**Research Article**

DBD non-thermal Plasma for decomposition of Volatile Organic Compounds

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Abstract

The most common air pollutants like Volatile Organic Compounds (VOCs) are the cause of different environmental degradation, causing secondary air pollution like Photochemical Smog, acid rain etc, which causes various health hazards. Therefore decomposition of VOCs is required. Abatement of VOCs can be done by non-plasma and plasma mediated methods. Plasma treatment is one of the effective methods for VOCs decomposition. In this review the decomposition as well as energy conversion is studied comparing both plasma and other conventional non-plasma methods. The decomposition process by Dielectric barrier Discharge (DBD) plasma assisted methods and its advantages are discussed. Decomposition efficiencies of DBD reactor depends on reactor size, applied potential, humidity; concentrations/flow rate of VOCs, pressure inside the system, gap between two electrodes and nature of different dielectric materials. Also the effect of various catalysts on VOCs decomposition is reviewed.

Graphical Abstract
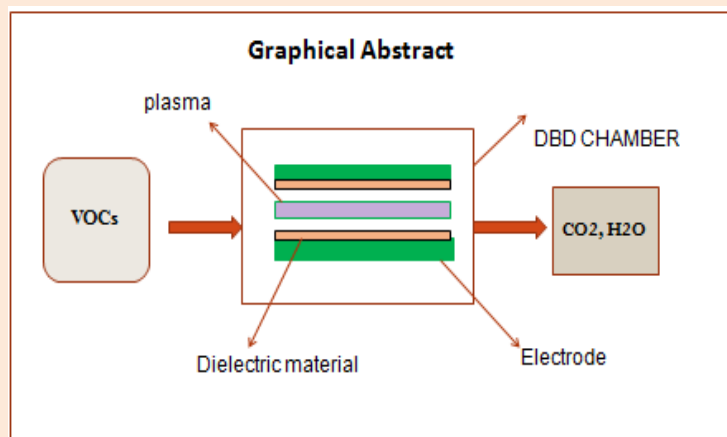
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Introduction

Air pollution has become a major cause of human distress both directly and indirectly. Highly Volatile, toxic gases and vapors released from chemical plants, various types of aerosols and particulate matter can be extremely hazardous to human health. VOCs are one of the air pollutants. **Table 1** shows the various air pollutants as part of classified groups [1].

Volatile organic compounds are molecules typically containing 1–18 carbon atoms that readily volatilize from the solid or liquid state into indoor air. All organic chemical compounds that can volatize under normal indoor atmospheric conditions of temperature and pressure are VOCs. VOC emissions result from natural and anthropogenic (manmade) sources. Natural sources of VOC include vegetation, forest fires and animals. Even though natural sources of VOC emissions are larger in general, it is the anthropogenic sources in populated and industrialized areas which are the main contributors to air quality problems. VOCs are emitted from many household products including paints and lacquers, paint strippers, cleaning supplies, combustion appliances, aerosol sprays, glues, adhesives, dry-cleaned clothing, and environmental tobacco smoke [**Table 2**]. VOCs mostly exist in the vapor phase in the atmosphere.

VOCs are primary precursors to the formation of particulate matter in the atmosphere which are the main ingredients of the air pollutant referred to as smog. VOCs can lead to acute and chronic health effects when anybody come contact with it. The possibility of health effects from inhaling any chemical depends on how much is in the air, how long and how often a person breathes it [2]. Some VOCs may persist from several months to years [3]. The large number of VOCs from Indian industries causing different health problems [4, 5, and 6] is listed in **Table 3**.

Table 1 Examples of air pollutants

Air pollutants	Examples
Acid Gases	SOx, NOx, HCl
Green house gases	COx, CH$_4$, NxOy, O$_3$, HFCs, PFCs, SF$_6$
Volatile Organic Compounds (VOCs)	**C$_7$H$_8$, C$_6$H$_6$, Chlorinated hydrocarbons and other substituted aromatics**
Ozone depleting substances (ODS)	CCl$_4$, CFCs, and HAPs
Toxic gases	Mercury, dioxin
Radioactive gases	Isotopes of Carbons, iodine, Cesium, radon
Particulate matter	PM$_{10}$ and PM$_{2.5}$

Hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulphur hexafluoride (SF$_6$) and hazardous air pollutants (HAPs). PM is Particulate matter of size 10micro-meters and 2.5 micro-meters respectively.

Table 2 Examples of different VOCs

Examples of Household Products	Possible VOC Ingredients
Fuel containers or devices using gasoline, kerosene, fuel oil and products with petroleum distillates: paint thinner, oil-based stains and paint, aerosol or liquid insect pest products, mineral spirits, furniture polishes	BTEX (benzene, toluene, ethylbenzene, xylene), hexane, cyclohexane, 1,2,4-trimethylbenzene
Personal care products: nail polish, nail polish remover, colognes, perfumes, rubbing alcohol, hair spray	Acetone, ethyl alcohol, isopropyl alcohol, methacrylates (methyl or ethyl), ethyl acetate
Dry cleaned clothes, spot removers, fabric/ leather cleaners	Tetrachloroethene (perchloroethene (PERC), trichloroethene (TCE)
Citrus (orange) oil or pine oil cleaners, solvents and some odor masking products	d-limonene (citrus odor), a-pinene (pine odor), isoprene
PVC cement and primer, various adhesives, contact cement, model cement	Tetrahydrofuran, cyclohexane, methyl ethyl ketone (MEK), toluene, acetone, hexane, 1,1,1-trichloroethane, methyl-iso-butyl ketone (MIBK)
Paint stripper, adhesive (glue) removers	Methylene chloride, toluene, older products may contain carbon tetrachloride
Degreasers, aerosol penetrating oils, brake cleaner, carburetor cleaner, commercial solvents, electronics cleaners, spray lubricants	Methylene chloride, PERC, TCE, toluene, xylenes, methyl ethyl ketone, 1,1,1-trichloroethane
Moth balls, moth flakes, deodorizers, air fresheners	1,4-dichlorobenzene, naphthalene
Refrigerant from air conditioners, freezers, refrigerators, dehumidifiers	Freons (trichlorofluoromethane, dichlorodifluoromethane)
Aerosol spray products for some paints, cosmetics, automotive products, leather treatments, pesticides	Heptane, butane, pentane
Upholstered furniture, carpets, plywood, pressed wood products	Formaldehyde

Therefore these should be reduced either by source minimization or decomposition methods. A lot of research is now being focused on finding new and more efficient techniques for decomposition of these compounds in elemental state or beneficiation of these hazardous emanations [7, 8].

A number of techniques used to decompose the VOCs are thermal oxidation, regenerative thermal oxidation, catalytic oxidation with recuperation, filtering/adsorption techniques like bio filters, scrubbers, condensation, membrane separation, physisorption [9-17].

Conventional methods (Non-Plasma mediated) for removal of VOC

Most of the direct fired Thermal oxidizers operate at temperature ranges between 980 °C (1,800 °F) to 1,200 °C (2,190 °F) with air flow rates of 0.24 to 24 standard cubic meters per second [18] .Thermal oxidizers are typically

used to destroy hazardous air pollutants (HAPs) and volatile organic compounds (VOCs) from industrial air streams. These pollutants are generally hydrocarbon based and when destroyed via thermal combustion they are chemically oxidized to form CO_2 and H_2O. Three main factors in designing the effective thermal oxidizers are temperature, residence time, and turbulence. The temperature needs to be high enough to ignite the waste gas. Most organic compounds ignite at the temperature between 590 °C (1,094 °F) and 650 °C (1,202 °F). To ensure near destruction of hazardous gases, most basic oxidizers are operated at much higher temperature ranges. When catalyst is used, the operating temperature range may be lower.

Table 3 Different VOCs with their health effects

VOC type	Health effects	Maximum permissible Emission standard (mg/m^3)	Emission source
Benzene	Headache, chest stuffy, paralysis of nerve center, carcinogen	0.5	Vehicle tail gases, Combustion, etc.
Toluene	Paralysis of nerve center, nausea, muscle weakness	0.3	Vehicle tail gases, Painting industries, Combustion, Chemical plants, etc
Xylene	Dizziness, paralysis of nerve center	1.5	Painting industries, Vehicle tail gases, Combustion, etc.
Phenol	Respiratory irritation, stupefaction	0.1	Combustion, Spice
Aniline	Liver and kidney disease	0.5	Aquatic products processing, Leather, etc.
Chlorobenzene	Paralysis of nerve center, headache, dizziness	0.5	Dye, Pharmacy, Leather, Painting industries, etc.
Nitrobenzene	Tinnitus, nausea, shock	0.05	Dye, Pharmacy, Pesticide, etc.
Benzopyrene	Carcinogen, teratogenesis	0.01×10^{-3}	Combustion, Vehicle tail gas, tar, etc.

VOCs can be removed by physisorption onto a high surface area of carbon. This process is relatively simple; disposal of spent carbon has to be carried out by thermal treatment but during the thermal treatment toxic compounds liberated into the atmosphere. In thermal oxidation, VOCs are oxidized at high temperatures in the range 700–900⁰C. Use of a catalyst decreases the operating temperature to 300–500⁰C. Catalytic techniques use less heat energy as compared to thermal oxidation and completely oxidize VOCs but limitation is related to the energy supply at low VOC concentrations. Conventional techniques for the cleaning of dilute gas streams work efficiently only when the VOC concentration is higher than 1000 ppm. Different non-plasma mediated methods and their limitations are listed in **Table 4**.

Plasma mediated Interactions

Plasma is a state of matter that generally consists of free electrons and ions in an ionized gas. Originally it was observed by Sir William Crookes during his experiment where plasma was formed in the discharge tube (1869-1875) and Irving Langmuir in 1927 who suggested that; more than 99% matter of the universe is in plasma state. **Table 5** depicts the general constituents of partially ionized plasma with the corresponding terminology and symbols.

The nature of properties and application of plasmas depend typically on temperature and charge density. While the high temperature fully ionized fusion grade plasmas have significant applications in generating unlimited resource of clean energy, the low temperature processing plasmas play an extremely significant role in materials processing, exotic chemistry, waste management and surface engineering. Due to the highly energetic particles available in the plasma and their energies, it is possible to carry out various particles triggered chemical reactions that are not possible in normal condition. Different activated species like electrons, positive and negatives ions, free radicals, gas atoms and molecules in the ground state or in the excited states are used in such exotic processes. A few examples are like VOC decomposition, surface modification of polymers, medical treatment, generation of conducting polymers etc. [19-24].

