Recent Progress and Applications of Non-Thermal Plasma

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Abstract—Atmospheric non-thermal plasma has been recognized as an important basic tool for promoting various chemical reactions at low temperature. Non-thermal plasma has potentially a wide range of applications, including environmental and biological fields, such as removal of NOx and soot in diesel exhaust, VOCs (volatile organic compounds), or plasma assisted combustion, sterilization of air and water, etc. In this review, recent progress of non-thermal plasma is introduced.

Keywords—Non-thermal plasma, Plasma chemical process, Packed bed, DeNOx, VOC

I. INTRODUCTION

Plasma chemical processes have been gaining attention for various applications, including environment and biological technologies [1]. Non-thermal plasma (NTP) can promote chemical reactions at a lower operating temperature range where a conventional catalyst cannot be activated. NTP can be used in various fields, such as indoor air cleaners, NOx removal from engine exhaust, fuel conversion and plasma-assisted combustion, VOC (volatile organic compound) decomposition, biological applications such as sterilization, etc. The combination of NTP with catalyst is an important method to improve selectivity and efficiency of the plasma chemical process promoted by NTP. In order to extend the capability of the application of plasma, the generation of suitable plasma, the characterization of fundamental parameters and the development of proper applications are important. For this purpose, a new journal, Int’l J. of Plasma Environmental Science & Technology has been published. In this review, several recent progresses in NTP are introduced, mainly from the articles in the journal.

II. GENERATION OF NTP

Several new methods have been developed to generate NTP. Using a silent discharge as an electrode, streamers can be extended along the surface. This process has been used to generate sliding discharges and honeycomb discharges. A micro-electrode system with holes has also been studied for better combination with catalyst.

A. Sliding Discharge

Dielectric barrier discharge (DBD) with a grounded electrode (sliding electrode) on the same surface as the high voltage electrode (three electrode DBD) was experimentally studied to generate homogeneous surface discharge [2-4]. Application of AC high voltage generated stable and homogeneous surface plasma between high voltage and grounded electrode without arcing. Electrical properties of the three electrodes DBD was experimentally studied. With the same peak voltage, lower DC component generated a more stable but less homogeneous plasma sheet. Lower AC/DC ratio reduced the electric field to initiate sliding discharge. With a sliding electrode, wide surface plasma was generated compared with normal DBD. The effect of the sliding
electrode was more significant when the gap between high voltage and the sliding electrode was increased.

B. Micro-discharge with Ceramic-coated Punching Metal

Ozone generation of micro plasma using a pair of electrodes covered with dielectric barrier is investigated. The discharge gap of micro plasma is in the order of micro meters, which is very small compared to other discharge methods [5]. Since the discharge gap is very narrow, non-thermal plasma occurs around 1 kV, which also produces a high electric field between the electrodes. By using micro plasma, pollutant gas control is possible with a very small power source and system.

C. Honeycomb Discharge

Inside the honeycomb catalyst, NTP can be generated. As shown in this figure, packed bed discharge is placed at one side of a honeycomb, and the other side is attached to a metal mesh electrode energized with DC. Fig. 4 shows the honeycomb discharge using a bundle of capillary tubes for visualization of the discharge inside the glass capillary.

III. OPTICAL MEASUREMENT OF NTP

Laser-induced fluorescence (LIF) [6, 7], laser absorption [8], and optical emission spectroscopy (OES) [9, 10] techniques have been applied for density and temperature measurements of OH radicals, NO molecules, ozone, atomic oxygen, atomic nitrogen, and N₂ (A3Σ⁺u) metastables in pulsed corona and pulsed dielectric barrier discharges under atmospheric pressure. These radical measurements are indispensable to develop an efficient non-thermal plasma reactor for decomposing atmospheric pollutants.

OH radicals can be measured using laser-induced predissociation fluorescence (LIPF). OH radicals in the ground state X2Π (v'' = 0) are excited to the upper state A2Σ+ (v' = 3) using a tunable KrF excimer laser at around 248 nm, then subsequent fluorescence from A2Σ+ (v' = 3) to X2Π (v'' = 2) is observed at around 297 nm. Fig. 5 shows the comparison between the streamer photograph and the spatial distribution of OH radicals observed using two-dimensional LIPF technique. Discharge occurs between a 13 mm point-to-plane gap at sufficiently low repetition rates (< 8 pps). The result shows that OH radicals are produced in the streamer channels.

