A Dielectric Barrier Discharge (DBD) Plasma Reactor: An Efficient Tool to Measure the Sustainability of Non-Thermal Plasmas through the Electrical Breakdown of Gases

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Abstract

Gas discharges in plasma atmosphere are known to consist of a collection of different particles, mainly electrons, ions, neutral atoms and molecules. In this piece of research work we aim for the complete decomposition of volatile organic pollutants in NTP system. So the formation of plasmas in DBD systems and its sustainability are the main goal. The present need is to characterize the plasmas and optimization of the designed and fabricated plasma system under variable conditions. One of most important issue is the electrical breakdown of gases and to find the point of electrical breakdown. The volatile organic pollutants taken are Benzene, toluene, xylene, chlorobenzene, dichlorobenzene, nitrobenzene, methylene chloride etc. Self-sustainability of DBD-plasmas is explained for different VOCs under different experimental conditions taking helium and argon as carrier gases in terms of Paschen’s curves. It explains the breakdown voltage as a function of the electrode spacing or gap (d), operating pressure (p), and gas composition [1]. The breakdown voltage is a function of the product of the pressure (p) and the inter-electrode distance (pd) also. It is verified that as the nature of substituent group changes, it varies the breakdown voltage and glow discharge zone following Townsend breakdown curve and eventually depends upon electron density of the system.

Keywords: Gas discharges, VOCs, DBD systems, Paschen’s curves, Townsend breakdown curve, self-sustainable plasma.

1. INTRODUCTION

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, it explained the breakdown voltage as a function of the electrode spacing or gap (d), operating pressure (p), and gas composition [1]. The breakdown voltage is a function of the product of the pressure (p) and the inter-electrode distance (pd).

\[ V_b = f(pd) \]  

\[ V_b \] is the breakdown voltage.

The mathematical formulation of Paschen’s curve is derived from Townsend’s assumption [2]. Description of the basic charge generation processes including electron impact ionization (α process) and secondary electron emission from the cathode due to primarily ion bombardment (the γ process), though other bombardment processes may play a vital role in this theory [3]. Historically, Paschen’s curve has proved to be accurate for large gaps and at low pressures [4-5], but it is often acknowledged that it fails to explain the behaviour of curve at extremely low or high pd values [6-7].

1.1 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 relations:
Paschen derived breakdown voltage from the above relationship as:

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

Finally expressing:

\[ V_b = f(pd) \]  

A and B are the constants and can also be calculated as:

\[ A = \frac{\sigma_n}{kT_n}, \sigma_n \text{ is electron-neutral collisional cross-section, } T_n \text{ is temperature of neutral atom, } k \text{ is the Boltzmann constant.} \]

\[ B = AV_i \text{ where } V_i \text{ is the ionization potential and } \gamma \text{ is secondary electron emission coefficient.} \]

From equation (1) it is clear that breakdown voltage depends on the product of p and d for a given gas. From the Paschen curve (figure 1), it is understood that 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 [8-19]. In order to optimize the newly designed DBD reactor, Paschen law and Townsend Theory were verified and the results were discussed in this piece of work.

\[ 1 - \gamma \left( e^{\alpha d} - 1 \right) = 0 \]

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

2. MATERIALS AND METHODS

In this work to optimize the DBD plasma system, we have performed a simple investigation on the electrical breakdown of Ar and He gas molecules between two parallel electrode plates separated by variable distance and voltage. The current is kept low so that the temperature is below the critical value beyond which thermionic emission occurs. In order to avoid emission of excess free electrons from the electrode, the low electric field is maintained. The parallel electrode
plates are used to avoid corona discharge due to accumulation of charges on cornered surfaces that can cause high potential gradients around them.

The experimental arrangement used to study DBD discharge at atmospheric pressure condition is sketched in Figure 2.

![Parallel Plate Plasma Reactor](image)

**Figure 2.** Parallel Plate Plasma Reactor

The discharge is generated between two plane electrodes that is covered by 3mm thick pyrex dielectric plates. The normal AC power supply is connected (frequency 50Hz) to a step-up transformer for generation of potential from 0-30kV. Two mass flow controller of the range 0-5 lit/min is connected to measure the gas flow to the reactor. The breakdown voltage for different VOCs with carrier gases like He and Argon are studied here.

Two MFCs are connected to the carrier gases Argon and Helium. The other end is attached to the reactor chamber. When high voltage is applied to the system, plasma is generated. Varying different voltages as well as gas gap the system is optimized. The gas gap distance can be varied from 3mm to 15mm. preliminarily break down voltages at different gaps are noted. By plotting a graph between break down voltage verses pd (pressure (p) X distance (d)), Paschen Curves for different gases are obtained.

In the second case we changed the flow rate of the gases, and then measured the discharge current. Pressure exerted was calculated from the flow rate. Then by plotting graphs between break down voltages and (P X d), we get Paschen’s Curve.

