

## **AUTOMOTIVE EMISSIONS:**

Emissions come principally from three automotive sources: the exhaust, the fuel system (evaporative), and crankcase ventilation gases. Regulations require exhaust emission measurements during the operation of the vehicle (or engine) on a dynamometer during a driving cycle that simulates vehicle road operation.

### **TYPES OF EMISSIONS:**

Emissions of many air pollutants have been shown to have variety of negative effects on public health and the natural environment. Emissions that are principal pollutants of concern include:

- **Hydrocarbons (HC)** - A class of burned or partially burned fuel, hydrocarbons are toxins. Hydrocarbons are a major contributor to smog, which can be a major problem in urban areas. Prolonged exposure to hydrocarbons contributes to asthma, liver disease, lung disease, and cancer. Regulations governing hydrocarbons vary according to type of engine and jurisdiction; in some cases, "non-methane hydrocarbons" are regulated, while in other cases, "total hydrocarbons" are regulated. Technology for one application (to meet a non-methane hydrocarbon standard) may not be suitable for use in an application that has to meet a total hydrocarbon standard. Methane is not directly toxic, but is more difficult to break down in fuel vent lines and a charcoal canister is meant to collect and contain fuel vapors and route them either back to the fuel tank or, after the engine is started and warmed up, into the air intake to be burned in the engine.
- **Carbon monoxide (CO)** - A product of incomplete combustion, inhaled carbon monoxide reduces the blood's ability to carry oxygen; overexposure (carbon monoxide poisoning) may be fatal. (Carbon monoxide persistently binds to hemoglobin, the oxygen-carrying chemical in red blood cells, where oxygen (O<sub>2</sub>) would temporarily bind. The bonding of CO excludes O<sub>2</sub> and also reduces the ability of the hemoglobin to release already-bound oxygen, on both counts rendering the red blood cells ineffective. Recovery is by the slow release of bound CO and the body's production of new hemoglobin—a healing process—so full recovery from moderate to severe [but nonfatal] CO poisoning takes hours or days. Removing a person from a CO-poisoned atmosphere to fresh air stops the injury but does not yield prompt recovery, unlike the case where a person is removed from an asphyxiating atmosphere [i.e. one deficient in oxygen]. Toxic effects delayed by days are also common.)
- **NO<sub>x</sub>** - Generated when nitrogen in the air reacts with oxygen at the high temperature and pressure inside the engine. NO<sub>x</sub> is a precursor to smog and acid rain. NO<sub>x</sub> is the sum of NO and NO<sub>2</sub>.<sup>[1]</sup> NO<sub>2</sub> is extremely reactive. NO<sub>x</sub> production is increased when an engine runs at its most efficient (i.e. hottest) operating point, so there tends to be a natural tradeoff between efficiency and control of NO<sub>x</sub> emissions.
- **Particulate matter** – Soot or smoke made up of particles in the micrometre size range: Particulate matter causes negative health effects, including but not limited to respiratory disease and cancer. Very fine particulate matter has been linked to cardiovascular disease.

- **Sulfur oxide (SO<sub>x</sub>)** - A general term for oxides of **sulfur**, which are emitted from motor vehicles burning fuel containing sulfur. Reducing the level of fuel sulfur reduces the level of **Sulfur oxide** emitted from the tailpipe.
- **Volatile organic compounds (VOCs)** - Organic compounds which typically have a boiling point less than or equal to 250 °C; for example **chlorofluorocarbons** (CFCs) and **formaldehyde**. **Volatile organic compounds** are a subsection of **Hydrocarbons** that are mentioned separately because of their dangers to public health.

## **ROLE IN AIR POLLUTION**

Pollutants from cars contribute to various types of air pollution. When hydrocarbons and NO<sub>x</sub> combine in sunlight, they produce **ozone**. High in the atmosphere, ozone protects us from the sun's ultraviolet rays. When holes in the atmosphere's ozone layer allows ozone to come closer to Earth, it contributes to smog and causes respiratory problems.

Air pollutants emitted from cars are believed to cause cancer and contribute to such problems as **asthma, heart disease, birth defects and eye irritation**.

Emissions from cars increase the levels of carbon dioxide and other greenhouse gases in the atmosphere. At normal levels, greenhouse gases keep some of the sun's heat in the atmosphere and help warm Earth. That said, many scientists believe that burning fossil fuels such as gasoline causes greenhouse gas levels to spike, leading to global warming.

Scientists use sophisticated instruments to measure concentrations of harmful substances in the air, but **it's tough to say exactly what percentage of air pollution comes from cars**. This makes sense, **because many other human activities contribute to air pollution as well**. In fact, the production of electricity by coal-fired power plants and other sources can cause more pollution than most cars. If that wasn't enough, we pollute the air when we heat our homes and public buildings with fuels other than electricity -- just as we do when we drive our cars. Even people who don't drive add to pollution when they buy goods and services that involve fuel when they're made or delivered.

Although the U.S. Environmental Protection Agency (EPA) declared cars "mobile sources" of pollution, they aren't the only culprits. Big trucks, bulldozers, ships and boats, and trains pollute the air.

According to the EPA, **motor vehicles collectively cause 75 percent of carbon monoxide pollution** in the U.S. The Environmental Defense Fund (EDF) estimates that **on-road vehicles cause one-third of the air pollution** that produces smog in the U.S., and **transportation causes 27 percent of greenhouse gas emissions**. The U.S. has 30 percent of the world's automobiles, yet it contributes about half of the world's emissions from cars.

The United States was long considered the world's biggest polluter in terms of carbon dioxide and other greenhouse gases, but by 2008, the United Nations had reported that China had moved into the top spot.

The percentage of air pollution caused by cars is higher in urban areas and higher still near major highways.

## **REMEDIES:**

<b>DO's</b>	<b>DON'Ts</b>
Walk to work, or ride a bicycle.	Don't use extensively your private vehicles, try to use <b>public transportation</b> whenever possible.
<b>Carpool.</b> Two - or four - can ride as cheaply as one.	Avoid congested road and rush hours.
Get a valid pollution under control certificate from authorized testing centre.	Don't idle away energy. <b>Beyond one minute</b> , it is more fuel - <b>efficient to restart your car.</b>
Keep automobiles <b>fuel filters clean</b> and save the fuel.	Don't forget to Keep your vehicle tuned up. When a vehicle is running well, it uses nine per cent less fuel and thus emits fewer toxic and noxious fumes.
Clean the <b>air filter</b> and <b>oil filter</b> regularly.	Don't try to replicate mechanical works and experiment with your car.
Clean the <b>carbon deposit</b> from silencer.	Don't forget to <b>replace your old battery with new battery</b> when it required.
Maintain recommended <b>tyre pressure.</b>	<b>Don't use clutch pedal as footrest.</b>

## **GREEN ENGINE**

The Green engine is a six phase, internal combustion engine with much higher expansion ratio. The term "phase" is used instead of "stroke" because stroke is actually associated to the movement of the piston.

The traveling of the piston from bottom dead centre to the top dead centre or vice versa is termed a stroke. But, in this engine pistons are absent and hence, the term "phase" is used. The six phases are: intake, compression, mixing, combustion, power and exhaust.

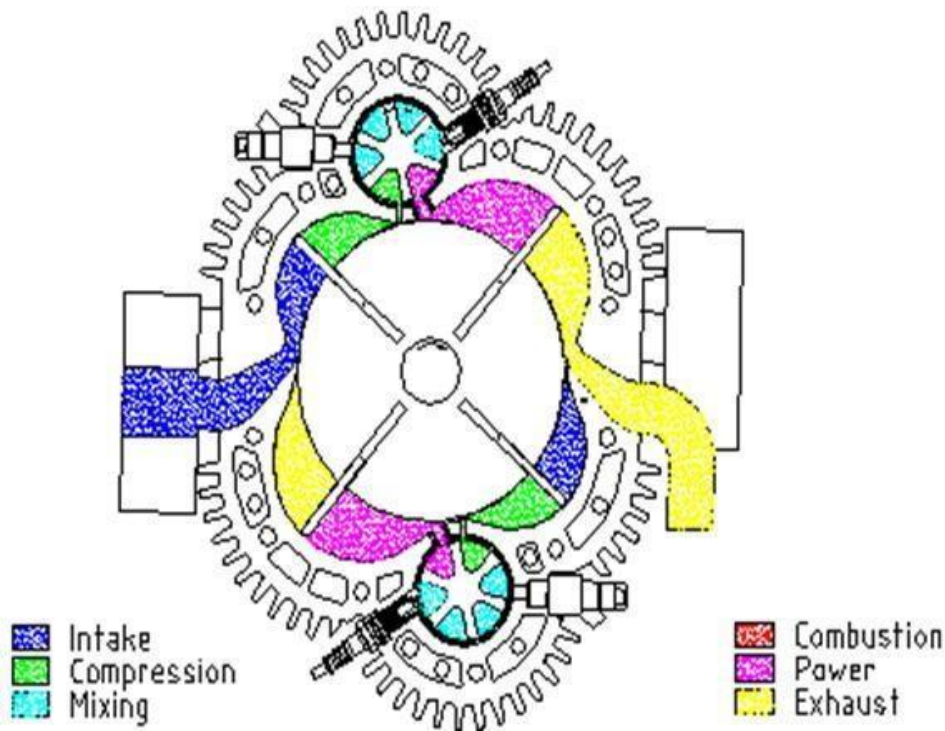
### **Construction & Working**

The engine comprises a set of vanes, a pair of rotors which houses a number of small pot-like containers. It is here, in these small containers that compression, mixing, combustion are carried out. The engine also contains two air intake ports, and a pair of fuel injectors and spark plugs. The spark plugs are connected in such a system so as to deactivate them, when a fuel which does not need sparks for ignition is used. The rotor is made of high heat resistance and low expansion rate material such as ceramic. Whereas, the metal used is an alloy of steel, aluminium and chromium.

