Pollutant emissions

Lecture in
TEP4170 Varme- og forbrenningsteknikk 2008
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Syllabus

Turns: Chapter 15 - Pollutant emissions
• Nearly 90% of the world’s energy requirement is covered by combustion

• **Combustion is a core process in many contexts**
  - e.g. internal combustion engines, wood stoves, in process industry, in district heating and gas- and coal-fired power stations

• **Challenges**
  - Reduction of emissions such as \( NO_x \), \( CO_2 \), etc.
  - Improvement of efficiency
  - Safety in connection with the use of gas and especially with regard to hydrogen

Simulation results, temperature and NOx values using detailed chemistry
Dept. of Energy Processes Combustion

- **Activity areas**
  - Power production with CO₂ capture
    - Hydrogen combustion
    - Oxy-fuel combustion
  - Low-NOₓ burners
  - Gas reforming and production of synthesis gas
  - Flame stability and pressure pulsations
  - Emissions and thermal impact from flames/flare
  - Modelling and simulation of pyrolysis and combustion of biomass

Source: [www.powergeneration.siemens.com](http://www.powergeneration.siemens.com)
Lecture content

• Overview
• Effects of pollutants
• Quantification of emissions
• Emissions from premixed combustion
• Emissions from nonpremixed combustion
• Summary
• Examples from Internal Combustion Engines
Overview

Control of pollutants is a major factor in the design of modern combustion systems. Pollutants of concern includes particulate matter (soot, fly ash, aerosols, etc.), SOx (SO2 and SO3), NOx (NO + NO2), N2O, hydrocarbons and CO, and CO2.

Table 15.1 summarizes general areas of concern and the various combustion-generated pollutants associated with each.
## Overview

### Table 15.1  Combustion-generated or related air pollution concerns

<table>
<thead>
<tr>
<th>Concern (International Treaty/U.S. Regulation)</th>
<th>Combustion-Generated or Related Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Local/Regional Air Quality (National Ambient Air Quality Standards [1])</td>
<td>Criteria pollutants: particles (PM$<em>{10}$)$</em>{a}$, O$_3$, NO$_2$, SO$_2$, CO, lead</td>
</tr>
<tr>
<td>Air Toxics/Hazardous Air Pollutants [2] (1990 Clean Air Act Amendments)</td>
<td>189 Substances: selected aliphatic, aromatic, and polycyclic aromatic hydrocarbons; selected halogenated hydrocarbons; various oxygenated organics; metals; and other compounds</td>
</tr>
<tr>
<td>Greenhouse Effect/Global Warming [3] (Kyoto Protocol, 1997)</td>
<td>CO$_2$, CH$_4$, N$_2$O, stratospheric H$_2$O, tropospheric and stratospheric O$_3$, C (soot), sulfates$_b$</td>
</tr>
<tr>
<td>Stratospheric Ozone Destruction [3] (Montreal Protocol, 1987)</td>
<td>CH$_4$, N$_2$O, CH$_3$Cl, CH$_3$Br, stratospheric H$_2$O, stratospheric O$_3$</td>
</tr>
</tbody>
</table>

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$a$ PM$_{10}$ designates particles having aerodynamic diameters equal to or less than 10 $\mu$m.

$b$ Sulfates ($SO_2/SO_4^{2-}$) act as anti-greenhouse gases.
**Effects of pollutants**

**Primary** pollutants (those emitted directly from the source) and **secondary** pollutants (those formed via reactions involving primary pollutants in the atmosphere) affect our environment and human health in many ways:

1. **Altered properties of the atmosphere and precipitation.**
   - Reduced visibility; resulting from the presence of carbon-based particulate matter, sulfates, nitrates, organic compounds and NO2.
   - Increased fog formation and precipitation; resulting from high concentrations of SO2 that form sulfuric acid droplets which serve as condensation nuclei.
   - Reduced solar radiation.
   - Altered temperature and wind distributions.
   - Regional climate, through acid rain.
   - Global climate, through greenhouse gases.

2. **Harm to vegetation.**
   - Harmed by the phytotoxictants SO2, peroxyacetyl nitrate (PAN), C2H4 and others. Phytotoxicants destroy chlorophyll and disrupt photosynthesis.
Effects of pollutants

- Particulate matter soils clothing, buildings and other structures, creating a reduced aesthetic quality and cleaning costs. Acid and alkaline particles, in particular those containing sulfur, corrode paint, masonry, electrical contacts and textiles, while ozone severely

4. Potential increase of sickness and mortality in humans.
- Pollutants can aggravate pre-existing respiratory ailments. deteriorates rubber.

- Secondary pollutants (ozone, organic nitrates, oxygenated hydrocarbons, photochemical aerosol; formed primary by the reactions among NO and various hydrocarbons) in photochemical smog cause eye irritation.