Fig. 6 shows the decay of OH density after discharge. It is observed around the tip of point electrode. The oxygen concentration is varied. It shows that the decay rate of OH density is faster at higher oxygen concentration. This result indicates that OH radicals react with some byproducts of oxygen, for example, atomic oxygen. The density and decay rate of OH radicals depends on the position between the discharge gap. From the measurement, the decay rate at 3.6 and 7.5 mm from the electrode tip is much faster than that at 1.0 mm. It is
probably caused by the difference in gas temperature in various positions.

Ozone absorbs UV light with a large absorption cross section. Ozone measurement by UV absorption is a popular technique and has been applied to the measurement in streamer discharge. Fig. 7 shows ozone distribution measured using needle-to-plane electrode, with a spacing of 16 mm. About 40 needles with 4 mm separation were used to increase the sensitivity of the UV absorption. The results show that ozone is produced after the discharge with a time constant of several tens μs via the well known three-body reaction. Then ozone density decreases due to diffusion.


IV. DECOMPOSITION OF VOC

Decomposition of VOC is of concern as a potential application of non-thermal plasma. Several efficient VOC treatment methods have been reported, such as plasma assisted combustion of concentrated VOC, use of plasma torch [11], and cyclic system of packed bed using oxygen plasma for oxidation of absorbed VOCs. Further understanding of the decomposition mechanism has been made through by-product analysis [12]. The synergetic effect of plasma and TiO₂ combination has also been confirmed [13, 14]. The combination will lead to the improvement of decomposition efficiency [15]. The effect of temperature for VOC decomposition is also important [16].

Fig. 8 shows a cyclic system for VOC decomposition [17]. Packed bed PDC (plasma driven catalytic reactors) were used. In the flow-type PDC reactor a trade-off relation was observed between the formation of nitrogen oxides and the decomposition of VOCs. Complete decomposition of VOC to CO₂ was achieved with the cycled system that used oxygen gas in a packed bed for oxidation of absorbed VOCs. The oxygen-partial pressure dependence of different catalysts on the decomposition of benzene and toluene was investigated. The results indicated no formation of CO, aerosol, and any nitrogen oxides. Fig. 9 shows the decomposition of toluene with different catalysts. The enhancement with the Ag/TiO₂ catalyst was confirmed.

V. PLASMA ASSISTED COMBUSTION

Rossocha has been proposing the idea of plasma assisted combustion. The concept written by Rossocha et al. is as follows [18]: Conventional combustion of hydrocarbon-fuel/air mixtures typically begins with spark ignition, whereby a spark thermally decomposes hydrocarbon and air molecules to produce free radicals and other reactive species. Burning then continues by subsequent reactions of the reactive species generated by the heat released by the combustion process. The overall rate of combustion is usually determined by how efficiently new reactive species are generated in the propagating flame front. However, this sort of self-generation of reactive species is sometimes insufficient to sustain combustion, particularly under lean-burn conditions.

