Module III: Air Pollution Monitoring & Control

(5)

Pollution Sources: Stationary & Mobile emission Sources, Monitoring & Control of air pollutants using high volume sampler, cyclone separators, wet scrubbers, electrostatic precipitators, etc. automobile emission control.

Topics to be covered

Pollution Sources: stationary & mobile emission sources Sampling methods for gaseous and particulate pollutants

- 1. Ambient air sampling
 - a. Sampling of gaseous pollutant
 - i. Grab sampling
 - ii. Absorption in liquid
 - iii. Absorption in solid
 - iv. Cold trapping, Condensation or Freeze out sampling
 - b. Sampling of particulate pollutant
 - i. Filtration
 - ii. High volume filtration
 - iii. Sedimentation
 - iv. Electrostatic precipitation
 - v. Thermal precipitation
- 2. Stack sampling

Analysis of air pollutants (NOx, SOx, hydrocarbons, CO, particulates)

Control of Air pollution

- 1. Control of particulate emissions
 - a. Gravitational settling chamber
 - b. Cyclone separator
 - c. Fabric filters
 - d. Electrostatic Precipitators
- 2. Control of gaseous pollutants
 - a. Control of NO_x emission
 - i. Modification in operating condition

- ii. Treatment of effluent gas
- b. Control of SO_x emission
 - i. Extraction of sulphur from fuel
 - ii. Coal gasification
 - iii. Desulphurization of flue gas (dry method)
 - iv. Flue gas wet scrubbing
- c. Automobile emission control
 - i. Use of alternative fuel
 - ii. Controlling exhaust emission (Internal Combustion Engines working & Modifications, Octane No., Knocking)
 - iii. Use of ecofriendly cars

Clean air act

Questions

- 1. Suggest measures for the control of SO_x/NO_x from mobile and stationary emission sources.
- 2. Describe methods applied for control of emissions from a coal-fired thermal power plant.
- 3. How can vehicular emissions be controlled?
- 4. Discuss the benefits using catalytic converters.
- 5. In a petrol run internal combustion engine what are the major pollutant emitted if (i) lean fuel-air mixture is taken (ii) if rich fuel air mixture is taken? How can we control these emissions?
- 6. Explain electrostatic precipitator with the help of labeled diagram and state its merits and demerits.
- 7. Discuss in detail the principle and application of (a) cyclone separator (b) electrostatic precipitator used for control of industrial emissions giving examples of the industries where they are used.
- 8. Write short notes on:
- a) Bag house filter (b) Dry and Wet Scrubbers (c) Catalytic converters.
- 9. Discuss the environmental implications, if the electrostatic precipitator of a thermal power plant stops functioning.

Pollution Sources: Stationary & Mobile emission Sources

Mobile source air pollution includes any air pollution emitted by motor vehicles, airplanes, locomotives and other engines and equipment that can be moved from one location to another. They can be broadly divided into i) **Road sources** (Cars, Light Duty and Heavy Duty Trucks, Buses, Motorbikes etc.) ii) **Non-road sources** (Aircraft, Motorboats, Locomotives, Construction, Equipment etc.)

A **stationary source** of air pollution refers to an emission source that does not move, also known as a point source. Stationary sources include dry cleaners, power plants, petroleum refineries, petrochemical plants, food processing plants and other heavy industrial sources etc.

Due to the large number of mobile sources of air pollution, and their ability to move from one location to another, mobile sources are regulated differently from stationary sources.

Air Quality Monitoring

Sampling and measurement of air pollutants, generally known as air quality monitoring and is an integral component of any air pollution control programme. Through monitoring, the current trends in air quality can be evaluated by comparing the data with the regulated standards. The information so obtained is helpful in implementing control measures for reducing pollutant concentrations to acceptable levels and in accessing the effect of air pollution control strategies. For monitoring purpose, sampling procedures are developed based on the pollutant being sampled, the collection technique and device being employed, the sensitivity and selectivity of the analytical method being used.

Procedures for Sampling of Gases

Several methods are available for the collection of gaseous pollutants from atmosphere. The common ones are:

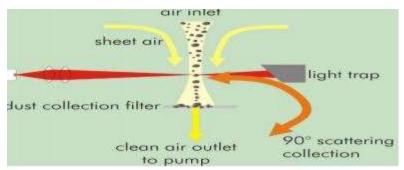
- 1. **Grab sampling:** Plastic bags, containers made up of glass or steel can be used. The containers are evacuated first and then air is allowed to fill them. When a representative sample is collected the air flow into the sample collector is stopped.
- 2. Absorption in liquid: Absorption separates the desired pollutant from air either through direct solubility in absorbing medium or by chemical reaction. The optimum conditions for efficient sampling are small bubble size and increased residence time in the absorbing device which ensures intimate contact between polluted air and absorbing medium. The absorbing devices used are glass scrubbers, packed columns etc. Example-

for absorption of SO₂ from air it is passed through an aqueous solution of H₂O₂, CO₂ can be absorbed in alcoholic solution of KOH etc.