- Carbon-based particles may contain adsorbed carcinogens.

- The health effect of CO is well documented (see Figure 15.1)

Stratosphere:
Catalytic destruction of stratospheric ozone by \( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \), where NO may be regenerated through \( \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \). The result is increased UV radiation on the Earth’s surface.
Quantification of emissions

Emission levels are expressed in many different ways, which can make comparisons difficult.

These differences arise from the needs of different technologies, e.g. g/km, mg/MJ or ppm at a reference O2 level.

**Emission indices**

The emission index for species $i$ is the ratio of the mass of species $i$ to the mass of fuel burned in the combustion process:

$$EI_i = \frac{m_{i,\text{emitted}}}{m_{F,\text{burned}}}.$$  \hfill (15.1)

In principle the emission index is a dimensionless quantity, however, units such as g/kg are used to avoid working with very small numbers.

The emission index is independent of any dilution of the product stream or efficiency of the combustion process, and is as such “uncoupled” from a specific application.
Quantification of emissions

Corrected concentrations

Concentrations, corrected to a particular level of \( \text{O}_2 \) in the product stream, are frequently used. The purpose of correcting to a specific \( \text{O}_2 \) level is to remove the effect of various degrees of dilution. Corrected concentrations may be expressed on either wet or dry basis.

Assuming stoichiometric or lean conditions and complete combustion with air of 1 mole of a hydrocarbon fuel, the global combustion reaction becomes:

\[
C_xH_y + a \text{O}_2 + 3.76a \text{N}_2 \rightarrow x \text{CO}_2 + (y/2) \text{H}_2\text{O} + b\text{O}_2 + 3.76a \text{N}_2 + \text{trace species.}
\]  

(15.3)

In many cases, the moisture is removed from a product gas sample before analysis, yielding so-called dry concentrations, while sometimes the gas is heated and the moisture retained.

The dry mole fraction for a species \( i \) is:

\[
\chi_{i,\text{dry}} = \frac{N_i}{N_{\text{mix,\text{dry}}}} = \frac{N_i}{x + b + 3.76a},
\]

(15.4a)

The wet mole fraction is:

\[
\chi_{i,\text{wet}} = \frac{N_i}{N_{\text{mix,\text{wet}}}} = \frac{N_i}{x + y/2 + b + 3.76a}.
\]

(15.4b)
Quantification of emissions

Various specific emission measures

Spark-ignition and diesel engines (e.g. g/kW-hr)

Mass specific emission = \( \frac{\text{Mass flow of pollutant}}{\text{Brake power produced}} \), \hspace{1cm} (15.10)

Mass specific emissions (MSE) are conveniently related to the emission index as:

\[
(MSE)_i = \dot{m}_F \frac{EI_i}{\dot{W}},
\]  

where \( \dot{m}_F \) is the fuel mass flowrate and \( W \) is the power delivered.

Another frequently employed specific emission measure is the mass of pollutant emitted per amount of fuel energy supplied (e.g. g/MJ):

\[
\frac{\text{Mass of pollutant } i}{\text{Fuel energy supplied}} = \frac{EI_i}{\Delta h_c},
\]  

where \( \Delta h_c \) is the fuel heat of combustion.

Other more specific measures of emission may be e.g. g/km.
Emissions from premixed combustion

The primary pollutants that we wish to deal with are oxides of nitrogen, CO, unburned and partially burned hydrocarbons and soot. SOx emissions in premixed combustion (typically using natural gas or gasoline) are low or zero.

Natural gas contains essentially no sulphur, and gasoline less than 600 ppm by weight.

For nonpremixed systems burning coal or low-quality oils, SOx is a major concern.

Oxides of nitrogen

NOx formation mechanisms:

1. The extended Zeldovich (or thermal) mechanism in which O, OH, and N₂ species are at their equilibrium values and N atoms are in steady state (Reactions N.1–N.3 in Chapter 5).

2. Mechanisms whereby NO is formed more rapidly than predicted by the thermal mechanism above, either by (i) the Fenimore CN and HCN pathways (Reactions N.7 and N.8), (ii) the N₂O-intermediate route (Reactions N.4–N.6), or (iii) as a result of superequilibrium concentrations of O and OH radicals in conjunction with the extended Zeldovich scheme.

3. Fuel nitrogen mechanism, in which fuel-bound nitrogen is converted to NO.
**Oxides of nitrogen formation (from Chapter 5)**

Nitric oxide can be formed from N2 in the air through three chemical mechanisms, the thermal or Zeldovich mechanism, the Fenimore or prompt mechanism, and the N2O-intermediate mechanism. A fourth route may be the NNH mechanism.

