What are advanced waste gas treatments used?

**Advanced physical-chemical waste gas treatment**

 These advanced oxidation process and are:

* Direct UV photolysis
* O3/UV process
* Heterogeneous photo catalysis (TiO2/UV)
* Advanced oxidative scrubbers (UV/H2O2, O3/H2O2)
* Non-thermal plasma technologies

**Advanced biotechnological waste gas treatment**

* Membrane bio-filtration
* Foamed emulsion bioreactor: an innovative bioreactor concept
* Microbial communities as indicator for bioreactor performance
* Biological waste gas treatment by fungi

**CO2-capture and sequestration**

Difference between the traditional chemical oxidation and advanced waste gas treatment

During the traditional chemical oxidation, we need to oxidize the pollutants and we use oxygen, the rate of oxidation with O2 at ambient temperature and pressure is too slow to be economically feasible and the high temperatures are needed (thermal oxidation: 800-1100°C), or alternative to reduce this temperature (catalytic oxidation: 300-400°C). This means that the traditional oxidation use high energy and cost and the hazardous by-products can be formed (*e.g.* dioxins). At high temperature when chlorine is present in the waste, dioxins are formed.

In the advanced oxidation process (AOP), we need to work at ambient temperature and pressure and we use high energy oxidants: O3, H2O2 and OH.

What is the principle of direct UV photolysis?

* We need UV photons and UV photons with energies from 4eV to 7eV (wavelength of 300 to175 nm, respectively) is used to break molecular bonds through photo-dissociation. The lower the wavelengths, the higher the energy.

1ev=1.6\*10-19joule; 1v=1joule/coulomb; E=hν=h\*c/λ

E=6.6\*10-34J\*3\*108ms-1/300\*10-9m=6.6\*10-19j/s =6.6\*10-19j/s/1.6\*10-19joule/eV=4eV

* The UV light is divided into UVa: 320-400nm; UVb: 280-320nm and UVc: 100-280nm. The UV b and UVc are harmful part and are arrested by O3 in atmosphere.
* The efficiency of direct photolysis depends on a number of factors:
* Molar absorptivity of the organic compounds at the used wavelength (beer Lambert law): A=ε\*c\*l with ε the molar absorptivity, c is the concentration and l is the path length. Log A=log I/Io.
* Quantum yield of the reaction( how many moles can be degraded for absorbed photons)
* Intensity of the UV-source
* Most compounds have extinction coefficients above 250nm, this techniques work at low wavelength and high energy UV light.



* By consequence, many organic compounds can undergo direct photolysis in the presence of UV radiation

**What is the Sources of UV light**

* The source of the UV sources is from low-pressure mercury lamps: monochromatic light at 254 nm (the second emission line at 185nm is absorbed by encasing). Effective for breaking hydrogen bonds, *e.g.* in DNA molecules (absorb light at 265 nm); commonly used for disinfection. At 254 nm the molar absorptivity of quite compounds is very low and cannot be used in this advanced techniques
* For the cleaving of intra-molecular bonds, more energetic deep UV photons (< 250nm) are more effective. Commercially available:
* Low-pressure mercury lamps with high purity silica encasing that does not absorb the mission line at 185 nm
* Medium- and high- pressure mercury lamps (second generation UV systems) with dopants (metal halides based on iodine) to increase the number of UV lines in the deep UV region
* Xenon flash lamps (third generation UV systems) that are based on pulsed corona discharge technology and emit a broad band of deep UV radiation
* Xenon excimer lamps that emit monochromatic light at 172 nm (vacuum UV) that can dissociate water molecules

What are the applications of UV photolysis

* Application of the UV photolysis of waste gas treatment is in chlorinated compounds to destroy the C-Cl bond
* Most research in this field has focused on chlorinated (volatile) organic compounds: These compounds pose major difficulties to traditional treatment technologies
* Because of the low bonding energy of the C-Cl bond, compared to C-C and C-H bonds the UV can be used to destroy this bond and you get the chlorine radical.

 HClC=CCl2 + h*v*  HClC=CCl. + Cl.

* The chlorine radical is more stable and attach another molecule and the chain reactions is initiated resulting in the high apparent quantum yields

 Cl. + HClC=CCl2 HCl2C-CCl2

* You need to monitor if other byproducts which are toxic are formed. The formation of noxious photo-stable by-products (*e.g.* phosgene or DCAC: Dichloroacetochloride can make necessary further treatment

 HCl2C-CCl2. + O2 HCl2C-CCl2OO.

 2 HCl2C-CCl2OO. 2 HCl2C-CCl2O. + O2

 HCl2C-CCl2O. HCl2C-CClO (DCAC) + Cl.

* Odor treatment: photolysis of sulphurous compounds is initiated by the photo-dissociation of the H-S bond:

 H2S + hυ → HS. + H.

 RHS + hυ → RS. + H.

