Atmospheric Pollution

- **SMOG**
  - Ozone \( \text{O}_3 \)
  - Nitrogen dioxide \( \text{NO}_2 \)
  - PAN (Peroxyacyl Nitrate) \( \text{R-C-OONO}_2 \)

- **TOXICS**
  - CO, Benzene, 1-3 butadiene, POM (Polycyclic organic Matters), Aldehydes

**Primary Pollutants:** Direct emissions from vehicles
- CO, HC, NOx, PM (Particulate matters), SOx, aldehydes

**Secondary Pollutants:** From interaction of emissions with the atmosphere
- \( \text{O}_3 \), PAN, \( \text{NO}_2 \), Aldehydes
Smog formation:
\[
\text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2 \\
\text{NO}_2 + h\nu (\leq 415 \text{ nm}) \rightarrow \text{NO} + O^{(3P)} \text{O}^{(3P)}, \text{HC}, \text{O}_2, \text{NO} \\
\text{O}_2 + \text{NO}_2 + \text{RCHO} \rightarrow O \text{R-C-OONO}_2 \\
\]

Acid rain:
\[
\text{SO}_2 + \text{OH} \rightarrow \text{HO}_2 \text{SO}_2 \\
\text{HO}_2 \text{SO}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{SO}_3 \\
\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \\
\text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2 \\
\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3 \\
\]

Emission requirements

Historic trend: Factor of 10 reduction every 15 years
At 28.5 miles per gallon, 100 g of fuel is burned per mile.
Emission of 0.01 g/mile means 10^-4 g/g-of-fuel

PZEV regulation
(120,000 miles guarantee):
NMOG 0.01 g/mile
CO 1.0 g/mile
NOx 0.02 g/mile
EMISSIONS MECHANISMS

- CO emission
  - Incomplete oxidation of fuel under fuel rich conditions
- NOx emission
  - Reaction of nitrogen and oxygen in the high temperature burned gas regions
- Particulate matter (PM) emission (most significant in diesel engines; there are significant PM emissions in SI engines in terms of number density, especially in direct injection engines)
  - Particulates formed by pyrolysis of fuel molecules in the locally fuel rich region and incomplete oxidation of these particles
  - Lubrication oil contribution
- Hydrocarbon emissions
  - Fuel hydrocarbons escape oxidation (or only partially oxidized) via various pathways
Typical steady state SI engine-out emissions

- NOx is a few thousand parts per million
- CO is around 0.5-1% for stoichiometric operation
- HC is 500-2000 ppm for fully warm up engine
- PM very small by mass

CO Emissions Mechanism

- CO is the incomplete oxidation product of the fuel carbon
- Significant amount in fuel rich condition
- Immediately following combustion, CO is in chemical equilibrium with the burned gas
- During expansion, as the burned gas temperature decreases, CO is ‘frozen’
  - Empirical correlation
    \[
    \frac{[CO][H_2O]}{[CO_2][H_2]} \approx 3.7
    \]
NO FORMATION CHEMISTRY

- Zeldovich Mechanism  
  \[ \text{See table 11.1 for rates} \]
  \[
  \begin{align*}
  N_2 + O & \leftrightarrow \text{NO} + N \\ 
  N + O_2 & \leftrightarrow \text{NO} + O \\
  N + OH & \leftrightarrow \text{NO} + H
  \end{align*}
  \]

  - NO formation is kinetically controlled
  - Reactions involving N is fast; N is in steady states (\(d[N]/dt \approx 0\))
  - Very temperature sensitive

- At high temperature (\(\geq 1000K\)), equilibrium favors NO versus NO\(_2\) formation
  - Engine-out \([\text{NO}_2]/[\text{NO}_x] \leq 2\%\)
\[
\frac{dx_{NO}}{dt}|_{t=0} = 10 \text{ (s)}
\]

\[
\frac{d[NO]}{dt} \quad (\text{Zeldovich})
\]

\[
= 2k_1^* [O][N_2] \left\{ \frac{1 - k_1^*k_2^*[NO]^2}{k_1^*k_2^*[N_2][O_2]} \right\}
\]

\[
= 2k_1^* [O][N_2] \quad \left( \text{Zeldovich} \right)
\]

\[
k_1^* = 7.6 \times 10^{13} \exp \left( \frac{-38000}{T(K)} \right)
\]

- O, O_2, N_2 governed by major heat release reaction
- In equilibrium in the hot burned gas
- Very temperature sensitive

---

**SI Engine NO formation**

Fig. 11-4

Dash line is adiabatic flame temperature for kerosene combustion with 700K 15 bar air

\[ P=15 \text{ bar} \]

\[ \phi = 1.2 \]

\[ T(K) \]

\[ [NO]_{0} \]

\[ k_1 \]

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**Thermodynamic state of charge**

Fig. 9-5 Cylinder pressure, mass fraction burned, and gas temperatures as function of crank angle during combustion.