The thermal mechanism dominate at high temperature combustion over a fairly wide range of equivalence ratios, while the Fenimore mechanism is particularly important in rich combustion.

The N2O mechanism play an important role in lean, low-temperature combustion processes.

The **thermal mechanism** consists of two chain reactions:

\[
\begin{align*}
O + N_2 & \rightleftharpoons NO + N \\
N + O_2 & \rightleftharpoons NO + O
\end{align*}
\]

which can be extended by adding the reaction:

\[
N + OH \rightleftharpoons NO + H.
\]

This three-reaction set is referred to as the extended Zeldovich mechanism.
The **N2O mechanism** is important in fuel lean, low-temperature conditions. The three steps of the mechanism are:

\[
O + N_2 + M \leftrightarrow N_2O + M, \quad \text{(N.4)}
\]

\[
H + N_2O \leftrightarrow NO + NH, \quad \text{(N.5)}
\]

\[
O + N_2O \leftrightarrow NO + NO. \quad \text{(N.6)}
\]

The N2O mechanism becomes important in NO control strategies that involves lean premixed combustion, especially relevant for gas turbines.

The **prompt NO** mechanism is intimately linked to the combustion chemistry of hydrocarbons:

\[
CH + N_2 \leftrightarrow HCN + N \quad \text{(N.7)}
\]

\[
C + N_2 \leftrightarrow CN + N, \quad \text{(N.8)}
\]
In the atmosphere NO ultimately oxidizes to form NO2, which is important to the production of acid rain and photochemical smog.

Many combustion processes, however, emit a significant fraction of their total NOx as NO2. The elementary reactions responsible for forming NO2 from NO in a combustion process are:

\[
\begin{align*}
\text{NO} + \text{HO}_2 & \rightleftharpoons \text{NO}_2 + \text{OH} \quad \text{(formation)}, \quad (N.12) \\
\text{NO}_2 + \text{H} & \rightleftharpoons \text{NO} + \text{OH} \quad \text{(destruction)}, \quad (N.13) \\
\text{NO}_2 + \text{O} & \rightleftharpoons \text{NO} + \text{O}_2 \quad \text{(destruction)}, \quad (N.14)
\end{align*}
\]

where \(\text{HO}_2\) is formed by:

\[
\text{H} + \text{O}_2 + \text{M} \rightleftharpoons \text{HO}_2 + \text{M}. \quad (N.15)
\]

The HO2 radicals are formed in relatively low-temperature regions, hence, NO2 formation occurs when NO from high-temperature regions diffuse or are transported by fluid mixing into the HO2-rich regions.

N.13 and N.14 are active at high temperatures, preventing NO2 formation.
Emissions from premixed combustion

The primary nitrogen oxide from combustion systems is NO, but NO2 may be formed from NO in significant amounts in low-temperature mixing regions of nonpremixed systems.

Calculation of NO formed via the thermal mechanism with equilibrium O and OH radicals is relatively straightforward, e.g. for the Zeldovich mechanism when also neglecting reverse reactions and assuming steady-state for the N concentration:

$$\frac{d[NO]}{dt} = 2k_{1f} [O]_e [N_2]_e$$  \hspace{1cm} (15.13)

The basic premise behind (15.13) is that the NO chemistry is much slower than the combustion chemistry, e.g. equilibrium assumptions for the radical concentrations are valid.

However, O and OH atoms may be formed in quantities well over equilibrium (up to 1000 times more) in flame zones. In this case NO will be formed in the flame zone much more rapidly than if O atoms were in equilibrium.

These superequilibrium concentrations are coupled to the fuel oxidation kinetics and the calculation becomes rather complex.

Within the flame zone, prompt-NO may also be important.

Table 15.2 presents calculated relative contributions of the various NO production pathways in premixed combustion systems.
At low pressures, the NO yield is dominated by the Fenimore and superequilibrium routes, while at atmospheric conditions the simple equilibrium thermal mechanism accounts for 50%. The N2O route increase in importance when the pressure increases.

**Equivalence ratio**: If the mixture is made increasingly rich at rich conditions the Fenimore mechanism dominates.

The well-stirred-reactor data show that under conditions of strong backmixing of reactants and products, the superequilibrium route dominates for lean mixtures, while the Fenimore mechanism controls for stoichiometric and rich conditions.
Emissions from premixed combustion

The fuel-N route is not generally important in premixed combustion applications since most fuels used in premixed combustion contain little or no bound nitrogen.

Pulverized coal and heavy distillate fuels, however, contain significant quantities of fuel nitrogen.

**NO control strategies**

For processes dominated by thermal NO formation, time, temperature and O2 availability are the primary variables affecting NOx yields.

