Combustion Generated Pollutants

New Delhi

Peking
Combustion Generated Pollutants

- Climate change
  - Greenhouse gases: CO$_2$, methane, N$_2$O, CFCs, particulates, etc.
- Hydrocarbons: Toxins and a major contributor to smog; prolonged exposure contributes to asthma, liver disease, lung disease and cancer
- CO: A product of incomplete combustion, carbon monoxide reduces the blood's ability to carry oxygen, overexposure may be fatal
- NOx (NO and NO$_2$): Produced when nitrogen in air reacts with oxygen at high temperatures, and lead to the generation of smog and acid rain
- SOx (oxides of sulfur): Generated from combustion of fuels containing sulfur
- NOx and VOCs (volatile organic compounds) react with the sun's ultraviolet rays and form ozone, which causes respiratory problems and other health problems, such as respiratory disease, damage to lungs, weaker immune system, chest pain, etc.
- PM (particulate matter)
Combustion Generated Pollutants: Particulates

- Particulate Matter (PM) is a complex mixture of solid particles and liquid droplets, suspended in the air. It may contain soot, dust, volatile matter, nitrates, sulfates, dust, etc.
- It may be emitted directly, as in smoke from fire and vehicles, or it can form in the atmosphere from reactions of gases such as sulfur and nitrogen oxides.
- Exposure to particulates, especially fine particles, cause both short-term and long-term health effects, including cardiovascular disease, respiratory irritation (coughing, wheezing), aggravated asthma, decreased lung function, etc.
- Particle size is directly linked to health problems. PM10 (10 microns) and smaller particles are inhalable. Finer particles (PM2.5) pose the greatest risk because they can get deep into lungs and some also into bloodstream.
Soot, Particulates and Aerosols

One study involving 312,944 people in nine European countries found that for every increase of 10 µg/m3 in PM10 (10 µm), the lung cancer rate rose 22%. The smaller particles (PM2.5) were particularly deadly, with a 36% increase in lung cancer.

Emission Standards (Heavy-Duty Engines)

<table>
<thead>
<tr>
<th>Region</th>
<th>Regulation and Year</th>
<th>Average Standard Values (g/kWh)</th>
<th>NOx</th>
<th>PM</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>2002-2004</td>
<td>2.7</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2007</td>
<td>1.6</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2010</td>
<td>0.27</td>
<td>0.013</td>
<td></td>
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<tr>
<td>European Union</td>
<td>Euro III (2000)</td>
<td>5</td>
<td>0.1</td>
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<tr>
<td></td>
<td>Euro IV (2005)</td>
<td>3.5</td>
<td>0.02</td>
<td></td>
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<tr>
<td></td>
<td>Euro V (2008)</td>
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<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Euro VI (2013)</td>
<td>0.2 - 1.0</td>
<td>0.01 - 0.02</td>
<td></td>
</tr>
<tr>
<td>Japan</td>
<td>2003-2004</td>
<td>3.38</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2005</td>
<td>2</td>
<td>0.027</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2009-2010</td>
<td>0.7</td>
<td>0.01</td>
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</tr>
</tbody>
</table>
NOx (NO and NO₂) Mechanisms

Thermal (Zeldovich) NO Mechanism
• Major contributor of NO at high temperatures (T > 1800 K) over a wide range of equivalence ratios
• Coupled to fuel oxidation chemistry through N₂, O, OH

\[ \text{N}_2 + \text{O} \leftrightarrow \text{NO} + \text{N} \] \hspace{1cm} (N1) \hspace{1cm} k_{1f} = 1.8 \times 10^{11} \exp(-38370 / T) \text{ m}^3 / (\text{kmol.s})

\[ \text{N} + \text{O}_2 \leftrightarrow \text{NO} + \text{O} \] \hspace{1cm} (N2)

\[ \text{N} + \text{OH} \leftrightarrow \text{NO} + \text{H} \text{ (extended zeldovich)} \] \hspace{1cm} (N3)

Prompt NO (Fenimore) Mechanism
• Strongly coupled to the fuel oxidation chemistry though CH
• More relevant at fuel rich conditions
• Fuel bound N₂ also contributes to NO as it is converted to HCN (hydrogen cyanide) or NH₃, which then form NO

\[ \text{CH} + \text{N}_2 \leftrightarrow \text{HCN} + \text{N} \] \hspace{1cm} (N4) \hspace{1cm} Primary initiation reaction

\[ \text{HCN} + \text{O} \leftrightarrow \text{NCO} + \text{H} \] \hspace{1cm} (N5)

\[ \text{NCO} + \text{H} \leftrightarrow \text{NH} + \text{CO} \] \hspace{1cm} (N6)

\[ \text{NH} + \text{H} \leftrightarrow \text{N} + \text{H}_2 \] \hspace{1cm} (N7)

\[ \text{N} + \text{OH} \leftrightarrow \text{NO} + \text{H} \] \hspace{1cm} (N8)

