Application of Non-thermal Plasmas in Medicine and Energy-Food-Water

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Abstract: Non-thermal plasma (NTP) due to their versatile nature have been successfully used in many applications ranging from hydrocarbon destruction to cancer treatment. The NTPs, can deliver high electron temperatures and high densities of radicals at near ambient conditions making it a unique source for applications ranging from treatment of extremely heat sensitive surfaces to complex chemical reactions which are feasible only at low temperatures. This work presents some of the recent understandings on how various NTP reactors can be designed and characterized for various applications. The results obtained from a pin-to-water plasma discharge system, in generating plasma activated water for agricultural applications are discussed. The application of NTPs in hydrocarbon reforming to obtain a tar-free gas from a waste to energy thermo-chemical process is discussed. The results of selective killing of cancer cells using a DBD is presented. Also, application of NTPs in wastewater treatment systems to treat household chemical products are presented.

Keywords: Index Terms—Non-Thermal Plasma, Hydrocarbon Reforming, Plasma Activated Water, Agricultural Applications, Cancer Treatment

Introduction

Non-thermal plasma technology

The Manmade plasmas can be classified into thermal and non-thermal plasmas (TP and NTP). While maximum achievable temperature through combustion is 2300 K, plasma species in thermal plasmas can equilibrate to very high temperatures of order 10^3-10^4 K reaching local thermodynamic equilibrium (LTE) [1]. This temperature governs the ionization and chemical processes, enhancing the overall process value. Hence, thermal plasma systems are used for applications that require enormous heat such as spray coating of metals and ceramics, welding, cutting and treatment of hazardous/municipal wastes. In thermal plasmas, most of the input
energy is spent towards heating the bulk of the gas to high temperatures. Hence, thermal plasmas typically have poor energy efficiency and poor chemical selectivity. However, NTP working at near ambient conditions are known to have higher energy efficiency and better chemical selectivity’s. The NTP are used in many applications such as pollution control, fuel conversion, dissociation of CO₂ and H₂S, H₂ generation from CH₄, water-gas shift reaction and syngas cleaning [2-4]. In NTP’s the highly reactive radicals are present at high concentrations and they initiate chemical reaction pathways even at room temperature. This feature of NTP’s can be utilized efficiently towards achieving increased chemical selectivity without heating the bulk of the gas, leading to less energy consumption. In NTP, the electron temperature (≈10000 K) governs ionization and chemical processes [1]. Due to these merits, NTP are considered as a potential replacement for catalysts. Using NTP, properties of water such as pH and conductivity can be regulated, when the air above water column is exposed to plasma for desired duration called as activation time (t). This activated water is referred to as plasma activated water (PAW) which has agricultural and bio-medical applications [5-7]. Exposing air to NTP also produces ozone which can be used for disinfection of water. This study reports on different NTP sources, their characterization and potential applications.

**Reactor sources - design and characterization**

Different NTP sources i.e. dielectric barrier discharge (DBD) and pin-to water discharge, as shown in Figure 1a and 1b respectively, was used for various applications such as enhanced seed germination, as a source of nitrogen for plant/algae growth, anti-microbial applications and treatment of grey water. Another plasma source having combined effect of TP and NTP called rotating gliding arc (RGA), as shown in Figure 1c, was used for hydrocarbon reformation and water-gas shift reactions. In the case of a DBD reactor, quartz tube was used as a dielectric material. Two aluminium wires electrodes which were wound, on both side of the quartz tube made the plasma electrode assembly. This electrode assembly was positioned in a glass breaker containing water below to generated plasma activated water (PAW). In the case of pin to water discharge, one of aluminium electrode submerged into the water column acted like an electrode whereas on aluminium wire positioned about 1 cm above the water column acted like a second electrode. In the case of RGA reactor, aluminium wires shaped as shown in Fig. 1c served as electrodes which was housed in a quartz tube serving as a plasma reactor. An AC 20 kHz–20 kV peak supply (M/s Information Unlimited PVM 500-4000) was used to power all these plasma reactors.