The rate coefficient $k_{1f}$ increase rapidly at temperatures above 1800 K.

The maximum equilibrium O-atom mole fraction lies near an equivalence ratio of 0.9, and corresponds approximately to the point where NO levels in spark-ignition engines peaks. This can be seen in Figure 15.2.

Unfortunately, from the viewpoint of emission control, maximum efficiency also is achieved near this equivalence ratio for many practical devices.

http://www.howstuffworks.com/engine1.htm
http://auto.howstuffworks.com/ignition-system1.htm
Emissions from premixed combustion

Reducing peak temperatures can significantly reduce NOx emissions.

This can be achieved by flue gas recirculation (FGR), or exhaust gas recirculation (EGR, for a spark-ignition engine).

The flue gas can be mixed with the air, the fuel, or with the post combustion gases.

The effect of FGR is to:
- increase the heat capacity of the burned gases
- dilute the flue gas
- cool the product gases
i.e. reducing the temperature.

Figure 15.3 shows experimental results for EGR.

Figure 15.3 Effect of exhaust-gas recirculation (EGR) on NOx emissions from a spark-ignition engine.

SOURCE: Reprinted with permission from Ref. [28], © 1973, Society of Automotive Engineers, Inc.
Figure 15.4 shows the correlation of NO reduction with diluent heat capacity for an SI engine.

Figure 15.4 Correlation of NO reduction with diluent heat capacity, $\dot{m}c_p$, for a spark-ignition engine.

SOURCE: Reprinted from Ref. [29], © 1971, Society of Automotive Engineers, Inc.
Emissions from premixed combustion

Another means to lower the combustion temperature in a SI engine is to **retard the spark timing**.

Late spark timing shifts the combustion event so that peak pressures occur when the piston is well beyond TDC (minimum volume), resulting in lower pressures and temperatures. This effect could be seen in Figure 15.2.

However, significant fuel-economy penalties result from retarded spark timings.

The amount of thermal NO formed is strongly linked to the time that combustion products spend at high temperatures.

For conditions where NO levels are well below their equilibrium values and reverse reactions are unimportant, the NO yield is directly proportional with time.

Therefore, the **temperature-versus-time relationship** is key to the control of NO emissions.

However, drastic alteration of the time-temperature relationship for the gas flow may compromise the useful operation of the device.
Emissions from premixed combustion

**Staged combustion,**
in which a rich-lean or lean-rich combustion sequence takes place, is also a NOx combustion strategy.

The idea here is first to take advantage of both the **good stability and low-NOx** emissions associated with **rich** combustion and, subsequently, to complete the combustion of the unburned gases (mainly CO and H2) in a **lean** stage where additional NO production also is low.

For staging to be effective, the mixing of rich products and air must be very rapid, or a substantial amount of heat must be removed between the stages.

The basic concept is illustrated in Figure 15.5 for a rich-lean sequence.

The ideal staged-combustion process is represented by the path 0-1-2’-2, and the bell-shaped curve represents the NOx yield for a fixed residence time $\Delta t = \Delta t_{\text{rich}}$.

In the rich stage, the amount of NOx formed in the time $\Delta t_{\text{rich}}$ is represented by the segment 0-1.

Secondary air is then instantaneously mixed with the rich products (segment 1-2’) with no additional NOx formed.

In the lean stage, CO and H2 are oxidized and an additional amount of NOx is formed (segment 2’-2) in the time associated with the lean stage.

If the mixing is not instantaneous (as in any real process…), additional NOx is formed during the mixing process as the stoichiometry passes through the regions of high NOx formation rates.

The success of staging depends on how well the mixing process can be controlled in practice.
Emissions from premixed combustion

Figure 15.5 Schematic representation of staged combustion on NO$_x$-equivalence ratio coordinates. The path 0–1–2′–2 represents the ideal case of instantaneous secondary air mixing, while 0–1–3 indicates the path for slow secondary mixing.
Emissions from premixed combustion

**CO**

CO is a major species in rich combustion products.

In normal operation of most devices, rich conditions are generally avoided, however SI engines employ rich mixtures during startup to prevent stalling, and at wide-open-throttle conditions to provide maximum power.

For stoichiometric and slightly lean mixtures, CO is found in substantial quantities at typical combustion temperatures as a result of the dissociation of CO2.

Other CO production mechanisms include quenching by cold surfaces, and partial oxidation of unburned fuel.
Emissions from premixed combustion

Unburned hydrocarbons

In most devices employing premixed reactants, unburned hydrocarbons are usually negligible. An exception to this is the SI engine.

The process of flame quenching, whereby a flame is extinguished a short distance from a cold surface, leaves a thin layer of unburned fuel-air mixture adjacent to the wall.