Table 4 Different non-plasma mediated methods and their limitations

Methods(Conventional And upcoming)	Technology involved	Limitations
Adsorption	Activated carbons, zeolites	Adsorbent is too specific and can saturate fast; risk of pollutant reemission
Incineration	Thermal oxidation	Not cost effective, incomplete mineralization and release of secondary pollutants.
Catalytic oxidation	Thermal catalysts (Pt, Al, ceramics)	Catalyst deactivation and its disposal, formation of by product.
Absorption	Washing gas with contaminated water	Not suitable for low concentrations, generates wastewater.
Condensation	Liquefaction by cooling or compression	Further treatment is required, applicable in high concentrations only.
Filtration	Air passed through fibrous material coated with viscous materials	Unable to remove gases, fouling, particle reemission can occur due to microbial growth.
Electrostatic precipitator with Ionization	Electric field is generated to trap charged particles	Generates hazardous by products.
Ozonation	Strong oxidizing agent	Generates unhealthy ozone and degradation products.
Photolysis	UV radiations to oxidize air pollutants and kill pathogens	Release of toxic photoproducts, UV exposure may be hazardous and energy consuming.
Photo catalysis	High energy UV radiation used along with a photo catalyst	Exposure to UV radiation may be harmful
Membrane separation	Separation through semi-permeable membranes	Membrane fouling and high pressure is needed
Enzymatic oxidation	Use of enzymes for treatment of air pollutants	Requirement of new enzymes periodically
Phytoremediation	Use of plants and microbes for the removal of contaminants	Large as compared to other technologies
Microbial abatement	Air passed through a packed bed colonized by attached microbes as bio-trickling filters or microbial cultures in bio-scrubbers	Need for control of biological parameters

Table 5 Types of Particles in a Plasma in General

Sl.	Particle Type	Symbol
1	Photon	Φ
2	Electron	e
3	Ground level atom or molecule	0 or 00
4	Excited atom or molecule	
	• electronic, one electron	0'
	• electronic, two electron	0''
	• electronic, metastable state	0^m
	• vibrational excitation	0^v
	• retational excitation	0^r
5	Positive ion (atom or molecule)	
	• singly charged	1
	• multiply ionized	2, 3….
	• singly ionized and electronically excited	1'
6	Negative ion (atom or molecule)	$\hat{1}$

The processing plasmas fall in two categories namely: thermal and non-thermal plasmas (**Table 6**) [25]. In thermal plasmas all the species are in thermal equilibrium. The non thermal plasmas are characterized by low gas temperature and high electron temperature thereby providing an ideal medium for conducting exotic chemistry.

The present paper is devoted to the cold plasma or non-thermal plasma processing of VOC gases. The different characteristics of Non-thermal Plasma (NTP) processing are strong non-equilibrium low gas temperature, presence of reactive chemical species and high conversion efficiency. Since the last decades NTP technologies are widely used for the decomposition of VOCs [25, 26]. Production of NTP is carried out in a strong electric field to create a neutral gas discharge and release electrons, generating radicals, neutral particles, ions and UV photons, which can non-selectively decompose most VOCs. As low-pressure discharge plasma is carried out in a sealed chamber which is expensive and time consuming, NTP is now being replaced by the atmospheric pressure non-thermal plasmas (ANTP) as extremely powerful processing tool for its economic and operational advantages. ANTP can be generated by various types of electrical discharges such as corona discharge, micro hollow cathode discharge, atmospheric pressure plasma jet, gliding arc discharge, atmospheric uniform glow discharge, dielectric barrier discharge and plasma needles with multiple technological applications. The characteristics of all the above atmospheric pressure plasma methods are shown in **Table 7** [25].

Table 6 Classification of plasmas [25]

Plasma	State	Example
High temperature plasma (Equilibrium plasma)	$T_e \approx T_i \approx T_g, T_p = 10^6 - 10^8 K$ $n_e \geq 10^{20} m^{-3}$	Laser fusion plasma
Low temperature plasma Thermal plasma (Quasi-equilibrium plasma)	$T_e \approx T_i \approx T_g, \leq 2 \times 10^4 K$ $n_e \geq 10^{20} m^{-3}$	Arc plasma, plasma torches, RF inductively coupled discharges
Non-thermal plasma (Non-equilibrium plasma)	$T_e \gg T_i \approx T_g = 300 \dots \dots \dots 10^3 K$ $n_e \approx 10^{10} m^{-3}$	Glow, corona, APPJ, DBD, MHCD, OAUGDP, plasma needle etc.

Atmospheric Pressure Plasma Jet (APPJ), Dielectric Barrier Discharge (DBD), Micro Hollow Cathode Discharge (MCHD), One Atmospheric Uniform Glow Discharge Plasma (OAUGDP).

Table 7 Plasma properties of different atmospheric pressure plasma processes

Parameters	Corona Discharge	DBD	APPJ	Atmospheric glow MHCD
Method and Type	Sharply pointed electrode	Dielectric barrier cover on electrodes	RF Capacitvely coupled	DC glow with micro hollow cathode electrode
Excitation	Pulsed DC	AC or RF	RF13.5 MHz	DC
Pressure (bar)	1	1	1	1
Electron energies (eV)	1-5	1-10	1-2	…………..
Electron Density,cm^{-3}	10^9-10^{13}	$\approx 10^{12}$-10^{15}	10^{11}-10^{12}	
Breakdown Voltage (kV)	10-50	5-25	0.05-0.2	……………
Scalability & Flexibility	No	Yes	Yes	Yes
Gas Temp T (K)	Ambient	Ambient	400	2000
Carrier Gas	……….	N_2^+ O_2^+ NO^+ Rare gas/Rare gas halides	Helium, Argon	Rare gas/Rare gas halides

In corona discharge [27-29] weekly ionized plasma is created. Corona discharge is characterized by (1) an asymmetric electrode configuration, (2) with high voltage; (3) an avalanche builds up near the sharp electrode,

(4) photons from the avalanche create charge carriers outside the space charge area and lastly (5) a new avalanche build up closer to the cathode. This is mostly used as electrostatic precipitators (ESP) for dust collection in industrial off gases. Also it is used in water purification, electri-photoghaphy, copying machine, printers and liquid spray gun and in power coating. But application of corona discharge in material processing is restricted due to inherent non-uniformity.

Atmospheric-pressure plasma jet is also used to generate non-thermal plasma [30-35]. APPJ consists of two concentric electrodes through which a mixture of helium, oxygen or other gases can enter. The inner electrode is coupled to 13.56MHz radio frequency power at a voltage between 100-250 V where the outer electrode is grounded. Discharging occurs when RF power is applied to it, then it functions on the feed stock gas and generates a high velocity effluent stream of highly reactive chemical species. Central electrodes driven by RF power, speed up the free electrons, which produces excited state molecules, atoms, free radicals and additional ion-electron pairs. No more ions and electrons are left when the gas exits the discharge volume due to the recombination process. This method has many applications including material processing, cleaning large industrial parts, sterilization of surgical and dental equipments etc. APPJ does not require any dielectric material and the gas temperature of the discharge is 50^0C.

Another method of plasma is the Micro-hollow cathode discharge (MHCD). This MHCD based on the use of Micro-hollow cathode electrode concept; on modification of cathode shape leads to increase the current density [36]. The modified cathode contains a hole or cavity or it may be a hollow cylinder. The energetic electrons formed is used in different fields like remediation of gaseous pollutants, medical sterilization and biological decontamination, cleaning of metallic surfaces, diamond deposition etc.

Among all these, the Dielectric barrier discharge (DBD) has been proved to be potent processing tool in myriads of applications. DBD was first investigated by Siemens in 1857 [37]. Atmospheric pressure DBD plasma characterization and its nature in air was studied latter by K. Buss [38], Klemene [39], Suzuki [40, 41], Honda [42], Gorbrecht [43], Basirov [44] with a planar parallel electrodes covered by dielectrics. Dielectric barrier discharge is also known as barrier discharge or silent discharge. It operates in AC voltage. This provides strong thermodynamic, non-equilibrium plasma at atmospheric pressure.

DBD reactor consists of two electrodes where at least one of the electrodes is covered with a dielectric material. Due to the presence of one or more insulating material on or between these two powered electrodes, non-equilibrium atmospheric discharge occurs. In general an AC voltage with amplitude of 1-100 kV, frequency from line frequency to several megahertz is applied to DBD. Cold plasma in DBD can be produced in various working mediums through ionization by high frequency and high voltage electric discharge.

DBD structure

Different geometrical configurations are shown below **Figure 1**. It may be planar DBD or cylindrical DBD reactor [40-43]. In case of planar DBD reactor the two electrodes are parallel to each other. The electrodes are covered with dielectric materials. The other type of arrangement is the co-axial arrangement where one electrode is inside the other.