- NO formed in burned gas
- Different “layers” of burned gas have substantially different temperature, hence different amount of NO production
- In reality, there is mixing between the layers
- Rate is non-linear in temperature

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Engine-out NO emission as function of $\Phi$

![Graph showing NO emission as a function of fuel/air equivalence ratio.]

**Fig. 11-9**
SI engine, 1600 rpm, MBT timing, $\eta_v=50\%$

In-cylinder NO control

- Temperature is the key
  - Spark retard
  - EGR (Exhaust Gas Recirculation)

![Graph showing in-cylinder NO control with MBT timing.]

**Fig. 11-13**

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NO control by EGR

- EGR is a dilution effect
  - Reduce burned gas temperature via increase in thermal inertia

Fig. 11-10

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HC emissions

- Importance
  - Photochemical smog (irritant; health effects)
  - Significant loss of fuel energy

- Measurement
  - Flame Ionization Detector (FID)
    - Chemi-ionization process
    - Signal proportional to C atom concentration

- Emissions regulation: NMOG as g/mile
  - EPA definition of HC
    - Normal gasoline $\text{CH}_{1.85}$
    - Reformulated gasoline $\text{CH}_{1.92}$
    - Compressed natural gas $\text{CH}_{3.78}$
  - Need speciation to detect $\text{CH}_4$
HC Impact on smog formation

- Species dependent
  - Assessed as MIR of individual VOC
- VOC = volatile organic compounds

Kinetic reactivity = \( \frac{\text{VOC reacted}}{\text{VOC input}} \)

Mechanistic reactivity = \( \frac{\text{Ozone formed}}{\text{VOC input}} \)

Maximum Incremental Reactivity (MIR)

\[ \text{MIR} = \frac{m_{\text{ozone, test case}} - m_{\text{ozone, base case}}}{\text{VOC increment to base case}} \]

EKMA (Empirical Kinetic Modeling Approach) methodology: follow air column (Lagrangian) from 0800 using O3 as indicator. Maximum O3 formation occurs at about 1500-1700 hr.

### APPENDIX

<table>
<thead>
<tr>
<th>Compound</th>
<th>MIR (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.265</td>
</tr>
<tr>
<td>Propane</td>
<td>0.178</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.150</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.131</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>0.123</td>
</tr>
<tr>
<td>1,2,4-Trimethylpentane</td>
<td>0.104</td>
</tr>
<tr>
<td>Isobutylene</td>
<td>0.098</td>
</tr>
<tr>
<td>2-Methylbutane</td>
<td>0.089</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>0.131</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.114</td>
</tr>
<tr>
<td>2,4-Dimethylpentane</td>
<td>0.110</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>0.098</td>
</tr>
<tr>
<td>1,1-Dimethylethylene</td>
<td>0.098</td>
</tr>
<tr>
<td>1,3-Dimethylpentane</td>
<td>0.098</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0.096</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>0.095</td>
</tr>
<tr>
<td>1,3-Dimethylbenzene</td>
<td>0.093</td>
</tr>
<tr>
<td>1-Chloro-2,4-dimethylbenzene</td>
<td>0.092</td>
</tr>
<tr>
<td>2-Chloro-1-methylbenzene</td>
<td>0.092</td>
</tr>
<tr>
<td>1-Chloro-3,5-dimethylbenzene</td>
<td>0.092</td>
</tr>
<tr>
<td>1-Chloro-4-methylbenzene</td>
<td>0.092</td>
</tr>
<tr>
<td>1-Chloro-3,4-dimethylbenzene</td>
<td>0.092</td>
</tr>
<tr>
<td>1-Chloro-2,3-dimethylbenzene</td>
<td>0.092</td>
</tr>
<tr>
<td>1-Chloro-2,6-dimethylbenzene</td>
<td>0.092</td>
</tr>
<tr>
<td>1-Chloro-2,4-dimethylbenzene</td>
<td>0.092</td>
</tr>
<tr>
<td>1-Chloro-3,4-dimethylbenzene</td>
<td>0.092</td>
</tr>
<tr>
<td>1-Chloro-2,6-dimethylbenzene</td>
<td>0.092</td>
</tr>
<tr>
<td>1-Chloro-2,3-dimethylbenzene</td>
<td>0.092</td>
</tr>
<tr>
<td>1-Chloro-2,4-dimethylbenzene</td>
<td>0.092</td>
</tr>
<tr>
<td>1-Chloro-3,4-dimethylbenzene</td>
<td>0.092</td>
</tr>
<tr>
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<td>0.092</td>
</tr>
<tr>
<td>1-Chloro-2,3-dimethylbenzene</td>
<td>0.092</td>
</tr>
<tr>
<td>1-Chloro-2,4-dimethylbenzene</td>
<td>0.092</td>
</tr>
</tbody>
</table>