Whether or not this quench layer contributes to unburned hydrocarbon emissions depends on subsequent diffusion, convection, and oxidation processes.

In an SI engine, most of the hydrocarbons from wall quenching ultimately mix with hot gases and are oxidized.

However, unburned hydrocarbons can results from flame quenching within and at the entrance to crevices, such as those formed by the piston topland and ring pack.

The helical spark-plug thread crevice can also be a source of unburned hydrocarbons emissions in SI engines.

Figure 15.7 illustrates this crevice-volume mechanism for unburned hydrocarbons emissions in engines.
Emissions from premixed combustion

Figure 15.7  Schematic representation of unburned hydrocarbon emission mechanism for spark-ignition engines.

SOURCE: After Ref. [34].
Other contributors to **unburned hydrocarbon** emissions in engines are absorption and subsequent desorption of fuel into **oil layers** on the cylinder walls.

A similar process can occur for **wall deposits**, which for unleaded-fuel operations are carbonaceous.

Unburned hydrocarbon emissions can also result from **incomplete** flame propagation in the bulk of the charge. This occurs for lean and/or dilute mixtures approaching the flammability limits.

Only about a third of the unburned hydrocarbons found in the untreated exhaust are **fuel molecules**. The remained are fuel pyrolysis and partial oxidation products, as shown in Table 15.3.
Emissions from premixed combustion

Catalytic aftertreatment

The primary technique applied to control, simultaneously, NO, CO, and unburned hydrocarbon emissions from SI engines.

Figures 15.8 and 15.9 illustrate the two principal types of catalytic converters currently employed.

In both types, noble-metal catalysts, e.g. platinum, rhodium and palladium, provide active sites for reactions that oxidize CO and unburned hydrocarbons while simultaneously reducing nitric oxide.

To achieve high conversion efficiencies, i.e. pollutant destruction, requires that the composition of the stream through the converter be maintained in a narrow range near the stoichiometric ratio.

Typical three-way catalyst conversion efficiencies are illustrated in Figure 15.10.
Emissions from premixed combustion

Figure 15.8  Pellet bed-type catalytic converter.
SOURCE: Reprinted from Ref. [39] with permission of the American Society of Mechanical Engineers.
Emissions from premixed combustion

Figure 15.9  Monolith catalytic converter.
SOURCE: Reprinted from Ref. [39] with permission of the American Society of Mechanical Engineers.
Emissions from premixed combustion

Figure 15.10 Conversion efficiencies for a typical three-way automotive catalyst, showing narrow air–fuel ratio window for simultaneous destruction of unburned hydrocarbons, CO, and NO.

SOURCE: Reprinted from Ref. [39] with permission of the American Society of Mechanical Engineers.
Emissions from premixed combustion

Particulate matter

Emissions of particulate matter from premixed combustion results only from rich operation or from fuel additives.

With the removal of tetraethyl lead from gasoline, this source of particulate matter from SI engines has been eliminated.

Fuel-air mixtures sufficiently rich to produce soot are usually the result of some malfunction, rather than typical operation.

The difference in sooting tendencies of various fuels is related not only to the fuel structure, but also to differences in flame temperature.
Emissions from nonpremixed combustion

The additional physical processes associated with nonpremixed combustion, e.g. evaporation and mixing, can produce a range of local compositions spanning a wide range of stoichiometries.

The overall combustion process may be stoichiometric, but within the combustion space there may be regions that are quite rich, while other may be quite lean.

This adds considerable complexity to the problem of pollutant formation in such systems.

In some situations combustion can occur essentially in a premixed mode when fuel evaporation and subsequent mixing is sufficiently rapid, even though the fuel and air are introduced separately into the combustion space.

Because of the great complexity involved in pollutant formation in non-premixed systems, and because emissions in such systems frequently depend on specific details of the system, we will here only briefly introduce the subject.
Emissions from nonpremixed combustion

Oxides of nitrogen

In simple turbulent jet flames, NO is suggested to be produced in thin laminarlike flamelet regions in the lower-to-mid regions of the flame and in relatively large and broadened reaction zones in the upper regions of the flame.

The simple thermal, superequilibrium-O and Fenimore mechanisms for NO formation are all likely to be active in hydrocarbon jet flames, while the determination of the relative contribution of each mechanism to the total NOx yield is not easily determined.

In applications where flame temperatures are quite high, such as flames in furnaces with reradiating walls or flames using oxygen enriched air, the thermal mechanism is likely to most important.

Hence, temperature, time and mixing are important also in nonpremixed flames. However, the composition will vary from point to point in the flow/flame, and the temperature will vary as well.