* Radicals formed are effectively degraded further by reaction with oxygen to odorless compounds such as sulfates and sulfonates

Principle of O3/UV process

* We use UV and add ozone; ozone (O3) is fed into a UV photo-reactor In the presence of water vapor, UV sensitized ozone decomposition yields OH radicals that oxidize organic compounds
* Since ozone exhibits an absorption maximum at 254 nm, traditional UV sources can be applied in the O3/UV process. In the O3/UV process, organic compounds are degraded via a combination of different reaction mechanisms :
* Direct UV photolysis(limited at 254nm)
* Direct ozonation
* Indirect OH radical oxidation
* Cl chain reactions (if pollutants are chlorinated compounds)
* Relative contribution of these mechanisms depends on UV radiation wavelength and intensity, ozone concentration, pollutant concentration and presence of moisture
* Since low wavelength UV light generates ozone, it could be said that gas-phase direct UV photolysis processes are essentially UV/O3 processes which combine UV and ozone:
* Direct photolysis pollutant + hυ to give non harmful products if no oxygen is present.
* Gas phase direct UV oxidation at 185nm gives ozone and you don’t need to doze ozone:

3 O2 + hυ (185 nm) → 2 O3

* oxidation at 254nm you have to dose ozone and the photolysis of ozone gives an oxygen radical:

O3 + hυ (254 nm) → O2 + O(1D) this oxygen radical is not stable and react with water to generate the OH radical which destroy the pollutants:

O (1D) + H2O → 2 OH

* At 254nm we don’t need the high energetic UV, we work at 254nm and we dose the ozone.

Application of O3/UV process

* Most of research in this field has focused on chlorinated (volatile) organic compounds: *e.g.*: chloroform, tetrachloromethane, trichloroethene, tetrachloroethene, 1,1,2- trichloroethane
* Direct ozonation contributed to the oxidation of chloroethenes
* OH reactions contributed to the oxidation of chloroform, 1,1,2-trichloroethane and to a lesser extent trichloroethene
* Neither ozone nor OH significantly enhanced the oxidation of tetrachloromethane
* UV/O3 process faces similar obstacles as direct photolysis:
* Although ozone promotes further decomposition, complete mineralization remains difficult
* Additional treatment remains necessary; you have to take care on the degradation products that can be formed
* Furthermore, ozone needs to be removed from the gas stream before discharge

Explain the heterogeneous photo catalysis principle

* Heterogeneous Photo-catalysis is a catalytic process during which one or more reaction steps occur by means of electron-hole pairs photo-generated on the surface of semiconductor materials illuminated by light of suitable energy
* Photo-catalysis makes use of the catalyst, heterogeneous means that you have 2 phases, the solid phase and gaseous phase.



* In a semi conductor you have the electron bands and the electrons need to fill the last band which is the valence band.
* If the semi conductor is irradiated, energy of the photons causes the electrons to left the valence band to the empty conduction band. Electrons can go back to the valence band by loosing energy and we have to avoid this
* We want to create a redox reaction, a reduction at the conduction band: oxidants like O2 are transformed to O2 radical which is a reductants and the oxidation is at the valence band to liberate electrons, this oxidation can be the oxidation of the reductants like H2O; OH and RH to give the oxidants such as OH radical and R radical.
* The energy (near UV light) to supply has to be higher than the band gap energy (ΔEg).
* A photo-catalytic reaction proceeds on the surface of semiconductors via several steps:
* Production of electron-hole pairs by irradiating the semiconductor with light having an energy higher than the band-gap energy of the semiconductor
* Separation of the photo-generated electrons and holes due to trapping by species that are adsorbed on the semiconductor
* Redox reactions between the trapped electrons and holes and the adsorbates present on the surface
* Desorption of the products and reconstruction of the surface

Choice of catalyst in the heterogeneous photo catalysis

* Semiconductor photocatalysts: TiO2, ZnO, WO3, CdS, ZnS, CdSe, CdTe can be used. by using these catalyst we can use the UVa. An increasing toward using high wavelength, low wnwegy lamps is needed.
* Research standard photocatalyst: *TiO2 (DegussaP25)*
* It has high absorptivities for UV radiation. Band-gap energy of 3eV(rutile) and 3.2eV (anatase), corresponding with near-UV radiation of 388 nm for anatase and 413 nm for rutile, produced by UV black light lamps
* It exhibits good adsorption characteristics for many contaminants
* The redox potential of its valence and conduction band edges are suitable for oxidizing organic contaminants
* It displays high photocatalytic activity while being highly resistant to photocorrosion
* It is inexpensive and non-toxic



* The higher the band gap, the more energy you need, but you cannot use the smaller band gap because the recombination is fast for the small band gap and this reduce efficiency. We have to avoid the recombination. You have to avoid the recombination by trapping the electrons either by the reaction O2/O2 radical or reaction of OH/OH radical.
* The valence band should have high redox potential. If the oxidation potential is more positive than OH/OH radical (valence band), the oxidation occurs and if the conduction band is more negative than O2/O2 radical (conduction band), the reduction occurs. The 2 condition are fulfilled with TiO2 atanase as you see on the diagram above.

Mechanisms of the heterogeneous photo catalysis

* **Initiating reaction step**

TiO2 + hν TiO2 (e- + h+) with λ ≤388 nm

* **Reaction with holes**
* Indirect reaction: catalyst react with water to produce OH radical or react with OH ions to produce the OH radical and OH radical destroy the pollutants:

TiO2 (h+) +H2Oads TiO2 + H2Oads.+ TiO2 + .OHads + H+

TiO2 (h+) + -OHads TiO2 + .OHads or indirect

* Direct reaction: the catalyst react with pollutants directly

TiO2 (h+) + RHads TiO2 + RH.+ads TiO2 + R.ads + H+

* **Reaction with electrons**
* indirect reactions that produce OH

 TiO2 (e-) + O2 TiO2 + O2.-

 O2. - + H+ HOO.

