 mg Nm$^{-3}$</td>
</tr>
</tbody>
</table>

* Note: in case of presence of several substances of the same class, the concentration limits is referred to the sum of all their concentrations. In case of presence of several substances of various classes, the concentrations of substances in each class have to be added with the concentrations of substances of the lower classes.

D.Lgs 152/06 includes a list of pollutants for each group and class. Limits for substances not included in the list should be proposed by the plan owner, based on similarities in hazardous properties with substances in the list. Proposed limits should be reviewed by the authority in charge for the permit issuing and confirmed (or modified, as necessary). It should be noted that most limits (originally defined in 1988) are higher than currently documented in IED or BAT Conclusions.

#### 7.5.4.3  Domestic Implementation of the IED

According to European regulation, industrial emissions should:

- Not exceed the BAT-Associated Emission Levels (BAT-AEL), as indicated in the BAT conclusions documents (when available and applicable);
- Not exceed the upper value of the range of BAT-Associated Emission Levels (BAT-AEL) reported in the applicable BREF, when BAT conclusions are not available. According to a note issued by the Ministry of Environment in 2015, when the BREF indicates a range of BAT-AEL, the upper value should be considered, though this is not mandatory. In reality, the local authority that issued the permit will request that the lower limit of the range be met (also known as Best In Class BAT-AEL). Best In Class BAT-AEL are almost always required in new developments, and existing developments are usually required to implement an upgrading plan that detail upgrades for the development’s eventual achievement of the Best In Class BAT-AEL.
7.5.4.4 Conditions included in the Permits

In most permits, only in-stack concentration limits are defined. In some Italian regions, the local regulations often prescribe more restrictive (temporary) concentration limits in case of adverse meteorological situations directly in the permit. In a very limited number of cases, an annual (mass) flux limit is also defined for high emitting facilities such as refineries, power plants, etc. The major city, in which a facility is located, has the authority to cease air emissions at any given source at any time, in cases of severe pollution and immediate hazard to the population.

7.5.5 The Netherlands

7.5.5.1 General Framework related to Air Emissions in the Netherlands

The Netherlands environmental policy to achieve good air quality has two objectives:

- limiting the emission of harmful substances; and
- preventing long-term human exposure to pollution.

Industrial emissions are limited by requiring all companies emitting substances into the ambient air to obtain an environmental permit. The companies must also adhere to all applicable source control policy to minimize air emissions at the source.

In the Netherlands, the key regulations on air quality can be found in Chapter 5 (title 5.2) of the Environmental Management Act (Wet milieubeheer or Wm in Dutch). The essence of the Dutch air quality regulations consists of air quality standards, based on European Directives. They also enforce the basic obligations imposed by European directives, namely assessment of air quality, reporting and actions to be taken.

Specific elements of the law are set out in Decrees and Ministerial Regulations.

Air emissions from industrial sources have been considerably reduced over the most recent years. This is partly attributed to reducing source emissions in accordance with the air emission allowances as defined in industrial environmental permits. In cases where companies do not require an environmental permit, the Activities Decree defines maximum emission of substances (until 2015 this was the NER, the Netherlands Guideline for Emissions). This is described further in the following section.

7.5.5.2 Requirements concerning industrial air emissions in the Netherlands

Air Quality within Dutch Jurisdiction

Regulatory threshold values and action values are usually a compromise between what is achievable and values defined from a health perspective. Many of the Dutch regulatory values are defined by EU standards, and methods of adherence to these values is described in title 5.2 and Annex 2 of the Environmental Management Act, as discussed above in section 7.5.5.1.
Activity Decree

On December 17th 2010, the Netherlands version of the EU IED was enacted. The full title reads “RICHTLIJN 2010/75/EU VAN HET EUROPEES PARLEMENT EN DE RAAD van 24 november 2010 inzake industriële emissies (geïntegreerde preventie en bestrijding van verontreiniging)” (herein referred to as “RIE”).