The kinetic effects in turbulent jet flames are complex, and we will here assume that NO is produced primarily in flame regions that have simultaneously high temperatures and high concentrations of O and OH atoms, i.e. conditions near stoichiometric.

These regions may be the thin laminarlike flame regions low in the jet flame or the broad regions near the flame tip.
Emissions from nonpremixed combustion

Industrial combustion equipment

In addition to boilers, this class of devices includes process heaters, furnaces, and ovens, all burning, primarily, natural gas.

Oil- and coal-fired devices is limited to utility boilers in this chapter.

Table 15.5 shows the wide range of NOx levels associated with such industrial processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Range, ppm at 3% O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-temperature direct</td>
<td></td>
</tr>
<tr>
<td>High preheat</td>
<td>500–2,000</td>
</tr>
<tr>
<td>Low preheat</td>
<td>200–800</td>
</tr>
<tr>
<td>High-temperature indirect</td>
<td>200–600</td>
</tr>
<tr>
<td>Low temperature</td>
<td>30–100</td>
</tr>
<tr>
<td>Boilers</td>
<td>25–100</td>
</tr>
</tbody>
</table>

a SOURCE: Courtesy of Energy and Environmental Research Corp.
### Emissions from nonpremixed combustion

Table 15.6 shows California South Coast Air Quality Management District standards.

<table>
<thead>
<tr>
<th>Process</th>
<th>Limit</th>
<th>Rule No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial boilers (5–40 MMBtu)</td>
<td>40 ppm (3% O₂)</td>
<td>1146</td>
</tr>
<tr>
<td>Industrial boilers (&gt; 40 MMBtu)</td>
<td>30 ppm (3% O₂)</td>
<td>1146.1</td>
</tr>
<tr>
<td>Refining heaters</td>
<td>30 ppm (3% O₂)</td>
<td>1109</td>
</tr>
<tr>
<td>Glass-melting furnaces</td>
<td>4 lb/ton of glass</td>
<td>1117</td>
</tr>
<tr>
<td>Gas turbines (no SCR)</td>
<td>15 ppm (15% O₂)</td>
<td>1134</td>
</tr>
<tr>
<td>Gas turbines (SCR)</td>
<td>9 ppm (15% O₂)</td>
<td>1134</td>
</tr>
<tr>
<td>Others</td>
<td>Best available current technology</td>
<td></td>
</tr>
</tbody>
</table>

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* Source: Courtesy of Energy and Environmental Research Corp.

* South Coast Air Quality Management District.
Figure 15.13 shows various strategies employed to reduce NOx emissions from gas-fired equipment.

Some of these techniques also apply to oil-fired devices.

The NOx reduction techniques are divided into those involving combustion modifications and those involving post-combustion controls.
Emissions from nonpremixed combustion

Combustion modifications

- Low excess air
- Staged combustion
- Temperature reduction
- Low NO$_x$ burners
- Oxy/gas combustion
- Reburn

Post-combustion controls

- Selective non-catalytic reduction
- Selective catalytic reduction

- Burners out of service
- Biased firing
- Overfire air
- Staged air
- Staged fuel
- Fiber burner

- Ammonia injection
- Urea injection
- Urea/methanol injection

Reduced air preheating
Water injection
Flue gas recirculation

Figure 15.13 The NO$_x$ control technologies for gas-fired industrial combustion equipment.

Emissions from nonpremixed combustion

Low excess air

Thermal NOx emissions peak at leaner than stoichiometric equivalence ratios. This NO reduction technique involves reducing the air down to stoichiometric conditions (see Figure 15.2). Only limited NOx reductions are possible with this method since CO emissions rise as the amount of excess air is decreased.

Staged combustion

Involves typically rich-lean design/operation of a burner or a system of burners.

Temperature reduction

In many combustion devices, the combustion air is preheated by hot exhaust gases to improve thermal efficiency. Reducing the amount of preheat reduces flame temperatures and NOx formation.

Water injection reduces flame temperatures because combustion energy is used to vaporize the water and superheat the steam to combustion temperatures.

FGR introduces diluents that reduces temperatures. Figure 15.14 shows the effect of FGR on NOx for burners operating with ambient and preheated combustion air. NOx reductions from 50 to 85 % are possible with FGR in gas-fired industrial boilers.
Emissions from nonpremixed combustion

Low-NOx burners

Burners designed for low NOx emissions employ fuel or air staging. Fuel staging creates a sequential lean-rich combustion process (Figure 15.15), while air staging creates a rich-lean process (Figure 15.16).

Another class of low-NOx burners are the fiber-matrix burners. These burners employ premixed combustion above or within a metal or ceramic fiber matrix. Because of radiation and convection heat transfer from the matrix, combustion temperatures are quite low.