Characteristics of DBD Plasma/ Electrical breakdown of gases

In 1889 Friedrich Paschen developed a law which is known as Paschen's law and the curve obtained from it is called the Paschen's curve, describing the breakdown voltage as a function of the electrode spacing or gap (d), operating pressure (p), and gas composition [45]. The breakdown voltage is a function of the product of the pressure p and the inter-electrode distance d (Figure 2):

$$V_b = f(pd)$$

The mathematical formulation of Paschen's curve is derived from Townsend's description of the basic charge generation processes including electron impact ionization (α process) and secondary electron emission from the cathode due primarily to ion bombardment (the γ process), though other bombardment processes may play a role [46]. Historically, Paschen's curve has proved to be accurate for large gaps and at low pressures [47], but it is often acknowledged that it fails to describe behavior at extremely low or high pd values [48].
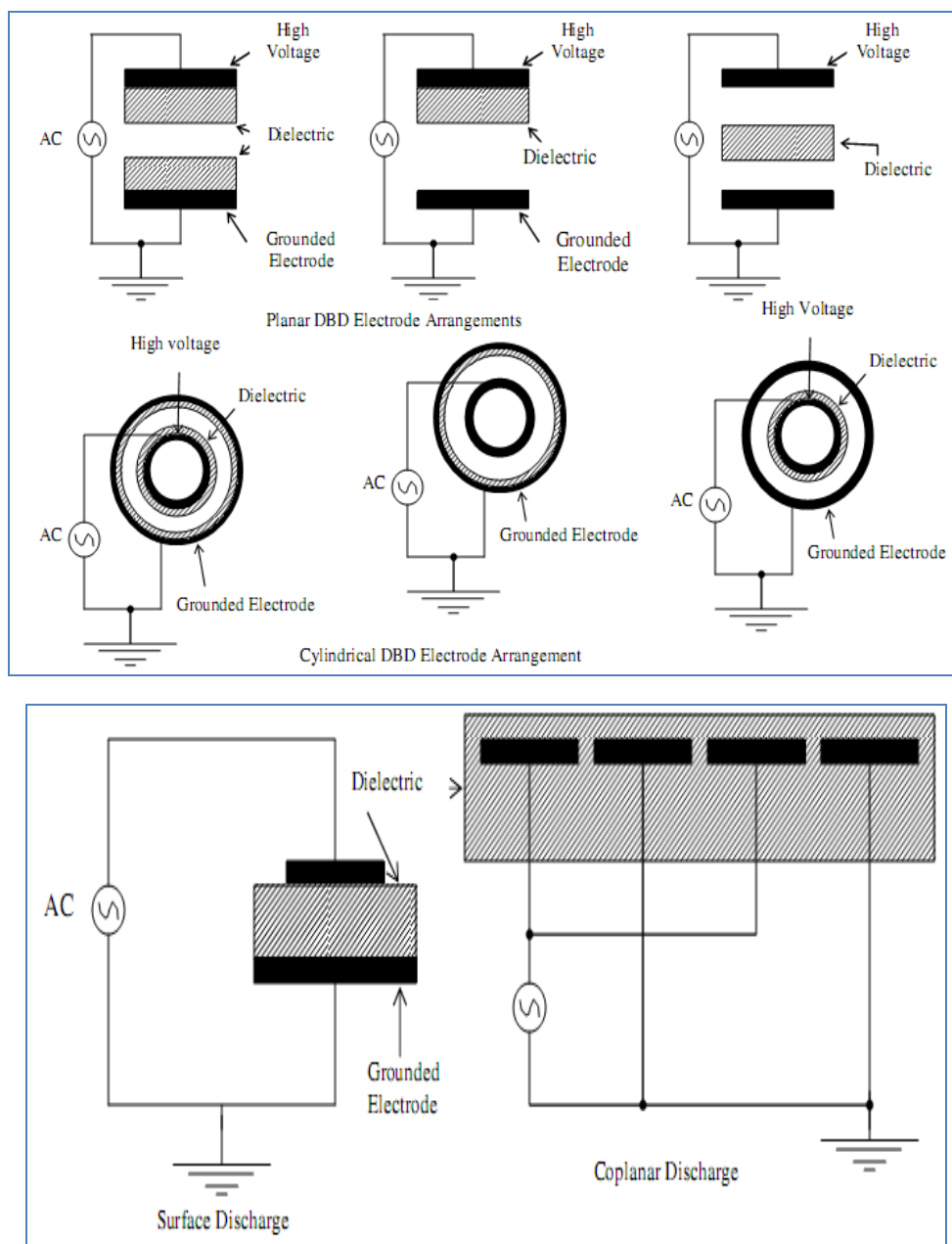
Figure 1 Typical electrode arrangements of DBD configurations

Conditions for self sustained discharge

Sustainability of plasma depends upon the applied voltage which must exceed the breakdown voltage of the gases. When this voltage is attained, the gases lose their dielectric properties and turn into conductors. It must satisfy the following condition:

$$1 - \gamma (e^{\alpha d} - 1) = 0$$

$$e^{\alpha d} = \left(1 + \frac{1}{\gamma}\right)$$

Paschen breakdown criteria

$$V_b = \frac{Bpd}{\left\{\ln\left(Apd - \ln\left[\ln\left(1 + \frac{1}{\gamma}\right)\right]\right)\right\}} \qquad (1)$$

$$V_b = f(pd)$$
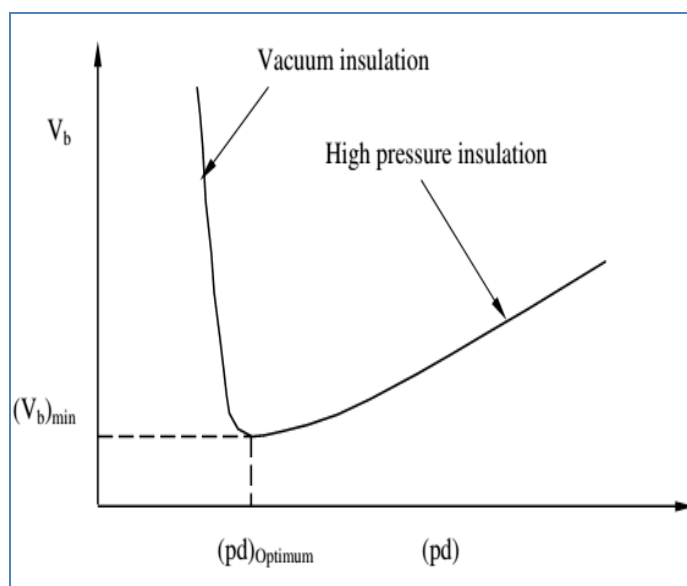
Figure 2 Paschen's curve

From eq. (1) it is clear that breakdown voltage depends on the product of p and d for a given gas and cathode materials, despite of the individual values of p and d. From the Paschen curve, it is clearly understood breakdown voltage is minimum for a certain pd product. But it is large for both small and large values of pd. This can be explained as there are too few collisions/ too large collisions at low and high values of pd respectively & it has been experimentally verified for a number of gases using the expression for the breakdown voltage as a function of the parameters A and B. (Figure 3) [49-51].
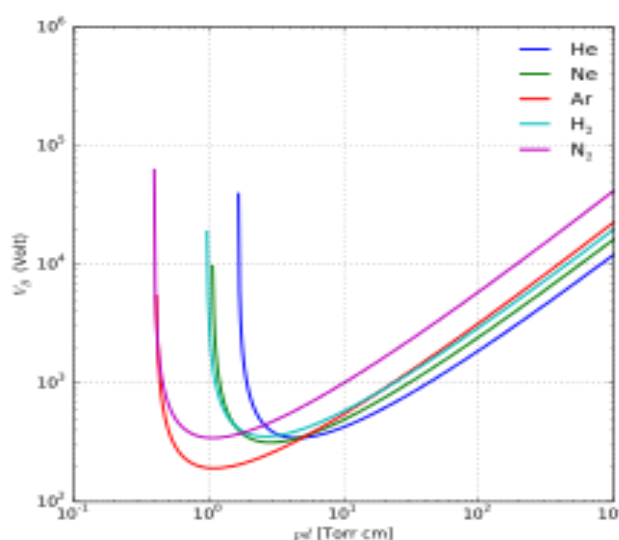
Figure 3 Paschen curves obtained for helium, neon, argon, hydrogen using the expression for the breakdown voltage as a function of the parameters A, B that interpolates the first Townsend coefficient [51].

Radio frequency (RF) plasmas

Electrical discharges could be energized and sustained by high-frequency electromagnetic fields. RF (radio frequency) discharges usually work in the frequency range 1 – 100 MHz. The corresponding wavelengths (λ = 300 – 3 m) are large compared to the dimensions of plasma reactor.

The power coupling in RF discharges can be consummate in different ways, as:
- Capacitively coupled discharges, 'E' discharges;

- Inductively coupled discharges, 'H' discharges [52].

Different actions of the electrons and ions at typical RF frequencies can be explained by their different masses. The light electrons can follow the instantaneous electric fields produced by the applied RF voltage [53, 54]. Capacitively coupled RF discharges also results from the differences in mass between electrons and ions by self-biasing. The 'self-bias' or 'DC bias' is a negative DC potential which develops between the plasma and the powered electrode as a consequence of; (i) the use of a coupling capacitor between the RF generator and the powered electrode and (ii) the use of appropriately shaped areas of the (smaller) powered electrode and the (larger) grounded electrode occurs. So it is assumed that the currents from the plasma to both electrodes must be equal. The higher current density at the small electrode requires a higher voltage between the plasma and electrode. But in case of other plasma devices, the application of an additional RF bias to the sample holder generates a self-bias with higher ion energies [55].

In a capacitively coupled RF discharge, the electron density is in the range ne = 10^9–10^{10}cm^{-3} and densities may be up to 10^{11} cm^{-3} are possible at higher frequencies [56]. The ion energy near the powered electrode can have energies of a few hundred electron-volts. CCPs are widely used in different fields like deposition of thin-films, plasma etching and sputtering of insulating materials as well as micro-fabrication in integrated circuit manufacturing industries for plasma enhanced chemical vapor deposition (PECVD).

Inductively coupled plasma (ICP) is similar to CCP. In ICP electrode consists of a coil wrapped around the discharge volume which inductively excites the plasma. ICP is excited by an electric field generated from a RF current in a conductor [53, 57]. Plasma electrons are accelerated by the changing magnetic field in this conductor. Simply the RF currents in the coil generate an RF magnetic flux which penetrates the plasma region.
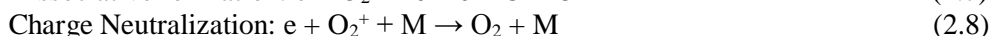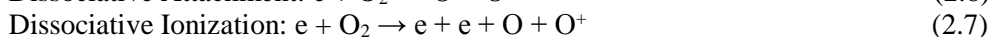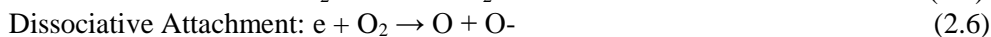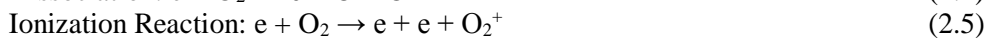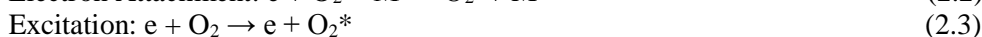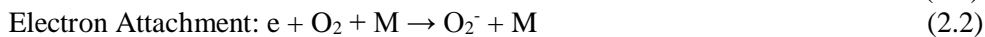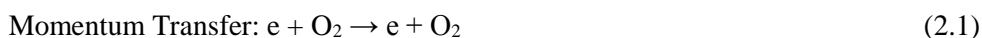
Advantages of DBD Plasma

DBD plasma has numerous applications [58-61] Starting from Ozone generation to material characterization and pollution control. DBD non-thermal plasma works at atmospheric pressure with large dimensions. DBD experiment can be carried out in a laboratory in room temperature. No spark or lighting, minimal medium heating and absence of cracking noise is normally noticed/ observed due to the presence of dielectric material.