Even though the engine is of symmetric shape, the vanes traverse an unsymmetrical or uneven boundary. This shape cannot be compromised as this a result of the path taken by the intake and exhaust air. This uneven boundary is covered by the vanes in a very unique fashion. The vanes are made in such a way that it comprises of two parts: one going inside a hollow one. At the bottom of the hollow vane is a compressive spring. On top of this spring is mounted the other part of the vane. Now, let us come to the working of the engine.

The air arrives to the engine through the direct air intake port in the absence of an air inlet pipe, throttle and inlet valves on the air intake system. A duct is provided on the sides of the vane and rotor. The duct is so shaped that when the air moves through, strong swirls generate when it gets compressed in the chamber. The air pushes the vane blades which in turn impart a proportionate rotation in the small rotor which houses the chambers. The inlet air duct ends with a very narrow opening to the chamber.

The Green engine's prototypes have been recently developed, and also because of the unique design, limitations have not been determined to any extent. But even in the face of limitations if any, the Green engine is sure to serve the purpose to a large extent.



The advantages of this innovative model of Green engine over the contemporary piston engines are many

- Small Size and Light Weight
- Limited Parts
- High Efficiency
- Multi-fuels
- Near-zero Emissions
- Smooth Operation
- Fast Accelerating Response
- Quietness and Low Exhaust Temperature

## **PHOTOCHEMICAL SMOG**

Photochemical smog is a mixture of pollutants that are formed when nitrogen oxides and volatile organic compounds (VOCs) react to sunlight, creating a brown haze above cities. It tends to occur more often in summer, because that is when we have the most sunlight.

### **Primary pollutants**

The two major primary pollutants, nitrogen oxides and VOCs, combine to change in sunlight in a series of chemical reactions, outlined below, to create what are known as secondary pollutants.

### **Secondary pollutants**

The secondary pollutant that causes the most concern is the ozone that forms at ground level. While ozone is produced naturally in the upper atmosphere, it is a dangerous substance when found at ground level. Many other hazardous substances are also formed, such as peroxyacetyl nitrate (PAN).

While nitrogen oxides and VOCs are produced biogenically (in nature), there are also major anthropogenic (man-made) emissions of both. Natural emissions tend to be spread over large areas, reducing their effects, but man-made emissions tend to be concentrated close to their source, such as a city.

### **Biogenic sources**

In nature, bushfires, lightning and the microbial processes that occur in soil generate nitrogen oxides. VOCs are produced from the evaporation of naturally-occurring compounds, such as terpenes, which are the hydrocarbons in oils that make them burn. Eucalypts have also been found to release significant amounts of these compounds.

### **Anthropogenic sources**

Nitrogen oxides are produced mainly from the combustion of fossil fuels, particularly in power stations and motor vehicles. VOCs are formed from the incomplete combustion of fossil fuels, from the evaporation of solvents and fuels, and from burning plant matter—such as backyard burning and wood-burning stoves.

## **Composition of Photochemical Smog**

The following substances are identified in photochemical smog:

Nitrogen dioxide (NO<sub>2</sub>) from vehicle exhaust, is photolyzed by ultraviolet (UV) radiation (hν) from the sun and decomposes into Nitrogen Oxide

$$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$$

The oxygen radical then reacts with an atmospheric oxygen molecule to create ozone, O<sub>3</sub>

$$\text{O} + \text{O}_2 \rightarrow \text{O}_3$$

Under normal conditions, O<sub>3</sub> reacts with NO, to produce NO<sub>2</sub> and an oxygen molecule

$$\text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2$$

This is a continual cycle that leads only to a temporary increase in net ozone production. To create photochemical smog on the scale observed in Los Angeles, the process must include Volatile organic compounds

VOC's react with hydroxide in the atmosphere to create water and a reactive VOC molecule

$$\text{RH} + \text{OH} \rightarrow \text{R} + \text{H}_2\text{O}$$

The reactive VOC can then bind with an oxygen molecule to create an oxidized VOC

$$\text{R} + \text{O}_2 \rightarrow \text{RO}_2$$

The oxidized VOC can now bond with the nitrogen oxide produced in the earlier set of equations to form nitrogen dioxide and a reactive VOC molecule

$$\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2$$

## **Effects of photochemical smog**

### **Health Effects**

Photochemical smog is capable of inflicting irreversible damage on the lungs and heart. Even short-term exposure to photochemical smog tends to have ill effects on both the young and the elderly. It causes painful irritation of the respiratory system, reduced lung function and difficulty breathing; this is more evident while exercising or working outdoors. High levels of smog also trigger asthma attacks because the smog causes increased sensitivity to allergens, which are triggers for asthma.

### **Effects on Environment**

Photochemical smog has devastating effects on the environment. The collection of chemicals found in photochemical smog causes problems for plants and animal life. Some plants such as tobacco, tomato and spinach are highly responsive to ozone, so photochemical smog can decimate these sensitive crops, trees and other vegetation. Ozone causes necrotic (dead) patterns on the upper surfaces of the leaves of trees. Ground-level ozone also can interfere with the growth and productivity of trees. The effects of smog on animals are also similar to its effect on humans; it decreases lung capacity and lung elasticity.

### **How can we reduce the occurrence of photochemical smog?**

The most effective way of reducing the amount of secondary pollutants created in the air is to reduce emissions of both primary pollutants.

#### **Reduction of nitrogen oxide**

The main method of lowering the levels of nitrogen oxides is by a process called ‘catalytic reduction’, which is used in industry and in motor vehicles. For example, a catalytic converter fitted to a car’s exhaust system will convert much of the nitric oxide from the engine exhaust gases to nitrogen and oxygen. In Australia, all motor vehicles built after 1985 must be fitted with catalytic converters. Nitrogen is not in the actual fuels used in motor vehicles or power stations; it is introduced from the air when combustion occurs. Using less air in combustion can reduce emissions of nitrogen oxides. Temperature also has an effect on emissions—the lower the temperature of combustion, the lower the production of nitrogen oxides. Temperatures can be lowered by using processes such as two stage combustion and flue gas recirculation, water injection, or by modifying the design of the burner.

#### **Reduction of VOCs**

There are various ways to reduce VOC emissions from motor vehicles. These include the use of liquefied petroleum gas (LPG) or compressed natural gas (CNG) rather than petrol, decreasing distances vehicles travel by using other modes of transport, such as buses and bikes, and implementing various engine and emission controls now being developed by manufacturers.

The other major contributor to VOC emissions, however, is not as simple to police because solvent evaporation occurs in many different places, from large factories to backyard sheds. Control strategies to reduce these emissions must be widely varied.

## What is Smog?

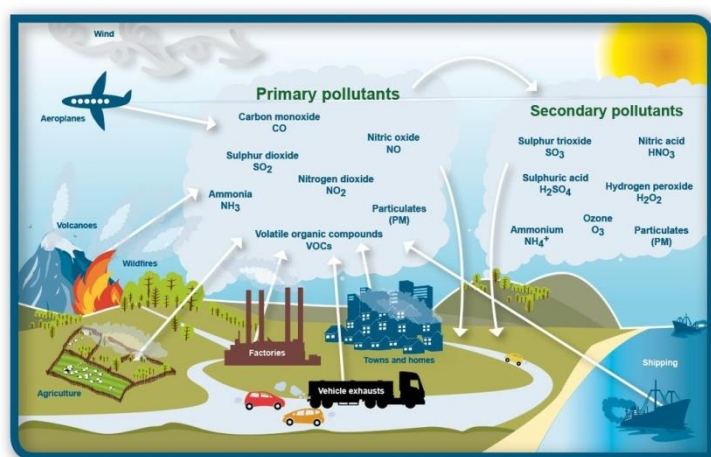
Smog is a common form of air pollution found mainly in urban areas and in large human centers. The term refers to any type of atmospheric pollution - no matter where it comes from, how it is constructed, or how concentrated it is - that produces significant damage to the atmosphere. Smog



encompasses a wide range of air pollution generated by a number of processes directly related to the atmospheric conditions of the constructed region. In the early 1900's, London was hit by a plume of smoke that came from a mixture of mist and coal from a coal fire. In modern times, the Los Angeles Basin is often associated with heavy chemical smoke, which is produced by a combination of car exhaust and sunlight. These are two of the plethora of examples of pollutants that are classified as smog, but they have nothing to do with chemicals. Smog refers to numerous categories of air pollution containing variegated chemicals; however, all forms of smoke create a visible blurry haze that reduces the visibility of the atmosphere.