A fiber burned is illustrated in Figure 15.17.
Emissions from nonpremixed combustion

Figure 15.16 Low-NOx burner employing air staging (rich–lean combustion).

SOURCE: From Ref. [48].
Emissions from nonpremixed combustion

Oxy-gas combustion

The N2 concentration in the air can be reduced by supplying additional O2, and with sufficiently large O2 additions, the decreased N2 concentrations outweighs the increased combustion temperatures and NOx levels can be reduced.

Operation with pure O2 eliminates all NOx production, assuming that no nitrogen is contained in the fuel.

Reburn

Reburn is a lean-rich-lean process, where about 15 % of the total fuel is introduced downstream of the main, fuel-lean combustion zone.

Within the reburn zone, NO formed in the first fuel-lean stage is reduced via reactions with hydrocarbons, forming intermediates such as HCN, which then may be reduced to N2.

Additional air is then supplied to provide the final burnout of the reburn fuel.

Reduction of NOx of about 60 % are typical for boilers employing reburn technology.

The reburn process is schematically shown in Figure 15.18.
Emissions from nonpremixed combustion

Figure 15.18  Industrial boiler equipped with reburn NOx control.
SOURCE: After Ref. [51].
Emissions from nonpremixed combustion

Selective non-catalytic reduction (SNCR)

A nitrogen-containing additive, either ammonia, urea (CON2H4 or (NH2)2CO) or cyanuric acid (C3H3N3O3), is injected and mixed with flue gases to effect chemical reduction of NO to N2 without the aid of a catalyst.

Temperature is a critical variable, and operation within a relatively narrow range of temperatures is required to achieve large NOx emissions. Imperfect mixing and nonuniform temperatures (in an actual flue gas) reduce the NOx reduction potential.

Figure 15.9 illustrates the temperature dependence.

Selective catalytic reduction

A catalyst is used in conjunction with ammonia injection to reduce NO to N2. The temperature window for effective reduction depends upon the catalyst used, but lies in the range between 480 K and 780 K.

Greater reduction are possible with SCR compared to SNCR, and operates at lower temperatures.

However, with SCR, the NOx removal cost are the highest of all NOx reduction technologies, due to high investment costs and the operating cost connected to catalyst replacement.
Emissions from nonpremixed combustion

Figure 15.19 The NO\textsubscript{x} reduction effectiveness for selective non-catalytic reduction (SNCR) techniques.

Utility boilers

Utility boilers (for electricity generation) are fired predominantly with coal, followed by gas and oil.

Burning coal and heavy oils provides an additional source of NOx because of the bound nitrogen in the fuel.

Table 15.7 compares the nitrogen content of coal and liquid fuels.

For gas-fired units, all of the combustion modification techniques and aftertreatment methods discussed in the previous section can be employed for NOx reduction.

In oil- and coal-fired units, about 20-40 % of the fuel-N is converted to NOx that appears in the flue gases, resulting in as much as half of the total NOx emitted.

Application of post-combustion NOx reduction techniques (SNCR and SCR) are complicated by the sulfur in coal and in heavy oils, and by particulate matter.

Ammonia used in either SNCR or SCR reacts with SO3 to form ammonium bisulfate (NH4HSO4), an extremely corrosive substance.

Poisoning of catalysts by SO3 and plugging of the catalyst surface by particulate matter make application of SCR much more difficult for oil and coal than for natural gas.
Emissions from nonpremixed combustion

Gas turbines and diesel engines

Gas turbines and diesel engines operate at high pressure; 10-15 atm for stationary gas turbines and 20-40 atm for aero-derivative gas turbines, while diesel engines operate at even higher pressures, up to 100 atm.

Compression of air from 1 atm to these high pressures results in the air entering the combustor at temperatures well above atmospheric, e.g. adiabatic compression of air at 300 K and 1 atm to 40 atm yields a temperature of 860 K.

Peak combustion temperatures are thus high, and thus NO formation is rapid.

Residence times in aero-derivative engines gas turbines are a few ms, and for stationary gas turbines 10-20 ms.

NOx are formed in the high-temperature, near-stoichiometric regions of the flame. Therefore, the combustion modification techniques employed to reduce NOx are those that lower temperatures.

This can be EGR or delayed injection timing in diesel engines, and water or steam injection in stationary gas turbines.

Diesel engines depends on diffusion burning, and are less flexible than gas turbines. Very low emission levels from diesel engines require post-combustion control (SNCR with cyanuric acid and SCR with ammonia).

For gas turbines, lean premixed combustion and rich-lean staging are the most prominent options for NOx reduction. Figure 15.20 illustrates rich-lean combustion.
**Emissions from nonpremixed combustion**

*Figure 15.20* Sketch of rich/quench/lean (RQL) staged gas-turbine combustor. Very rapid mixing of the rich combustion products with air is required to keep peak temperatures low (cf. Fig. 15.5).