In 2008, the Dutch Activities Decree was enacted and depending on a company’s commercial activities, companies were then classified into one of three categories ‘A’, ‘B’ or ‘C’ pursuant to the Activities Decree. The aim of Activities Decree is to regulate companies that impact the environment under general environmental rules.

A type ‘C’ facility requires an environmental permit (“omgevingsvergunning” or formerly “milieuvergunning”) issued by the regulatory authority. In cases where the company’s activities are listed in Annex 1 of the RIE, specific conditions relating to IPPC installations are defined by the regulatory authority. Type B facilities are not required to obtain a permit but must notify the competent authority (e.g. municipal authority) when they commence, change, or expand operations. Type A facilities do not have to notify the competent authority when they commence, change, or expand operations.

In section 2.3 of the Activity Decree, the applicability of the regulations is stated. Article 2.5 of the Activities Decree sets out the air emission standards. The article defines several substance categories (e.g. ZZS, sO, sA, gO and gA), each of which have subcategories (termed substance classes) based on the chemical, physical and toxicological parameters. Technical opportunities for emission reduction are also considered in the definition of these substance classes. Table 40 presents the mass flow limits and emission thresholds for the different substance categories and classes listed in the Activity Decree.
Table 40  Overview of air emissions standards in Netherlands’ Activity Decree

<table>
<thead>
<tr>
<th>Substance category</th>
<th>Substance class</th>
<th>Mass flow limit (g hr(^{-1}))</th>
<th>Emission threshold (mg Nm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>sA (dust like inorganics)</td>
<td>sA.1</td>
<td>0.25</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>sA.2</td>
<td>2.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>sA.3</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>gA (gaseous inorganic)</td>
<td>gA.1</td>
<td>150</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>gA.2</td>
<td>2,000</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>gA.3</td>
<td>2,000</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>gA.4 (SO(_2))</td>
<td>2,000</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>gA.5 (NO(_X))</td>
<td>2,000</td>
<td>200</td>
</tr>
<tr>
<td>gO (hydrocarbons)</td>
<td>gO.1</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>gO.2</td>
<td>500</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>gO.3</td>
<td>500</td>
<td>100</td>
</tr>
<tr>
<td>sO (dust)</td>
<td>sO</td>
<td>≥200</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>sO</td>
<td>≤200</td>
<td>200</td>
</tr>
</tbody>
</table>

Conditions related to odour are described in article 2.7 of the Activities Decree. The main concept is to minimize or reduce to an acceptable minimum level all odour emission from the facility.

Article 2.4 of the Activities Decree relates to substances defined as ZZS, meeting the requirements of article 57 REACH. This article requires facility emitting these substances to evaluate, every 5 years:

- The current quantities of the substance’s emissions to air; and
- The ability to eliminate emissions of these substances or, if elimination is not possible, to limit the emissions.

*Note: Activities Decree in Development

Regulations in the Activities Decree are currently being updated and developed. Since enacting the Activities Decree in 2010, activities and industries have been regulated in stages. For example, the first tranche of activities required several industries to be brought wholly or partially under the Activities Decree such as sheet-fed offset printing and laboratories. The second tranche in 2011 included waste related companies such as recycling companies and wind turbines to be brought under the Activities Decree. The third tranche in 2013 required agricultural companies to be incorporated into the Activities Decree. In January 2016, the “fourth tranche” has been published where links to other legal documents have been amended.

In addition, several industries have been brought wholly or partially under the Activities Decree such as gas turbines. This change will facilitate authorities in adding conditions for existing installations that have medium size combustion equipment. This concerns conditions related to the NO\(_X\) emission thresholds for different combustion equipment and a C\(_x\)H\(_y\) emission threshold for gas-fired engines. This change is most likely to be implemented from January 2017 onwards.