## Photochemical Smog : Formation and Causes

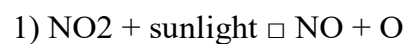
Photochemical smog is a type of smog produced when ultraviolet light from the sun reacts with nitrogen oxides in the atmosphere. It is visible as a brown haze, and is most prominent during the morning and afternoon, especially in densely populated, warm cities



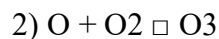
Photochemical smog is produced when sunlight reacts with nitrogen oxides and at least one volatile organic compound (VOC) in the atmosphere. Nitrogen oxides come from car exhaust, coal power plants, and factory emissions. VOCs are released from gasoline, paints, and many cleaning solvents. When sunlight hits these chemicals, they form airborne particles and ground-level ozone—or smog.

### **Photochemical Smog : Reactions and Composition**

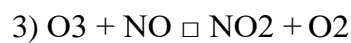
Nitrogen dioxide (NO<sub>2</sub>) can be broken down by sunlight to form nitric oxide (NO) and an oxygen radical (O):



Oxygen radicals can then react with atmospheric oxygen (O<sub>2</sub>) to form ozone (O<sub>3</sub>):



Ozone is consumed by nitric oxide to produce nitrogen dioxide and oxygen:



Harmful products, such as PAN, are produced by reactions of nitrogen dioxide with various hydrocarbons (R), which are compounds made from carbon, hydrogen and other substances:



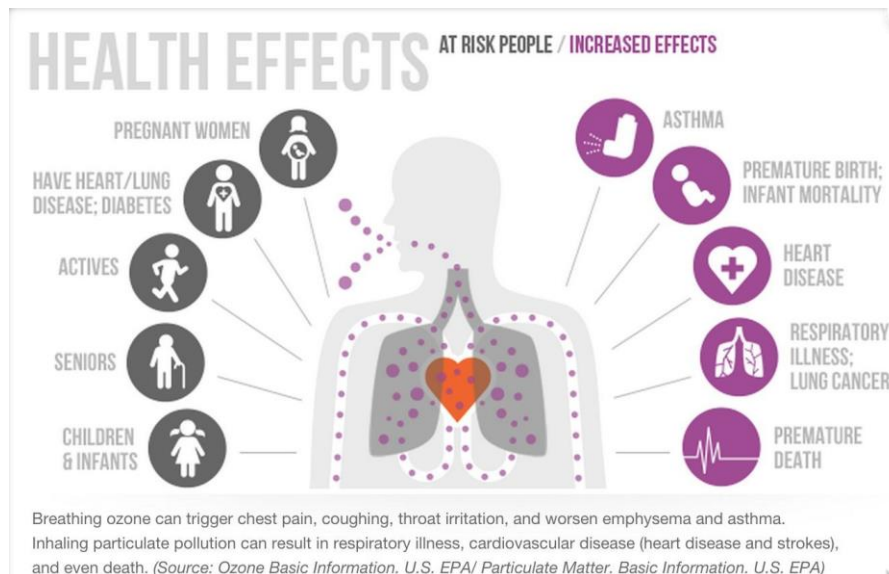
The main source of these hydrocarbons is the volatile organic compounds or VOCs. Similarly, oxygenated organic and inorganic compounds (RO<sub>x</sub>) react with nitric oxide to produce more nitrogen oxides:



The importance of the presence of VOCs in these two approaches is very important. Ozone is commonly used by nitric oxide, as seen in reaction 3. However, when VOCs are present, nitric oxide and nitrogen dioxide are consumed as in reaction of 4 and 5, allowing the formation of ozone ground level.



## Adverse Effects of Smog



Smog is a major problem in many cities and continues to damage human health. Low levels of ozone, sulfur dioxide, nitrogen dioxide and carbon monoxide are particularly dangerous in the elderly, children, and people with heart and lung conditions such as emphysema, bronchitis and asthma. It can irritate the respiratory tract, reduce lung function, cause shortness of breath, pain when inhaling deeply, breathing and coughing. It can cause irritation of the eyes and nose and dry up the protective lining of the nose and throat and impair the body's ability to fight infections, making it easier to get sick. Hospital admissions and respiratory deaths often increase at times when ozone levels are high.

## How to Reduce Smog Formation

- Keep your car serviced regularly and tires filled using the manufacturer clarification. This will ensure that the car is running smoothly and does not emit pollutants.
- If you are trading in your old car, replace it with a smaller, fuel-efficient car.
- Instead of using a car, try cycling or walking, and use buses, trams or trains whenever you can.
- Use energy-saving devices. Check the Energy Star logo when you buy a computer, printer, air conditioner, clothes dryer, dishwasher, refrigerator or freezer you buy.
- When renovating or building, use energy-efficient designs and materials.
- Turn off unnecessary electrical appliances when possible.

- Make it your goal to buy 'green energy' - energy produced by clean, renewable energy sources.
- Use your green energy - investigate Government Discount Solar Hot Water, Photo-voltaic discount and Remote Renewable Power Generation grants.
- Schools can join Airwatch, a primary and secondary school system where students can become pollinators in their local environments.

## **Smog in Delhi, India**

A few years ago, cities in northern India were shrouded in smoke during the winter. The situation has worsened at National Capital, Delhi. The smoke is caused by the accumulation of Particulate Matter (a type of dust and toxic gases) in the air due to the constant movement of air during the winter.

Delhi is the most polluted city in the world and according to some estimates, air pollution causes the deaths of an estimated 10,500 people in Delhi every year. During 2013-14, the high levels of fine particulate matter (PM) in Delhi increased by about 44%, mainly due to high car and industrial emissions, construction work and burning of crops in the combined areas. Delhi has a very high level of carbon dioxide. , PM2.5 is considered to be the most dangerous to health, at 153 micrograms. The increase in air pollution levels has significantly increased lung-related diseases (especially asthma and lung cancer) among children and women in Delhi. Heavy smoke in Delhi during the winter causes severe disruptions to air trains and trains every year. According to Indian meteorologists, temperatures in central Delhi during the winter have dropped significantly since 1998 due to rising temperatures.



## **HOMOGENOUS AND HETROGENOUS**

Homogeneous simply means suppose if we put a pinch of salt in water it takes time to be dissolved completely once it is dissolved it is called homogeneous mixture but in the case of water and iron nail it is not dissoluble so it is a heterogeneous mixture.

Similarly in the case of diesel engine combustion process there is air which is compressed 40 to 50 bar is highly dense and diesel which is atomized and thrown with 100 to 200 bar into cylinder gets not mixed properly and meanwhile, combustion takes place.

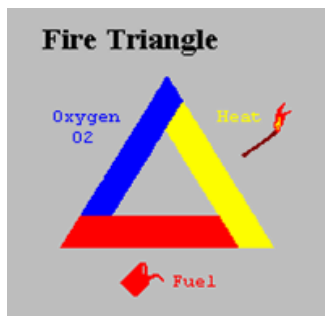
And in the case of petrol engine, there is air and petrol previously mixed in carburettor which made it homogeneous and thrown into a cylinder with high pressure and combustion takes place when the piston moves from BDC to TDC.

### **What is combustion**

**Combustion** is a chemical process or a reaction between Fuel (Hydrocarbon) and Oxygen. When fuel and oxygen react, it releases the heat and light energy. Heat and light energy then result in the flame. So, the formula for **Combustion** reaction is Hydrocarbons + Oxygen = Heat energy

## **The Fire Triangle**

Three things are required in proper combination before ignition and combustion can take place--**Heat, Oxygen** and **Fuel**.