At Atmospheric DBD discharges, the gas molecules collide with electrons, forms excited gas molecules. The gas temperature remains in the same levels as the atmospheric condition whereas discharge electrons in NTP acquire temperatures of (1-25 eV). Various processes like excitation, ionization or dissociation occur with release of secondary electrons where it reacts with the VOCs to decompose it. In the presence of oxygen atmosphere and water vapor/ hydrogen gas form OH radicals which made easy decomposition of VOCs to CO_2 and H_2O with other byproducts. In the presence context ANTP has wide applications for the decomposition of VOCs like benzene, xylene, toluene, acetylene, naphthalene etc [62-66]. Catalytic action also plays important role to decompose VOCs to CO_2 and H_2O as main products by increasing the rate of decomposition/removal efficiency [67]. Different catalyst having different decomposition efficiency is also reported [68-73].

Reactions in plasma in a DBD system:

The plasma chemistry in plasma is generated by electron-impact reactions. This electron-impact reaction is very unpredictable and complex. Some of the most common electron impact processes are discussed below.
Taking O_2 molecule as an example, the types of electron-impact reactions include:
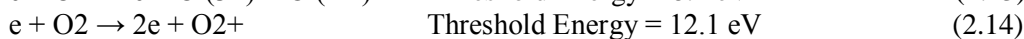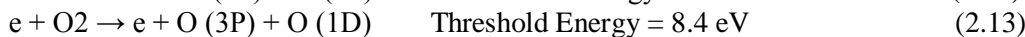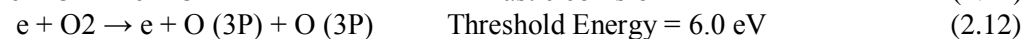
Momentum Transfer: $e + O_2 \rightarrow e + O_2$ (2.1)
Electron Attachment: $e + O_2 + M \rightarrow O_2^- + M$ (2.2)
Excitation: $e + O_2 \rightarrow e + O_2{*}$ (2.3)

Dissociation: $e + O_2 \rightarrow e + O + O$ (2.4)
Ionization Reaction: $e + O_2 \rightarrow e + e + O_2^+$ (2.5)
Dissociative Attachment: $e + O_2 \rightarrow O + O-$ (2.6)
Dissociative Ionization: $e + O_2 \rightarrow e + e + O + O^+$ (2.7)
Charge Neutralization: $e + O_2^+ + M \rightarrow O_2 + M$ (2.8)

where e is the electron, O_2^* is the O_2 molecule in excited state, O- is the negative ion of oxygen atom, O_2^- and O_2^+ are the negative and positive ions of O_2 molecule respectively.

Electron-impact dissociation of molecular oxygen produces the ground state atomic oxygen O (^{3}P) and excited atomic O (^{1}D):

$$e + O_2 \rightarrow e + O\ (^3P) + O\ (^3P) \hspace{3cm} (2.9)$$
$$e + O_2 \rightarrow e + O\ (^3P) + O\ (^1D) \hspace{3cm} (2.10)$$

which is explained in terms of energy as,

|		
$e + O2 \rightarrow e + O2$	Elastic collision	(2.11)
$e + O2 \rightarrow e + O\ (3P) + O\ (3P)$	Threshold Energy = 6.0 eV	(2.12)
$e + O2 \rightarrow e + O\ (3P) + O\ (1D)$	Threshold Energy = 8.4 eV	(2.13)
$e + O2 \rightarrow 2e + O2+$	Threshold Energy = 12.1 eV	(2.14)

Except for the momentum transfer, there is threshold energy for all the other reactions. For example, the threshold energy for reaction 2.11 is < 6 eV. The cross section of this reaction below 6 eV is zero. Moreover, at the electron energy of 10 eV, the cross sections for 2.12 to 2.14 are in the sequence as: 2.13 > 2.14 > 2.12, suggesting the probabilities of the occurrence for these reactions are in the same order. The products from electron-impact reactions (positive ion, negative ion, radical excited species and meta-stable) would react with each other and with the background gas, leading to the complexity of plasma chemistry [74-75].

In humid air mixtures, OH radicals can be produced in a variety of ways. In discharge reactors for which the electron mean energy is low, the OH radicals are produced via three types of reaction:
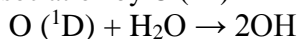
Electron Attachment

$$e + H_2O \rightarrow H^- + OH$$
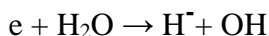
Direct dissociation by electron impact
$$e + H_2O \rightarrow e + H + OH$$
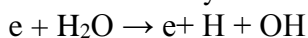
Dissociation by O (^{1}D)
$$O\ (^1D) + H_2O \rightarrow 2OH$$

Case study for decomposition of some common VOCs.
Decomposition of Xylene

Non-thermal plasma produced in low-temperature and atmospheric pressure condition is a powerful tool for exciting, atomizing or desorbing harmful substances in ambient condition by collision-induced energy transfer of electrons which is used as an ideal excitation/ionization source or atomizer for trace pollutant detection by Z.Wu et al. [76]. Non-thermal plasma assisted air purifier system was investigated by S. Schmid et al [77] for the decomposition of VOCs in absence of catalyst. VOCs like Cyclohexane, Benzene, Toluene, Ethylbenzene and Xylene isomers are treated with the air purifier. The degradation products are absorbed by charcoal tubes and the efficiency rate was found to be $11\pm1.6\%$ for Cyclohexane, < 2% for Benzene, $11\pm2.4\%$ for Toluene, $3\pm1\%$ for Ethylbenzene, $1\pm1\%$ for *o*-Xylene and $3\pm0.4\%$ for m-/p-Xylene. Different oxidizing products indicate the formation of alcohols, aldehydes, ketones and epoxides. The other byproducts also suggest the reaction with OH radicals and ozone formation during the decomposition. This is an oxidative decomposition process, most likely involving OH radicals. Humidity during the process is in the range 10–14 gm^{-3} which helps for the formation of OH radicals due to reaction of H_2O with exited NO_2 [78]. Also processes such as dissociative excitation of H_2O or dissociative electron attachment can lead to OH radical formation may be due to collisions of H_2O with electrons [79, 80]. An H-atom abstraction from the C–H bond of the ethyl group induced by OH radicals, followed by further reaction with O_2 catalyzed by NO has been reported to be a possible reaction of ethylbenzene to acetophenone [81]. Based on the work by B. Eliasson and U. Kogelschatz, [82], it is assumed that an electron transfer from the plasma region to the air molecules is to form reactive species such as O, O_2, O_3, OH which then react with the analyzed molecules.
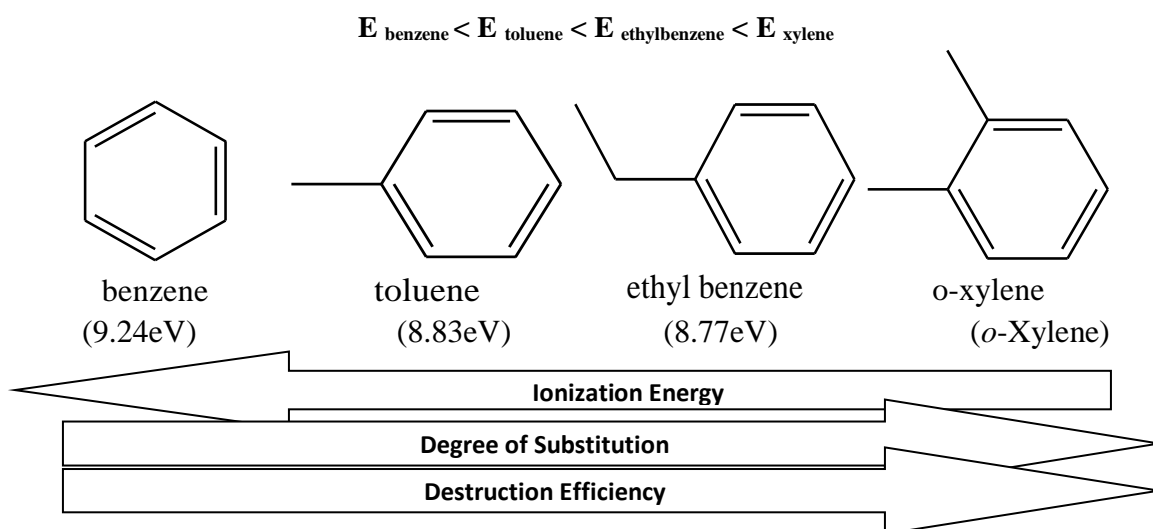
Destruction efficiencies of volatile aliphatic and aromatic hydrocarbons are studied in a non-thermal, ambient-pressure, capillary discharge plasma reactors. The contaminant destruction efficiency (DE, %) is defined as

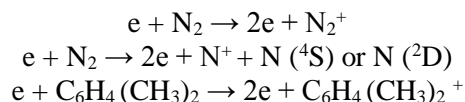$$E = \frac{C_0 - C}{C_0} \times 100$$

Where C_0 = influent concentration and C = effluent concentration in ppm scale

$$\text{Where SE (specific energy)} = \frac{\text{input power (P)}}{\text{gas flow rate (Q)}}$$