2HOO. H2O2 + O2

H2O2 + O2.- HO. + O2 + OH

H2O2 + hν 2 HO.

TiO2 (e-) + H2O2 TiO2 + -OH + .OH

* direct reaction with halogenated compounds

TiO2 (e-) + RXads TiO2 + RXads.- TiO2 + Rads. + X

Applications of the heterogeneous photo-catalysis

* works at ambient temperature and pressure conditions
* Large volumes of slightly contaminated air (pollutant concentration < 500 ppmv)
* Wide range of organic and inorganic pollutants:
* Alkanes and alkenes
* Alcohols and ketones
* Aromatic compounds
* Organic acids
* Heteroatom containing organic compounds (*e.g.* odorous compounds)
* Halogenated compounds (TCE: research standard)
* NH3, H2S,

Heterogeneous photo-catalysis process parameters

* Relative humidity: competitive adsorption versus OH-radicals; too much water will stick on surface of catalyst and catalyst will not have access to pollutants. only one monolayer of water is minimal
* Temperature: affect adsorption-desorption equilibrium, reaction kinetics. At low temperature adsorption will occurs and at high temperature desorption will occur.
* Irradiation conditions: wavelength, light intensity
* Oxygen concentration: threshold concentration, oxygen has to trap electrons
* Pollutant concentration: the techniques is used for low concentration of pollutants
* Photocatalyst properties: e.g. specific surface area(m2/g; how much surface to adsorb a particular mass), UV-VIS absorbance
* Desactivation of the photocatalyst during reaction. Polymer at high concentration can be formed and block the surface( toluene at high concentration)
* Reactor-related parameters: residence time, flow regime, mass transfer.

Principle of advanced oxidative scrubbers

**Physical scrubbing**

* Scrubbers: mass transfer from gas to liquid phase. The concentration in the gas decrease and the concentration in the liquid increases. The Henry constant H=Conc in water at eq/Conc in gas at eq. if another compound apart from water is used the equilibrium constant Ka is the term used.
* The driving force is the difference between the concentration in gas at the starting minus the concentration of gas at equilibrium and is equal to the concentration in water at the start minus the concentration in water at equilibrium
* No driving force, no mass transfer if the concentration in the start is equal to the concentration at the equilibrium

**Reactive scrubbers/chemical scrubbing**

* It is physical combined to chemical scrubbing, there is a mass transfer and when the pollutants are in liquid we add the chemical to convert pollutants to non harmful compounds. The equilibrium is not reached.
* Reactive scrubbers (alkaline, acid or oxidative scrubbers) : reagents are added to the scrubbing liquid and contaminants react upon absorption and the driving force is maintained

**Advanced oxidative scrubbers**

* Advanced oxidative scrubber : OH-radicals generated via an advanced oxidation process are used as oxidants instead of traditional oxidants (O3, H2O2, NaOCl)
* Due to high reactivity of OH radical, advanced oxidative scrubbers can also be used for less reactive compounds
* Since the life time of OH radical is very short, OH radical should not be dosed in the scrubbing liquid storage tank (as in traditional oxidative scrubbers), but initiation of the oxidation process should take place in the scrubber reactor itself
* Two advanced oxidation processes haven been applied in advanced oxidative scrubbers : UV/H2O2 and peroxone process (O3/H2O2)

**UV/H2O2 advanced oxidative scrubber**

* Waste gas stream is contacted with a scrubbing liquid, *e.g.* in a bubble column. A column with small bubbles of liquid and the H2O2 is dosed via the scrubbing liquid inside the column. The column is surrounded UV light to irradiated the system by photons of 254 nm. Pollutants are present in gas stream and the gas is allowed to pass in the column with scrubbing liquid+H2O2.The OH radicals are created inside the scrubber itself
* H2O2 + hυ → 2 .OH
* .OH + RH → R.+H2O(hydrogen abstraction: alkanes)
* .OH + R2C=CR2 → R2C(OH)-CR2.(electrophylic addition: alkenes, aromatics)
* .OH + RX → RX+. + -OH (electron transfer)
* .OH + .OH → H2O2 (radical-radical recombination)
* **Reactions to avoid**
* If an excess of H2O2 is used, OH radicals will produce hydroperoxyl radicals (.OOH), which are much less reactive
* Scavenging of reactions OH radicals by HCO3- and CO32- has to be avoided in this system

.OH + HCO3- → H2O + CO3.-

.OH + CO32- → HO- + CO3. -

* Advantages of H2O2 as an oxidant:
* readily commercial available
* Thermal stability and storage on-site
* Infinite solubility in water
* Costs are less sensitive to scale of operation than for ozone