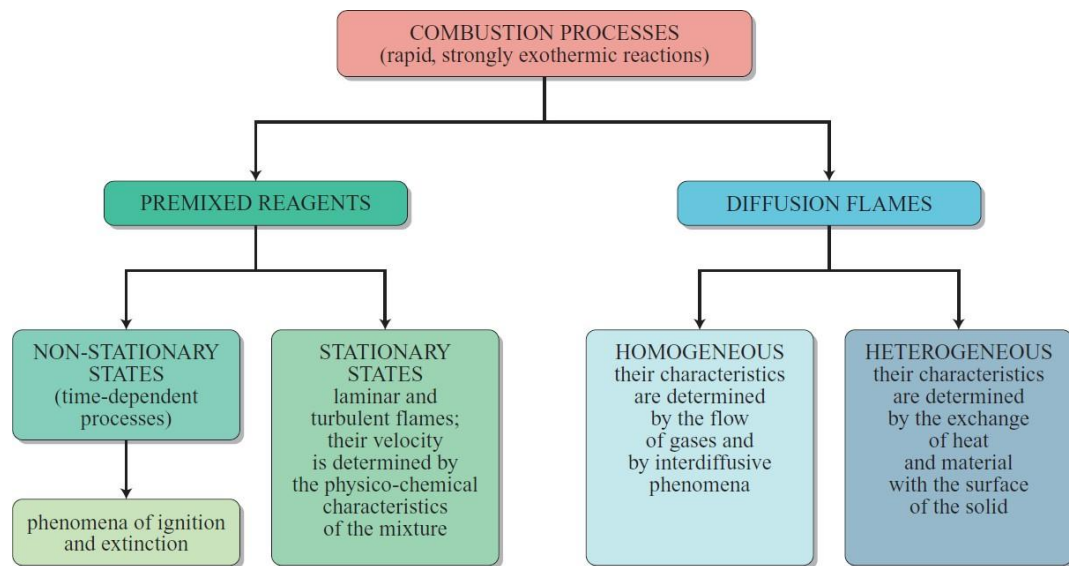
1. There must be **Fuel** to burn.
2. There must be **Air** to supply oxygen.
3. There must be **Heat** (ignition temperature) to start and continue the combustion process.

Combustible mixture

Homogenous- fuel and oxygen molecules are uniformly distributed.

Heterogenous- combustion in porous media, is a type of combustion in which a solid and gas phase interact to promote the complete transfer of reactants to their lower energy potential

products.



## HOMOGENEOUS COMBUSTION

Our understanding of the phenomenon of combustion dates from the second half of the Eighteenth century, when Antoine-Laurent Lavoisier demonstrated that the process was not due to the release of phlogiston, then considered to be one of the constituent parts of matter, but instead to the combining of one component of the air, oxygen, with particular gaseous, liquid or solid combustible materials. Its special characteristic is the manifest emission of light and heat which often takes on the typical aspect of flames. In reality, combustion processes have been the main source of energy for mankind ever since prehistoric times, and even today they play a central role in our economy, supplying about 90% of the energy we consume. In spite of the relentless and, in certain respects, challenging search for alternative sources of energy, this pre-eminent position is bound to remain unchallenged for a long time to come. The fuels commonly used as sources of energy are natural gas, which is principally made up of methane; petroleum products, which are composed of mixtures of hydrocarbons; and coal. When these combine with oxygen (the *carburant* substance) carbon dioxide and water are formed through a series of chemical reactions that, as a rule, are very complex because they take place in various stages and involve, as will be explained further on, many intermediate species. Leaving aside these details, it is nevertheless easy to formulate the global reactions through which combustion products are formed from the fuels mentioned. These can be expressed as follows:

[1]  $\text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2$  for methane

[2]  $\text{C}_n\text{H}_m + (n + \frac{m}{4})\text{O}_2 \rightarrow n\text{CO}_2 + \frac{m}{2}\text{H}_2\text{O}$

for a generic hydrocarbon

[3]  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$  for coal

These reactions release significant quantities of heat energy whose values can be calculated from the enthalpies of formation of the various species involved (see below). Alongside the preceding combustion reactions, there is also, for example, the combination of oxygen with hydrogen to form water, and the combination of hydrogen with chlorine and bromine to form the corresponding hydrochloric and hydrobromic acids. In short, the category of combustion processes includes all reactions that are very rapid and strongly exothermic. The peculiar nature of combustion processes stems from the interaction of an ensemble of physical and chemical phenomena which give rise to particular and diversified situations. The simplest is that of a gaseous mixture containing a fuel, methane, for example, oxygen and any inert gases such as nitrogen which may be present, in which a very rapid exothermic reaction is triggered that produces a strong heating effect with consequent sharp variations of the temperature and concentrations of the reagents in time and space. The geometrical configuration and the physical conditions of the mixture, in particular the temperature, of the mixture create the right conditions for its *ignition* to take place. If the fluids are in motion, changes in components and operating conditions cause different identifiable situations to arise, each of which is characterized by specific problems for the description and handling of combustion processes. The case of a gaseous mixture formed by a fuel and a carburant (combustion-support) that moves with laminar flow in a given direction at constant rate will be considered first. If a combustion reaction is triggered at a particular position in the direction of the flow, a flame is generated which causes a sharp increase in the temperature of the mixture. The reactive event takes place in a thin layer in which, besides the temperature increase, an abrupt decrease in the concentration of the reagents also occurs, while the concentration of the reaction products increases at an equivalent speed and attains its corresponding value in the final mixture. In substance, one can identify a reaction front that moves at a given rate of direct propagation in the direction opposite to that of the gaseous flow. If the numerical values of the two velocities are identical, the position of the flame front remains unchanged in time and the flame is said to be *stationary*. This description identifies the behavior of what are known as *premixed one-dimensional flames*. A different situation occurs in the case of *diffusion flames*, in which the two gaseous reagents flow into two separate zones and then converge in a third zone where the combustion takes place.

## Emission Formation :

The enormous increase in environmental pollution caused by combustion processes makes it essential that solutions are found for their reduction. Soon after World War II it was recognized that a major portion of this problem is caused by the exhaust emission from the internal-combustion engines (Taylor, 1985). The causes and the control of this problem have been the objective of an enormous amount of research and development, which is still continuing. The reactions that occur in the engine combustion process not only produce substances such as  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2$ , but also various pollutants which are found in the engine exhaust. The three main pollutants which are subject to exhaust emission legislation are carbon monoxide (CO), unburned hydrocarbons (HC) and nitrogen oxides ( $\text{NO}_x$ ). These emissions are worse from the spark-ignition engine than from the compression ignition engine. Other important pollutants contained in exhaust emissions are aldehydes (H—C—O compounds), lead components produced by use of leaded fuels, Sulphur dioxide ( $\text{SO}_2$ ), and particulates (including soot), especially with diesel engines. A typical exhaust composition (ECE test) is shown in Figure 1. Emissions of pollutants vary between different engines and are dependent on such variables as ignition timing, load, speed, and in particular, fuel/air ratio. Figure 2 (Stone, 1991) shows typical variations of pollutant concentrations with the fuel/air ratio for a spark-ignition engine.

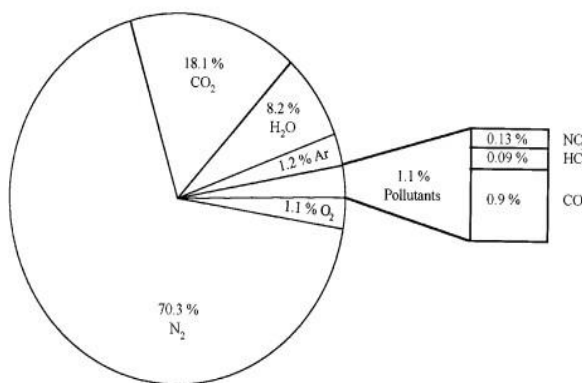


Figure 1 Mean exhaust composition without catalytic converter in ECE test (medium-size vehicle)

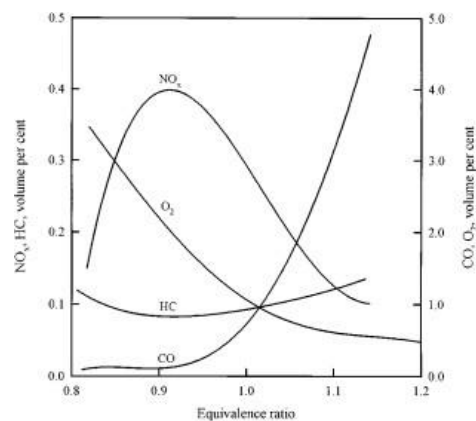


Figure 2 Spark ignition engine emissions for different fuel/air ratios

The share of toxicity that may be attributed to the ICE pollutants is well realized, an outline of which is given in the following section along with the maximum workplace (MAK) concentrations.

**Carbon monoxide (CO):** Due to its strong adherence to haemoglobin, even low concentrations may therefore be sufficient to cause suffocation. The MAK value is  $33 \text{ mgm}^{-3}$ .