Destruction efficiency for n-heptane increases up to 95% with increasing specific energy above 2 J/cm^3. And the specific energy depends slightly on the residence time. It is observed that after the particular SE, the DE remains constant [83]. Similar result was also been reported for toluene (SE=1.3 J/cm^3, RT= 0.6 s, DE= 80%). Greater DE may be due to the straight chain aliphatic group. DE also depends on reactor volume that at a particular SE. DE is higher in smaller reactor volume. This may be explained in terms of plasma density. At a particular SE, plasma in a larger reactor volume has a lower plasma density, which decreases chemically reactive radicals required for VOC destruction. Depending upon the compound chemical nature, DE is inversely proportional to ionization energy and is directly proportional with the degree of chemical substitution. This is in agreement with the result obtained by Ogata et al group [84]. This may be due to the presence of aliphatic group present in the side chains. Already it is discussed that aliphatic HC are more easily destructed than aromatic HC. Also it is experimentally found that benzene is more difficult to decompose than toluene comparing the DE [85]. DE for benzene, toluene, ethylbenzene, xylene are in the order:
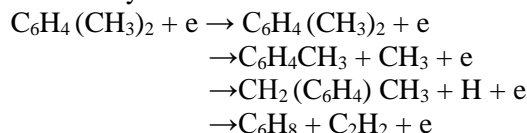
$$E_{\text{benzene}} < E_{\text{toluene}} < E_{\text{ethylbenzene}} < E_{\text{xylene}}$$

benzene (9.24eV)   toluene (8.83eV)   ethyl benzene (8.77eV)   o-xylene (o-Xylene)

Ionization Energy

Degree of Substitution

Destruction Efficiency

p-xylene decomposition in DBD can be generalized as (i) electron-impacts, (ii) ion collisions, and (iii) gas-phase radical attacks.

$$e + N_2 \rightarrow 2e + N_2^+$$
$$e + N_2 \rightarrow 2e + N^+ + N \, (^4S) \text{ or } N \, (^2D)$$
$$e + C_6H_4 \, (CH_3)_2 \rightarrow 2e + C_6H_4 \, (CH_3)_2{}^+$$

The chemical kinetics for plasma chemistry is quite complex usually involving tens of species and hundreds of reactions. Therefore the reaction rate constants for electron impact dissociation and ions' rearrangement of p-xylene are not understood at present. As toluene and p-xylene are of similar chemical structures and nature, comparing the value with toluene, reaction rate constants for p-xylene is found to be of the order of 10^{-6} and 10^{-10} cm^3. S^{-1}.

Another mechanism can be predicted for p-xylene that does not react with nitrogen molecules directly so the following reaction may lead to ion collision reaction.

$$C_6H_4 \, (CH_3)_2 + e \rightarrow C_6H_4 \, (CH_3)_2 + e$$
$$\rightarrow C_6H_4CH_3 + CH_3 + e$$
$$\rightarrow CH_2 \, (C_6H_4) \, CH_3 + H + e$$
$$\rightarrow C_6H_8 + C_2H_2 + e$$

Decomposition of Toluene

Removal of VOCs especially toluene by using different catalysts at different concentrations was studied in the atmospheric plasma conditions. Decomposition of Vinyl Chloride, Ethyl Acetate, Toluene and Acetone was studied in cylindrical and planar DBD reactors by R. Rudolph et al [86]. Ozone in zero air and OH radical in humid air plays the main role for decomposition. EA and Toluene show the good result.

Small values < 1ppm / (Wh/m^3) in zero air,
Medium values in the range of 2-5 ppm/ (Wh/m^3) in laboratory air
Large values >10 ppm / (Wh/m^3) in the case of Vinyl Chloride treatment (planar)

For improvement in the destruction efficiency and to reduce undesirable byproducts, a TiO_2/-Al_2O_3 / nickel foam catalyst was combined in and after the non-thermal plasma. It gives very good result enhancing toluene removal with increasing CO_2 selectivity and carbon balance and the byproducts reduced interestingly. It may be due to the presence of catalyst.

The bond dissociation energy of C-H in methyl is 3.7eV, where as that of C-H in aromatic ring is higher than this i.e 4.3eV. Similarly C-C bond energy in methyl group and aromatic rings is 4.4 eV that of aromatic ring is 5.0-5.3 eV [87] and C=C bond energy in aromatic ring is 5.5 eV. It is reported that mean energy of the energetic electrons ranges from 1 to 10 eV [88]. As the C-C energy between methyl and benzene ring is 4.4eV, C-C can be broken by the energetic electrons beyond the energy 4.4eV. The aromatic bonds in the intermediate compounds can be directly ruptured by the O/OH radical attack. Formation of small molecular mass compounds like formic acid, acetic acid and CO on further oxidation with O/OH radicals converted to CO_2 and H_2O. Interestingly the conversion of Toluene to benzene is explained by the attack of energetic electrons, where as no benzene is found to be formed in O/OH radical attack. Decomposition of benzene is difficult than toluene [89, 59].

Possible reaction pathways for the toluene decomposition depending upon the product are given in the following pathways (R-1 to R-2). It is a complex mechanism. So it can be explained as toluene in presence of H_2O (OH$^{\cdot}$) gives phenol free radicals, which in presence of O$^{\bullet}$ /HO$_2$$^{\bullet}$ in O_2 gas with H_2O forms benzaldehyde. Then it is oxidized to benzoic acid, and then it gives aliphatic aldehyde which lastly converts to CO_2 and H_2O. The mechanisms given below involve oxidation reactions causing a ring retaining or ring opening product which finally gives CO_2 and H_2O (**Scheme 1**) [90-93]. Another possible mechanism can also be predicted starting from toluene to glyoxal via various intermediate products, which finally gives CO_2, H_2O (**Scheme 2**).
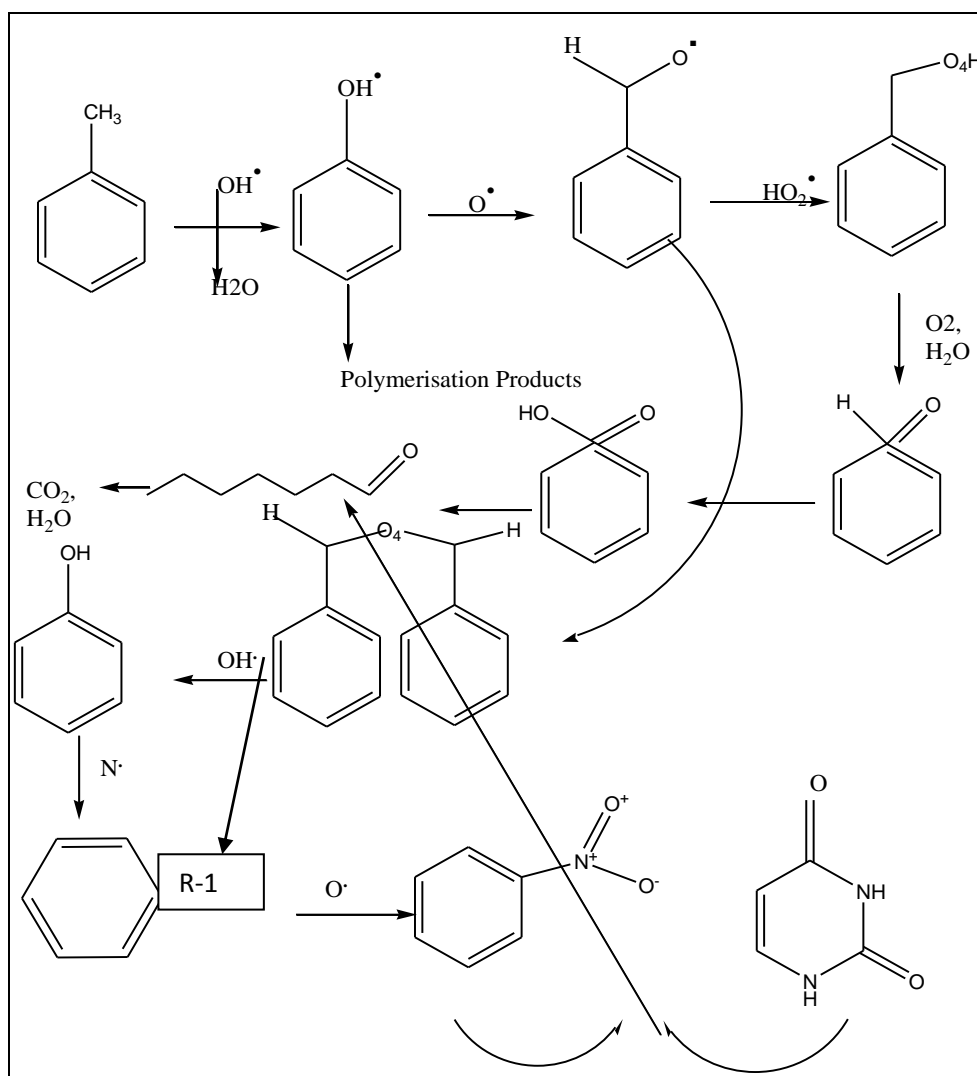
Decomposition rate of toluene in ceramic Raschig rings packing increases as compared to the reactor without packing significantly from 48% to 97%. In this case the energy yield also increases in presence of packing material [94].formation of ozone does not react in the toluene decomposition process [95-96].

Removal of toluene in a DBD reactor and in a catalyst bed reactor was studied at atmospheric pressure. Toluene is oxidized in both of the above systems via ozone to Oxygen radical conversion. Post plasma catalysis also oxidized byproducts like CO, formic acid and formaldehyde [97].

Toluene decomposition in presence of different background gases and catalysts at NTP condition was studied and compared. Depending upon the removal efficiency the reaction mechanism and dynamics are also suggested. In presence of Ar gas the removal is better as compared to the other gases like N_2, N_2/Ar and N_2/O_2. Moreover the presence of catalysts increases further removal efficiency, carbon dioxide selectivity and decrease the byproducts. Manganese oxide/alumina/Nickel foam proves to be the most effective catalyst [98]. Depending upon the reaction mechanisms like (1) electron impact dissociation (2) gas-phase radical (3) ion-molecule reactions Y –F. Guo, D –Q. Ye et al reported the feasibility of reactions [99]. The first one suggests that O and O_3 reactions are negligible [100, 101].