NTP ‘activation’ does not rely on the self-generation of reactive species. Two possible mechanisms for fuel cracking and fuel activation (creation of more reactive species) exist. The first is based on electron-impact processes, such as dissociation, dissociative ionization, vibrational excitation, and electronic excitation of the parent fuel molecule, which produce molecular fragments, radicals, or excited states relevant to the promotion of combustion reactions. The second mechanism involves ion-molecule reactions, in which ions created by electron impact react with neutral gas species and produce species which can promote combustion reactions.
Fig. 10 shows a DBD reactor for fuel-cracking. Propane gas is passed through the active, annular region (approximately 14 cm in length) of the ceramic-dielectric, coaxial-cylinder plasma reactor. The plasma-activated propane is then mixed with air (which flows through the center-ground tube) and is ignited by an electrical spark at the end of the region where the two gases mix. A portion of the exhaust from the burning propane-air mixture is collected by a sampling system and directed to a mass spectrometer (MS), which measures the fractional concentrations of the effluent gas species. Mass fragments of particular relevance to a propane mass spectrum are atomic masses 26 (C\textsubscript{2}H\textsubscript{2}), 27 (C\textsubscript{2}H\textsubscript{3}), 39 (C\textsubscript{3}H\textsubscript{3}), and 43 (C\textsubscript{3}H\textsubscript{7}). During operation, the flame was ignited and allowed to burn without plasma for two minutes. Then the power supply was turned on, and the activated fuel burned for two minutes. This procedure was repeated several times in order to test the repeatability of any enhanced combustion provided by the plasma. Fig. 11 shows typical data (with one mass fragment of propane, M = 43 shown, along with plots for the expected combustion products M = 18, water and M = 44, carbon dioxide). The partial pressures of the propane fragments decrease while water and carbon dioxide increase when the plasma is turned on. The plateaus at the end of the traces are the result of extinguishing the flame (last gray region) – these are the partial pressures in the absence of any combustion. It is clear that the plasma significantly decreases the partial pressure of unburned hydrocarbons, indicating that propane is being burned more completely with plasma activation. Future experiments are expected to be conducted to examine how changes in plasma energy density affect unburned hydrocarbons, other products of combustion of relevance to pollution (e.g., CO and NO\textsubscript{x}), the production of combustion intermediate species, combustion temperatures, and the spatial characteristics of flames under plasma-activation conditions.

The potential applications are quite broad, ranging from ignition to flame stabilization, to pollution reduction and increased fuel-utilization efficiency. Even though plasma-based combustion has been studied for many decades, the field of plasma-assisted combustion is still in a nascent state. Proof-of-principle works have demonstrated promising results for gaseous fuels, but more research and development must be carried out to understand the basic combustion-enhancement mechanisms and optimize the process. If applications to other fuels (e.g., gasoline, diesel, jet fuel) are successful, NTP-assisted combustion may prove to be highly beneficial to the energy-usage and pollution-reduction needs of modern society.

VI. STERILIZATION USING NTP

Investigation on sterilization by NTP has been increasing [19-21]. Argon NTP plasma has recently been receiving attention for the application of sterilization of surfaces associated with the medical industry [22, 23]. Investigation of argon plasma ‘cleaning’ of surfaces has also been made. A major advantage of non-thermal plasma technology is its ability to operate at or near room temperature, thereby allowing treatment of polymer surfaces which cannot be subjected to conventional dry or wet heat treatment. It is important to note that any use of plasma technology in the application of sterilization must consider the requirement of not doing major physical damage to the material(s) underlying the bacteria. In addition, since plasma treatment of polymer surfaces is well-known to increase surface hydrophilicity, thereby increasing the future capacity of surfaces to support bacterial growth, this issue should be carefully considered.
To produce argon NTP, a dielectric barrier discharge was used with a cylindrical reactor with a Pyrex tube as the dielectric. A rod with a 2 mm diameter was centered as an HV electrode, and the counter-electrode was a copper sheet wrapped around the exterior of the Pyrex tube, which had an inner diameter of 3 mm. The counter-electrode was 4 cm in length, giving a plasma volume of 0.157 cm³. Several ppm of hydrogen peroxide can be generated, and sterilization can be made. Under the conditions studied, hydrogen and oxygen are produced in quantities at least one order of magnitude greater than that of hydrogen peroxide. A result of the simulation, shown in Fig. 12, is the implication that 10 ms downstream of the discharge, that hydperoxyl radical persists in hundreds of ppb and oxygen atom and hydroxyl radical in tens of part-per-billion, suggesting a possible role of these species for the purpose of surface sterilization. The results of experiments for sterilization were that up to 5 orders of magnitude of E. coli inactivation were observed within a 20 minute treatment time and that this sterilization was spatially dependant.

Dielectric Barrier Discharge in air can also be used as an efficient tool for direct sterilization of surface [24]. It can also be used to destroy the membrane or outer shell of microbes and viruses to extract genes for rapid analysis of bio-particles [25].