3. RESULTS AND DISCUSSION

3.1. Optimization of the reactor in presence of Ar at a fixed gap.

The optimization parameters for different gases (argon and He) varying voltage and distance were analyzed. Townsend breakdown and Paschen Curve were analyzed for different pressure and distance [6]. Impedance matching resistor was installed between HV power supply and DBD reactor for maximum power transfer at optimized operating condition.

The curve (figure 3) for Ar is obtained when gas-gap is kept fixed at 11mm and mass flow rate is varied from 0.5-5.0 lit/min. It is observed from the figure 4 that when P X d value is 24.75 (Torr X mm) the minimum value of Vb corresponds to 2.1 KV and at this condition the system is optimized.
3.2 Optimization of the system in Ar with volatile organic compound.

In presence of Ar, different volatile organic compounds ionize in different voltage (figure 4, 5, and 6). Benzene, xylene and toluene and in Ar plasma ionize at 2.8 kV, 4.5 kV and 2.6 kV. Between benzene and toluene, due to branching, toluene reacts first. In spite of presence of two substituted methyl groups in xylene its breakdown voltage is higher than others. This may be explained in terms of steric effect. During the course of experiment we also found that xylene decomposes at higher voltages than benzene and toluene indicating presence of some stabilizing energy in xylene between methyl substituent.
3.3 Optimization of the plasma reactor depending upon the two different gap distances between the electrodes for He plasma

From the figures 7 and 8 it is clear that He plasma is best explained when its mass flow rate is 1.0lit/min. but the breakdown voltage is higher (6.5 KV) when the gas gap is 7mm (figure 7) as compared to 4mm distance (i.e 3.9 KV) (figure 8). The system can work efficiently for formation of sustainable helium plasma at a gas gap distance 4-7mm and the applied voltage in the range of 3.9-6.5 kV. So the formation and existence of He plasma in this system can be understood in following ways:

i. It depends upon the distance between the electrodes.
ii. Also on the flow rate of the gas i.e. concentration of the gas present in the reactor volume
iii. Volume of the chamber as its volume depends upon the inter electrode distance

Figure 6. Paschen Curve for Ar + Toluene

Figure 7. Paschen Curve for He (d=7mm fixed and mass flow is varied)
Figure 8. Paschen Curve for He (d=4mm fixed and mass flow is varied).

3.4. Optimization of He plasma in presence of volatile organic compounds in different flow rates

From the figure 9, 10 and 11, it is clear that all the above system is optimized in the gas gap of 4mm for the formation of He plasma. In three cases mass flow rate is 1lit/min. The gas gap distance is 5mm and 4mm in figure 10 and 11 respectively. For figure 10 the breakdown voltage is 3.2kV and it is slightly greater than in figure-11 i.e 3.0 kV. The deviation may be due to the atmospheric humidity (condition) and gas gap. But in case of figure 9 as the gas gap (pd) is 8mm the minima broadened the Paschen curve and we get higher breakdown voltage at 5.5KV.

Figure 9. Paschen Curve for He + Benzene (d=8mm)

Figure 10. Paschen Curve for He + Benzene (MFC= 1lit/min) (d=5mm)
Comparing the figures 11, 12, 13 and 14, the breakdown voltages of the volatile organic compounds like benzene, toluene, xylene and chlorobenzene are found to be 3.0kV, 3.0kV, 3.8kV and 2.7kV respectively. Which shows for a particular mass flow rate (1lit/min), the breakdown voltages differs for different compound. In case of nitrobenzene (in figure 15) the breakdown voltage is about 4.0kV which is much greater than chlorobenzene i.e.2.7kV. As the gap distance is more (6mm).So it required more voltage to break the compound at higher gas gap. It indicate breakdown voltage (i) depends upon the nature of the VOC compound and bond energies of the compounds.

**Figure 13.** Paschen Curve for He + Xylene
3.6. Verification of Townsend breakdown curve.

Plasma breakdown as an important fundamental process in plasma science has been a subject of enormous studies from the early days of gaseous electronics. Due to its relevance in a wide range of applications, it is used for a deeper understanding of fundamental plasma behaviour [21-24]. Renewed interest in breakdown phenomena, especially breakdown in small gaps, emerged from the possibility of lower facility and process costs for a variety of plasma processing and micro-manufacturing techniques. At the same time, direct current (DC), pulsed DC and radio-frequency (RF) discharges are widely used in the microelectronics industry, in plasma display panels, for depositing thin films, for semiconductor processing, surface modification, analytical chemistry, biotechnological and environmental applications, waste treatment etc. [25-31]. As already pointed out, a better understanding of voltage breakdown, besides being scientifically interesting, will aid progress in many fields and technologies, which generally fall into two categories: those that require high electric fields, and those that require high electric currents. On the other hand, unwanted voltage breakdown limits many technologies involving high electric fields [32]. Electric breakdown is referred to as a process that transforms a non-conducting material to a conducting one when a sufficient strong electric field is applied comprising an involved set of transient processes such as collision of electrons, ions and photons with gas molecules and electrode processes which take place at or near the electrode surface. Other possible gas processes include ion-atom collisions, excited atom-molecule collisions, and atom-atom collisions. In 1928, Langmuir [33] introduced the word plasma to describe the ionized gas that is created in a gas discharge.
From above facts here we conclude that