SOURCE: From Ref. [72]. Reprinted with permission of the authors.
Emissions from nonpremixed combustion

Unburned hydrocarbons and CO

In nonpremixed combustion systems there are two sources of unburned hydrocarbons and CO, that results directly from the nature of nonpremixed combustion.

1) **Overly lean regions** are created within the combustion chamber, due to fuel injector characteristics and fuel-air mixing patterns. Since a normal flame does not propagate through overlean regions, fuel pyrolysis and partial oxidation products are formed.

2) **Overly rich regions** that subsequently do not mix with sufficient additional air, or if they do, insufficient time is available to achieve complete combustion.

Additional mechanisms that can result in unburned and partially burned species are:

- Wall quenching (diesel engines)
- Quenching by secondary or dilution air jets (gas turbines)
- Uncontrolled fuel dribble/leakage (diesel engines)
- Too large fuel droplets (gas turbines using liquid fuels)
Emissions from nonpremixed combustion

Particulate matter

Except for mineral matter ash particles (from coal), soot is the primary particulate matter produced in nonpremixed combustion.

Mineral matter ash is removed by e.g. electrostatic precipitators or baghouse filters.

Soot can be considered an intrinsic property of most diffusion flames.

Soot is formed in the rich regions of diffusion flames, and whether or not soot is emitted from a flame depends upon competition between soot formation and soot oxidation processes.

Soot can be reduced by combustion system modifications or post-combustion control devices.
SOx

In combustion processes all the sulfur in the fuel appears as SO2 or SO3 (not true for biomass!).

There are only two ways to control SOx emissions, remove the sulfur from the fuel, or clean the flue gases.

Both techniques are used in practise.

Table 15.8 provides estimates of the sulfur content of various fuels.

The amount of SO3 formed is typically only a few percent of the amount of SO2, although the SO3 is usually found in greater than equilibrium concentrations.

SO3 readily reacts with H2O to form H2SO4, thus, sulfuric acid is formed in the flue gas.

SO3 also poisons three-way catalysts, thus, sulfur levels are low in gasoline.

The fate of SO2 in the atmosphere is reactions leading to sulfuric acid.

The most commonly method of removing SO2 from flue gases involves reacting SO2 with limestone (CaCO3) or lime (CaO). An aqueous slurry of limestone or lime is sprayed into a tower through which the flue gases pass.
Summary

In this relatively long chapter, we discussed first the implications of pollutant emissions from combustion systems. You should have a knowledge of the major effects of the primary pollutants, NO$_x$, CO, unburned and partially burned hydrocarbons, particulate matter, and SO$_x$; that is, what is it that makes these species pollutants? Next we investigated the various ways used to quantify pollutants. The bases for all of the measures are simple species or atom balances and mass conservation. You should understand why some measures are more useful than others depending on the application, and be able to convert from one measure to another. The next major topics dealt with the formation and control of emissions; first, from premixed systems, and second, from nonpremixed systems. Much of the material concerning pollutant formation relies on previous chapters, particularly sections of Chapters 4, 5, 8, and 9.

Review of that material would be appropriate now to consolidate your understanding. Although not comprehensive, many practical applications were also discussed in this chapter. You should be able to discuss the most important pollutant formation and control mechanisms and how they apply to spark-ignition engines, gas-fired industrial combustion equipment, utility boilers, and diesel and gas-turbine engines. Particular emphasis was placed on NO$_x$ emissions because of their current importance.
ICE

Reliable technology
No real short term alternatives
→ Going to be around for a long time

Local emissions
PM, NOₓ, HC, ...

Emission legislations

Improved combustion technologies
- Control systems
- New engine concepts
- Additives

Improved after-treatment
- Catalysts
- SCR
- Particle filters

Alternative fuels
- Natural gas
- H₂
- FT
- DME, ....

Global emissions
CO₂

CO₂ neutral fuels

Improved efficiency

- Biofuels
- H₂ from renewables
- H₂ prod. with CO₂ capture
<table>
<thead>
<tr>
<th>Time (ms)</th>
<th>CH4</th>
<th>5% H2</th>
<th>30% H2</th>
</tr>
</thead>
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<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
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<tr>
<td>2 ms</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>3 ms</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
<tr>
<td>4 ms</td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
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<tr>
<td>5 ms</td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
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<tr>
<td>6 ms</td>
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<tr>
<td>7 ms</td>
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<td><img src="image20.png" alt="Image" /></td>
<td><img src="image21.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Transition to cellular structure

\( \lambda = 1.0 \)