7.5.5.3  Specific requirements for chemical and fertilizer sectors

Article 4.1 of Annex 1 of RIE 2010/75/EU (IPPC) lists chemical plants that require an environmental permit. Chemical plants considered in this study that require an environmental permit include:

- Ethylene plants;
- Polyethylene plants;
- Ethylene oxide plants;
- Ethylene glycol plants;
- Methanol plants; and
- Ethanol plants.

The facility’s environmental permit would include specific conditions that state air quality requirements for the plant.

Stand-alone hydrogen production plants are listed in Annex 1 of RIE 2010/75/EU (IPPC), Article 4.2. Therefore, these plants would also require an environmental permit. Again, the permit would likely have conditions that specify air quality requirements for the plant.

Article 4.3 of Annex 1 of RIE 2010/75/EU (IPPC) lists fertilizer plants that require an environmental permit. Fertilizer plants considered in this study that require an environmental permit include:
- Ammonia plants;
- Urea plants;
- Nitric acid plants; and
- Ammonium nitrate plants.

Again, the facility’s environmental permit would include specific conditions that state air quality requirements for the plant.

An example of how air emissions standards are applied in the Netherlands is illustrated using an ethanol plant. Activities related to this plant are IPPC (IED), and hence an environmental permit is required (Type C facility). Emission thresholds defined in article 2.3 of the Activities Decree are not applicable for IPPC-installations if BAT conclusions cover these. In this case, only the requirement to eliminate or limit the use and emissions of substance class ZZS applies (substance meets the requirements listed in article 57 of European REACH regulations). Specific requirements related to emission reduction are defined in conditions in the environmental permit.

7.5.6 Spain

7.5.6.1 Regulatory context

Spanish Environmental Legislation consists of several levels, the most important of which are Acts ("Leyes"), Decrees / Royal Decrees ("Decretos / Reales Decretos"), Orders ("Órdenes") and Technical Regulations ("Reglamentos").

The 1978 Constitution is the fundamental Spanish Law. As a consequence of the environmental distribution of powers set out by the Spanish Constitution, both the Spanish Parliament and the Legislative Assemblies of the Autonomous Regions have the power to issue environmental laws. Such laws are usually implemented by regulations, which set out a more detailed content of the principles and provisions established in the relevant law. The regulations may either adopt the form of a Royal Decree ("Real Decreto"), Decree ("Decreto") or Order ("Orden"), depending on the body that approves the relevant regulation. In addition, Local Entities may also enact environmental rules, which usually adopt the form of Municipal Ordinances ("Ordenanza Municipal").
The Spanish State is divided in 17 Autonomous Regions (AR) called "Comunidades Autónomas", which have their own administrative bodies, such as a parliament, a cabinet, etc. The Spanish Government has the duty to framework environmental legislation. Each autonomous region has the power to develop and implement national framework legislation depending on the degree of legislative competences transferred (which changes from one region to another). The Spanish Government has exclusive power to enact basic legislation on the protection of the environment, notwithstanding the powers of the AR to issue additional protection regulations. From a practical standpoint, an AR can issue a law before the State issues a basic rule. These regional laws have to be at least as restrictive as the national laws.

Environmental issues in Spain are normally the responsibility of the Ministry of Environment, which is divided into three Secretariats:

1. the Sub-secretariat of Environment ("Subsecretaría de Medio Ambiente"),
2. the General Secretariat for the Land and the Biodiversity ("Secretaría General para el Territorio y la Biodiversidad") and
3. the General Sub-secretariat for the Prevention of the Contamination and the Climate Change ("Secretaría General para la Prevención de la Contaminación y el Cambio Climático"), which are subsequently subdivided into six General Directorates:
   1. The General Directorate of Water ("Dirección General del Agua"),
   2. the General Directorate of Coasts ("Dirección General de Costas"),
   3. the General Directorate for Biodiversity Conservation ("Dirección General para la Biodiversidad"),
   4. the General Directorate for Quality and Environmental Assessment ("Dirección General de Calidad y Evaluación Ambiental"),
   5. the General Directorate of the Spanish Office of Climate Change ("Dirección General de la Oficina Española del Cambio Climático") and
   6. the General Directorate of the National Institute of Meteorology ("Dirección General del Instituto Nacional de Meteorología").