Decomposition of Toluene and Nitric Oxide was studied by NTP discharge process such as corona and DBD. Benzene ring of toluene is so stabilized that it is too difficult to break the C-C bond [102]. Nitrogen radical reduces NO to N_2 but formation of NO cannot be restricted [103]. Alkene and substituted alkene were found having much larger

decomposition rate constants than aromatic and substituted alkane compounds. Both the systems showed similar effect [104].
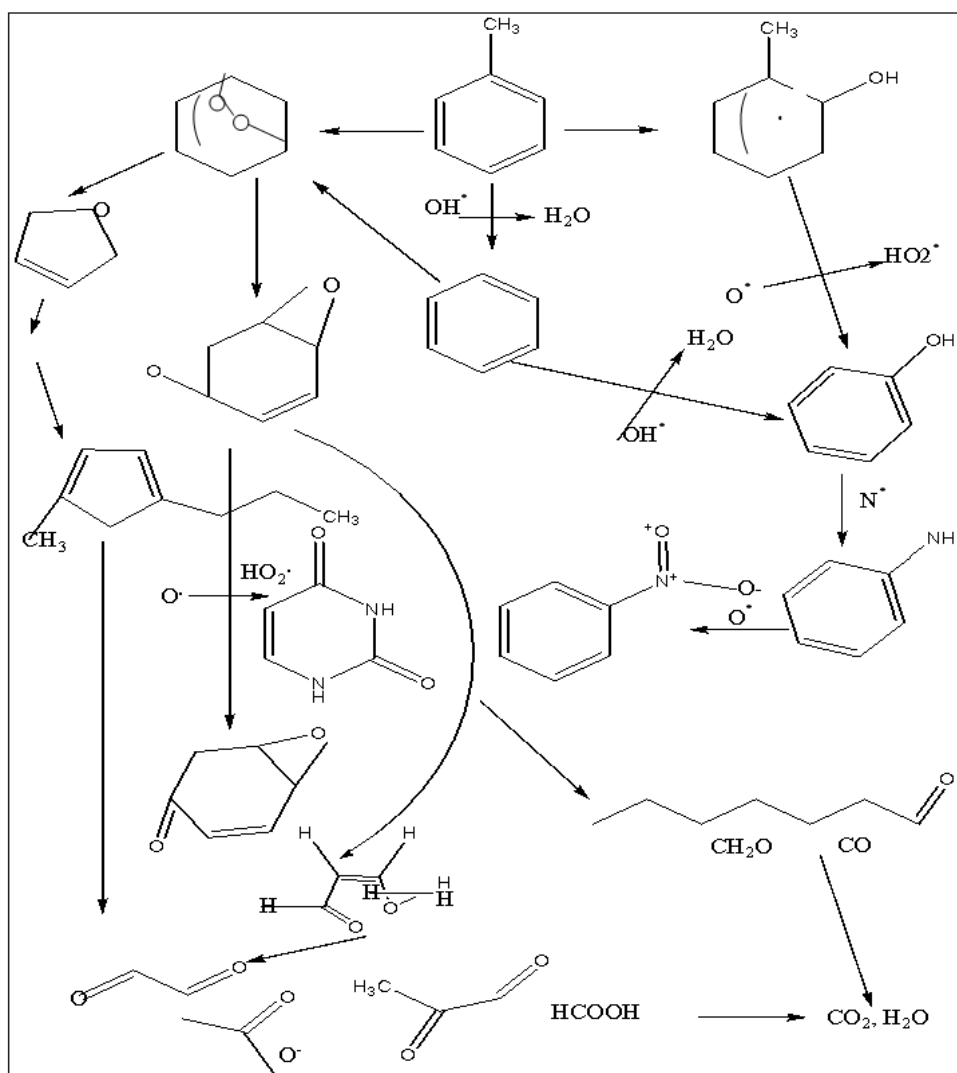

Scheme 1

Decomposition of Chlorinated VOCs

Much work has not done on chlorinated VOCs either by conventional or plasma methods (from literature). Decomposition of dilute trichloroethylene was studied by non-thermal plasma reactor. Effect of humidity and OH radical behavior was discussed. Increase in the humidity, decreases the ozone exhaust and decomposition increases up to 20% of the total humidity by Y. Nakagawa et al [105].

Removal of Chlorobenzene in a DBD reactor and effect of catalyst was studied by means of bipolar pulse power. In the presence of bipolar pulse power supply, the reactor produced instant strong discharge and energetic particles. The catalyst present just before the outlet gives better yield [106].

Decomposition of benzene using hybrid systems of a NTP and catalyst like Ag/TiO_2 increases the CO_2, CO selectivity. At lower Specific Input Energy (SIE) a trace amount of formic acid was detected as minor product. The carbon balance shows no other products are formed. The removal efficiency is better in hybrid systems of a NTP than the conventional pulsed corona discharge reactor and surface discharge reactor. Amount of catalyst does not affect the removal efficiency where as formation of N_2O decreases with larger amount of catalyst [107].
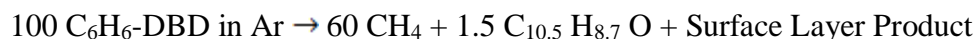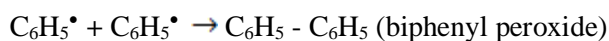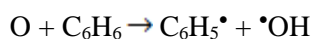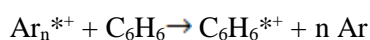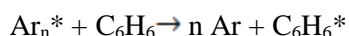
Scheme 2

Decomposition of Benzene and Styrene

Gas-to-particle conversion of Benzene and its implications on atmospheric chemistry was studied; the products are in solid form found on the surface indicating formation of polymer like substrates [108-109]. SEM study shows the formation of nano-particles and C=O band. During the decomposition of styrene similar polymer deposition (polymeric by-product of phenol) was observed [110, 111]. Another undesirable product i.e aerosol was found and can be removed by using catalysts [112, 113].

DBD is also proven its utility as a very fundamental technique for the decomposition VOCs due to its simple design. Moreover its working principles involve different free radicals, positive ions and negatives ions with reactive electrons adding to its advantage. In the presence of O_2 the decomposition rate of benzene is significant. The probable mechanism which depends upon the product type and concentration are given in the following reactions. Conversion rate of benzene to methane is greater than the conversion rate of toluene and *p*-Xylene to methane [114, 115].

$Ar_n^* + C_6H_6 \rightarrow n\ Ar + C_6H_6^*$

$Ar_n^{*+} + C_6H_6 \rightarrow C_6H_6^{*+} + n\ Ar$

$O + C_6H_6 \rightarrow C_6H_5^{\bullet} + {}^{\bullet}OH$

$C_6H_5^{\bullet} + C_6H_5^{\bullet} \rightarrow C_6H_5 - C_6H_5$ (biphenyl peroxide)

$100\ C_6H_6\text{-DBD in Ar} \rightarrow 60\ CH_4 + 1.5\ C_{10.5}H_{8.7}O + \text{Surface Layer Product}$

Decomposition of pure and mixture form of VOCs

Methanol decomposition in NTP process is studied and shows that the effect of OH radical plays important role for the decomposition processes. Presence of excited species like O˙, N˙, and OH are also important [108]. Decomposition of butane under ambient temperature in a DBD non-thermal plasma reactor was studied considering the effect of various parameters [116]. Decomposition rate is higher in presence of O_2 as compared to the argon and helium gas. But there is a difference in the product formation like formation of CO, CO_2, acetone and acetaldehyde in presence of O_2 where as in the presence of Ar and He, acetylene and methane are formed. From the emission spectra various reactive species including radicals, ions, excited molecules, Ozone formation were identified [117-122].

Different VOCs like Benzene, Xylene, P-cumene, Diethylether and Dichloromethane were tested for their decomposition by DBD and Packed-Bed DBD. Decomposition of benzene required higher energy as compared to other aromatic hydrocarbons with side branches. Also the decomposition efficiency is higher in Cumene and Xylene and low for toluene and diethyl ether. But the dichloromethane can destroy the atmospheric Ozone layer. But that can be decomposed in double dielectric barrier discharge system in low power consumption and the rate is slightly higher than in Packed-bed reactor [123].

Effect of catalysts

Sometimes the byproducts may be more harmful than parent VOCs which is reduced significantly in the presence of various catalysts. The reaction pathways of toluene removal from a gaseous influent at NTP were studied by T. Zhu et al. [124]. Different catalysts like nano MnO_2/Al_2O_3 coupled with modified ferroelectric of nano-$Ba_{0.8}Sr_{0.2} Zr_{0.1}Ti_{0.9}O_3$ plays an important role for increase in removal efficiency of toluene which is also a good inhibitor for ozone formation.

Effect of catalyst and plasma reactor studied together for decomposition of VOCs.

Decomposition of styrene in air stream with and without packing material was studied. Selectivity of CO_2 as major product is higher in packed bed reactor than the non-packed reactor. Also increase in the concentration of styrene decreases its removal efficiency. Plasma reactor packed with Pt-Pd/Al_2O_3 pellets shows good results for decreasing the concentration of O_3 [120].

Decomposition of benzene was studied by NTP coupled with nano-titania catalyst. The resulting byproducts are mainly CO_2, H_2O and small quantity of CO. Here the effect of photo catalyst increases the removal efficiency of benzene [125].

Decomposition of benzene in presence of catalyst was studied in a DBD reactor. Using catalysts like TiO_2, Pt/TiO_2 and V_2O_5/TiO_2 are chosen in the NTP reactor for the decomposition of dilute Benzene. Where 1.00 W% V_2O_5/TiO_2 proves as an effective catalyst for the decomposition. The use of catalyst decreases the N_2O formation and increases CO_2 as by-product. Also it is noticed that increase in the discharge voltage increases the decomposition rate of benzene [126].

For the first time the effect of TiO_2/GAC, ZnO/GAC, and TiO_2-ZnO/GAC catalyst for the decomposition of chlorinated volatile organic compounds was studied in pin-to-plate corona discharge NTP reactor. Better result is obtained for TiO_2-ZnO/GAC catalysts [127]. Oxidative decomposition of Chlorobenzene in air was studied in a DBD reactor which is modified to the ground electrode with different substances like silver paste, copper wire and aluminum foil; where electrode with silver paste gives best result. Also increase in the flow rate decreases the removal efficiency [128].

Catalytic non-thermal plasma reactor for total oxidation of VOCs like Toluene, isopropanol and trichloroethylene was studied in presence of metal oxides of Ti, Mn and Co for a fixed concentration of the treated gas. Total oxidation of isopropanol seems to be best as compared to the other two. MnOx/SMF show the best result may be due to formation of active species [129].