**Unburned hydrocarbons (HC):** They generally cause irritation to mucous membranes in humans.

**Nitrogen dioxide ( $\text{NO}_2$ ):** Even low concentrations cause lung irritation, tissue damage and irritation of mucous membranes. A risk of acid formation is present. The MAK value is  $9 \text{ mgm}^{-3}$ .

**Nitrogen monoxide (NO):** It modifies the function of the lungs and irritates mucous membranes in humans. There is a risk of nitric acid formation. The MAK value is  $9 \text{ mg m}^{-3}$ .

**Aldehydes (H—C—O compounds):** They have a narcotic effect. Some of these compounds are believed to cause cancer, the MAK value (for example, of formaldehyde) is  $0.6 \text{ mg m}^{-3}$ .

**Lead:** Reduces oxygen absorption of the blood. The MAK value is 0.1 mgm<sup>-3</sup>.

**Sulphur dioxide (SO<sub>2</sub>):** Causes irritation of mucous membranes. It is the main cause of producing sulphuric acid in the atmosphere. The MAK value is 2 mgm<sup>-3</sup>.

**Particulates:** Part of the particulates can enter the lungs, which results in health hazard. Particulates also contain soot (as pure carbon or with deposited hydrocarbons). Soot is believed to have a carcinogenic effect.

**Carbon dioxide (CO<sub>2</sub>):** Excessive concentrations may lead to suffocation. It generally contributes to the long-term environmental damage caused by atmospheric changes (global warming or greenhouse effect). The MAK value of carbon dioxide is 9000 mgm<sup>-3</sup>.

The following two sections will give a short account on the causes of emissions from internal combustion engines for both spark-ignition engines and compression-ignition engines.

### **Causes of emissions in spark-ignition engines CO:**

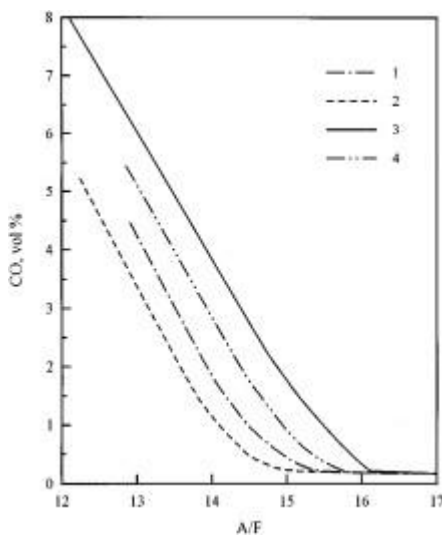


Figure 3 Variation of SI engine CO emissions with fuels of different H/C ratio with air/fuel ratio

Emissions of CO are influenced primarily by the air/fuel ratio. Figure 3 shows the CO levels in the exhaust of a conventional spark-ignition engine for several fuel compositions differing in the H/C ratio (Novak and Blumberg, 1978). For a specific air/fuel ratio, CO concentrations vary with the composition of the used fuel; the higher the H/C ratio the lower the concentrations will be. For a given fuel composition, for fuel-rich mixtures, CO concentrations increase steadily with decreasing air/fuel ratio. For fuel-lean mixtures, CO concentrations vary little with air/fuel ratio. SI engines often operate on nearly fuel rich composition at full load, which means significant emissions of CO. Even for fuel-lean mixtures, some CO will be generated because of poor mixing, local rich regions, incomplete combustion and also because there is not enough time to reach equilibrium of oxidation of CO to CO<sub>2</sub>.

**Unburned HC:** Emissions of HC are primarily due to incomplete combustion of hydrocarbon fuel. Essential components of unburned hydrocarbons are aromatics (benzene, toluene, ethyl benzene), olefins (e.g. propane, ethylene), acetylene and paraffines (e.g. methane). Unburned hydrocarbons will remain only in those areas where the flame does not propagate such as gaps close to the cylinder head gasket, piston top land, piston rings and spark plugs. HC emissions are also formed due to the quench effect, misfire as well as due to the detachment of lubricating film.

**NO<sub>x</sub>:** Figure 2 shows that the nitrogen oxides reach a maximum at a slight excess of air. Generation of these components is enhanced by high, local peak temperatures and a corresponding excess of air. The high-temperatures encourage splitting of N<sub>2</sub> and O<sub>2</sub> into their atomic constituents. Excess air ensures that sufficient oxygen is present. All engine-related parameters (e.g. load, air/fuel ratio, ignition angle, compression ratio) influence NO<sub>x</sub> emissions. NO emissions account for approx. 90—98% of all NO<sub>x</sub> emissions during engine operation.

**Aldehydes:** Aldehydes are hydrocarbons with additional embedded oxygen atoms. These O—H—C compounds are produced mainly during the combustion of fuels with high oxygen contents, e.g. alcohols.



One major representative of this pollutant group is formaldehyde (HCHO) which is already subject to regulations in places like California.

**Lead compounds:** Lead emissions of spark-ignition engines are caused exclusively by lead additives contained in gasoline. Lead is usually found in anti-knock additives based on chlorine and bromine compounds that are used to reduce the high boiling temperature of lead. The use of lead additives is decreasing rapidly as they contaminate the catalytic converters used today. A qualitative illustration of the formation mechanisms of HC, CO and NO in a spark-ignition engine is given in Figure 4 (Heywood, 1988).

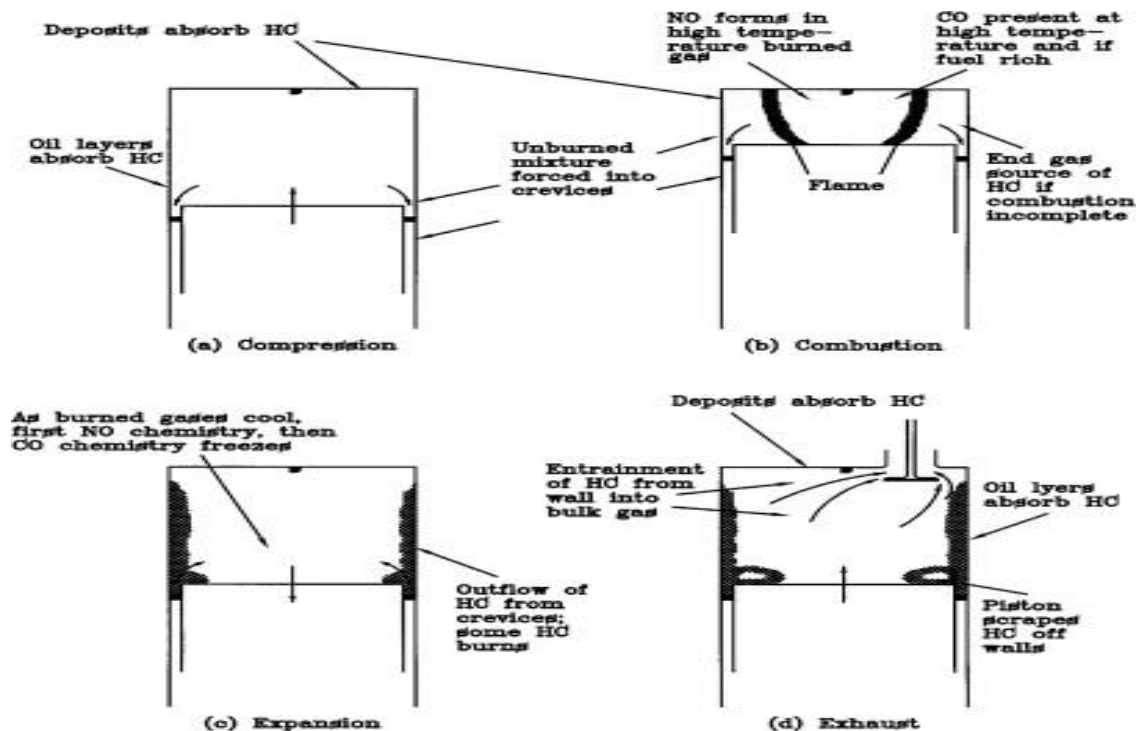


Figure 4 Summary of HC, CO, and NO pollutant formation mechanisms in spark ignition engine

### **Causes of emissions in compression-ignition engines:**

**CO:** The mean air/fuel ratio present in the combustion chamber per cycle is far higher in the diesel engine than in the SI engine. Due to a lack of homogeneity of the mixture built up by stratification, however, extremely 'rich' local zones are present. This produces high CO concentrations that are reduced to a greater or lesser extent by post-oxidation. When the excess-air ratio increases, dropping temperatures cause the post-oxidation rate to be reduced (the reactions 'freeze-up'). The CO concentrations of diesel engines therefore are far lower than in SI engines. The basic principles of CO formation, however, are the same.