Carter Index for Ozone Forming Potential (CARB July, 1992)

Table from SAE Paper 932718 (Tauchida et al)

Methodology explained in SAE Paper 900710 (Lowi and Carter)

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HC sources

• Non-combustion sources
  – Fueling loss
  – Diurnal emissions
  – Running loss
  – Hot soak
  – Blow by
    ➢ A few L/min; depends on load and RPM
    ➢ At light load, 1500 rpm, blow by ~ 4L / min

HC sources (cont.)

• Combustion sources
  – 300 to 3000 ppmC1 typical
    ➢ Stoichiometric mixture is ~120,000 ppmC1
  – Main combustion: very little HC except for very lean/ dilute or very late combustion (misfires/ partial burns)
    ➢ Various mechanisms for HC to escape from main combustion
  – Cold start emissions (wall film) especially important
SOURCES OF UNBURNED HC IN SI ENGINE

a) Crevices
b) Absorption and desorption in oil layers
c) Absorption and desorption in deposit
d) Quenching (bulk and wall layer)
e) Liquid fuel effects
f) Exhaust valve leakage

Crevice HC mechanism
Absorption and desorption of fuel vapor

Absorption of fuel vapor

Fuel/air mixture

Compression stroke

Desorption of fuel vapor

Burned gas

Expansion stroke

Ishizawa and Takagi (Nissan)

HC pathway

Unburned HC sources:
Creves
Wall phenomena
Bulk quench

Oxidation products

Post-combustion in-cylinder mixing

Residual gas

Exhaust port

Exhaust pipe

Fig. 11-31

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Hydrocarbon Pathway - Steady State, cruise condition

Flame converts fuel to CO₂, CO, H₂O, H₂ etc.

Fuel (100%)

Liq. Fuel 1.2% Deposits (1%) Oil Layers (1%)

Quenching (0.5%) Crevices (5.2%) Exh. Valve Leakage (0.1%)

Crevices (0.7%) - Recycled - Blow-by (0.6%) - Recycled -

In-Cylinder Oxidation

1/3 Oxidized 2/3 Oxidized

Unburned HC in Residual (1.3%) - Recycled -

Valve Leakage (0.1%)

In-Cylinder Oxidation

1/3

2.5% 3.4% 2.3%

1.7% 1.7% 1.5%

Catalyst

Fully Burned Exhaust Tailpipe-out HC (0.1-0.4%)

HC Sources: Magnitudes and Percent of Total Engine-out Emissions*

(SAE Paper 932708)

<table>
<thead>
<tr>
<th>Source</th>
<th>% Fuel Escaping Normal Combustion</th>
<th>Fraction Emitted as EOHC</th>
<th>% Fuel as HC Emissions</th>
<th>% of Total EOHC Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crevices</td>
<td>5.2</td>
<td>0.15*</td>
<td>0.682</td>
<td>42.6</td>
</tr>
<tr>
<td>Quench</td>
<td>0.5</td>
<td>0.15</td>
<td>0.074</td>
<td>4.6</td>
</tr>
<tr>
<td>Oil Layers</td>
<td>1.0</td>
<td>0.097</td>
<td>0.090**</td>
<td>5.6</td>
</tr>
<tr>
<td>Deposits</td>
<td>1.0</td>
<td>0.30</td>
<td>0.300</td>
<td>18.7</td>
</tr>
<tr>
<td>Liquid Fuel</td>
<td>1.2</td>
<td>0.30</td>
<td>0.356</td>
<td>22.2</td>
</tr>
<tr>
<td>Valve Leakage</td>
<td>0.1</td>
<td>1.00</td>
<td>0.100</td>
<td>6.3</td>
</tr>
<tr>
<td>Total</td>
<td>9.0</td>
<td>1.60</td>
<td>1.600</td>
<td>100</td>
</tr>
</tbody>
</table>

* Blowby (0.6%) subtracted
** Amount to crank case (0.7%) subtracted

*steady state cruise condition (1500 rpm, 2.8 bar NIMEP)
HC control

• Reduce crevice volume
• Keep liner hot
• Spark retard
  – Higher burned gas temperature in the later part of expansion stroke and higher exhaust temperature
• Comprehensive cold start strategy
  – Retard timing, fuel rich followed by exhaust air injection