7.5.6.2 Integrated Pollution Prevention and Control

General Considerations

The key pieces of legislation in Spain relating to Integrated Pollution Prevention and Control are the following:

- Royal Decree 508/2007, enacted April 20th 2007, regulating the submittal of information on emissions related to the European Pollutant Release and Transfer Register (E-PRTR) Regulation and Integrated Environmental Authorizations; and
- Royal Decree 815/2013, on Industrial Emissions; approving the Regulation for the development and implementation of Act 16/2002, enacted July 1st 2002.
Act 16/2002 creates a new administrative instrument known as the Integrated Environmental Authorization (IEA). The authorization merges environmental permits in Spain. The Ministry of Environment is the responsible body for the implementation of the IPPC Directive at State level. Act 16/2002 provides for the Government to set regulations under the IPPC Act within the scope of its competences. The Ministry of Environment has the power to modify the annexes of the Act should there be any changes introduced by European Community legislation.

EU Directive on IPPC (96/61/EC) was transposed into Spanish legislation in Law 16/2002 on July 1st 2002. This law aims to ensure the prevention or reduction of emissions from potentially polluting industries to various receptors (i.e. air, water, land), in order to maintain EU environmental quality standards and other EU legislation. IED directive has been partially transposed into Spanish legislation in Law 5/2013, modifying the IPPC Law 16/2002.

Regional Governments are responsible for implementing / regulating IPPC in their respective regions. The Autonomous Communities and their Environmental Departments can either directly adopt the state legislation and develop the regulations for the implementation at regional level or implement the state act by virtue of a single new piece and develop its correspondent regulations to set forth the specific requirements. Some regions have implemented the IPPC regime by virtue of a single new piece of legislation such as Catalonia, Valencia and Basque Country.

The owners or operators of existing installations defined in Act 16/2002 must comply with the terms of the Act and secure an IEA before October 30th, 2007. IEAs will be valid for a maximum period of eight years and can be renewed and, eventually, updated for successive periods. Non-existing (i.e., new) facilities must apply for an IEA no less than ten months prior to the start of operations.

Contents of the Integrated Environmental Authorizations under Act 16/2002 include:

- Emission limits applicable to the facility or activity, in particular, those limits applicable to the contaminating substances listed in Annex 3 of the Act;
- Requirements in connection with the prevention of soil and groundwater contamination;
- Procedures and methods to manage waste to be generated;
- Systems and procedures to be applied to treat and control emissions and waste, also describing the measuring methods, frequency thereof, and the applicable assessment procedures;
- Requirements applicable to the operation of the facility under abnormal operation circumstances such as malfunctions, temporary halts or final closing;
- If applicable, the Impact Assessment Study and the prevention and control measures required by the regulations applicable to the prevention of serious accidents involving dangerous substances; and
- Any other requirement applicable pursuant to specific sector regulations.

Exceptions to emission limits can be authorized provided the operator produces the following:

- A rehabilitation plan assuring that the maximum value limits shall be again respected within six months; and
- A project to minimize contamination.
The facilities that have to adjust their obligations to the new requirements under Act 16/2002 and 5/2013 will be operating under the existing operating authorization until 2007, when all Annex I facilities must obtain the new authorization.