**Unburned HC:** Since the air—fuel mixture is not homogeneous throughout, extremely high excess-air ratios are present in certain zones during the diesel combustion process. The higher the air/fuel ratio, the lower is the local temperature. This means that chemical reactions proceed fairly slowly or may even 'freeze-up', thus leading to increased HC emissions. In general, HC concentrations of diesel engines are lower than those of spark-ignition engines.

**NOx:** NOx concentrations are lower than in spark-ignition engines; the share of NO in the NOx emissions is slightly higher. The type of combustion process has a significant effect on nitrogen oxide formation. In engines with a divided combustion chamber, combustion initially occurs in the pre-combustion or swirl chamber under conditions of extreme oxygen deficiency. This generates high temperatures, and NOx levels are low due to a lack of air and, hence, oxygen. This process is reversed in the main combustion chamber.



Extreme excess air ratios and, hence, low temperatures also result in low NO<sub>x</sub> formation. The direct-injection diesel engine does not have the above features that keep NO<sub>x</sub> emissions low. As a result, NO<sub>x</sub> formation is approximately twice as high as in an engine with divided combustion chamber.

**Sulphur compounds:** Sulphur compounds are caused exclusively by the sulphur content of the fuel. When combined with the water produced during the combustion process, SO<sub>2</sub> produces sulphuric acid. Sulphur compounds cause problems with regard to acid rain and particulate formation via sulphates.

**Particulates:** Basically, soot emissions are part of particulate emissions. Soot formation occurs at extreme air deficiency. This air or oxygen deficiency is present locally inside diesel engines. It increases as the air/fuel ratio decreases. Soot is produced by oxygen deficient thermal cracking of long-chain molecules. A separation of hydrogen leads to C-structures showing an increasing lack of hydrogen. Acetylene and other polymerization processes lead to formation of molecules rich in carbon that form soot particulates (Homann, 1985). Once soot has formed, it can be oxidized only to a limited extent. Soot formation produces molecules with an increasingly low hydrogen content and higher weight that will finally agglomerate to form soot particulates. Particulates consist of solid (organically insoluble) and liquid (organically soluble) phases. The solid phase consists of amorphous carbon, ash, oil additives, corrosion products and abrasion products. The liquid phase consists of fuel and lubricant contents which are, in most cases, combined with soot. The hydrocarbons contained in the hot exhaust are still largely gaseous and are converted into a liquid, organically soluble phase (particulates) after cooling by turbulent intermixing with air. Particulate composition is largely dependent on the operating point and the combustion process. Figure 5 shows a typical particulate composition of diesel engine exhaust. Figure 6 illustrates how various parts of the fuel jet and the flame affect the formation of NO, unburnt HC and soot during the pre-mixed and mixing-controlled phases of diesel combustion in a direct-injection engine with swirl (Heywood, 1988).

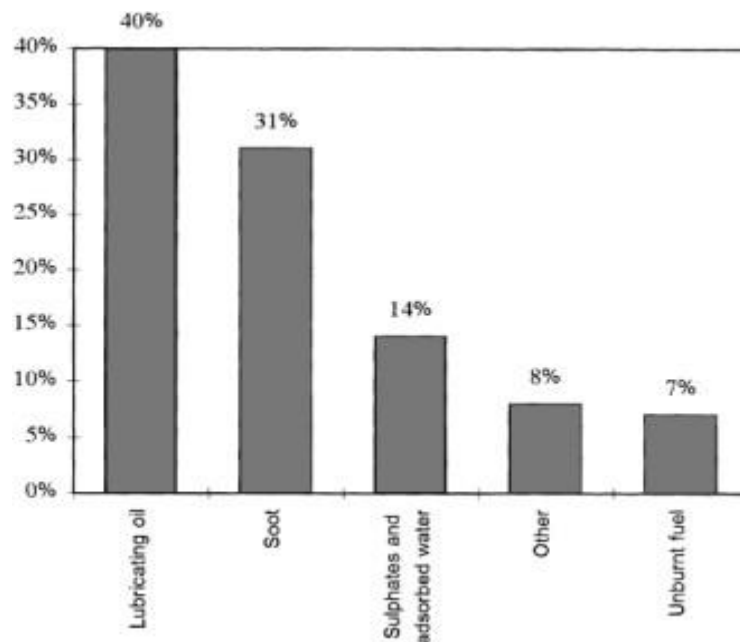


Figure 5 Particulate composition of diesel engine exhaust

# Incomplete Combustion

Internal combustion engines (ICE) are the most common form of heat engines, as they are used in vehicles, boats, ships, airplanes, and trains. They are named as such because the fuel is ignited in order to do work inside the engine. Carbon monoxide is the product of incomplete combustion in IC engine. But when there is not enough oxygen for the combustion process Carbon monoxide (CO) forms, that is incomplete combustion. Complete combustion needs ample amounts of oxygen

## Incomplete combustion

The urban air pollution is a very complicated problem. The exhaust emissions from internal-combustion engines account for a major portion of this problem. It is realized that the content and concentrations of the exhaust emissions depend on various parameters. These parameters include engine design parameters, operational parameters, exhaust gas aftertreatment, fuel types, fuel additives and lubricants.

Incomplete combustion occurs when the supply of air or oxygen is poor. Water is still produced, but carbon monoxide and carbon are produced instead of carbon dioxide.

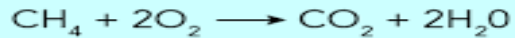
In general for **incomplete combustion**:

**hydrocarbon + oxygen → carbon monoxide + carbon + water**

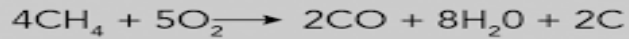
The carbon is released as **soot**. Carbon monoxide is a poisonous gas, which is one reason why complete combustion is preferred to incomplete combustion. Gas fires and boilers must be serviced regularly to ensure they do not produce carbon monoxide.

Carbon monoxide is absorbed in the lungs and binds with the haemoglobin in our red blood cells. This reduces the capacity of the blood to carry oxygen.

Complete combustion of methane



Incomplete combustion of methane



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**Carbon monoxide(CO):** Due to its strong adherence to haemoglobin, even low concentrations may therefore be sufficient to cause suffocation. The MAK value is  $33 \text{ mg m}^{-3}$ .

**Unburned hydrocarbons(HC):** They generally cause irritation to mucous membranes in humans.

**Nitrogen dioxide(NO<sub>2</sub>):** Even low concentrations cause lung irritation, tissue damage and irritation of mucous membranes. A risk of acid formation is present. The MAK value is  $9 \text{ mg m}^{-3}$ .

**Nitrogen monoxide(NO):** It modifies the function of the lungs and irritates mucous membranes in humans. There is a risk of nitric acid formation. The MAK value is  $9 \text{ mg m}^{-3}$ .

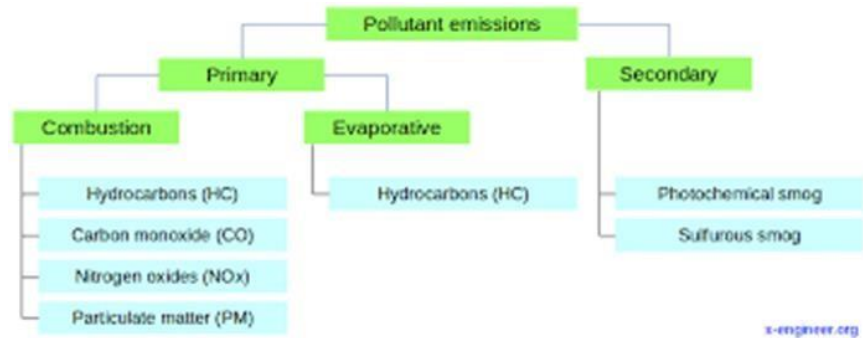
**Aldehydes(H–C–O compounds):** They have a narcotic effect. Some of these compounds are believed to cause cancer, the MAK value (for example, of formaldehyde) is  $0.6 \text{ mg m}^{-3}$ .

**lead:** Reduces oxygen absorption of the blood. The MAK value is  $0.1 \text{ mg m}^{-3}$ .

**Sulphur dioxide(SO<sub>2</sub>):** Causes irritation of mucous membranes. It is the main cause of producing sulphuric acid in the atmosphere. The MAK value is  $2 \text{ mg m}^{-3}$ .

**Particulates:** Part of the particulates can enter the lungs, which results in health hazard. Particulates also contain soot (as pure carbon or with deposited hydrocarbons). Soot is believed to have a carcinogenic effect.

