Engine Emissions and Air Pollution

The Lecture Contains:

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Principal Engine Emissions

SI Engines	CO, HC and NOx
CI Engines	CO, HC, NOx and PM

CO = Carbon monoxide, HC = Unburned hydrocarbons, NO_x = Nitrogen oxides mainly mixture of NO and NO_2 ,
PM = Particulate matter
Other engine emissions include aldehydes such as formaldehyde and acetaldehyde primarily from the alcohol fuelled engines, benzene and polyaromatic hydrocarbons (PAH).

Sources of Engine/Vehicle Emissions

Figure 1.3 shows the sources of emissions from a gasoline fuelled SI engine viz., exhaust, crankcase blow by and fuel evaporation from fuel tank and fuel system

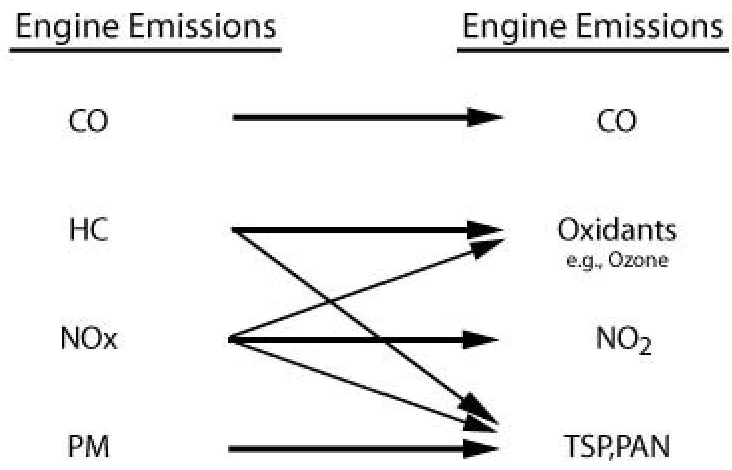
Figure. 1.3	Emission sources in a gasoline fuelled car

From a diesel engine powered vehicle the emission sources are shown in Fig. 1.4.

Figure 1.4	Emission sources in a diesel engine powered bus.

Emissions and Pollutants

Engine emissions undergo chemical reactions in atmosphere known largely as ‘*photochemical*’ reactions and give rise to other chemical species which are hazardous to health and environment. Linkage of engine emissions and air pollutants is shown in Fig. 1.5.



TSP = Total suspended particulate matter in air
PAN = Peroxy- acetyl nitrate

Figure. 1.5	Air pollutants resulting from engine emissions

Photochemical Smog

Photochemical smog is a brownish-gray haze resulting from the reactions caused by solar ultraviolet radiations between hydrocarbons and oxides of nitrogen in the atmosphere. The air pollutants such as ozone, nitric acid, organic compounds like peroxy- acetylnitrates or PAN ($CH_3CO\text{-}OO\text{-}NO_2$) are trapped near the ground by temperature inversion experienced especially during winter months. These chemical substances can effect human health and cause damage to plants. The photochemical reactions are initiated by nitrogen oxides emitted by vehicles into atmosphere. A simple set of reactions leading to photochemical smog formation is as follows:

$$NO_2 + h\nu \xrightarrow{UV} NO + O$$
$$O + O_2 \rightarrow O_3$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$h\nu$ is energy of a photon and UV is ultraviolet light radiations .

The above reactions form NO_2 photolytic cycle. However, if only these reactions are involved then, NO_2 concentration in the atmosphere would remain constant. But, volatile organic compounds (VOCs) that include unburned hydrocarbons and their volatile derivatives also react with NO and O_2 to form NO_2 . The reactions between HC and NO do not necessarily involve ozone and provide another route to form NO_2 and thus, the concentration of ozone and NO_2 in the urban air rises. The most reactive VOCs in atmosphere are olefins i.e., the hydrocarbons with C=C bond. The general reaction between hydrocarbons (RH) and NO may be written as

$$RH + NO + O_2 \xrightarrow{\text{UV(Sunlight)}} NO_2 + PAN$$

The overall global reaction is

$$VOCs + NO \longrightarrow O_3 + HNO_3 + Organics$$

Main processes in photochemical smog formation are shown in Fig. 1.6.

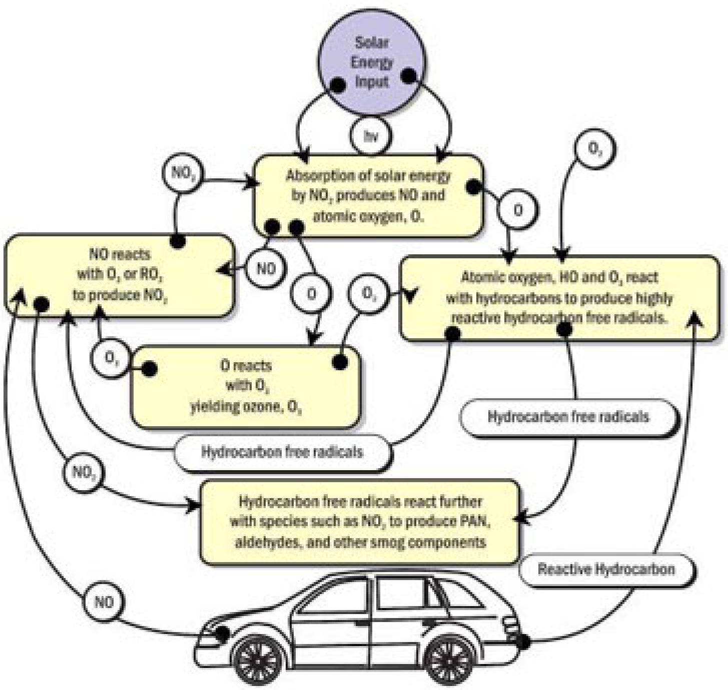


Figure1.6	Main processes in photochemical smog formation (adapted from http://mtsu32.mtsu.edu:11233/Smog-Atm1.htm)

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The harmful constituents of photochemical smog are, NO_2, O_3, PAN and aldehydes. The PAN and aldehydes cause eye irritation. NO_2 and ozone are strong oxidants and cause damage to elastomeric/ rubber materials and plants.