**Chemical and Fertilizer Sector**

Regarding the chemical and fertilizer sector, the following industries are included in Annex 1 of the Act 16/2002:

- Chemical installations for the manufacture of basic organic chemicals, in particular:
  - Simple hydrocarbons (linear or cyclic, saturated or unsaturated, aliphatic or aromatic);
  - Oxygenated hydrocarbons, such as alcohols, aldehydes, ketones, organic acids, esters, acetates, ethers, peroxides, resins, epoxides;
  - Sulphur hydrocarbons;
  - Nitrogenous hydrocarbons, in particular amines, amides, nitrous compounds, nitrates or nitrates, nitriles, cyanates and isocyanates;
  - Phosphorus hydrocarbons;
  - Halogenated hydrocarbons;
  - Organic metal compounds;
  - Basic plastic materials (polymers, synthetic fibers, cellulose fibers);
  - Synthetic rubbers;
  - Colorants and pigments; and
  - Surfactants and surfactants.

- Chemical installations for the manufacture of basic inorganic chemicals, such as:
  - Chemical installations for the manufacture of fertilizers based on phosphorus, nitrogen or potassium (simple or compound fertilizers).

Royal Decree 508/2007 regulates the submittal of information on emissions related to the Regulation on the European Pollutant Release and Transfer Register (E-PRTR) and Integrated Environmental Authorizations. Operators of activities listed under Annex I of this Royal Decree that exceed the applicable capacity thresholds are required to submit annually to the competent authority, information on emissions to atmosphere, water and soil, waste transfer and transfer of wastewater for off-site treatment in accordance with its article 3.

Royal Decree 815/2013 approves the Regulation for the development and implementation of Act 16/2002 which is further modified by the Law 34/2007. Additionally, this Royal Decree modifies Royal Decree 1383/2002, enacted December 20th 2002, on the management of end-of-life vehicles. This Regulation allows public administrations to adapt administrative procedures for the authorization of activities that fall under its scope of application, by establishing technical measures that simplify administrative procedures for the authorization of new activities as well as the adequacy of existing activities and establishes a simplified procedure for the application for an integrated environmental authorization. Additionally, it allows ARs to simplify inspection procedures as part of the authorization procedure for installation for which either an Environmental Management System or an Eco-Management and Audit Scheme is in place.
Air emissions are covered by several acts, royal decrees and orders. The main pieces of legislation regarding air emissions at national level are the following:

- Royal Decree 100/2011, enacted January 28th 2011, by updating the list of activities potentially polluting the atmosphere and sets the basic rules for its implementation;
- Law 34/2007, enacted November 15th 2007, on air quality and atmospheric protection;
- Royal Decree 833/1975 developing the Air Protection Act;
- Royal Decree 102/2011, enacted January 28th 2011, on air quality;
- Royal Decree 1613/1985, establishing new air quality values regarding pollution by SO2 and particulates and partially modifying Decree 833/1975 (this Royal Decree was subsequently modified by further regulations);
- Royal Decree 2102/1996, on the regulation of VOCs emissions from the storage and distribution of fuel in petrol stations;
- Royal Decree 117/2003, on VOCs emissions restrictions due to the use of certain solvents in some industrial activities;
- Royal Decree 227/2006, enacted February 24th 2006, complementing the legal regime on the limitation of emissions VOCs in certain paints and varnishes and vehicle refinishing products.

Royal Decree 833/1975, developing the Air Protection Act implemented by former Act 38/1972, establishes the air pollution prevention, monitoring and correction regime at a national level. It regulates all aspects in relation to potentially polluting activities (as defined in Annex II). Titles V, VI, VII and Annex I of this Act have been repealed by Royal Decree 100/2011. Moreover, it should be noted that this Royal Decree has been partially replaced by IPPC. Annexes II and III of this Decree have been revoked by Law 34/2007, enacted November 15th, 2007.

Law 34/2007, on air quality and atmospheric protection, establishes three categories (A, B or C) of air emission activities depending on their polluting potential. Annex IV of Law 34/2007 defines the specific industries in each category; in general though, categories A and B contain industries with greater emissions. This Law establishes a more stringent regime for the protection of the atmosphere than previous Act 38/1972, and requires groups A and B activities to apply for an authorization, whereas group C activities shall notify the regional governments on the construction, operation, transfer, substantial modification or cease of their operations. Deadlines for compliance with these administrative requirements are defined at the regional level by the different Autonomous Communities.