**O3/H2O2 oxidative scrubber**

* Instead of using UV; you add ozone in the waste gas stream; the gas phase contains pollutant and ozone (O3). PH will be an important parameter.
* Hydrogen peroxide (H2O2) is dosed in the scrubbing liquid inside the reactor. Hydroxyl radicals are produced by combination of H2O2 and O3. Both liquid and gas phases are contacted with each other in a scrubber (e.g. bubble column).
* H2O2 will dissociate and gives HO2 radical that react with ozone to give back this radical and ozone radical or this radical dissociates to give oxygen radical and hydrogen. The combination of ozone radical and hydrogen radical gives HO3 radical which is dissociated to provide OH radicals.
* H2O2 ↔ HO2-. + H+ pKa = 11.7
* HO2-. + O3 → HO2.+ O3.-
* HO2. ↔O2.- + H+ pKa = 4.8
* O2.- + O3 → O2 + O3.-
* O3.- + H+ ↔ HO3.  pKa = 6.15
* HO3.→ O2 + .OH
* Overall reaction: H2O2 + 2 O3 → 3 O2 + 2.OH
* Decomposition of organic compounds is by two mechanisms: direct oxidation by O3 (selective) and indirect oxidation by OH radicals (non selective). The kinetics are fast for OH radicals (TCE=17M-1s-1) than O3(TCE=4\*109M-1s-1). TCE: change of concentration/time.
* Important parameters for O3/H2O2 process
* PH of the liquid phase has effects on OH radical production and scavenging.
* Gas and liquid flow rate has effects on mass transfer from gas to liquid phase.
* The concentration ratio H2O2/O3 has an effect on the radical concentration and scavenging
* Pollutant concentration
* The target compounds are benzene,toluene, xylene; 1,1,1trichloroethane,trichloroethene,tetrachloroethene and dimethylsulphide.

Principle of non thermal plasma thecnology

* Possibility of destroying pollutants by using plasma whichis a partial ionized gas containing neutral atoms and molecules and a quasi equal concentrations of positive and negative charged particles (electrons, ions). Plasma is quasi neutral.
* In an electric field, charged particles accelerate and collisions with other gas constituents occur, resulting into the formation of new charged particles. Charge losses result finally into stable plasma.

**Thermal plasma (equilibrium plasma)**

* the constituents of the gas are in thermal equilibrium, at higher pressure, the frequency of collisions is higher, resulting into a higher energy transfer to the background gas
* The energy is also transferred to the gas and heat the gas.

**Non-thermal plasma (non-equilibrium plasma)**:

* The mass of electron (me) is 9.02.10-31 kg and the mass of ion (mion) is 5000-50000 me. There is a large difference in mass.
* Due to large difference in mass, electrons in the plasma have a higher mean energy (Te) which is greater than 1 eV than the other constituents of the gas which are ions, atoms and molecules with energy (Tg) and is less than 0.1 eV.
* The energy putted in the system is selectively transferred to electrons and the bulk gas does not get energy.
* The non thermal plasma technology is good as compared to thermal plasma technology. The essential of a non-thermal plasma technique is that the available energy is added selectively to the plasma electrons (no energy loss by heating the background gas). Energy is putted in electrons and the electrons are homogeneously distributed
* Through electron-impact dissociation and ionization of the background gas molecules, the energetic electrons produce free radicals (oxygen and hydroxyl radicals) and additional electrons which, in turn, oxidize or decompose organic molecules
* Electrons may also react directly with the pollutants, which allows the treatment of perhalogenated saturated compounds (*e.g.* freons)
* 2 processes can be used, either by using electron beam irradiation or by electrical discharge process
* In electron beam irradiation: High energy electrons are generated outside the reactor chamber under high vacuum in an electron accelerator. The electron beam generated is injected into the reaction chamber through a thin foil titanium window
* In electrical discharge process: High energy electrons are produced by an electric field generated between two high voltage electrodes within the reactor chamber. Plasma is generated by accelerating electrons in the field under atmospheric conditions; collisions with other gas constituents will transfer energy from the electrons to the rest of the gas. Local heating of the gas will result in a spark discharge in which the plasma is confined to a small filament. However, different reactor configurations have been developed that extend non-thermal discharge plasma processing to atmospheric pressure conditions
* Dielectric barrier discharges: sparks are prevented by a dielectric barrier between the metal electrodes
* Pulsed corona discharges: the applied voltage time during pulses is too short to generate spark discharges
* Flow stabilized discharges: a fast gas flow cools the electrodes, preventing spark discharges
* Application of non thermal plasma technology include:
* **Destroying NOx that cause** acid rain and photochemical smog by oxidation of NOx by means of O3, O, OH or by reduction of NOx to N2 by means of NH3, ureum
* **Destroying Sox that cause** acid rain and photochemical smog by oxidation : SO → SO2 → SO3 → H2SO4 or by synergetic effect between SO2 and NOx
* **Destroying the COx:** toxic monoxide carbon and a greenhouse gas CO2 by CO2 + e → CO + O + e or CO2 + e → C + O2 + e
* **Destroying VOC: the Target compounds are**: ethane, propane, butane, pentane, vinyl chloride, ethyl chloride,chloromethane, bromomethane, dichloromethane,1,1,1trichloroethane,trichlorofluoroethane,tetrafluoromethane,tetrachloromethane, tri-chloroethene, formaldehyde, methanol, acetone, methyl ethyl ketone, benzene, toluene, styrene. The reactor configurationscan be pulsed corona discharge, dielectric packed bed, silent discharge, electron beam, surface discharge. The electron beam is more effective than pulsed corona. Hybrid systems exists as a combination of non-thermal plasma and adsorbents or (photo)-catalysts which is the possibility to combine plasma technology with UV. Large variety on experimental conditions and reactor configurations makes it difficult to compare results
* **Deodorization:** the Target compounds are acetaldehyde, NH3, sulphurous compounds (H2S, SF6, CH3SH, (CH3)2S, CS2, COS and SO2

Traditional biotechnological waste gas treatments



* In traditional biological waste gas treatment, the bio-film is covered by a water layer, forming a barrier between the micro-organisms and hydrophobic compounds in the air phase.
* You have a carrier material and on the carrier material you have the bio-film, the waste gas pollutants has to be transferred from gas to liquid before they are degraded. Hydrophobic compounds like hexane do not transfer to water and cannot be removed.
* We use microorganisms which are brought in contact with waste gas and pollutants become the food for microorganisms. The decomposition of food by microorganisms gives CO2, minerals and transformation to biomass. The pollutants itself should be biodegradable.