A DBD reactor for toluene removal shows enhanced removal efficiency from 10% (only plasma) to 100% (with Mn-based composite catalyst). 100% ozone removal was found in the presence of catalyst at a SED of 28.8 JL^{-1}. Among the alumina supported Mn- based composite catalysts Mn-Co/Al catalyst showed better result may be due to the larger BET specific surface area with supported Al_2O_3 [130]. Catalysis chart of the combination of catalysts in the process of gas discharge in different plasma system is given in **Figure 4**.
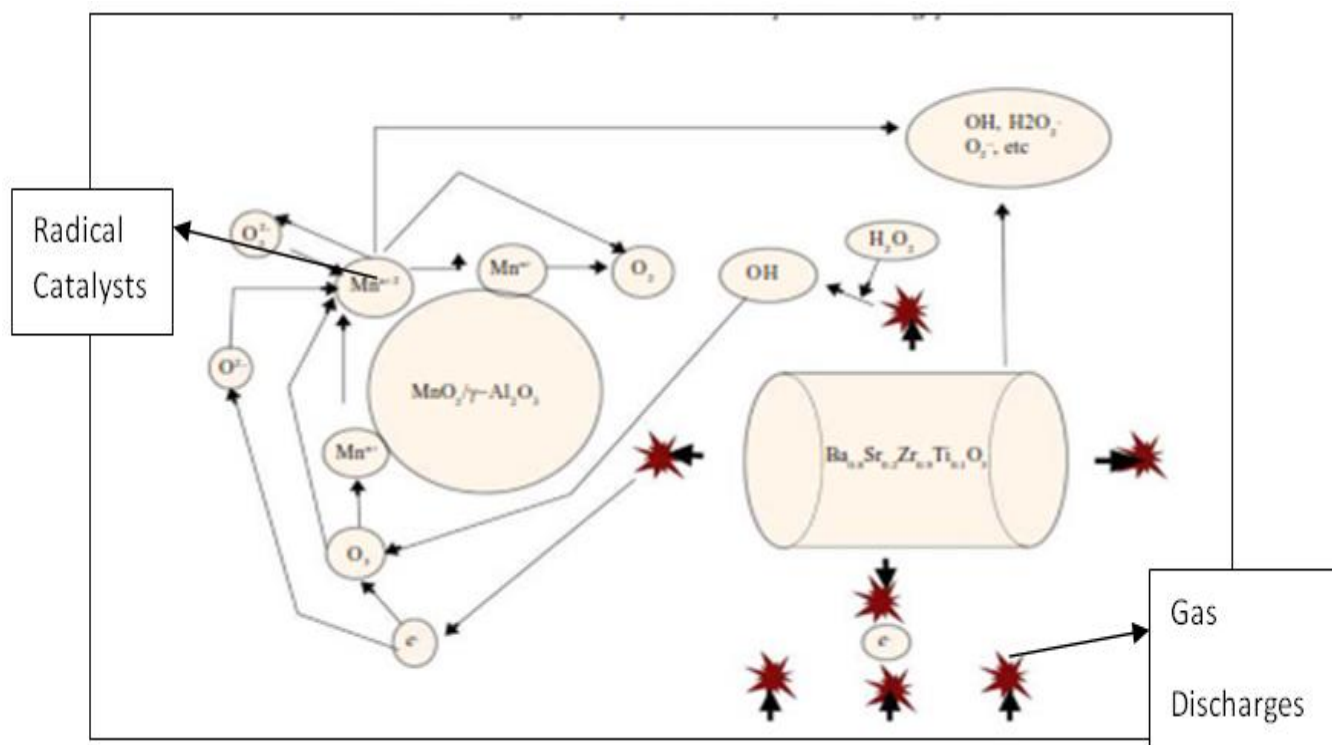
Figure 4 Catalysis chart of the combination of catalysts in the process of gas discharge

Effect of Humidity on VOC Oxidation

The presence of humidity has shown mixed effects in different VOC treatment systems depending on the chemical nature of the substrate. The presence of humidity was the inhibiting factor in the decomposition of TCE. Hence, the destruction of TCE was optimized in dry air stream. But in case of perchloroethylene (PCE), the presence of humidity enhanced the overall destruction of the compound. Humidity in a plasma system alters the reaction mechanism as it introduces [OH] species which can also react with molecules to form different intermediates [131-134].

Effect of Temperature

Increasing temperature increases the removal efficiency in most of the decomposition process in NTP reactor. But in case of toluene the decomposition rate either remains constant or decreases. This may be due to the catalytic action of some catalysts [135-138].

Work done at author's laboratory

A planar DBD reactor has already set up in the department of chemistry, Ravenshaw University. DBD reactor has area 600 cm^2 (20cm x 30cm). It works in AC voltage power supply from 0-30kV and frequency of 50 Hz at atmospheric pressure and room temperature condition. The schematic diagram of the set up of DBD is shown below **Figure 5**.
    Decomposition of various VOCs is studied in the Planar DBD reactor at atmospheric condition. Basic plasma parameters like Paschen curve, I-V curve, Townsend breakdown, comparison of bond dissociation energies of different VOCs by non-thermal plasma are verified; electron temperature and density are calculated.

Verification of Paschen's law in author's laboratory

The optimization parameters for different gases (Ar and He) for voltage and distance were analyzed. Townsend breakdown and Paschen Curve were analyzed for different pressure and distance (Figure 6)
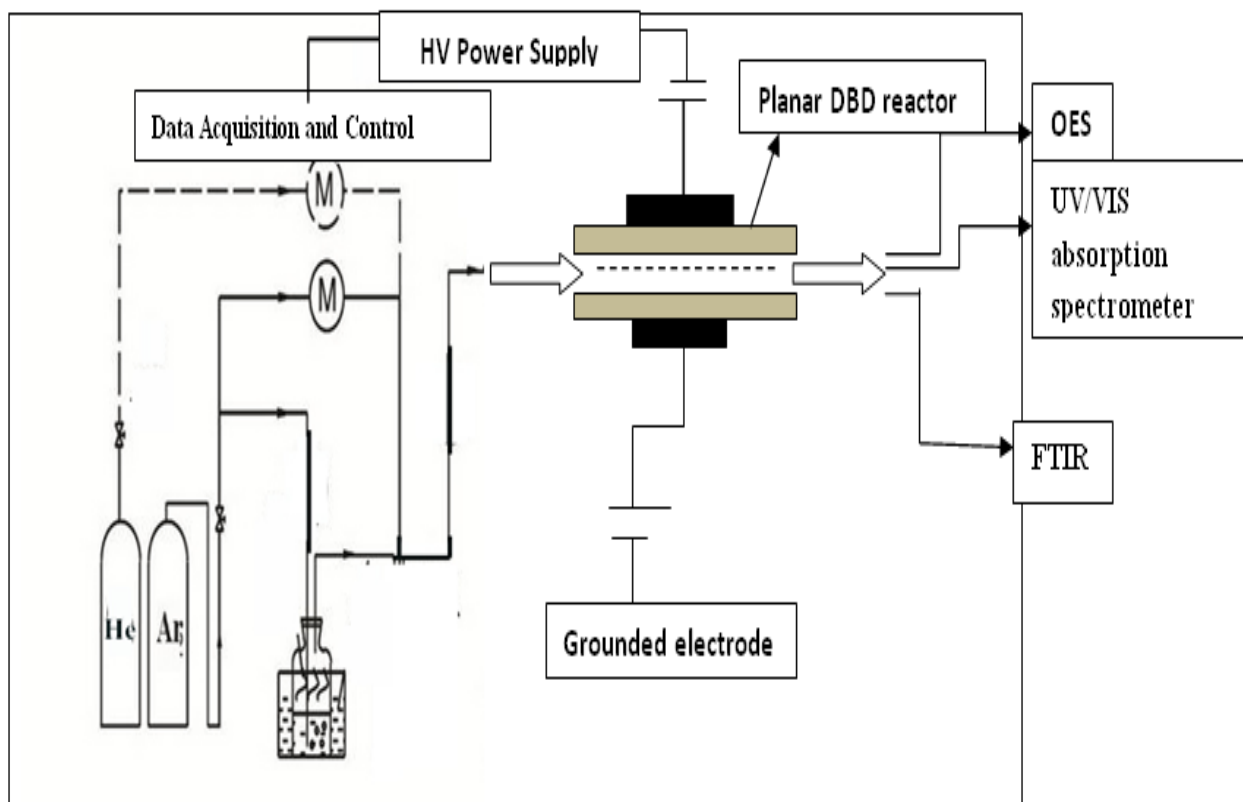
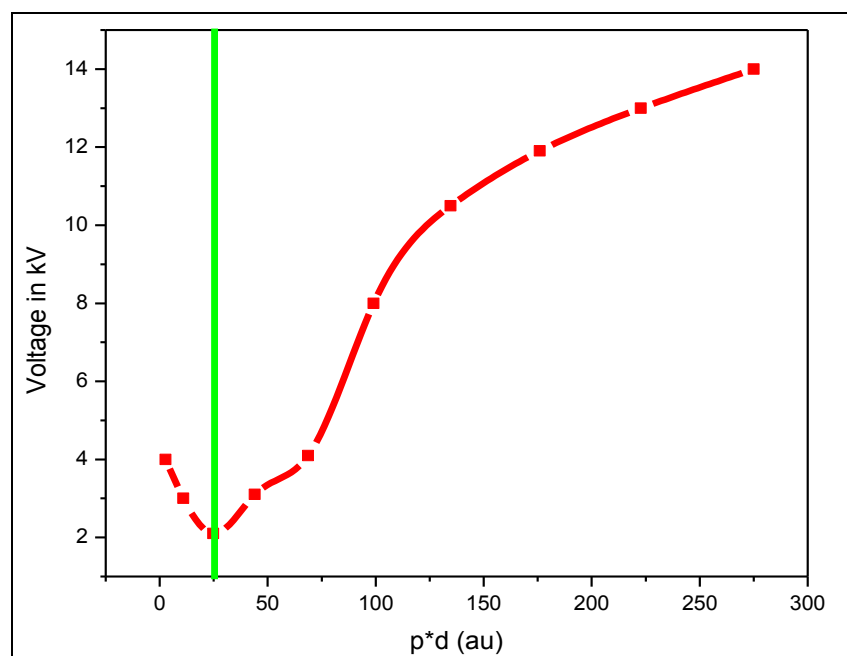**Figure 5** Schematic diagram of DBD set up

Figure 6 Paschen Curve for Ar

Plasma parameters like electron temperature and density is determined by UV/VIS emissive spectrophotometer, by taking the ratio of intensities of spectral lines of some element of same degree of ionization/ excitation may be written as

$$I_2/I_1 = (Ag\upsilon)_2 / (Ag\upsilon)_1 [\exp (E_1-E_2)/kT]$$

Hence electron temperature

$$T_e = [\{(E_2-E_1)/k\}/[\ln\{(A g\upsilon)_2/(A g\upsilon)_1\}-\ln(I_2/I_1)]$$

$$\mathbf{Electron\,Density} = \frac{I_a}{I_i} \times \frac{(Ag)_i\,\lambda_a}{(Ag)_a\,\lambda_i} \times 2\left(\frac{2\pi mkT_e}{h^2}\right)^{3/2} \times \exp^{-\left[(U-\Delta U)-\frac{(E_a-E_i)}{kT_e}\right]}$$

Different spectral lines obtained for various VOCs are given in the following **Figure 7**. From the below figure, it is clear that the intensities of spectral lines of Ar decreases when it is combined with chloro- or nitro group attached benzene with respect to when it is studied without VOCs.