3. Adsorption on solids: Adsorbents used in this method include activated charcoal, activated alumina, silica gel, diatomaceous molecular sieves etc. The amount of pollutant adsorbed is directly proportional to the surface area and physicochemical property of the adsorbent, temperature and pressure maintained in the sampling device. After adsorption, the sample gases are desorbed by heating the adsorbent in a current of an inert gas like N₂ or Ar at elevated temperature. In this method the gas is adsorbed on solid material at reduced temperature and then evacuated with an inert gas like N₂ or Ar.

Procedures for Sampling of particulates

- 1. Filtration: It is the most common technique for sampling particulates. The filter media could be cellulose filter paper for determination of metals and anions, silica felts for trace inorganic species, glass fibre for organic compounds.
- 2. High volume sampler: Large volume of air (up to 2000 m³ at a flow rate of 1.7 m³/min) is pumped into the sampler in which glass fiber is used as the filtration medium.



- 3. Sedimentation: Dust fall collector is used for sampling particles having diameters exceeding 5 µm (the particles with larger size drop due to gravity).
- **4. Impingement:** Dry impinger operates on the principle of impaction on a dry surface for particle collection. It contains a four-stage cascade impactor which directs the air stream against collection slides through increasingly small orifices and provides for stepwise collection of smaller particles.

Monitoring of Air Pollutant

Monitoring of NOx:

Spectroscopic and chemiluminescence are the two widely used methods for monitoring of NOx.

Spectroscopic method: Sample is collected over a solution of NaOH. To this sulphanilic acid and NEDA is added. NO₂ reacts with them and produce a reddish purple dye. Then 10 mL of this solution is taken out and H₂O₂ is added. Absorbance is taken at 543nm. The concentration of NO₂ is calculated from comparing the data with absorbance of blank and standard solutions taken at 543nm.

$$NO_2$$
 + NH_2 + NH_2 + NH_2 N

Chemiluminescence method: The air is passed through a photo thermal converter which converts NO₂ to NO. Now the sample is injected to a chemiluminescence instrument where it is treated with O₃ in presence of UV light. NO reacts with O₃ to form NO₂. At the time of its formation it is in higher energy state and return to ground state through emission of light in the range of 600-3000nm. The intensity of this light is measured by a photomultiplier. From this concentration of NO₂ and NO is calculated as the air sample also contains NO. In the next experiment the air sample is directly injected to the chemiluminescence instrument and which gives the concentration of NO₂ in the difference in the two results is the concentration of NO₂ in the air sample.

Monitoring of SO₂:

The air sample is passed through a solution of sulphamic acid which reduces NO_2 to N_2 . The out coming gas is then passed onto a solution of $HgCl_2 + KCl + HCHO$. Then *p*-rosaniline hydrochloride is added. A Reddish violet dye is produced. The absorbance of the sample is taken at 548nm. The concentration of SO_2 is calculated from comparing the data with absorbance of blank and standard solutions taken at 548nm.

$$\begin{array}{c} O \\ HO^{-}S^{-}NH_2 + NO_2 + \text{ other gases} \end{array} \longrightarrow \begin{array}{c} N_2 + \text{ other gases} \\ + HCHO \end{array} \longrightarrow \begin{array}{c} SO_2 + HCHO + H_2O \\ HOCH_2SO_3H \end{array}$$

$$\begin{array}{c} NH^{-}CH_2 - SO_3H \\ NH^{-}CH_2 - SO_3H \end{array} \longrightarrow \begin{array}{c} NH^{-}CH_2 - SO_3H \\ NH^{-}CH_2 - SO_3H \end{array} \longrightarrow \begin{array}{c} NH^{-}CH_2 - SO_3H \\ NH^{-}CH_2 - SO_3H \end{array} \longrightarrow \begin{array}{c} NH^{-}CH_2 - SO_3H \\ NH^{-}CH_2 - SO_3H \end{array} \longrightarrow \begin{array}{c} NH^{-}CH_2 - SO_3H \\ NH^{-}CH_2 - SO_3H \end{array} \longrightarrow \begin{array}{c} NH^{-}CH_2 - SO_3H \\ NH^{-}CH_2 - SO_3H \end{array} \longrightarrow \begin{array}{c} NH^{-}CH_2 - SO_3H \\ NH^{-}CH_2 - SO_3H \end{array} \longrightarrow \begin{array}{c} NH^{-}CH_2 - SO_3H \\ NH^{-}CH_2 - SO_3H \end{array} \longrightarrow \begin{array}{c} NH^{-}CH_2 - SO_3H \\ NH^{-}CH_2 - SO_3H \end{array} \longrightarrow \begin{array}{c} NH^{-}CH_2 - SO_3H \\ NH^{-}CH_2 - SO_3H \end{array} \longrightarrow \begin{array}{c} NH^{-}CH_2 - SO_3H \\ NH^{-}CH_2 - SO_3H \end{array} \longrightarrow \begin{array}{c} NH^{-}CH_2 - SO_3H \\ NH^{-}CH_2 - SO_3H \\ NH^{-}CH_2 - SO_3H \end{array} \longrightarrow \begin{array}{c} NH^{-}CH_2 - SO_3H \\ NH^{-}CH_2 -$$

Monitoring of Ozone:

A sample of air is passed to an aqueous solution of KI. The I_2 thus released is measured at 352nm.

$$KI + O_3 + H_2O \rightarrow O_2 + KOH + I_2$$

One mole of ozone releases one mole of I_2 . Therefore, this method directly calculates the amount of ozone in the sample.

