Effect of molecular structure of C1 – C7 hydrocarbons on PAH formation

Hamisu Adamu Dandajeh
Nicos Ladommatos
Paul Hellier

Department of Mechanical Engineering
University College London
Introduction: Poly-aromatic hydrocarbons (PAHs)

<table>
<thead>
<tr>
<th>Sn</th>
<th>PAHs</th>
<th>PAH Abbreviation</th>
<th>Toxicity Group</th>
<th>Toxicity Factor</th>
<th>PAH Rings</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Naphthalene</td>
<td>NPH</td>
<td>D</td>
<td>0.001</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Acenaphthylene</td>
<td>ACY</td>
<td>D</td>
<td>0.001</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Acenaphthene</td>
<td>ACN</td>
<td>NA</td>
<td>0.001</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Fluorene</td>
<td>FLU</td>
<td>D</td>
<td>0.001</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Phenanthrene</td>
<td>PHN</td>
<td>D</td>
<td>0.001</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Anthracene</td>
<td>ATR</td>
<td>D</td>
<td>0.01</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Fluoranthene</td>
<td>FLT</td>
<td>D</td>
<td>0.001</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Pyrene</td>
<td>PYR</td>
<td>NA</td>
<td>0.001</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Benzo[a]anthracene</td>
<td>B[a]A</td>
<td>B2</td>
<td>0.1</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Chrysene</td>
<td>CRY</td>
<td>B2</td>
<td>0.01</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Benzo[b]Fluoranthene</td>
<td>B[b]F</td>
<td>B2</td>
<td>0.1</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Benzo[k]Fluoranthene</td>
<td>B[k]F</td>
<td>B2</td>
<td>0.1</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Benzo(a)pyrene</td>
<td>B[a]P</td>
<td>B2</td>
<td>1.0</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>[123cd]P</td>
<td>B2</td>
<td>0.1</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Dibenzo[a,h]anthracene</td>
<td>D[ah]A</td>
<td>B2</td>
<td>1.0</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Benzo[g,h,i]perylene</td>
<td>B[ghi]P</td>
<td>D</td>
<td>0.01</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>
Introduction: PAHs Vs Soot

Motivation

- Rise in human mortality rate → Stringent global particulate legislation

  - Example of London Borough of Camden:

    - Population = 165,000
    - Number of annual deaths = 1126
    - Particulate related deaths = 87
    - Statistically, the 87 deaths caused a reduction of life average expectancy of 13.3yrs
    - 1 in every 15 people will have their lifespan reduced by 13.3 years due to particulates

Control of particulates

- **Control of Particulates**
  - **Combustion based**
    - e.g. Low temperature combustion to reduce particulate emissions
  - **Fuel based**
    - e.g. use of DPFs to reduce particulate emissions

**Exhaust after Treatment**

- But reduction of particulates do not necessarily imply reducing the amount of toxic PAHs left on the remaining particulates

**Two fuel-based approaches to eliminating the toxicity of particulates:**

a) Eliminate the formation of carbon particles which act carriers of toxic substances such as PAHs
b) Reduce the formation of toxic substances on the particulates such as PAHs
# Methodology

<table>
<thead>
<tr>
<th>Fuel Molecules</th>
<th>Molecular Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
</tr>
<tr>
<td>Ethane</td>
<td>CH₃CH₃</td>
</tr>
<tr>
<td>Ethylene</td>
<td>H₂C = CH₂</td>
</tr>
<tr>
<td>Acetylene</td>
<td>HC ≡ CH</td>
</tr>
<tr>
<td>Dimethyl-Ether (DME)</td>
<td>H₃C−O−CH₃</td>
</tr>
<tr>
<td>Propane</td>
<td>CH₃ CH₂CH₃</td>
</tr>
<tr>
<td>Propene</td>
<td>CH₃ CH = CH₂</td>
</tr>
<tr>
<td>Butane</td>
<td>CH₃ CH₂ CH₂CH₃</td>
</tr>
<tr>
<td>Iso-butane</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
</tr>
</tbody>
</table>