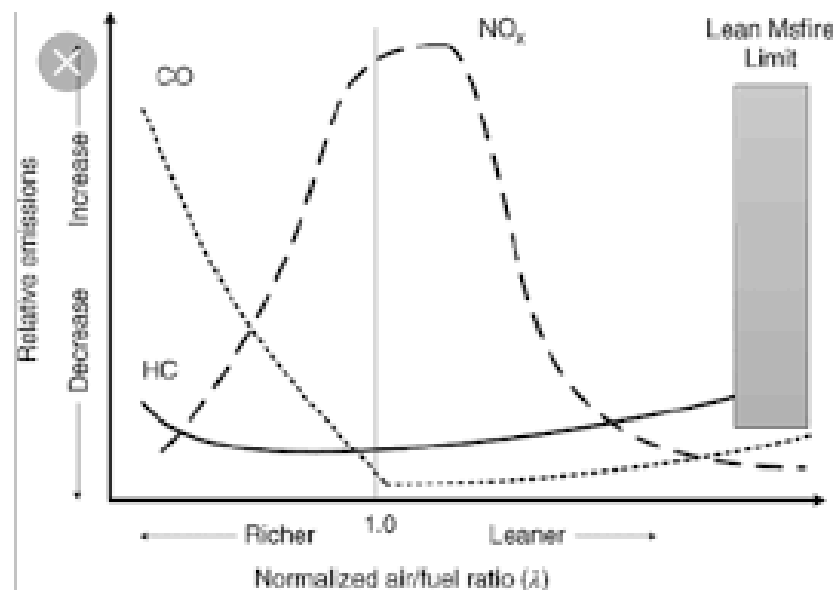
**Carbon dioxide(CO<sub>2</sub>):** Excessive concentrations may lead to suffocation. It generally contributes to the long-term environmental damage caused by atmospheric changes (global warming or greenhouse effect). The MAK value of carbon dioxide is  $9000 \text{ mg m}^{-3}$ .



**Precautions to be taken to prevent incomplete combustion are :-**

**Proper air to fuel ratio:** For complete combustion of the fuel each droplet should be surrounded by air which is equal or greater to the air-fuel ratio.

**Proper atomisation of fuel:** Fuel should be sprayed in the form of mist so that it can mix with air for proper combustion.



**Heat:** Heat required for combustion of different fuels are also different. Petrol or Gasoline need very less heat to ignite as it vaporises but not the diesel fuel. It needs much higher heat than the gasoline counterparts. Proper heat should be provided for complete combustion.

**Engine timing:** Engine timing is very crucial for complete combustion as early spark can lead to a flame travelling into the intake valve and also it can lead to knocking.

**After-burning:** Prevent afterburning by introduction of multiple spark plugs so that the entire charge ignites simultaneously because there are chances that fuel exits the chamber unburnt. So make sure all the parts in the combustion chamber gets equal heat.

## **Hydrocarbon:**

A hydrocarbon is an organic compound consisting entirely of hydrogen and carbon.

[1] 620 Hydrocarbons are examples of group 14 hydrides. Hydrocarbons from which one hydrogen atom has been removed are functional groups called hydrocarbyls.

[2] Hydrocarbons are generally colorless and hydrophobic with only weak odors.

Hydrocarbons can be gases (e.g. methane and propane), liquids (e.g. hexane and benzene), waxes or low melting solids (e.g. paraffin wax and naphthalene) or polymers (e.g. polyethylene, polypropylene and polystyrene).

The vast majority of hydrocarbons found on Earth occur in petroleum, coal, and natural gas. Petroleum (literally "rock oil" – petrol for short) and coal are generally thought to be products of decomposition of organic matter. In contrast to petroleum, is coal, which is richer in carbon and poorer in hydrogen. Natural gas is the product of methanogenesis.

## **Combustion of hydrocarbon fuels**

Hydrocarbon fuels can undergo complete combustion or incomplete combustion, depending on the amount of oxygen available.

### **Complete combustion**

- Complete combustion happens when there is a good supply of air. Carbon and hydrogen atoms in the hydrocarbon fuel react with oxygen in an exothermic reaction:
- carbon dioxide and water are produced energy is given out

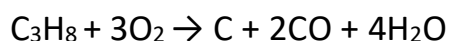
Carbon dioxide is an atmospheric pollutant. Incomplete combustion produces other pollutants.

### **Incomplete combustion**

- Incomplete combustion happens when the supply of air or oxygen is poor.
- Water is still produced, but carbon monoxide and carbon are produced. Less energy is released than during complete combustion.

For example, here is one possible equation for the incomplete combustion of propane:

**propane + oxygen → carbon + carbon monoxide + water**



### **Soot**

The carbon is released as fine black particles. We see this in smoky flames, and it is deposited as soot. Soot can cause breathing problems and it blackens buildings. It may block boilers and other appliances, or cause a fire.



**Fig:** Incomplete combustion produces smoke and invisible carbon monoxide

### **Carbon monoxide**

Carbon monoxide is a toxic gas. It is absorbed in the lungs and binds with the haemoglobin in the red blood cells. This reduces the capacity of the blood to carry oxygen. Carbon monoxide causes drowsiness, and affected people may fall unconscious or even die.

### **Hydrocarbon Combustion and Fossil Fuels**

Note that  $\text{CO}_2$  is always produced in hydrocarbon combustion; it doesn't matter what type of hydrocarbon molecule. Producing  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is actually how useful energy is obtained from fossil fuels. For this reason, it is important to distinguish between carbon dioxide and other "waste" products that arise from impurities in the fuel such as sulfur and nitrogen compounds. Wastes that arise from impurities can be eliminated with the right technology;  $\text{CO}_2$  cannot be eliminated unless the fossil fuels are not burned (used) in the first place. Not all fossil fuels have the same composition. Natural gas is composed of over 90% methane ( $\text{CH}_4$ ) which is the smallest hydrocarbon molecule. Oil tends to be composed of medium sized molecules, although composition varies greatly from one grade of crude to the next. In general, the denser the oil, the longer the carbon chains in the molecules. Finally coal contains the largest and most complex hydrocarbon molecules.

Since different hydrocarbons have different ratios of hydrogen to carbon, they produce different ratios of water to carbon dioxide. In general, the longer and more complex the molecule, the greater the ratio of carbon to hydrogen. For this reason, combustion of equal amounts of different hydrocarbons will yield different quantities of carbon dioxide, depending on the ratio of carbon to hydrogen in molecules of each.

Since coal contains the longest and most complex hydrocarbon molecules, burning coal releases more CO<sub>2</sub> than burning the same mass of oil or natural gas. This also changes the energy density of each of these fuels.

Incomplete combustion is generally due to poor mixing of the air and fuel, insufficient residence time, insufficient temperature and low total excess air.



# **CARBON MONOXIDE EMISSION IN I.C. ENGINES**

## **CARBON MONOXIDE GAS**

Carbon monoxide is a colorless, odorless gas that is very stable and has a life of 2–4 months in the atmosphere. It is a component of motor vehicle exhaust, which contributes about 53% of all CO emissions nationwide. (including CO from wildfires), and 74% of all CO emissions excluding wildfires. High concentrations of CO occur in areas with heavy traffic congestion where as much as 95% of all CO emissions may come from automobile exhaust.

## **FORMATION OF CARBON MONOXIDE IN IC ENGINES**

Carbon monoxide is the product of incomplete combustion in IC engine. It is produced by the partial oxidation of carbon containing compounds. Generally in combustion process carbon dioxide(CO<sub>2</sub>) is formed after combustion. But when there is not enough oxygen for the combustion process Carbon monoxide (CO) forms, that is incomplete combustion.

## **HARMFUL EFFECTS OF CARBON MONOXIDE**

High concentrations of CO can cause physiological and pathological changes and ultimately death. Carbon monoxide enters the bloodstream through the lungs and reduces oxygen delivery to the body's organs and tissues. The health threat from lower levels of CO is most serious for those who suffer from cardiovascular diseases, such as angina pectoris. At much higher levels of exposure, CO can be poisonous, and even healthy individuals can be affected. Visual impairment, reduced work capacity, reduced manual dexterity, poor learning ability, and difficulty in performing complex tasks are all associated with exposure to elevated CO levels. Carbon monoxide appears to have no detrimental effects on material surfaces. At ambient concentrations, experiments have not shown CO to produce any harmful effects on plant life. Carbon monoxide has been found to be a minor participant in photochemical reactions, leading to ozone formation.

## **CARBON MONOXIDE MITIGATION TECHNIQUES**

The catalytic converter is used in internal combustion engines fueled by petrol or diesel used in automobiles to reduce the emission of carbon monoxide into the atmospheric air. Shifting BS4 vehicles to BS6 vehicles and moving from diesel or petrol vehicles to electric vehicles.