Monitoring of CO:

The air sample is reduced catalytically with H₂ over Ni at 360 °C. The produced CH₄ is measured by Gas chromatographic analysis.

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

One mole of CO is reduced to form one mole of CH₄. Therefore, this method directly calculates the amount of CO in the sample.

Monitoring of hydrocarbon:

The air is passed through a column packed with a porous styrene divinyl benzene polymer. The sample collector is subsequently heated to desorb the sample for Gas chromatographic analysis. The Gas chromatography instrument is attached with a mass spectrometer. The information obtained from analyzing the sample using this technique is adequate for unambiguous identification of different hydrocarbons present in the sample.

Monitoring of particulate matter:

The particulate matter monitoring is carried out using X-ray fluorescence. The sample is first bombarded with X-ray/gamma-ray radiation. This gives rise to secondary X-ray fluorescent radiation which is passed through a monochromator. The radiation coming out of it is counted by a detector. The output is printed as a spectrum.

Control of Air pollution

The most effective method of controlling air pollution is to prevent the formation of the pollutants or minimize their emission at the source itself. The formation of pollutants at the source can be minimized by i) raw material change ii) Process change and iii) Equipment modification or replacement. The emission of pollutants at the source can be minimized by

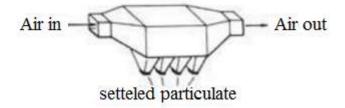
1. Control of particulate emissions

Particulate matter emitted generally range from $100 \, \mu m$ to $0.1 \, \mu m$ and even less. Therefore, choice of collection device depends upon physical and chemical characteristic of the particulates, the particle size, its concentration in the effluent gas, volume of effluent to be handled, the temperature and humidity of the effluent gas. The following equipments are in use for this purpose.

- a. Gravitational settling chamber
- b. Cyclone separator
- c. Fabric filters
- d. Electrostatic Precipitators
- 3. Control of gaseous pollutants
 - a. Control of NO_x emission
 - i. Modification in operating condition
 - ii. Treatment of effluent gas
 - b. Control of SO_x emission
 - i. Extraction of sulphur from fuel
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 - iii. Desulphurization of flue gas (dry method)
 - iv. Flue gas wet scrubbing
 - c. Automobile emission control
 - i. Use of alternative fuel (CNG, Propane, Bioethanol, Biodiesel)
 - ii. Improvement in automobile technology
 - iii. Prevention and control of vehicular pollution (Internal Combustion Engines working & Modifications, Octane No., Knocking)
 - iv. Use of ecofriendly cars

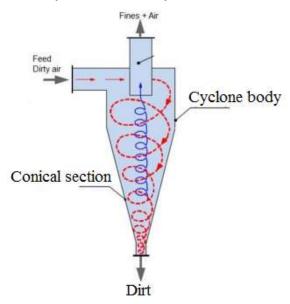
Gravitational settling chamber

The flue gas is passed onto the big chamber, where the velocity is reduced. Therefore, larger particles settle due to gravitational force. However, only particles of size $> 50 \, \mu m$ are settled. Since most of the troublesome particles have sizes much smaller than $50 \, \mu m$, these devices are normally used as precleaners prior to passing the gas stream through high efficiency collection devices. However, they require less capital, easy to install and operate and their maintenance is simple.



Cyclone separator

Cyclonic separation is a method of removing particles from gas stream through establishing a high speed rotating flow within a cylindrical or conical container called a cyclone. Air flows in a helical pattern, beginning at the top (wide end) of the cyclone and ending at the bottom (narrow) and then the flow is reversed. This generates a centrifugal force and particles in the rotating stream find difficulty to follow the tight curve of the stream and strike the wall. Then fall to the bottom of the cyclone where they can be removed. The cleaner air exit from the top of the cyclone.

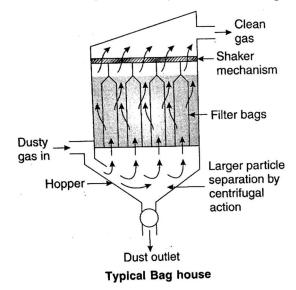


Cyclones are often used as precleaners to remove particles greater than 20µm in diameter. Smaller particles that escape the cyclones can then be collected by more efficient control equipment like bag filters and electrostatic precipitators. Cyclones are relatively inexpensive since they have no

moving parts and they are easy to operate. They are able to operate at high temperatures and pressures. The most common type of cyclone is known as reverse flow cyclone separator.

Fabric filters

A baghouse or fabric filter is an air pollution control device that removes particles from effluent gas using high-temperature fabrics capable of withstanding temperatures from 70 °C and up to 260 °C depending on the fabric material used. Most baghouses use long, cylindrical bags made of high-temperature fabrics as a filter medium. Dust-laden gas or air enters the baghouse through hoppers. Here, larger particles are separated and collected by centrifugal action and then the gas is directed into the baghouse compartment. The gas is drawn through the bags, dust particles strike the fibers and get collected on the filter media surface. The collection is continued until air can no longer move through the filter. At this point, sufficient pressure drop occurs and the cleaning process begins through shaker mechanism. Cleaning can take place while the baghouse is online (filtering) or is offline (in isolation). When the compartment is clean, normal filtering resumes.