**VII. WATER TREATMENT USING DISCHARGE**

In addition to traditional UV-activated hydrogen peroxide and/or ozone oxidation, many studies have reported on the removal of trace contaminants in aqueous solutions and sterilization using plasma chemical reactions [26-28]. Corona discharge, including streamer discharge in water, spark or pulsed arc [29, 30], or gliding arc discharges [31], have been used. Hydroxyl radicals, a very powerful and nonselective oxidant, are produced directly in the aqueous solution. Direct discharge in water produces active species as well as intense ultraviolet rays. Corona/streamer discharge in air on the water surface also produces active species, and injects them into water. The lifetime of the hydroxyl radical is usually very short, in the order of 0.1 ms, therefore, the main cause of the reaction could be due to radicals having a long life, such as ionic ozone and O₂⁻, etc. With streamer discharge on water, streamers tend to propagate along the water surface, therefore, ionization can take place in the vicinity of water. This enables the utilization of OH radicals with a short lifespan [32, 33]. For example, wet-plasma reactor oxidizes SO₂ effectively.

Fig. 13 illustrates the reactors using discharge above water. An experiment was made to evaluate the phenol-decomposition efficiency using different geometries of the discharge electrode and the ground[34]. Reactor #a is made of an aluminum cylinder with an inner diameter of 36 mm, a length of 100 mm, and a center electrode with 1 x 1 mm tungsten square wire. Reactor #b has a Plexiglas cylinder (ID: 36 mm, L: 100 mm) with a point electrode located at the top of the cylinder, and grounded metal foil is glued at the bottom of the cylinder. Reactor #c is almost the same except the discharge electrode of 20 mm diameter disk. Reactor #d uses the same disk set at the middle of the cylinder and grounded electrodes are glued at the top and the bottom of the Plexiglas cylinder. The sample liquid was circulated by a peristaltic pump with a flow rate of 0.3 – 1.0 L/min, in which the water fell down along with the inner surface of the cylinder forming wetted-wall. Gas (air, oxygen, argon, or their mixture) flowed through the upper part of the reactor with a flow rate of 0.3 - 1.0 L/min. The total volume of the sample liquid was 200 mL including 50-ppm phenol
dissolved in water. Positive 30 kV, 100 Hz pulsed voltage was applied to the reactors. Reduction of the phenol concentration was analyzed using high performance liquid chromatography every 10 minutes. Air, argon, oxygen and their mixtures were used as surrounding gas to observe discharge characteristics.

Fig. 14 shows the comparison of decomposition rate of phenol with varying reactors #a to #d in the case of argon. Streamer discharge took place from the discharge electrode to the water surface. When reactor #c or #d was used, the discharge path in argon gas was strong and elongated on the water surface (compare to the case with oxygen gas). The decomposition of phenol could be dependent on the region of discharge plasma near the water surface. Longer streamer discharge generated in argon resulted in a higher decomposition rate of phenol than in oxygen. On the other hand, in the case of reactor #a, the decomposition rates in argon and oxygen were almost the same, though the strength of plasma was quite different between corona in oxygen and streamer in argon. Corona discharge in oxygen gas would generate ozone efficiently, and the ozone seemed to contribute to the decomposition of phenol in water.

VIII. CONCLUSIONS

Some examples of recent progress on NTP in environmental applications are introduced. NTP generates radicals that will be beneficial in various emerging fields such as nano and bio-technologies. One of these potentially important applications seems to be diesel exhaust cleaning because NTP promotes chemical reactions at low temperature at which normal catalysts do not work [35, 36]. Conversion of fuels is also of concern [37, 38]. Understanding of radical formation and chemical processes has been advanced using optical and other measurements. The mechanism of the synergetic effect of the combination of NTP and catalyst, however, has still to be clarified. Further understanding of the interaction of NTP and solid/liquid surface is challenging, but will lead to various applications.

ACKNOWLEDGMENT

The author is very grateful for the support and cooperation of the co-editors, Prof. T. Oda, Prof. J. S. Chang, Prof. G. Touchard, Prof. J. Mizeraczyk, of International Journal of Plasma Environmental Science and Technology, advisory board and members of the assembly of electrostatic societies. The author is also grateful for the discussion and support of the engineers of collaborating research institutions and companies.

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