* As you see on the diagram above, the characteristics of the waste is very important, the system works for low concentration of waste gas stream and medium to high flow loading rate. By combining the concentration g/m3 and the loading rate m3/h you get g/m3\*m3/h=g/h which is the amount of g entering in the bioreactor per hour.
* The traditional biological waste gas treatment techniques were biofilter, biotrickling filter and bioscrubber.

Discuss the bio-filter as tradition biological techniques



* It is a container filled with organic carrier material which can be peat or compost. The filter material should not be dry; it should have 60% of humidity because enough water is a requirement for the microorganisms. Microorganisms grow as a bio-film in the bio-filter. Nutrients like N,P and others are necessary. The PH is important because the the bacteria do not work on acid condition. You have to add PH buffering compounds to maintain PH to neutral
* Waste gas stream is humidified and allowed to pass from the bottom to the top and microorganisms grew in the bio-filter as a bio-film assimilates the pollutants. The residence time depends on the type of wastes.
* The filter material should have a high specific surface area, you need a lot of space and this can be a problem.
* Can treat agriculture waste gas stream and industrial effluents

Discuss the bio-scrubber as tradition biological techniques



* It is has an absorption column and a bioreactor. The scrubbing aqueous solution passes in the column from up to down the column and the air with pollutants from bottom to top in the column.
* There is a transfer of pollutants from the gas to the scrubbing liquid and the scrubbing liquid with pollutants is transferred in the reactor with an activated sludge, suspended in a nutrient solution and the pollutants are degraded.
* After the pollutants are degraded the content of the bioreactor is decanted to remove the biomass and the water is recirculated back in the absorption column
* It is easy to control the PH and nutrients because the bioreactor is separated with the absorption column.

Discuss the bio-trickling as tradiion biological techniques



* The column is packed with the inert materials and the bio-film grows on the surface of the packaging materials. The polluted air passes from top to bottom and at the same time the scrubbing liquid is sprinkled at the top of the column. You need aqueous solution to adjust the PH and nutrients
* There is a scrubbing and biodegradation at the same time
* The treated air and treated water is collected at the bottom

Advanced biotechnological waste gas treatments

* the advanced biological waste gas treatment includes:
* the membrane bio-filtration,
* 2 phases partitioning bioreactor: Foamed emulsion bioreactor and 2 phase portioning membrane bioreactor
* Study of microbial communities as indicator for bioreactor performance
* biological waste gas treatment by fungi

Discuss the membrane bio-filtration reactor



* Liquid and air phase are separated by a membrane. Pollutants like VOC diffuse through the membrane , reach the bio-film and are subsequently degraded by the micro-organisms in the bio-film. The membrane act as the carrier of the bio-film
* Because of the separation of the liquid and air phase, waste air containing hydrophobic compounds like hexane can be treated effectively
* Oxygen is supplied from the air phase, while nutrients are present in the liquid phase
* Since the liquid phase is continuously recirculated, the pH can easily be corrected and toxic degradation products can be removed
* Types of the membrane bio-filtration include:
* **Porous membranes:** The advantage of this is that has low mass transfer resistance. The pollutants diffuse easily through the poles and reach the bio-film. The disadvantage of the porous membranes is the bio-fouling.
* **Dense membranes:** has no poles in the membranes, the compounds dissolves in the membranes and diffuse through the membranes. The permeability is equal to the solubility times the diffusion. The advantage is that you have less chance on bio-fouling but you have a higher mass transfer resistance as a disadvantage of this type of the membrane
* **Composite membranes:** combine the porous and non porous, one part is porous and another part is non porous. It has a porous support layer and a dense top layer. Combines the advantages of both types of membranes
* Different types of membranes configuration includes:
* flat membranes : plate-flame and spiral wound ; they are mainly UF/RO
* Cylindrical membranes: tubular, capillary and hollow fiber, they are mainly MF/UF. The hollow fibers membrane bioreactor has an internal diameter < 0.5 mm and a very large specific membrane-gas contact area. the capillary membrane bioreactor has an internal diameter between 0.5 mm-10 mm

Process taking place in membrane bio-filtration

* Mass transfer and microbial kinetics of a gaseous pollutant within a membrane bioreactor module can be described as a sequence of events:
* Bulk mixing of the contaminant in the air entering the bioreactor
* boundary layer transport
* transport through membrane
* exit from the membrane and dissolution and diffusion into the bio-film
* diffusion through and degradation within the bio-film
* Boundary layer transport through the liquid phase
* Subsequent mixing and degradation within the cell suspension

Factors affecting the flux over the membranes

* Flux :J=Kov\*A(Cgas–H Cliquid)

With J the flux in g/s; Kov : is the kinetic parameter and is the overall mass transfer coefficient (m/s) and depends on the permeability ; A is the membrane surface area (m²); Cgas and Cliquid are concentrations is gas, liquid phase (g/m3) and H is the dimensionless Henry-constant and depends on vapor pressure and the solubility.