For achieving maximum chemical performance in these reactors, especially in the case of pin-to-water discharge and RGA, reduced electric field (E/N) becomes an important optimizing parameter, since the E/N is a function of electron temperature. In the case of pin-to-water discharge, E/N was varied by recirculating the water to interact with the arc with/without stirring the water by providing magnetic stirrer at the bottom. By this way, the arc’s length and voltage varied in both these cases as it can be inferred from Figure 1. In the case of RGA where
swirl flow was employed, the influence of turbulent eddies on the discharge was used as a control parameter to achieve the desired E/N. Table 1 shows the E/N values achieved in pin-to-water discharge and RGA reactors. With pin-to-water and RGA discharge, the maximum E/N of 60 Td and 100 Td were achieved respectively.

Table 1. Reduced Electric Field for Different Plasma Sources.

| Method                                | E/N during operation, in Td |
|---------------------------------------|-----------------------------|
| Pin to water discharge                | Continuous power            | < 20                        |
| Pin to water discharge                | Power supplied as duty cycled | < 60                       |
| RGA                                   | Transient flow              | < 50                       |
| RGA                                   | Turbulent flow              | < 100                      |

In the case of the DBD reactor, plasma volume was varied by varying the length of the wound wire electrodes. As it can be seen from Fig. 1, by using the coils as electrode, the area of overlap between two coils and the pitch of the coil was designed such a way that the plasma volume was large and uniform.

Figure 1. Schematic (top) and plasma volume (bottom) of plasma sources (left to right): a) coil type DBD, b) pin-water discharge and c) rotating gliding arc.
Discussion

Agricultural applications

Plasma activated water (PAW) is a mixture of reactive nitrogen and oxygen species, of which nitrate and nitrite are the dominant species. The PAW can be used to enhance plant growth and seed germination [5]. Water was activated through, pin-to-water discharge for plant growth applications, and DBD for seed germination. The PAW was generated in-situ at the point of consumption, making it suitable for decentralization.

1) Seed germination studies: The effects of seed germination using maize and green gram seeds were studied. Figure 2 shows the average root length (mm) variation of green gram over a period of 120 hours. The seeds supplied with PAW showed a longer root length (almost twice—see Fig. 2) compared to those supplied with tap water.

![Figure 2. Average root length (mm) variation of green gram over a period of 120 hours.](image)

2) Plant growth studies: Tomato seeds were used to study the plant growth. Figure 3 shows view of the grown plants fed with tap water and PAW activated with $t_a$ of 10, 20 and 30 min.

![Figure 3. Pictorial view of plants grown fed with tap water and PAW (different activation time).](image)
The results indicate that plants fed with PAW of \( t_a = 30 \) min have nearly 1.5 times higher shoot length, 4 times higher leaf count, twice the chlorophyll content in the leaves than the plants fed with tap water.

**Biomedical applications**

After powering the DBD plasma reactor for the desired activation time \( t_a \), the reactor was shaken well to assist in the mixing and transfer of the newly formed species from air to the water. Some of the species present in PAW used for this study were \( H^+ \), \( H_2O_2 \), nitrates (\( NO_3^- \)) and nitrites (\( NO_2^- \)). The concentration of these species can be varied by regulating the \( t_a \).

1) **Antimicrobial studies** *Pseudomonas aeruginosa* is an opportunistic, multidrug resistant bacterium that targets the immunocompromised patients. *P. aeruginosa* is one of the predominant bacteria responsible for hospital acquired infections. Figure 4 shows the patches of *P. aeruginosa* (left) which were not found when exposed to PAW (right). The results showed that PAW was effective at inactivating *P. aeruginosa*.

![Figure 4. Pseudomonas aeruginosa colonies in patches (left). Absence of colonies after exposing to plasma activated water (right).](image)

2) **Cancer cell death studies**: Breast cancer ranks first in cancer-related deaths in women. A study was performed to investigate the effectiveness of PAW against human breast cancer cells (MDA MB-231). Figure 5 shows the cancer viability result. These initial results showed a significant reduction in the cancer cell viability without significantly reducing the viability of healthy cells. The PAW retained its effectiveness against cancer cells following two weeks of storage at -20 deg C.