Advantages:

- High removal efficiency for rough and fine substance with efficiency of 99%
- Relatively simple in use
- Relatively low pressure drop

Disadvantages:

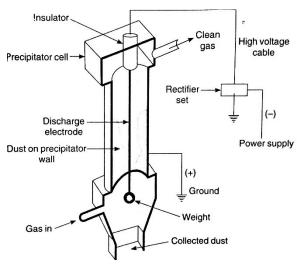
- Their large size
- High construction cost
- Can be operated for effluent gas below 260 °C

- Sparks must be extinguished before they reach the filter cloth in order to avoid explosion.
- Soot must be avoided as they can combust spontaneously which may lead to explosion.
- Sticky substance must be avoided

They can be applied in Chemical industry, Metallurgical industry, Cattle feeding industries, Feeding industry, Waste disposal industry etc.

Electrostatic Precipitators

An electrostatic precipitator (ESP) is a filtration device that removes fine particles, like dust and smoke, from a flowing gas using the force of an induced electrostatic charge (a corona discharge). The precipitation system consists of a positively charged (grounded) collecting surface and a high voltage discharge electrode suspended from an insulator (at the top) and held in position by a weight at the bottom. A very high DC voltage, generally of the order of 50 kV, is used which causes a corona discharge near to the negative electrode, setting up an electric field between the emitter and the grounded surface. The particle ladden gas enters near the bottom and flows upward. The gas near to the negative electrode is ionized upon passing through the corona. as the negative ions migrate towards the grounded surface, the electrostatic field draws the particles to the collector surface where they get deposited.



Advantages of electrostatic precipitator:

- Pressure drop and hence power requirement is small compared to that in other devices, economical and simple to operate.
- An ESP applies energy only to the particulate matter being collected and therefore is very energy efficient (in the form of electricity).
- 99% efficiency obtainable, very small particles can be collected wet or dry.

• Can handle both gases and mists for high volume flow.

Disadvantages of electrostatic precipitator:

- Relatively high initial cost and large space requirement.
- Sensitive to variable particulate loadings or flow rates.
- Not suitable for combustible particles.
- Performance may vary significantly depending on process and electrical conditions.
- Safeguard of operating personnel from high voltage is necessary.

In electricity, a **corona discharge** is an electrical discharge brought on by the ionization of a fluid surrounding a conductor that is electrically charged. Spontaneous corona discharges occur naturally in high-voltage systems unless care is taken to limit the electric field strength. The corona will occur when the strength (potential gradient) of the electric field around a conductor is high enough to form a conductive region, but not high enough to cause electrical breakdown or arcing to nearby objects. It is often seen as a bluish glow in the air adjacent to metal conductors carrying high voltages.

Control of gaseous pollutants

The most detrimental effect comes from NO₂ which forms from the reaction of NO and oxygen. Once in the atmosphere, the NO₂ is involved in a series of reactions that form secondary pollutants. The NO₂ can react with sunlight and hydrocarbon radicals to produce ground level ozone/photochemical (urban) smog and acid rain constituents. NOx is associated with respiratory disorders, corrosion of materials and damage to vegetation. NO₂ also absorbs the full spectrum of light and can reduce visibility in excess concentration (brownish color).

SO₂ is a colourless gas with a pungent, irritating odour and taste. It is highly soluble in water forming weakly acidic sulphurous acid. When SO₂ combines with the O₂ in air, SO₃ is slowly formed which may combine with water vapor to produce H₂SO₄ (contributing to acid rain). In addition, H₂SO₄ may react with NH₃ or other cations (in atmosphere) to form particles of ammonia sulfate or some other sulfate. These small particles are responsible for urban particulate material (PM₁₀, PM_{2.5}) and visibility problems. SO₂ can harm crops and trees, turns leaves yellow and decreases the growth rate of crops. SO₂ corrodes metal, and causes building materials and textiles to deteriorate and weaken. SO₂ irritates the throat and lungs and can damage respiratory system.

1. Control of NO_x emission

a. Modification in operating condition

- i. Low-excess air combustion: Generally combustion is done in presence of 10 to 20% excess air to ensure complete combustion of the fuel. However, this excess air provides sufficient O₂ for reacting with nitrogen. Lowering the % of excess air significantly decreases formation of NO_x. Ex- in case of pulverised coal firing, NO_x decreases from 600 ppm at 20% excess air to 175 ppm when only 1.4% excess air is supplied. However, lowering the % of excess air results in lowering of carbon combustion efficiency. It has been observed that combustion efficiency fell from 99% at 20% excess air to 90% at 1.4% excess air.
- ii. Two stage combustion process: Power plants emit about 50 to 1000ppm of NO_x. Such emission can be reduced by 10% through the most effective two stage combustion method. In this method all the fuel is fired with only 90-95% of the total air required at the bottom of the furnace followed by secondary air injection higher up in the furnace to complete the combustion.