**Mechanism:** mechanism of Townsend theory involves three steps which is represented as below

Let A is a gas molecules or atoms undergo ionization involving following steps:

1. **Step-1 photo ionization:**
   
   \[ A + h\nu \rightarrow A^{-} + e \]

2. **Step-2 ionization by excited atoms or molecule**
   
   \[ A + A^{*} \rightarrow A^{-} + e + A \]
   
   \( \text{Or} \)

   **Associative ionization**
   
   \[ A + A^{*} \rightarrow A_{2}^{+} + e \]

3. **Step-3 Dissociative Recombination**
   
   \[ A_{2}^{+} + e \rightarrow A + A^{*} \]
   
   \( \text{Or} \)

   **Associative recombination**
   
   \[ A^{+} + e \rightarrow A + \gamma \]

![Figure 16. Electron avalanche on the basis of Townsend’s theory](image)

Following the Townsend theory (shown in figure 16) in this work, Voltage-current characteristic of low temperature discharge between electrodes for a wide range of currents is plotted in figure 17, plasmas become self-sustaining, i.e. the breakdown occurs. The simplest breakdown condition can be expressed as: each primary electron generated in the initial avalanche and lost at the anode is replaced by another electron generated by secondary emission at the cathode. This represents a steady self-sustained current in the homogeneous field:

\[ E_{t} = \frac{V_{b}}{d} \]

(Point B in Figure 17), where \( V_{b} \) is the breakdown voltage and is determined from Equation (3) as a function of \( d, \gamma \) and the known function \( \alpha \) (EA: region of non-self-sustaining discharge, (BC) Townsend discharge, (CD) subnormal glow discharge, (DE) normal glow discharge EF) abnormal glow discharge. All these data shows the existence and sustainability of the plasma in the designed reactor.

![Figure 17. I-V curve of He + Benzene](image)
3.7. Comparison of breakdown voltages for different substrates (VOCs) from current-voltage curve.

Influenced by Townsend experiment we have calculated the breakdown voltages (in figure 18 & 19). Breakdown voltage starts at 3.0kV, 2.7kV, 3.0kV and 3.8kV for benzene, chlorobenzene, toluene, xylene respectively in figure 18. But it is 3.2kV, 6.0kV for ortho-dichlorobenzene and methylene chloride in figure 19. Here all these vocs are taken in combined with He as carrier gas. The bond dissociation energy of C-H bond in benzene is ~390kCal/mole [8], in toluene is ~77.5kCal/mol and in xylene ~77.5Kcal/mole [9], and that for C-Cl bond in chlorobenzene is ~399.19kCal/mole, for ortho- dichlorobenzene it is 385.4 kCal/mol and that for methylene chloride is 310.0 kCal/mole[10].

It is observed that C-Cl bond energy is highest, but its breakdown voltage is 2.7kV and 3.2kv in case of chloro and dichlorobenzene. For benzene bond energy is ~390kCal/mole, but dissociates at 3.0kV. Similarly, the glow region also starts at 11.5kV for chlorobenzene and 5.0kV for di-chlorobenzene where as that of benzene is 14.0kV. Since the electron affinity of Cl is appreciable, as soon as the chamber is filled with He plasma, Chlorine atom gets detached from chlorobenzene and dichlorobenzene quickly becoming neutral recombining with free electron in the plasma. Again for benzene the maximum current is drawn i.e. 0.67mA and for chlorobenzene it is lower than benzene i.e. 0.41mA whereas for dichlorobenzene it is much less i.e. 0.1mA justifying chlorine as a strong electron scavenger. In both the cases the chlorine ions get detached from chlorobenzene and dichlorobenzene in plasma medium by using DBD reactor at low breakdown voltage and current producing sustainable plasma.
But it is found that in case of aliphatic dichloro compound i.e. methylene chloride, bond dissociation energy is comparatively less i.e. 310.0kV whereas breakdown voltage starts at 6.0kV and glow region starts immediately at 6.5kV. It may be due to low molecular mass, high volatile nature (B.P. -39.5) of the compound which gets dissociated completely in plasma medium due to electron induced reaction.

4. CONCLUSION

Dielectric barrier discharge assisted plasma technique is a novel green technique with high energy evolution. The developed DBD assisted plasma reactor is optimized using various diagnostic methods. Optimization of a plasma reactor depends on size, gap between the electrodes, gas flow rate as well as applied potentials and stability of carrier gases. It also depends upon the nature of the compounds and type of bond which has been verified taking different volatile organic compounds like benzene, toluene, nitrobenzene, chlorobenzene, dichlorobenzene, methylene chloride etc. Different aspects discussed above give the reliability of the Paschen curve and Townsend breakdown theory verified from our DBD plasma system operating in room temperature and atmospheric pressure.

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