* The factors affecting the flux are:
* Concentration gradient
* Membrane surface area
* Permeability
* Vapor pressure and Solubility

Application of membrane bio-filtration

* Target compoundsare compounds with a broad range of air-water partitioning coefficients (five orders of magnitude) , both inorganic and organic compounds , most research on single compounds degradation, less research on the degradation of mixtures of compounds, lab-scale experiments. These target compounds are mostly hexane, propylene , methanol, 1-butanol,dichloromethane,1,2-dichloroethane, trichloroethylene, benzene, toluene, ethylbenzene, xylene, ammonia, dimethyl sulphide, nitric oxide ,
* Below is the application of the traditional biological waste gas treatment as compred to the membrane.
* Biowasfilter is the biotrickling filter with 2 types of carrier material(grof and fijn), this works only at low concentration and low henry constant (hydrophyric compounds) and the compounds with a very high Henry constant (hydrophobic compounds) cannot be degraded in this system
* Biowasser is the bio-scrubber and works at high concentration and low Henry constant
* The bio-filter works at low concentration and can works for more hydrophobic compounds as compared to bio-scrubber and trickling filter except the membrane.
* The membrane covers a wide range from low to high concentration and works for both hydrophilic and hydrophobic compounds.The gas residence time is equal to the volume of the reactor/flow rate and is very small for membrane reactor compared to bio-filter and bio-trickling filter. Membranes bio-reactor can handle the more heavily polluted waste gas at a small residence time while the bio-filter and bio-trickling can handle only less heavily polluted gas streams. The residence gas time for the bio-filter is small compared to the bio-trickling filter.



Advantages of membrane bio-filtration

* Incorporation of mass transfer of gaseous pollutants across a media with high specific surface area and low diffusion length
* Presence of high biomass concentrations
* Ability to continuously remove biomass to prevent clogging at high loading rates
* Ability to remove by-products and add pH buffers, nutrients, co-metabolites
* Ability to treat low solubility compounds (e.g. hexane, ethene)
* Ability to treat gas streams at elevated temperatures
* Ability to inoculate bioreactor with specific cultures for poorly biodegradable compounds
* Separation of the microbial process from the gas being treated
* Operation at lower pressure drop than in bio-filters
* Gas and liquid flow rates can be varied independently without flooding or foaming
* Modular design and so easy to scale-up by adding more membrane
* No gas channeling

Disadvantages of the membrane bio-filtration

* High investment costs
* The technology has not been demonstrated at full-scale
* Removal declines over time as the bio-film ages resulting in decreased biomass activity and the bio-film thickness increases
* Hollow fiber bundles tend to clump when bio-film growth is high, resulting in fiber tangling and thus reduction of available membrane surface area
* Biomass grows in porous membranes, resulting in declining reactor performance; there is no good method available for cleaning the porous membrane bioreactor systems

Principle of 2 phase partitioning bioreactor

* The limitation of traditional techniques to degrade the hydrophobic compounds can be solved by the 2 phase partitioning bioreactor or membrane bioreactor
* This system use foamed emulsion bioreactor (FEBR) which is emulsion of highly active pollutant degrading microorganisms and a water-immiscible organic phase. Instead of working with pure water, this system use emulsion which is a combination of non aqueous phase (organic phase) and a water phase.
* The emulsion is converted into foam (by addition of a surfactant) during waste air treatment. The microorganisms are in water phase and at the boundary of the organic phase.
* Pollutants are transferred from air to the emulsion phase; the hydrophobic compounds are transferred to organic phase and degraded.



* Contaminated air stream is introduced into the foam column through a gas sparger
* Emulsion consisting of mineral medium, active culture, organic phase (oleyl alcohol) and surfactant (DC-100 silicone) are introduced at the bottom of the reactor
* The pollutants are degraded inside the tank and clean air comes out with the foam and sent to the defoamer for de-foaming. The de-foaming is done by continuously spraying the foam with the emulsion from the cell reservoir this cell reservoir contains the emulsion that was de-foamed before or you can use the water as a deforming agent.
* Liquid is returned to the cell reservoir prior to being recycled to the foam column
* Less energy is required to pass air in moving foam than passing air through the solid material.

**Advantages of 2 phase portioning bioreactor**

* Increased gas/liquid interfacial area provided by the fine foams
* Increased driving-force for mass transfer resulting from the presence of a water-immiscible organic phase (Henry coefficient>>partition coefficient between gas and organic phase)
* Since no packing material is present in the FEBR, bed clogging and associated pressure drop problems are avoided
* High-density culture of actively growing organisms is present, resulting in high volumetric pollutant removal rates

Challenges of the 2 phase partitioning bioreactor

* Foam stability at high air velocity
* Supply enough oxygen to the cell culture

Principle of 2 phase partitioning membrane bioreactor



* It is the same as the 2 phase portioning bioreactor except that the membrane is introduced between air and the emulsion phase. The non aqueous phase is putted on the membrane and the hydrophobic pollutants are degraded in a non aqueous phase.
* The use of this Non aqueous phase extent the capacity of a bioreactor to treat high concentration stream.