b. Treatment of effluent gas

i. Absorption of NO_x by liquid:

• The effluent gas is passed onto an aqueous suspension of Calcium hydroxide (absorbing medium), the NO_x reacts to form calcium nitrite and results in reduction of NO_x upto 200 ppm. The calcium nitrite can then be treated with H₂SO₄ to convert it to more valuable calcium nitrate.

$$NOx + Ca(OH)_2 \longrightarrow Ca(NO_2)_2$$

$$2H_2SO_4 + 3Ca(NO_2)_2 \longrightarrow 2CaSO_4 + 4NO + Ca(NO_3)_2 + 2H_2O$$

$$Calcium nitrite$$

$$Calcium nitrite$$

Calcium nitrate is used as a fertilizer and the evolved NO may be used in nitric acid plant as raw material.

• Similarly aqueous Mg(OH)₂ can be utilized for the purpose.

ii. Reduction of NO_x

• Selective reduction may be carried out using catalyst or in absence of a catalyst. In the **Selective catalytic reduction** (SCR), nitrogen oxides are converted to N₂, and H₂O with the aid of a catalyst such as titanium oxide, zeolites (are micro porous, aluminosilicate minerals) and NH₃.

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O$$

 $2NO_2 + 4NH_3 + O_2 \longrightarrow 3N_2 + 6H_2O$
 $NO + NO_2 + 2NH_3 \longrightarrow 2N_2 + 3H_2O$

several secondary reactions:

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

 $2NH_3 + SO_3 + H_2O \longrightarrow (NH_4)_2SO_4$

The porous nature of catalyst provides high surface area essential for reduction of NOx. However, the pores are easily clogged by a variety of compounds present in the flue gas. Therefore, many SCRs have a finite life due to unknown amounts of contaminants in the untreated gas.

• In a selective non-catalytic reduction process either ammonia or urea is injected into the firebox at a location where the flue gas is between 760 and 1,090 °C to react with the nitrogen oxides formed in the combustion process to form N₂, CO₂ and H₂O.

$$NH2CONH2 + H2O \longrightarrow 2NH3 + CO2$$

$$4NO + 4NH3 + O2 \longrightarrow 4N2 + 6H2O$$

$$NO + NO2 + 2NH3 \longrightarrow 2N2 + 3H2O$$

2. Control of SO_x emission

- i. Extraction of sulphur from fuel: Sulphur in coal is present in both inorganic (mainly as iron disulphide, Fe₂S) and organic forms (cystin, thiols, sulphides). Washing of coal can reduce the inorganic sulphur upto 30%. But such methods may add 20% or more to the cost of coal. The organic sulphur can be removed by chemical processing.
- ii. <u>Coal gasification</u>: Gasification is done by blowing oxygen and steam (water vapor) over coal while being heated. It is essential that the oxygen supply should be insufficient for complete oxidation of the fuel. Thus partial oxidation of coal produce a gaseous mixture of CO₂, CO, methane, water vapor, and H₂. Sulfur impurities in the coal are converted to hydrogen sulfide and carbonyl sulfide, from which sulfur can be easily extracted, typically as elemental sulfur or sulfuric acid, both valuable byproducts. Nitrogen oxides, another potential pollutant, are not formed in the oxygendeficient (reducing) environment of the gasifier; instead, ammonia is formed from reaction of nitrogen with hydrogen. The ammonia can be easily stripped out of the gas

stream. Another advantage is that when oxygen is used in the gasifier (rather than air), the carbon dioxide produced by the process is in a concentrated gas stream, making it easier and less expensive to separate and capture. Once the carbon dioxide is captured, it is prevented from escaping to the atmosphere, where it could otherwise potentially contribute to the "greenhouse effect."

- iii. <u>Desulphurization of flue gas (dry method):</u> The dry techniques for the desulphurization can be achieved by
 - Alkalized alumina process: In this process, the dust-free flue gas is fed to a reactor wherein the adsorbent, a porous form of sodium aluminate (Na₂O.Al₂O₃), adsorbs SO₂. during adsorption, The SO₂ and O₂ in the flue gas react with adsorbent

$$Na_2O.Al_2O_3 + SO_2 + O_2 ---> Na_2SO_4 + Al_2O_3$$

The spent material is then treated with H_2 in a reactor at about 680 °C to produce H_2S and regenerate the adsorbent.

$$Na_2SO_4 + Al_2O_3 + 4H_2 ---> Na_2O.Al_2O_3 + H_2S + H_2O$$

The sodium aluminate pillets are reused and H₂S gas is used for production of sulphur. The major problem of this method is related to maintenance of the granular strength of the adsorbent.