Photochemical Reactivity of Hydrocarbons

The exhaust gases of gasoline engines contain more than 150 different hydrocarbons and their derivatives. Some hydrocarbons are more reactive than the others. The photochemical reactivity of hydrocarbons has been measured in terms of the rate at which the specific hydrocarbon causes oxidation of NO to NO_2. To determine the rate of photo-oxidation, NO in presence of the specific hydrocarbon is irradiated by ultra violet radiations in a reaction chamber and the buildup of NO_2 in terms parts per billion/per minute is recorded. Another photochemical reactivity scale has been defined in terms of ozone formation. Reactivity of different classes of hydrocarbons based on formation of NO_2 is given in Table 1.4

It has been noted that the reactivity of a given hydrocarbon depends also on the initial concentrations of pollutants in the environment in which a particular hydrocarbon is added when emitted. A reactivity termed as ***incremental activity*** has been determined in terms of ozone formed. It is defined as the change in ozone formation rate when specific VOC is added to the base reactive organic gas mixture in the environment divided by the amount of the specific VOC added. This reactivity is considered to bge of more practical relevance.

Table 1.4

Photochemical Reactivity of Hydrocarbons (General Motor Scale)

Hydrocarbon	Relative Reactivity*
C1-C4 paraffins AcetyleneBenzene	0
C4 and higher paraffins Monoalkyl benzenes *Ortho*- and *para*-dialkyl benzenes Cyclic paraffins	2
Ethylene Meta- dialkyl benzenes Aldehydes	7
1-olefins (except ethylene) Diolefins Tri- and tetraalkyl benzenes	10
Internally bonded olefins	30
Internally bonded olefins with substitution at double bondCyclo-olefins	100

*based on NO_2 formation rate for the specific hydrocarbon relative to that for 2,3 dimethyl-2-benzene

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Health Effects of Air Pollutants

The effect of pollutants on human health depends on pollutant concentration in the ambient air and the duration to which the human beings are exposed. Adverse health effects of different pollutants on human health are given in Table 1.5 for short term and long term exposures. Carbon monoxide on inhalation is known to combine with haemoglobin at a rate 200 to 240 times faster than oxygen thus reducing oxygen supply to body tissues and results in CO intoxication. Nitrogen oxides get dissolved in mucous forming nitrous and nitric acids causing irritation of nose throat and respiratory tract. Long term exposure causes nitrogen oxides to combine with haemoglobin and destruction of red blood cells. Long term exposure resulting in more than 10% of haemoglobin to combine with nitrogen oxides causes bluish colouration of skin, lips fingers etc

Table 1.5

Adverse Health Effects of IC Engine Generated Air Pollutants

Pollutants	Short-term health effects	Long-term health effects
Carbon monoxide	Headache, shortness of breath, dizziness, impaired judgment, lack of motor coordination	Effects on brain and central nervous system, nausea, vomiting, cardiac and pulmonary functional changes, loss of consciousness and death
Nitrogen dioxide	Soreness, coughing, chest discomfort, eye irritation	Development of cyanosis especially at lips, fingers and toes, adverse changes in cell structure of lung wall
Oxidants	Difficulty in breathing, chest tightness, eye irritation	Impaired lung function, increased susceptibility to respiratory function
Ozone	Similar to those of NO_2 but at a lower concentration	Development of emphysema, pulmonary edema
Sulfates	Increased asthma attacks	Reduced lung function when oxidants are present
TSP/Respirable suspended particulate	Increased susceptibility to other pollutants	Many constituents especially poly-organic matter are toxic and carcinogenic, contribute to silicosis, brown lung

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Historical Overview: Engine and Vehicle Emission Control

Beginning with the identification during early 1950s that mainly the unburned hydrocarbons and nitrogen oxides emitted by vehicles are responsible for formation of photochemical smog in Los-Angeles region in the US, the initiatives and milestones in pursuit of vehicle/ engine emission control are given in Table 1.6

Table 1.6
Engine Emission Control – A Historical Perspective

Year	Event and Milestone
1952	Prof A. J. Haagen- Smit of Univ. of California demonstrated that the photochemical reactions between unburned hydrocarbons (HC) and nitrogen oxides (NOx) are responsible for smog (brown haze) observed in Los-Angeles basin
1965	The first vehicle exhaust emissions standards were set in California, USA
1968	The exhaust emission standards set for the first time throughout the USA
1970	Vehicle emission standards set in European countries
1974	Exhaust catalytic converters for oxidation of carbon monoxide (CO) and HC were needed in the US for meeting emission targets. Phasing-out of tetra ethyl lead (TEL), the antiknock additive from gasoline begins to ensure acceptable life of the catalytic converters
1981	Three-way catalytic converters and closed-loop feedback air-fuel ratio control for simultaneous conversion of CO, HC and NOx introduced on production cars
1992	Euro 1 emission standards needing catalytic emission control on gasoline vehicles implemented in Europe
1994	Catalytic emission control for engines under lean mixture operation introduced
1994	US Tier -1 standards needing reduction in CO by nearly 96%, HC by 97.5% and NOx by 90%
2000-2005	Widespread use of diesel particulate filters and lean de-NOx catalyst systems on heavy duty vehicles
2004	US Tier -2 standards needing reduction in CO by nearly 98 %, HC by 99% and NOx by 95%