**NOx Mechanisms**

**Prompt NO**

**N₂O Intermediate Mechanism**
- More important under fuel-lean ($\phi < 0.8$) and low-temperature conditions

\[
\begin{align*}
N_2 + O + M & \leftrightarrow N_2O + M \quad (N9) \\
N_2O + H & \leftrightarrow NO + NH \quad (N10) \\
N_2O + O & \leftrightarrow NO + NO \quad (N11)
\end{align*}
\]

**NNH Mechanism:**
- Remaining steps follow the prompt-NO mechanism
- NO can be converted to $NO_2$ through $NO + HO_2 \leftrightarrow NO_2 + OH$
- NO is also converted to nitrogen dioxide in the atmosphere, and form acid rain and smog
NO Formation in Triple Counterflow Flames

Temperature and NO in n-heptane and 1-heptene triple flames with $\phi_R=1.5$ and $\phi_L=0.8$

NO produced through thermal, prompt, N2O and NNH mechanisms in n-heptane and 1-heptene triple flames
NO Formation in Triple Counterflow Flames

ROP of total NO, and NO through thermal, prompt, N2O and NNH mechanisms in n-heptane and 1-heptene triple flames with $\phi_R=1.5$ and $\phi_L=0.8$

Xu, Aggarwal, Brezinsky, E&F 2013
NO and NO\textsubscript{2} in a Turbulent Spray Flame

Mass fraction contours in a turbulent spray flame in a constant volume (Sandia) reactor

Xu and Aggarwal, Fuel, 2015
Soot Formation Processes

- Soot refers to impure carbon particles resulting from incomplete combustion of hydrocarbons. It is a major pollutant and the second most contributor to global warming.
- PM (PM10, PM2.5 and smaller) emissions from diesel represent a serious health concern, with long term exposure causing lung and vascular diseases.
- Soot formation strongly depends on fuel structure and flame type, with aromatics producing much higher amount of soot compared to aliphatics.
- Soot models are generally based on semi-empirical approaches.

\[ 2 \text{C}_8\text{H}_6 \rightarrow \text{C}_{16}\text{H}_{10} + \text{H}_2 \]

Acetylene (C\(_2\)H\(_2\)), propadiene (allene, C\(_3\)H\(_4\)), benzene (C\(_6\)H\(_6\)), phenylacetylene (C\(_8\)H\(_6\)), Acenaphthylene (C\(_{12}\)H\(_8\)), pyrene (C\(_{16}\)H\(_{10}\))
Soot Formation Processes

- Important steps include (i) formation of precursor species (fuel chemistry important here), (ii) nucleation (particle inception), (iii) surface growth through chemical reactions and coagulation (agglomeration), and (iv) oxidation.

- As fuel decomposition is initiated, intermediate hydrocarbon species are formed in the fuel rich region, which undergo further reactions to form PAHs. C2H2 and C6H6 are considered as major precursors.

- Once a primary particle is formed through nucleation and polymerization, it can grow through surface reactions and coagulation and also undergo oxidation.

- The kinetic models used for fuel oxidation is capable of simulating the formation of PAHs up to pyrene (C16H10).

- The nuclei interact with each other through coagulation as well as with the gaseous species on its surface.

- Some of the soot is oxidized.

- Smoke point is used to define fuel’s propensity to form soot; minimum fuel flow rate until smoke is observed to escape from the flame tip (jet flame). Its values for C2H2 and n-C6H17 are 0.51 and 7.0 mg/s.
Figure 9.14  Measured soot volume fractions as functions of height above burner for propylene and butane at both sooting and nonsooting conditions.


Kent, Combustion Flame, 1986
Counterflow Partially Premixed Flame Structure & Soot Emissions

Two reaction zones (RPZ & NPZ)

Soot formation: soot volume fraction, number density, and particle diameter (nm)

Precursors:
Acetylene and pyrene

N-heptane Flame ($\phi = 2$)

Xiao & Aggarwal, E&F 2013
Counterflow Partially Premixed Flame Structure & Soot Emissions

N-heptane Flame ($\phi=8$)
Soot & Partial Premixing

$\phi = \infty \quad 24 \quad 20 \quad 15 \quad 10 \quad 5 \quad 3$

Ethylene/air flames
C$_2$H$_2$, OH, NO and PAH Species in a Partially Premixed Spray Flame

N-heptane flame in a constant volume reactor at diesel engine conditions

Xu and Aggarwal, Fuel, 2015