- Activated Carbon process: In this process activated carbon is used as adsorbent which provides larger surface are for adsorption of SO₂. This process is attractive due to its low cost. However, main limitation of activated carbon as adsorbent is its tendency towards spontaneous ignition and problems associated with thermal regeneration.
- iv. <u>Flue gas wet scrubbing:</u> One of the most widely used process is **Stone and Webster-Ionics scrubbing process**. It is based upon reaction of caustic soda (NaOH) solution with SO₂ to form sodium sulphite and bisulphites.

$$2NaOH + CO_2 ---> Na_2CO_3 + H_2O$$

 $Na_2CO_3 + SO_2 ---> Na_2SO_3 + CO_2$
 $Na_2SO_3 + \frac{1}{2}O_2 ---> Na_2SO_4$
 $Na_2SO_3 + SO_2 + H_2O ---> 2NaHSO_3$

The resulting solution is treated with H₂SO₄ in desorption tower to get sodium sulphate and concentrated SO₂ gas which is captured and removed from the solution.

$$2NaHSO_3 + H_2SO_4 ---> Na_2SO_4 + 2SO_2 + 2H_2O$$

The resulting solution is passed on to an electrolytic regeneration cell which converts Na₂SO₄ into NaOH and H₂SO₄. The NaOH is returned back to scrubber and the acid is used in the desorption tower. The overall reaction is:

$$Na_2SO_4 + 3H_2O \longrightarrow 2NaOH + H_2SO_4 + H_2 + \frac{1}{2}O_2$$

SO₂ is used in many industrial processes such as chemical preparation, refining, pulp-making and solvent extraction. SO₂ is also used in preservation of food because it prevents bacterial growth.

http://www.eia.gov/todayinenergy/detail.cfm?id=10151

3. Automobile emission control

. Use of alternative fuel

Alternative fuels are non-conventional or advanced fuels other than conventional fuels like; *fossil fuels* (petroleum, coal, and natural gas), nuclear fuels (uranium and thorium, as well as artificial radioisotope fuels that are made in nuclear reactors). Some well-known alternative fuels include compressed natural gas (CNG), propane, biofuels like biodiesel and bioethanol.

CNG: Natural gas, a fossil fuel, is comprised mostly of methane and is one of the cleanest burning alternative fuels. It has to be used in the form of compressed natural gas (CNG) or liquefied natural gas (LNG) to fuel cars and trucks due to less energy density in its natural form. Dedicated natural gas vehicles are designed to run on natural gas only, while bi-fuel vehicles can also run on gasoline or diesel.

Advantages:

- The auto-ignition temp of CNG is 540 °C which is much higher than auto-ignition temp of petrol (250 °C) and diesel (225 °C). Safest gaseous fuel.
- Octane number of CNG (127) and petrol (97). Superior fuel than petrol, don't need any anti knock additive.
- CNG is currently cheaper than petrol and diesel.
- CNG offers the cheapest mileage cost per kilometer.

• CNG is much more environmental friendly, as it is completely combusted. The CO emission is reduced by 70 to 90% and CO₂ emission reduced by 15 to 20%.

Disadvantages:

- Cetane no of CNG (10) and diesel (45) which makes it unsuitable for compression engine.
- Initial cost of installing a CNG kit is high (~ Rs. 50,000)
- Lacks initial pick up
- Very few CNG stations
- CNG kit adds extra weight to car and occupies space that could have been used for carrying bags and other goods.
- High maintenance cost
- Higher insurance cost

Propane: HD₅ contains 95% propane and 5% propylene. It is used as fuel in liquefied form.

Advantages

- Easier to compress than natural gas.
- Much lighter than CNG tank.
- It's a by-product of oil refinery.
- Minimum NO_x emission

Disadvantage

- Low pick-up
- Slower speed
- Starting troubles
- Frequent adjustment requirement

Biodiesel: It is made from the reaction of lipids (e.g., vegetable oil, soybean oil, animal fat) with an alcohol producing fatty acid esters mainly long-chain alkyl (methyl, ethyl, or propyl) esters. Biodiesel can be used alone, or blended with petrodiesel (diesel obtained from refining of petroleum, generally we call it diesel) in any proportions.

- 100% biodiesel is referred to as **B100**
- 20% biodiesel, 80% petrodiesel is labeled **B20**

- 5% biodiesel, 95% petrodiesel is labeled **B5**
- 2% biodiesel, 98% petrodiesel is labeled **B2**

Advantages

- is a renewable energy source unlike petroleum.
- Reduces the dependency of a country on foreign oil reserve as it is produced domestically.
- It has better fuel economy.
- It can be blended with other energy resources and oil.
- Less polluting. Lack of sulphur in **B100** (100% biodiesel) extends the life of catalytic converter.
- Biodiesel fuel can also be used in existing diesel engines without making any alterations.
- Can be distributed through existing diesel fuel pumps, which is another advantage of biodiesel fuel over other alternative fuels.
- The lubricating property of the biodiesel may lengthen the lifetime of engines.

Disadvantages

- Quality of Biodiesel may vary depending on the biofuel crop from which it is prepared.
- Not Suitable for use at low temperatures as it forms gel
- Food Shortage: Since biofuels are made from animal and vegetable fat, more demand for these products may raise prices for these products and create food crisis in some countries.
- **Increased use of Fertilizers:** As more crops are grown to produce biofuels, more fertilizer is used which can have devastating effect on environment.
- Water Shortage: The use of water to produce more crops can put pressure on local water resources.
- Use of Petroleum Diesel to Produce Biodiesel: It requires much amount of energy to produce biodiesel fuel from crops as energy is needed for sowing, fertilizing and harvesting crops. Apart from that, raw material needs to be transported through trucks which may consume some additional fuel. Some

scientists believe that producing one gallon of biofuel needs energy equivalent to several gallons of petroleum fuel.