![Figure 5. Picture indicating cancer cell viability. Light purpleness indicates lower cancer cell viability.](image)

Further feasibility studies need to be conducted to expand the scope of the application from laboratory to hospitals, where PAW can be used in two critical biomedical applications.
Industrial chemical applications

1) Water gas shift reaction using DBD: A dielectric barrier discharge reactor (DBD) was used to generate hydrogen from CO and H₂O. A simple co-axial geometry was chosen as DBD [8]. As part of the systematic experimental investigations, this study focused to evaluate the effect of the following parameters on cold plasma powered WGS reaction. i.e., the effect of:

1. Steam to CO molar ratio (MR), defined as the ratio of moles of steam to that of CO in the feed mixture. The MR investigated were 2, 5, 10, 14 and 20.
2. Reactor gas residence time is the ratio of reactor volume to the volumetric flow rate of the gas mixture. Gas residence times of 350, 450, 650, 1300 and 2600 ms were studied.
3. These parameters were studied for plasma discharge powers of 40, 70, and 100 W.

Figure 6 shows variation of CO conversion and H₂ generation for a given discharge power. Results depict that, for a given power, increasing the MR, the CO conversion and H₂ concentration in the product gas increased. Increasing the plasma power at a lower MR increased the H₂ concentration in the product gas.

![Figure 6](image)

**Figure 6.** The effect of steam to CO molar ratio on the avg. CO conversion % (left) and avg. H₂ concentration (right) for molar ratios 2, 5, 10, 14 & 20.

It was also noticed that at higher MR, the influence of plasma power on the CO conversion was negligible. The results show that, at MR of 20, with 2600 ms gas residence time and plasma discharge power of 70 W, a maximum CO conversion of 63 ± 4 % was achieved with H₂ concentration of 48 ± 2 % in the product gas.

Further studies are being pursued to optimize the energy consumption and scaling up the reactor.

2) Tar destruction studies: A novel RGA was developed and fully characterized for its physical and electrical parameters [9]. Since RGA has combined features of both TP and NTP, it can be a suitable plasma source for aromatic hydrocarbon destruction. A preliminary experiment was conducted to destruct toluene compound at concentration of 20 g m⁻³, using N₂.
as carrier gas, at a total flow rate of 25 LPM. Preliminary observation showed toluene destruction of > 90% by spending 0.09 kWh. Fig. 7 shows the soot formed during the tar destruction in RGA reactor.

Further works are planned to understand the chemistry of toluene destruction using syngas as a carrier gas in the presence of steam.

Figure 7. Picture of toluene-N\textsubscript{2} plasma during destruction of toluene. Soot deposited on quartz can be seen indicating dissociation of toluene.

Environmental Applications

Developing decentralized technological solutions for greywater recovery from households and small communities is a way forward to reduce freshwater consumption. Towards this, a compact laboratory scale greywater treatment system was designed which produced ozone to remove surfactants, mal-odour and color of the grey water coming from a kitchen and hand wash sink of a consumer home. The drop in concentration of surfactant, turbidity and malodour were monitored. Results achieved from lab-scale studies, indicated 50% reduction in surfactant concentration and 90% water recovery. Figure 8 shows ozone throughput for various flow rates of air.

Figure 8. Ozone throughput as a function of flow rate in a co-axial DBD plasma reactor.
Based on the findings from the laboratory scale system, a decentralized greywater treatment system for a school in rural India was designed and deployed as a pilot plant. The goal was to direct the treated greywater for reuse in toilet flushing. To do this, grey water was channelled through a grease trapper, trickling bed filter (a bed made of gravel of different sizes), aerator, and a DBD plasma ozonation system. The ozonation disinfects the greywater to achieve reuse water standards. Ozone was produced using a high throughput ozonator designed by the authors [10], powered by solar energy. Figure 9 shows the installed ozonators at the pilot plant.

**Figure 9.** High throughput ozonator in pilot plant.

**Conclusion**

This work reports an overview of the potential applications of the non-thermal plasma systems. Various non-thermal plasma reactor systems were designed, and their preliminary characterization was discussed. This work also discusses various interesting applications of plasma activated water such as enhanced seed germination and plant growth. Also, the other interesting biomedical application such as antimicrobial application of PAW and its capabilities to kill cancer cells are discussed. Industrial applications such as production of hydrogen from carbon monoxide and steam through water gas shift reaction and destruction of high molecular weight tar compounds which are often found to be clogging if not removed in waste to energy application is also discussed. The study also shows demonstrate the versatility of plasma systems for its application in decentralized grey water treatment and recycling.
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