Microbial communities as indicators for bioreactor performance

* Bio-filters are nowadays used in industry for treating odorous airstreams or airstreams containing low pollutant concentrations.
* However, little information is available about the composition and the dynamics of the complex microbial communities present in the bio-filter material, and about their relationship with *e.g.* pollutant removal and resistance towards stress conditions.
* Recent research aims at finding a relationship between parameters obtained from microbial community fingerprinting and pollutant removal efficiencies in compost bio-filters.
* By changing the parameters the efficiency can change and by improving the microbial communities, the performance can be improved. The following can be adopted in case the system is not working:
* Adapt the flow
* Adapt the humidity
* Adapt the PH
* Adapt nutrients

Analytical techniques to study microbial communities

**Traditional techniques**

* Microscopic analysis: can give information on unstable morphology of microorganisms and small differences between bacteria
* Plating bacteria: there is a need for choice of nutrient medium for the selectivity and counting number of bacteria and/or isolation of one group of bacteria, it is only applicable to 0.1 to 10% of bacteria
* PLFA (polyfosfolipid fatty acid) analysis: the Polyfosfolipid fatty acids are characteristic components of cell membrane. You perform extraction of PLFA and GCMS analysis

**Molecular techniques**

* Analysis of nucleic acids : DNA and RNA)
* polymerase chain reaction: PCR
* denaturating gradient gel electrophoresis: DGGE
* Fluorescence in situ hybridization: FISH ; by using this, you can visualize the biological toluene degraders and you can investigate the active bacteria and its distribution to see whether it is homogeneous distributed or if it is distributed only in one part

Microbial communities evaluation tools

**Presence of microbial species**

* DGGE profiles of bacteria for different subgroups like eubacteria, ammonium oxidizing bacteria are analyzed
* Each band represents a species
* Appearance or disappearance of species can be followed as a function of time and operational parameters

**Community diversity**

* From DGGE-profiles, diversity indices is the number of species (S) which is the number of bands
* From DGGE-profiles, diversity indices can be calculated as Shannon diversity index (H)
* H = - ∑Pi log Pi with Pi = ni/N with ni as the intensity of one band and N as the ∑ ni or total intensity

**Community dynamics**

* Community dynamics (CD) = 100 – R with R is the mean Pearson correlation (%) of samples during time interval of 15 days and is a measure for similarity between two different lanes of bands
* If the bands are the same, R=100% and no dynamic community in this case.

Microbial communities state of the art (achievement)

* Molecular microbial community fingerprinting analysis allows to:
* identify the dominant active bacteria
* determine community diversity
* observe spatial heterogeneity
* observe dynamics of community change
* The link between microbial community composition/dynamics and bio-filter H2S removal can now further be explored

Principle of biological waste gas treatment by fungi

* We can use fungi instead of using the bacteria; fungi can work at conditions that the bacteria cannot work with.
* Possible problems with traditional bioreactors that fungi cn solve:
* n-alkanes smaller than octane are not assimilated by most hydrocarbon-degrading bacteria and fungi can assimilate those alkanes
* Poor performance often caused by acidification and drying out of the bioreactor. The fungi can work on low moisture content and are less sensitive to acid conditions.
* Degradation of highly hydrophobic compounds (*e.g.* hexane, ethene) is problematic because of mass transfer limitations of compounds with high Henry coefficients through the water layer covering the bio-film. Fungi can deal with hydrophobic compounds.
* For specific compounds, specialized pure or mixed cultures are needed to inoculate the bioreactor.

Advantages of fungi driven biodegradation:

* Fungi are generally tolerant to relative low pH-values
* Fungi are generally tolerant to relative low water activity
* Fungi form a three-dimensional network (hyphae) which provide a large surface area in contact with the gas stream so that a direct mass transfer from gas phase to the biological phase is realized
* Since fungi can work at lower moisture contents, mass transfer limitations for hydrophobic compounds are less
* For specific hydrophobic compounds, higher elimination capacities can be obtained in bioreactors inoculated with specialized fungi

Limitation of fungi as active species

* Difficult to purify complex waste gases by bioreactors inoculated only with fungi (specificity). Fungi are more specific toward a certain pollutant while bacteria have a wide application range to degrade pollutants than fungi.

Why the CO2 capture and sequestration

* CO2 is among the greenhouse gases: H2O, CO2, O3, CH4, N2O, CFC (chlorofluorohydrocarbons). The green house gases have effects on transmission of solar irradiation and absorption of IR irradiation cause the earth’s temperature to increase to 15°C instead of -18°C
* The heating up of the earth surface is 0.6 – 1.0°C during the last 150 years. The prediction is that further increase of average year temperature of 1.4°C– 5.8°C (1990-2100) this will results in big climatological and ecological problems (*e.g.* floods, disappearance of plant and/or animal species) can be expected
* Increase of CO2 concentrationfrom 280 ppmv (1750) to > 400 ppmv (since 2013), caused by anthropogenic emission: Combustion of fossil fuels (70-90%): domestic, traffic, industrial activities and reduction of forest areas
* CO2-emission for 2/3 responsible for global warming effect

CO2 international registration

* 1991 : first meeting of Intergovernmental Negotiation Committee (INC)
* 1992 : United Nations Framework Convention on Climate Change (UNFCCC)
* 1992 : United Nations Conference on Environment and Development (UNCED) → Earth Summit declaration (implementation in 1994)
* 1997: Kyoto-protocol on Industrial countries: emission reduction of greenhouse gases of 5% in 2008- 2012 compared with that in 1990 and European Union: emission reduction of 8%
* 2015: United Nations Climate Change Conference in Paris
* 20-20-20: European policy for 2020 compare to 1990. The policy is that there should be 20% reduction of energy consumption, 20% reduction of the green house gases and 20% of energy that is used should come from the renewable energy