Royal Decree 102/2011, on air quality, transposed the content of Directive 2008/50/EC (May 21st, 2008) into Spanish law. It is approved for the purpose of avoiding, preventing, and reducing the harmful effects of air emissions on human health, and the environment.

Industries classified as group A or B require an authorization, with pre-established measurement frequencies for each source of emission and control regulations (also regulated by the Autonomous Community). This classification is the responsibility of the corresponding Autonomous Community, with the following criteria taken into consideration:

- Size and production of the facility;
- Its energy consumptions;
- Type of contamination generated and associated quantities; and
• Level of pollution in the area, in relation to established air quality objectives.

The owners of such type of installations must follow certain parameters, such as:

1. Notify the proper authorities in case of transition, cessation or closure of activities and/or facility;
2. When applied, the facility must have contamination level measuring stations, which should be integrated in the autonomous community network;
3. Keep an updated register of emissions control and contamination levels and submit the facility to regular inspections of such parameters, as by applicable regulation;
4. Minimize emissions and diffuse emissions applying the best techniques as possible;
5. All necessary elements for normative compliance regarding air emissions should be operative at start of operations and during all activity period, except when stated otherwise (in the Authorization), according to Law 34/2007;
6. As per the Authorization requirement, apply emission controls to every activity performed on the facility;
7. If there are suspects/evidences of incompliance of the authorization conditions/applicable normative, the authorities may ask for additional control sources of the facility;
8. The authorities may exempt a facility of total or partial emissions control, in case of technical impossibilities or non-systematic emission sources.
9. Respect the emission limit values, if established (also regulated by the Autonomous Community);
10. In case of threat of significant damage caused by atmospheric contamination from the facility, immediately warn the authorities and adopt mitigation measures;
11. In case of significant damage caused by atmospheric contamination from the facility, immediately adopt avoidance measures and warn the authorities; and
12. Provide information to the Public Administration regarding atmospheric emissions issues, as necessary.

Additionally, this law sets the basis for the update and/or further development of emission limit values and other legislation on the matter.

As indicated above, emission limit values and monitoring periodicity is regulated by the each Autonomous Community.

Royal Decree 100/2011 aims to provide an update to the catalogue of activities which potentially pollute the air. These activities are given in annex IV of Law 34/2007, enacted November 15th 2007, on air quality and protection. It establishes the specific basic legal requirements to allow its application as well as some minimum common criteria concerning measures for monitoring emissions, which the Autonomous Communities can adopt for activities included in the aforementioned catalogue. The Erratum to Royal Decree 100/2011 was published on April 7th 2011, and provides updates the catalogue of activities which potentially pollute the air. It also establishes the basic legal requirements for their application.

The chemical and fertilizer plants catalogued in the Erratum to Royal Decree 100/2011 are presented in Table 41 below.
Table 41  Classification of the chemical and fertilizer sector according to the Royal Decree 100/2011

<table>
<thead>
<tr>
<th>Group</th>
<th>Chemical plants</th>
<th>Fertilizer plants</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ethylene oxide plants</td>
<td>Ammonium nitrate plants</td>
</tr>
<tr>
<td></td>
<td>Ethylene plants</td>
<td>Nitric acid plants</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Urea plants</td>
</tr>
<tr>
<td>B</td>
<td>Ethanol plants</td>
<td>Ammonia plants*</td>
</tr>
<tr>
<td></td>
<td>Polyethylene plants</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>Ammonia plants*</td>
</tr>
</tbody>
</table>

*Ammonia plants can be classified as group B or C, depending on the type of production

According to the Resolution of the Autonomous Community of Madrid, published March 12th 2011, classified industries in all AR are required to carry out air emission monitoring (as specified in the Authorization) according to the following periodicity:

- Group A facilities, every two weeks;
- Group B facilities, every year and a half; and
- Group C facilities, every two and a half years.