Bioethanol: This is created through the fermentation of beet, sugar cane, potato, wheat barley etc. It can be blended with petrol.

Advantages

- The octane number of bioethanol is at around 105. More complete combustion. It has better fuel economy
- The use of ethanol-blended fuels such as E85 (85% ethanol and 15% gasoline) can reduce the net emissions of greenhouse gases by as much as 37.1%, which is a significant amount. Ethanol-blended fuel as E10 (10% ethanol and 90% gasoline) reduces greenhouse gases by up to 3.9%.
- is a renewable energy source unlike petroleum.
- Reduces the dependency of a country on foreign oil reserve as it is produced domestically.

Disadvantages

- Quality of bioethanol may vary depending on the biofuel crop from which it is prepared.
- Burning 1 liter of ethanol gives 34% less energy than burning the same amount of petrol.
- Food Shortage: Since biofuels are made from animal and vegetable fat, more demand for these products may raise prices for these products and create food crisis in some countries.
- **Increased use of Fertilizers:** As more crops are grown to produce biofuels, more fertilizer is used which can have devastating effect on environment.
- Water Shortage: The use of water to produce more crops can put pressure on local water resources.
- ethanol is hygroscopic and thus has high corrosion aggressiveness.
- ii. Exhaust emission control (Internal Combustion Engines working & Modifications, Octane No., Knocking, Improvement in automobile technology)

The four stroke internal combustion engines based on petrol contains-

Intake stroke: The descending piston draws in a mixture of fuel and air through intake valve.

Compression stroke: the raising of piston compresses the air/fuel mixture in the cylinder. As the piston approaches the top of the compression stroke, the spark plug fires, igniting the mixture.

Power stroke: the burning mixture expands and forces the piston down which turns crankshaft and delivers power to drive the engine.

Exhaust stroke: the exhaust valve opens and the raising piston forces the combustion products out of the cylinder through the exhaust system and into the air. [this is the exhaust system, which need to be controlled to minimise the emission of the pollutants]

The internal combustion engines based on diesel comprises of the same four strokes as petrol engine, however, in intake stroke only air is drawn and is compressed in the compression stroke. Then diesel is injected into the cylinder where it is self-ignited by the hot compressed air.

Air to fuel ratio (AFR) and lean/rich fuel:

The single most important factor in determining emissions from a four stroke internal combustion engine is the ratio of air to fuel in the mixtures. To analyze that mixture ratio and its impact on emission, let us begin with the stoichiometry of the gasoline combustion. Modern gasolines are blend of various hydrocarbons, an average formulation can be represented as C₇H₁₃.

For complete combustion in oxygen,

$$C_7H_{13} + 10.25 O_2 \longrightarrow 7CO_2 + 6.5 H_2O$$

In air N_2 is present, 3.76 mol of N_2 accompanying in every mole of oxygen (based on air contains ~78% nitrogen and 21% O_2 by volume). Thus $10.25 \times 3.76 = 38.54$ moles of N_2 can be placed each side of the reaction which will give-

$$C_7H_{13} + 10.25 O_2 + 38.54 N_2 \longrightarrow 7CO_2 + 6.5 H_2O + 38.54 N_2$$

Where any oxidation of N₂ to nitrogen oxides has been neglected.

Stoichiometric Air to fuel ratio:

1 mol of $C_7H_{13} = 97 g$

 $10.25 \text{ mol of } O_2 = 328 \text{ g}$

 $38.54 \text{ mol of } N_2 = 1079 \text{ g}$

Considering air to be made up only oxygen and nitrogen, the air fuel ratio needed for complete oxidation of gasoline is = air/ fuel = 14.5 ()

Therefore, AFR of 14.5:1 is the stoichiometric ratio for gasoline. An air-fuel mixture having < 14.5 (air): 1 (fuel) ratio is called a rich mixture or rich AFR. An air-fuel mixture having > 14.5 (air): 1 (fuel) ratio is called a lean mixture or lean AFR.

Example for gasoline:

15.0:1 = Lean

14.5:1 = Stoichiometric

13.0:1 = Rich

When the air-fuel mixture is ignited by the spark plug, a flame front propagates from the spark plug. The now-burning mixture raises the cylinder pressure and temperature, peaking at some point in the combustion process. The rich AFR mixture (denser) raises the peak cylinder pressure, therefore increasing the probability of knock. As the AFR is leaned out, the temperature of the burning gases increases (combustion moves towards near completion), which also increases the probability of knock. The probability of knock can be reduced by adjusting the AFR to richer mixture, and retarding ignition timing. These parameters need to be optimized together to yield the highest reliable power.