CO2 emission reduction strategies

**Preventive strategies**

* Decreased use of fossil fuels (currently 85% of energy supply)
* Use of alternative energy sources
* Use of nuclear energy
* Use of Renewable energy : solar and wind energy

**CO2-fixation in biomass**

* forests, wetlands, agriculture areas, humus

**End-of-Pipe strategies**

* Separation and capture of CO2 from waste gases by chemical / physical absorption , adsorption, cryogenic methods , gas separation membranes , gas absorption membranes
* Once the CO2 is captured, it needs to be securely stored (sequestered)

Chemical absorption as end of pipe technology

* CO2 containing gas stream in contact with solvent
* Reaction between solvent and CO2 which gives an intermediate
* Solvent regeneration by heating
* Mostly applied when CO2-concentration is low
* Most applied solvent : monoethanolamine (MEA – HOCH2CH2NH2): high affinity for CO2



* The flue gas with CO2 is allowed to pass from bottom to top into an absorber (scrubber) with packaging material.
* The liquid phase which is the water with monoethanolamine (MEA) to increase the solubility of CO2 is allowed to pass from top to bottom.
* The air is cleaned inside the absorber by absorption of CO2 into the liquid phase; the clean air is collected at the top.
* The CO2 rich solvent is collected at the bottom of the absorber (scrubber) and passed through a heat exchanger to increase the temperature of the CO2 rich solvent, in this heat exchanger there is a pass of hot solvent from the stripper and this hot solvent exchange the temperature with CO2 rich solvent.
* After the CO2 rich solvent has passed through the heat exchanger, it is passed at the top to bottom through the stripper and the stream is added from the bottom to top. This process separates the CO2 rich solvent into the CO2 stream at the top and the solvent at the bottom. The hot CO2 steam is condensed and the CO2 is obtained and stored while the hot solvent is allowed to pass through the heat exchanger.
* We minimize energy by using the heat exchanger. In heat exchanger the hot solvent exchange the heat with the CO2 rich solvent from the scrubber and it is cooled down. After it is passing through the heat exchanger, it is passed through the cooler to further decrease the temperature of the solvent and the solvent is recirculated in the scrubber.
* In general the system has 2 parts, the first part where the absorption of CO2 occurs at low temperature in a chemical absorption unit and the second part to recover the solvent by stripping at high temperature. The chemical absorption unit comprises of an absorber, heat exchanger and a stripper
* Absorption is performed by a mass transfer from gas to liquid phase , due to reaction of CO2 with solvent mass transfer rate is increased
* In heat exchanger CO2-rich solvent is preheated by the CO2-lean solvent coming from the stripper
* In stripper: preheated CO2-rich solvent is stripped by steam and CO2 is released at the top of the stripper and CO2-lean solvent is cooled in the heat exchanger and cooler and returns to the absorption unit
* There is a Continuous regeneration of the solvent

Physical absorption as end pipe strategy

* Absorption according to Henry’s law
* Solvent regeneration by decreasing pressure
* Mostly applied for gas mixtures with high partial pressures of acid gases (high CO2 concentrations)

Adsorption as end pipe strategy

* Physical attraction between CO2 and active sites of solid. The system uses a kind of sorbent material that has a high affinity with CO2. Adsorbents :aluminium, molecular sieves, active coal can be used
* Limitations: low selectivity and capacity of adsorbents. The sorbents have also affinity with other pollutants, the obtained CO2 is not pure and it is difficult to make it pure.

Cryogenic methods as end pipe strategy

* CO2 physically separated from other gases by condensation of CO2 at cryogenic temperature. Low temperatures and high pressures

Gas separation membranes as end pipe strategy

* Due to different physical-chemical properties, some compounds of the gas stream diffuse faster through membrane than others do
* Multi-step systems are necessary due to low membrane selectivity
* By increasing pressure, increased driving force
* The diffusion of CO2 is high through the membrane

Gas absorption membranes as end pipe strategy

* Gas and liquid (solvent) stream are separated by membrane. Choice of a selective absorption liquid (solvent, e.g. MEA).
* By putting the membranes between 2 phases , you increase the selectivity

Utilization of captured CO2

* You can use the CO2 in the production of ureum and dry ice
* It can be used in Food and beverage industry
* It can be used to enhanced oil recovery (EOR) : increased mobility of oil by injecting CO2 in existing oil field and increased efficiency

Sequestration of CO2 (safe storage)

* CO2 can be sequestered in geologic formations like deep saline reservoirs, depleted oil and gas wells, unmineable coal seams
* Or can be sequestered in oceans, they have a very high CO2 capacity and CO2 can be injected below thermocline (100-1000 m below sea level) where there is a very slow mixture with surface water

A research project: sequestration of CO2 in Lake Kivu and see if it can be transformed into methane gas. The Lake Kivu samples with methane can be used in lab and CO2 is added and see the increase in CH4.

The second project: the reaction of H2O2 +2O3 produce the oxygen and the OH radicals ; this reaction can be used in water treatment because it generate oxygen that can do the oxidation.