In addition, Royal Decree 117/2003 restricts VOCs emissions resulting from the use of certain solvents in some industrial activities. The list of activities and processes falling under this new piece of legislation are included in Annex I of this Royal Decree. Installations also falling under the IPPC Act, as well as the VOCs Royal Decree will be required to hold an Integrated Environmental Permit. For those falling under the VOCs Royal Decree, a “notification” is required from the competent authority prior to the beginning of the operations. For existing installations, the deadline for complying with the new requirements is October 31st, 2007. A special regime is established for those activities using hazardous and risky substances and compounds. In the case of non-compliance with the emission limit values, the owner of the facility is required to either notify the competent authority or cease operations by requirement of a competent authority.

Royal Decree 227/2006, enacted February 24th 2006, complements the legal regime on the limitation of VOC emissions in certain paints and varnishes and vehicle refinishing products. This Royal Decree modifies the scope of application of Royal Decree 177/2003 on VOCs and adopts Directive 2004/42/CE of the European Parliament and of the Council, published April 21st 2004, on the limitation of VOC emissions resulting from the use of organic solvents in certain paints and varnishes and vehicle refinishing products, which amends Directive 1999/13/EC, dated March 11th 1999. The purpose of this Royal Decree is to limit the total content of VOCs in certain paints and varnishes and vehicle refinishing products listed under its Annex I in order to prevent or reduce air pollution resulting from the contribution of VOCs to the formation of tropospheric ozone.
7.5.7 United Kingdom

7.5.7.1 Overview of Air Quality Framework in the UK

In the United Kingdom (UK), air quality is a devolved matter; administrations in Scotland, Wales and Northern Ireland are responsible for their own air quality policy and legislation.

The 2007 Air Quality Strategy establishes the policy for ambient air quality in the UK. It includes the National Air Quality Objectives (NAQOs) for the protection of human health and vegetation for 11 pollutants (Defra, 2011). The Air Quality (England) Regulations 2000 (and 2002 amendments) set out the NAQOs for local authorities in England. The NAQOs are policy objectives; local authorities are not required to achieve them, but have to work towards their achievement. The objectives mirror limits set in EU legislation (2008/50/EC).

Local authorities have a duty under section 83(1) of the UK 1995 Environment Act to designate those areas where the air quality objectives are unlikely to be, or are not being, met as air quality management areas (AQMA). These are known as non-attainment areas (NAA). Within England, the main contributor to non-attainment is from vehicle emissions and not industrial sources given the highly urbanized nature of the country and the limited amount of heavy industry. There are no specific requirements for industry within NAA, and there is no obligation on the regulators to set emission limits any more stringent than those associated with the use of Best Available Technology (BAT).

The NAQOs apply to external air where there is relevant exposure to the public over the associated averaging periods within each objective. Guidance is provided within Local Air Quality Management Technical Guidance 2016 (LAQM.TG (16)) issued by the Government Department for Environment, Food & Rural Affairs (DEFRA) for Local Authorities, on where the NAQOs apply (Defra, 2016). The objectives do not apply in workplace locations, to internal air or where people are unlikely to be regularly exposed (i.e. centre of roadways).

7.5.7.2 Requirements concerning industrial air emissions in the UK (England and Wales)

Air pollution emissions from industrial sources are controlled under the Environmental Permitting (England and Wales) Regulations (and 2013 amendments) which implement the Industrial Emissions Directive on Integrated Pollution Prevention and Control (IPPC) (2010/75/EU). The Environmental Permitting Regulations set out the type and size of processes requiring an environmental permit to operate.