[Diagram with molecular structures]
Methodology

Accelerated Solvent Extraction (ASE)

Extracts in Dichloromethane

PAH Standards

Deuterated PAH

Extracted PAHs

Results

PC

GCMS

Fuel pyrolysis

PAHs Adsorbed on Soot

PAHs Adsorbed on XAD-2 resin
Generation of particulates and gas phase PAHs

Schematics of the experimental set-up: 1) mass flow controller (MFC) 2) vaporiser 3) static mixer 4) circulating cooling water 5) tube furnace 6) DMS 500 sampling probe 7) soot sampling probe

Temperature range of 1050 to 1350 °C

Fixed hydrocarbon concentration of 10,000 ppm on C1 basis

N₂ flowrate of 20L/min
Results - effect of unsaturation on PAHs

Gas phase PAHs

a) 

Particle phase PAHs

b) 

Total PAHs

c) 

- Increase in Degree of unsaturation of fuels favoured GP PAHs in C2 fuels
- Increase in Degree of unsaturation of fuels favoured PP PAHs in C3 fuels
Results – Weighted carcinogenicity of PAHs (WC- PAHs)

$$WC-PAHs = \sum_{i=1}^{16} (TEF_i \times C_i)$$

$\text{TEF} = \text{Toxicity equivalent factors}$

$C_i = \text{PAH concentrations}$

WC-PAHs is higher at low temperature
The total PAH concentrations tended to increase with increasing carbon number (excluding heptane) at the temperature of 1050 °C but an opposite (decreasing) trend was observed at 1350 °C.
Gas phase and particle phase PAH distributions - Summary

GP PAHs

- High vapour Pressure
- Low Boiling Point
- Hence, highly volatile

PP PAHs

- Low vapour Pressure
- High Boiling Point
- Hence, highly less volatile

- From Naphthalene to pyrene, the amount of gas phase PAHs (ppm) decreases
- From Pyrene to Benzo (g,h,i)Perylene, the amount of particulate PAHs (ppm) increases
- Pyrene was considered as vital PAH in transition from gas to particle phase
- Majority of PAH growth passes through pyrene
Formation of a two ring naphthalene PAH via HACA mechanism

Possible Phenyl/benzene routes from acetylene

- $n$-C4H3 + C2H2 $\rightarrow$ C6H5
- $n$-C4H4 + C2H2 $\rightarrow$ C6H6
- 2(C2H2) $\rightarrow$ C6H6
- 3 (C2H2) $\rightarrow$ C6H6
- 2(C3H3) $\rightarrow$ C6H6 (Propargyl dimerization)

HACA – Hydrogen Abstraction, Acetylene Addition
PAHs having 3 to 4 rings were detected in roughly similar concentrations regardless of the molecular structure of the hydrocarbon tested.
Growth of a five-membered ring acenaphthylene to Pyrene

- PAH growth from Naphthalene → Acenaphthylene → Pyrene
Growth of a benzenoid phenanthrene to benzenoid Pyrene

- Pyrene can also grow via Phenanthrene by HACA
- PAH growth from Naphthalene → Phenatherene → Pyrene
Further information on PAH formation of some C1 – C7 hydrocarbons can be found in:

Conclusions

- Increasing pyrolysis temperature of the tube reactor decreased the total PAH concentration regardless of the carbon number and degree of unsaturation of the hydrocarbons.

- The concentration of gas phase PAHs generated from the C_2 and C_3 fuels increased with increasing unsaturation in the fuels tested.

- The total PAH concentrations tended to increase with increasing carbon number of the hydrocarbons from C1 – C7 (excluding heptane) at the temperature of 1050 °C but an opposite (decreasing) trend was observed at 1350 °C.

- The weighted carcinogenicity of PAHs was found to have the highest concentration for all the fuels at the lowest temperature tested and this concentration decreased with rise in temperature to 1350 °C.