Decomposition of Benzene, Chlorobenzene, Toluene, Xylene was studied in the above mentioned plasma reactor with large surface area in presence of He as carrier gas, depending upon the bond dissociation energies Chlorobenzene having high bond energy but dissociate first than benzene with lower bond dissociation energy (Figure 8) [139, 140, 141, 142].

Different deposited by products are studied in FTIR and UV/VIS spectrometer and found that pure VOCs transmittance differs from the spectra of deposited by products [143]. Other VOCs like nitrobenzene, Chlorobenzene were studied in presence of Ar as carrier gas in the planar DBD at NTP condition and their plasma parameters are determined. Interestingly it is found that electron temperature and density like parameters of Ar plasma increases in presence of VOCs indicating the decomposition of the target [144].
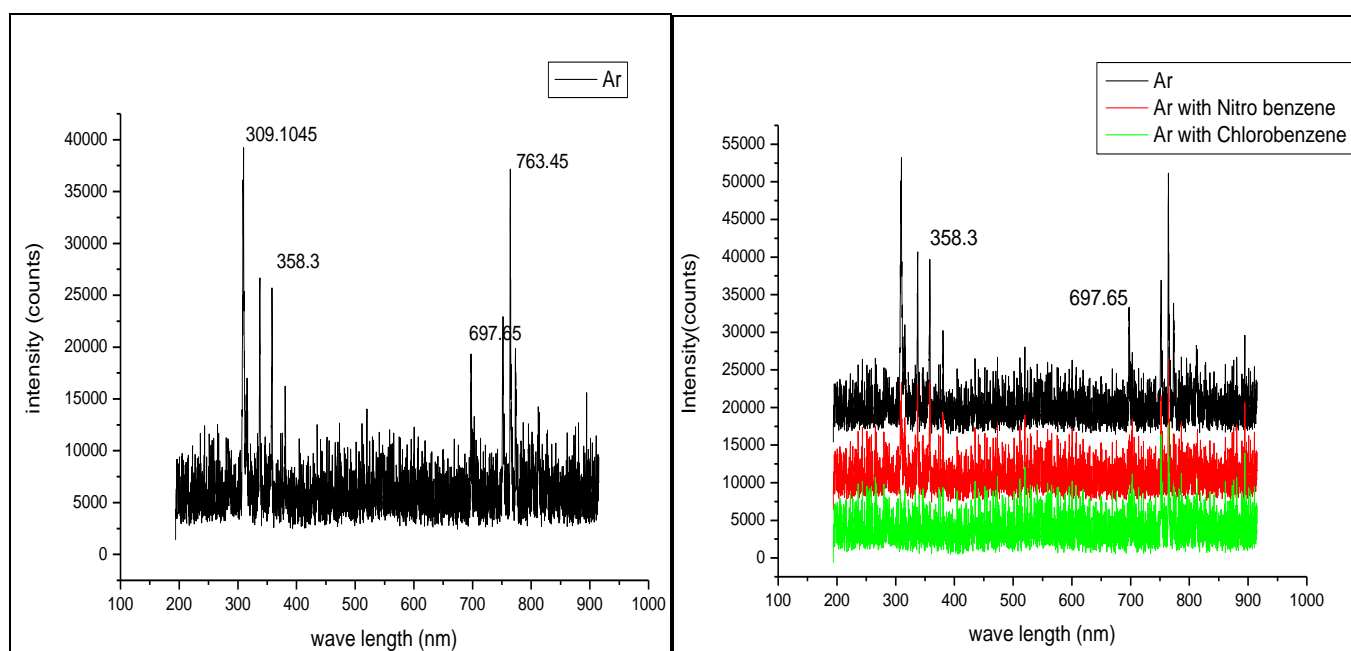

Figure 7 Spectral data obtained for Ar and Ar with VOCs by UV-VIS spectrophotometer

Summary and conclusion

VOCs are the most important air pollutants. Therefore decomposition of VOCs is the present need of the society. Various conventional methods (non-plasma methods) have been used to control these VOCs. But those have many shortcomings and the byproducts are more harmful than the parent compounds. This problem can be overcome by plasma techniques. The high temperature fully ionized fusion grade plasmas have significant applications in generating unlimited resource of clean energy, the low temperature processing plasmas play an extremely significant role in materials processing, exotic chemistry, waste management and surface engineering. Due to the highly energetic

particles available in the plasma and their energies, it is possible to carry out various particles triggered chemical reactions that are not possible in normal condition. DBD non-thermal plasma is one of these plasma techniques, which has many wide applications in different fields. It is a novel method for the decomposition of low-concentrated VOCs releasing to the environment. It can be done in a laboratory condition, which is widely used to industrial sectors. VOCs decomposition mainly depends upon types of VOC, catalysts, temperature, humidity etc. It is also noticed that the deposited by-products are more or less polymeric in nature. Different deposited byproducts are studied in FTIR and UV/VIS spectrometer and found that pure VOCs transmittance differs from the spectra of deposited byproducts. Increase in removal efficiency in presence of catalyst is a great achievement. Catalytic non-thermal plasma reactor for total oxidation of VOCs like toluene, benzene, xylene, styrene, substituted aromatics, isopropanol and trichloroethylene were studied in presence of metal oxides of Ti, Mn and Co for a fixed concentration of the treated gas. Catalytic action plays important role to decompose VOCs to CO_2 and H_2O as main products by increasing the rate of decomposition/removal efficiency. Humidity in a plasma system alters the reaction mechanism as it introduces [OH] species which can also react with molecules to form different intermediates. All the advantages of DBD non-thermal plasma have discussed in the review.
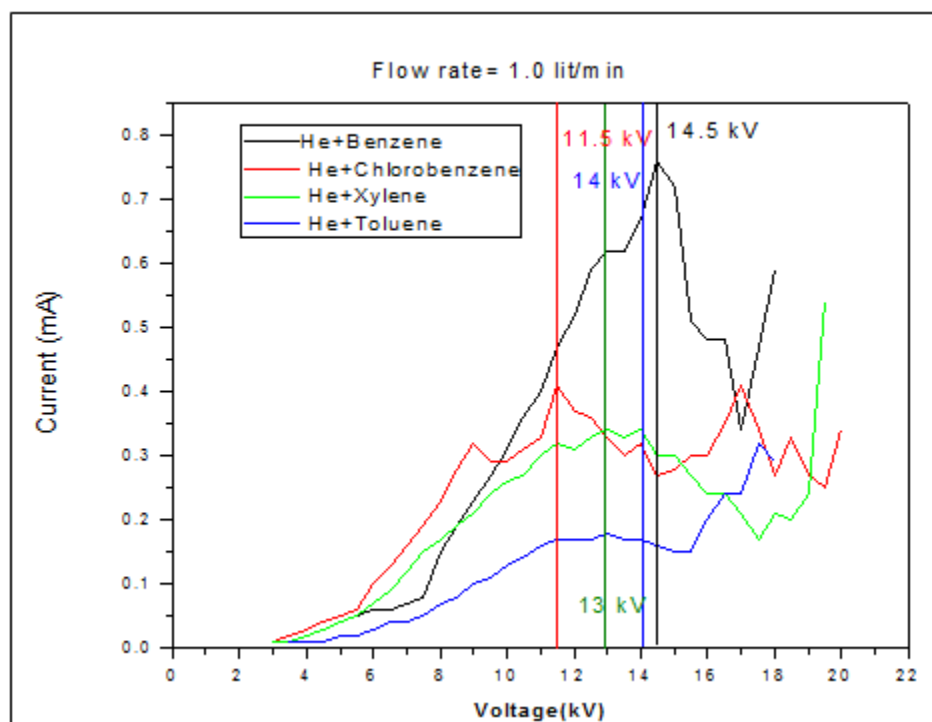

Figure 8 Breakdown voltages of different VOCs[142]

While the breadth and depth of application of DBD non-thermal plasma research is impressive for applications in present days and in future. There are a number of concerns which need to be added to fully realize the potential of this method. This process can be utilized in other fields like surface treatment, conducting polymers, medicine, cancer treatment etc .Novelty of this process is that the system is easy to fabricate, easy to handle, working in room temperature and atmospheric condition. It has also a wide industrial application. Pollution control, waste water treatment, thin film deposition, new polymer preparation, surface modification etc are mostly industrial applications. The modification of polymer surface by plasma treatment has great potential for applications as biomaterials, sensors and medical devices. For plasma pollution control, incomplete oxidation of VOCs leads to the formation of various intermediate and unwanted by-products. Although for certain compounds decomposition mechanisms are proposed, there is still need to expand the knowledge on plasma-chemical kinetics. The derived information about e.g. the distribution of by products can be very useful to choose an appropriate catalyst or to enhance existing catalytic formulations in order to increase the efficiency of the hybrid system. With all mentioned qualities DBD plasma technology is considered as a green technology

Acknowledgements

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