## OXIDES OF NITROGEN DURING EMISSION IN I.C ENGINES

Exhaust gases of an engine can have upto 2000ppm of oxides of nitrogen. Most of this will be nitrogen oxide , with a small amount of nitrogen dioxide .  $\text{NO}_x$  is very undesirable . Released  $\text{NO}_x$  reacts in the atmosphere to form ozone & is one of the major cause of photochemical smog. .

At low temperatures , atmosphere nitrogen exists as a stable diatomic molecule. Therefore , only very small trace amounts of oxides of nitrogen are found. However at very high temperatures that occur in the combustion chamber of an engine , some diatomic nitrogen breaks down to monoatomic nitrogen which is reactive.

The higher the combustion reaction temperature , the more diatomic nitrogen will dissociate to monoatomic nitrogen & the more  $\text{NO}_x$  is formed. Although the maximum flame temperature will occur at a stoichiometric air fuel ratio (  $\phi=1$  ) . The maximum  $\text{NO}_x$  is formed at a slightly lean equivalence ratio of about  $\phi=0.95$ . At this condition flame temperature is still very high & in addition there is an excess of oxygen that can combine with the nitrogen to form various oxides.

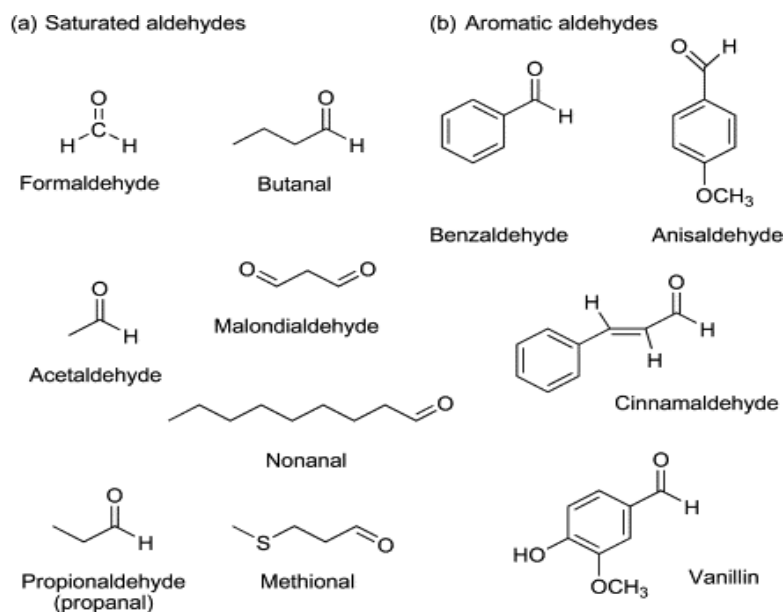
In addition to temperature the formation of  $\text{NO}_x$  depends on the pressure & air fuel ration . Combustion duration plays a significant role in  $\text{NO}_x$  formation within the cylinders .  $\text{NO}_x$  vs time relationship & supports the fact that  $\text{NO}_x$  is reduced in modern engines with fast burn combustion chambers . The amount of  $\text{NO}_x$  generated also depends on the location of the spark plug within the combustion chamber. If the spark is advanced , the cylinder temperatures will be increased & amount of  $\text{NO}_x$  created will increase . Because CI engines have a high compression ratio & higher temperature & pressure they with divided combustion chambers & indirect injection IDI tend to generate higher level of  $\text{NO}_x$  .

**Exhaust gas recirculation** is an emission control technology allowing significant  $\text{NO}_x$  emission reduction from most types of diesel engines : from light duty engines through medium & heavy duty applications right up to low speed , two stroke marine engines.



## **Introduction**

An aldehyde is a hydrocarbon group that chemically comprises a carbon atom that is doubly-bonded to an oxygen atom. It is commonly represented as the R-CHO group in organic chemistry and is known as the carbonyl group. Aldehydes are common in organic chemistry, and many fragrances contain aldehydes.



*Fig 1: Different forms of aldehydes*

## **Formation**

Aldehydes do not freely occur in nature. The most common method of synthesizing aldehydes is through the oxidation of an alcohol. This is precisely what happens in Internal combustion engines as well.

To earn savings on fuel prices, adding ethanol and other alcohol derivatives to gasoline has been a common practice since the 1980s. Brazil was the first country to adopt this policy. Due to an abundance of sugarcane, there is a vast supply of resources for the production of ethanol from sugarcane. Once this was synthesized, it was added to the fuel to improve fuel economy. Today, the United States has more than 98% of its gasoline containing ethanol additives.

Ethanol additives result in fuel blends with a lower fuel calorific value as compared to standard gasoline. Further, the Internal combustion engines would need to be specifically modified to allow the use of these ethanol-based fuels.

The advantage of using ethanol-based additives is that while they result in lower fuel economies, they are naturally synthesized. This results in lower dependence on fossil fuels and other conventional sources. In the big picture, this is actually a much more economical method. Also, if synthesized sustainably it can result in a very low carbon footprint.

Furthermore, Acetaldehyde is also formed during the incomplete combustion of hydrocarbon-based fuels. In both gasoline as well as diesel fueled vehicles, acetaldehyde is a primary pollutant in tailpipe emissions.



*Fig 2: An ethanol-based fuel petrol station in Brazil*

## **Emission**

Unfortunately, ethanol additives result in the formation of Aldehyde emissions. These emissions are harmful for humans. It is well documented that Aldehydes such as Acetaldehyde and Formaldehyde are known carcinogens. In addition to being directly harmful to humans, they also cause various environmental degradations. Formaldehyde is a major precursor to photochemical

smog. This reacts with other chemicals to ultimately result in the formation of ozone. Exposure to aldehyde emissions is known to cause acute as well as long term respiratory distress in humans. It can cause severe headaches, nausea and nosebleeds. Long term exposure to aldehydes is known to considerably increase the chances of humans developing lung cancer.

Formaldehyde, acetaldehyde and other aldehydes are produced when alcohols are oxidised. When only a 10 per cent mixture of ethanol is added to gasoline (as is common in American E10 gasohol and elsewhere), aldehyde emissions increase 40 per cent. Some study results are conflicting on this fact however, and lowering the sulphur content of biofuel mixes lowers the acetaldehyde levels. Burning biodiesel also emits aldehydes and other potentially hazardous aromatic compounds which are not regulated in emissions laws.

### **Aldehyde emissions through various fuel engines**

In alcohol run engines there is an increased emission of carbonyls (aldehydes and ketones), compared with pure gasoline on conventional engines. Aldehyde emissions (both formaldehyde and acetaldehyde), major exhaust pollutants formed as intermediate compounds due to incomplete combustion of the fuel, cause many human health disorders.

Aldehyde and alcohol emissions are the primary concerns for emission control for vehicles fueled with methanol and ethanol. Both emissions contribute to the formation of ozone. Also, aldehydes are considered to be toxic materials. However, gasoline engines emit less aldehydes than alcohol engines and have higher exhaust gas temperatures which promote the catalytic destruction of emitted aldehydes.

### **Control of Aldehyde Emissions**

The primary means of removing gaseous hydrocarbons from exhaust emissions is via complete oxidation to carbon dioxide. The ease of oxidation increases in the order:

methane < paraffins < aromatics < olefins < oxygenates

In general, when operating near stoichiometry, palladium catalysts are superior to platinum catalysts for the oxidation of methane and unsaturated hydrocarbons, while platinum catalysts are better for the oxidation of paraffins. Rhodium is an excellent catalyst for steam reforming under rich conditions, and in addition it improves the durability of platinum and palladium catalysts and has high activity for the reduction of nitrogen oxides. Therefore, the catalyst formulation can greatly influence the hydrocarbon reactivity in automotive exhaust and allows emission control catalysts to be tailored for specific fuel-vehicle-catalyst systems.

The aldehydes (formaldehyde and acetaldehyde) in the exhaust were estimated by wet chemical technique with high-performance liquid chromatography (HPLC). Aldehyde emissions increased with an increase in alcohol induction. The low heat rejection (LHR) engine showed a decrease in aldehyde emissions when compared to a conventional engine. However, the variation of injection pressure showed a marginal effect in reducing aldehydes, while advancing the injection timing reduced aldehyde emissions. LHR engine marginally reduced aldehyde emissions at the peak load operation with pure diesel. Advanced injection timings reduced aldehyde emissions in the LHR engine, while increased the same in conventional engine. Aldehyde emission decreased marginally with the increase of injection pressure in both versions of the engine.

Formaldehyde emissions were higher with methanol induction, while acetaldehyde emissions were observed to be higher with the ethanol induction in both versions of the engine. Control of aldehyde emission from alcohol fueled vehicles is needed to meet emission control requirements. “Five-Way” catalysts placed close to the engine manifold to make use of higher exhaust gas temperatures are effective for suppressing aldehyde and alcohol emissions from flexible fuelled vehicles.

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