For new major industrial developments, the EU EIA Directive (2011/92/EU) will also apply. In the UK, this is implanted as the Town and Country Planning (Environmental Impact Assessment) Regulations. There are no official guidelines on quantifying significance of air quality impacts in EIA, however Environmental Protection UK (EPUK) and the Institute of Air Quality Management (IAQM) Planning Guidance considers both absolute and relative changes in air quality on receptors and compliance with NAQOs (EPUK and IAQM, 2015).

The Environmental Permitting Regulations classifies industrial installations into three groups:

- Part A1: The largest and most polluting installations (as listed in the EU directive) which are permitted by the Environment Agency;
• Part A2: Less polluting installations which are regulated for emissions to air, water and land permitted by the Local Authority; and
• Part B: Less polluting installations which are only regulated for emissions to air; these are also permitted by the local authority.

For Part A1 processes, the EU has produced a series of BREF notes setting out appropriate Best Available Technique (BAT) AEL (Associated Emission Limits) and other management techniques to prevent emissions (see Europe section above). Similar less stringent guidance is produced by Defra for Part A2 and Part B processes. New sources would need to demonstrate that they meet BAT and the AEL, and would also be expected to demonstrate that the predicted emissions would not result in a significant effect on air quality through production of a risk assessment; a generic risk assessment produced by the Environment Agency for standard rules permits or a bespoke risk assessment for bespoke permits.

A new industrial facility classed as an A1 installation must apply to the Environment Agency to operate. There are 2 types of permit which can be applied for:
• Standard rules - a set of fixed rules for common activities; and
• Bespoke - tailored to your business activities.

The UK government provides detailed guidance on when each type of permit is applicable and the process for applying for one. In general, chemical and fertilizer plants would not qualify for standard rules permits given certain characteristics of these facilities that preclude them from qualifying; for example, to apply for a standard rules permit, the installation must not:
• Have to use equipment to reduce or remove emissions before they are released into the outside environment;
• Produce more than 1 tonne of waste or 10 kg of hazardous waste per day, averaged over a year, with not more than 20 tonnes of waste or 200 kg of hazardous waste being released in any one day; or
• Consume energy at a rate greater than 3 MW or, if the installation uses a combined heat and power installation to supply any internal process heat, 10 MW (through both imported electricity and by burning fuel on site).

New industrial developments resulting in significant impacts of a pollutant, for which an AQMA has been declared, are unlikely to be granted a permit by either the Environment Agency or the Local Authority without mitigation to reduce impacts to an acceptable level.

Where an existing industry is considered to be resulting in excessive emissions, an improvement timetable would be implemented to gradually improve the emissions so that they comply with BAT.

7.5.7.3 Specific requirements for chemical and fertilizer sectors

Schedule 1 of the Environmental Permitting Regulations lists the activities, installations and plants that fall under these regulations. Chapter 4 relates specifically to the chemical industry and identifies which part of the regulations, Part A1, A2 or B, would apply.

• **Organic Chemicals** - Under section 4.1 activities, installations and plants producing organic chemicals such as hydrocarbons, organic compounds containing oxygen, nitrogen phosphorus

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or halogens, organometallic compounds, plastic materials (e.g. polymers), synthetic rubbers, dyes/pigments and surface active agents, are categorized as part A1 activities and therefore an environmental permit will be required from the Environment Agency.

- **Inorganic Chemicals** - Under section 4.3 activities, installations and plants producing inorganic chemicals such as gases (e.g. hydrogen), acids (e.g. nitric acid), bases, salts, halogens or a range of other inorganic compounds are categorized as a part A1 activity and therefore an environmental permit will be required from the Environment Agency.

- **Chemical Fertilizers** - Under section 4.3 on chemical fertilizer production, activities, installations and plants producing (including any blending which is related to their production) phosphorus, nitrogen or potassium-based fertilizers (simple or compound fertilizers) are categorized as a part A1 activity and therefore an environmental permit will be required from the Environment Agency.
8.0 References


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