Exhaust emission can be controlled by following improvement in automobile technology:

- Developing exhaust system reactors for complete combustion.
- Treating exhaust gases with devices such as absorbers/adsorbers
- Updating engine design
- Using additives to improve combustion (reduce CO)
- Using catalytic converters

Earlier two way catalytic converter were used to control the hydrocarbon (HC) and CO pollutant, but as NOx has also immense effect on the atmosphere, a three way catalytic converter was developed which can control all the three important pollutants.

Three way catalytic converter: A three way catalytic converter is able to oxidize HC and CO to H₂O and CO₂ while reducing NOx to N₂. It is very effective in controlling emissions near stoichiometric conditions where the engine performance and efficiency are greatest. Finely divided Pt used as a catalyst (Pd and Rh can also be used) which reduces NOx to N₂ (through NH₃) and oxidize HC and CO to CO₂ and H₂O.

Lead (Pb) free gasoline should be used to avoid poisoning of Pt catalyst by Pb which reduces the catalytic activity of Pt.

A three-way catalytic converter has three simultaneous tasks:

- o Reduction of NO_x: $2NO + 2CO ---> N_2 + 2CO_2$, $2NO + 5H_2 ---> 2NH_3 + 2H_2O$
- Oxidation of CO, NH₃ and HC: In order to oxidize residual CO, NH₃ and HC, air is passed over a second catalyst Pd or Pt

$$RH + O_2 ---> CO_2 + H_2O$$

 $2CO + O_2 ---> CO_2$
 $4NH_3 + 3 O_2 ---> 2 N_2 + 6 H_2O$

However, the major disadvantage is during warm up period of engine, at that time the temperature in the catalytic chamber is not high enough to bring about efficient reaction.

iii. Use of ecofriendly cars

Helium based cars: Cars using Helium as a fuel are experimentally running in US and Japan. Costwise helium will cost less than 25% of the conventional fuels (petrol and diesel) and will be 100 times more ecofriendly and will not give any kind of exhaust gas. However, its mass scale utilization have not started yet. In countries with temperate weather these cars have chances for blown up. Hence, scientists are working hard to find a catalyst which can keep the temperature under control even in tropical countries so that car can run smoothly.

Electric Cars: The electric car is under development since 1990. A two seater electric car weighs up to 1060 Kg, 40% of which consists of 26 lead acid batteries. With full charge, the car can run up to 144 km and then recharge is needed. It can accelerate to 96 km/hr in 8.5 sec with maximum speed of 128 km/hr. In order to compensate its heavy weight and to maximize the distance it can cover, the following measures are under research for the use of;

- low rolling resistance tyres
- Aluminum chassis
- wind cheating plastic skin
- regenerative braking system that helps to recapture energy that is lost when brake is applied

Nickel metal hydride batteries that doesn't depend on H₂SO₄ as an electrolyte. It
may last up to 10 years while the lead batteries have to be replaced every two to
three years.

Fuel cell cars: The fuel cell technology is based on mixing H₂ and O₂ to form water, heat and a lot of electricity. In its basic form, a fuel cell consists of two chambers containing two oppositely charged electrodes, separated by a semipermeable membrane. Therefore, this type of fuel cell is also known as PEM (polymer exchange membrane or proton exchange membrane) fuel cell. Hydrogen is introduced into the chamber in which it gets split into hydrogen atoms in the presence of platinum catalyst and ionized immediately due to the electrical potential between the electrodes. The proton passes through the membrane and combines with oxygen atom in the other chamber to form water. In the meantime the electron in the first chamber are drawn as electric current. Therefore, the utility of fuel cell lies in their ability to harness efficiently the energy released by the chemical reaction and converting it into electricity. In addition to use in car, if fuel cells ever worked properly, they would make small scale electricity production cheap and environmentally clean (end product is water vapor).

Advantages

- It is a zero-emission fuel when used in a contained cell capable of 'reversing' the reaction.
- No harmful emission.
- Hydrogen is readily available and renewable.
- Non-toxic, therefore, environmental friendly

Disadvantages

- Production of hydrogen is expensive, time consuming and lot of processing is required for its purification
- Storage and transport is a concern.
- It's highly inflammable
- We may reduce our dependency on fossil fuels by using hydrogen but in turn we are actually using them for its production.

Types of fuel cell

PEM fuel cells (sometimes called **PEMFCs**) are currently favored by engineers for powering vehicles, but they're by no means the only design possible. Just as there are many kinds of batteries, each using different chemical reactions, so there are many kinds of fuel cell too. Spacecraft use a more primitive design called an **alkaline fuel cell** (AFC), while much greater amounts of power could be generated by an alternative design known as a **solid-oxide fuel cell** (SOFC). **Microbial fuel cells** have an extra feature: they use a tank of bacteria to digest sugar, organic matter, or some other fuel and produce either an electric current (which can be used to power a motor) or hydrogen (which can power a fuel cell in the usual way). Another possibility is to have a vehicle with a solar panel on the roof that uses the Sun's electricity to split water into hydrogen and oxygen gases with an electrolyzer. These gases are then recombined in the fuel cell to produce electricity. (The advantage of doing things that way, rather than using the Sun's energy directly, is that you can store up hydrogen in the daytime when the Sun's shining and then use it to drive the fuel cell at night.)