

Plasma Acid Production in a Gliding Arc Plasmatron

Ryan D. Robinson,* Kirill Gutsol, Alexander Rabinovich, & Alexander Fridman

Department of Mechanical Engineering and Mechanics, Drexel University, Philadelphia, Pennsylvania

*Address all correspondence to: Ryan D. Robinson, Department of Mechanical Engineering and Mechanics, Drexel University, Philadelphia, Pennsylvania; rdr34@drexel.edu

ABSTRACT: Plasma acid is an acidic solution simply produced from water and a carrier gas in an electrical discharge. These produced solutions are of high value for biological decontamination and industrial pollutant abatement applications. While several electrical discharges have been shown to produce plasma acid, the subject of this study is the gliding arc plasmatron, a rotating gliding arc discharge. Air and oxygen were used as gases to carry for distilled water through the discharge, and pH and conductivity of the resulting solution was measured. Consistent with other studies of plasma acid, solutions with a lower pH were obtained with air at the carrier gas than with oxygen, and the conductivity increased appropriately with the pH decrease. Other studies noted a transient change in plasma acid after treatment in an air carrier gas, whereas in this study, oxygen also was observed to temporally decrease the acidity over several days.

KEY WORDS: quasi-thermal plasma, plasma acid, water treatment, gliding arc, post treatment transient water chemistry, aqueous ions and radicals

I. INTRODUCTION

The production of acidic solutions from various nonequilibrium electrical discharges in water/gas environments, termed plasma acids, have many applications in the biological and industrial fields. In industrial settings, the radicals formed in plasma-treated solutions chemically degrade organic compound solutions, such as phenols, dyes, and aqueous volatile organic compounds found in wastewater.^[1–3] The properties of plasma acid that are beneficial in industrial applications are also applicable in biological fields. Solutions of microorganisms can be sterilized by reactive oxygen species formed. Commonly identified produced in plasma acids include hydroxyl (OH), superoxide anions (O_2^-), hydroperoxyl radicals (HO_2), and singlet [$O_2(a^1\Delta_g)$] and atomic oxygen (O).^[4,5]

In general, the nonequilibrium electrical discharges and water interactions comprise three configurations: (1) an electrode gap is submerged and the discharge is electro-

hydraulic; (2) one electrode is above the volume in the gas phase and the discharge interacts directly with the surface; or (3) a water spray or vapor is introduced to the gas flow through a discharge.^[2,6]

Electrohydraulic discharges usually have point-to-plane geometry and produce pulsed corona discharges in the liquid, where the high voltage is on the point (needle-like) electrode. The small radius and curvature at the tip helps to concentrate the electric fields needed in submerged liquid-phase discharges. Because of these large electric field required, 10^7 – 10^9 V/m, and streamer core temperatures near 5000 K, erosion of the high-voltage electrode is a common difficulty. The radical species in the vaporized solution formed by the streamer then diffuse into the liquid.^[2,7]

The plasma surface interacts with a liquid in electrode configurations where one of the electrodes is submerged in the solution while the other is in the gas phase above the solution. In air, pulsed corona and dielectric barrier discharges in the gaseous space above the liquid form species such as nitric oxide (NO), nitrogen dioxide (NO₂), and ozone (O₃), which lead to mechanisms resulting in acidic solutions.^[8] Some planar gliding arc systems also have been developed in which the extending arc, in its non-equilibrium stage, touches the surface of the solutions below it or the second electrode in a planar gliding arc is the water.^[2,9] In these configurations, the build-up of an acidic solution relies on diffusion of radical species to the gas-liquid interface and ion bombardment from direct streamer contact. Therefore, the surface area-to-volume ratio affects the rate at which plasma acid is produced.

The configuration that is the subject of this study introduces a water spray or stream into a nonequilibrium discharge. The nonequilibrium discharge commonly used under these experimental parameters is a gliding arc. The idea is that the water spray through a gliding arc utilizes the gas discharge chemistry and the large surface area permits a faster diffusion of the gaseous species into the droplets, while a portion of the liquid itself also contributes to the discharge chemistry. Most other gliding arc discharges used have a linear arc path.^[10–13] The system in this study utilizes a gliding arc plasmatron (GAP) where the arc rotates through the volume as it extends. The water spray and gas mixture are then injected along this axis of rotation. The GAP is a more optimal choice for both full-volume and continuous treatments of solutions rather than batch treatments that corona and dielectric barrier discharges typically provide.

Typically, changes in pH and conductivity of the solutions are measured during the experiment to characterize the plasma acid strength. The acidic strength can be interpreted as the plasma acid concentration. Using the treatment time, power applied, and

concentration of plasma acid, a basis for comparison between systems can be developed.

II. MATERIALS AND METHODS

The experimental setup for this study (a diagram of which can be seen in Fig. 1) mainly comprised a sealed, stainless steel system. Gases were tangentially injected at 28 L/min to the 2 mm gap (3) between the cathode (1) and anode (2). The cathode is a hollow cylinder, 3 cm in diameter. Distilled water is pumped (5) through the cathode, along the axis of gas rotation. The gas and vapor mixture is introduced to the discharge for treatment and then exits the plasmatron through a 1 cm opening to a concentric cylinder heat exchanger (7) and then exits the plasmatron through a 1 cm opening to a concentric cylinder

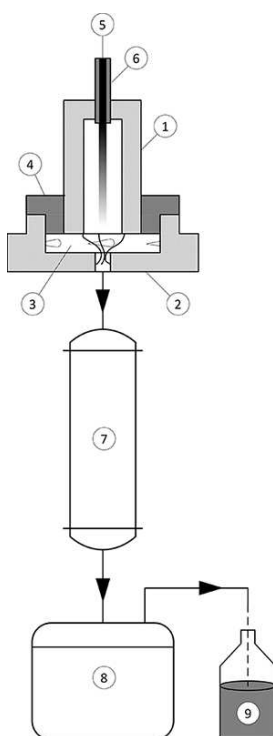


FIG. 1. Diagram of gliding arc plasmatron and plasma acid collection setup: (1) cathode, (2) anode, (3) plasma gap, (4) insulator, (5) water inlet, (6) quartz capillary tube, (7) concentric cylinder heat exchanger, (8) condenser, (9) sample collection.

heat exchanger (7), 45 cm long and 5 cm in diameter. Then the vapor is condensed (8) in coiled tubing submerged in an ice bath, and the condensate drips out into plastic vials with the exhaust gas for collection (9).

The discharge power across the gap was monitored during each experiment. The power supply (Universal Voltronics, Inc.) was capable of supplying 10 kV maximum in open-circuit voltage or a constant current in conjunction with a ballast resistor. In each experiment, 600 mA was maintained, while voltage was measured by a digital phosphor oscilloscope (DPO 3014 Tektronix) with a maximum sampling frequency of 100 MHz. Because of the relatively shorter time scale of the ignition and extinction phases in the gliding arc life cycle, an averaged 128 periods was used to measure voltage. Voltage varied from 0.9 to 1.5 kV during experiments.

The distilled water was continuously injected at 18, 38, 57, and 77 mL/min, with an accuracy of 10%. In the case of air as the gas, the average initial pH was 5.4 and conductivity 1.4 $\mu\text{S}/\text{cm}$. When oxygen was the carrier gas, distilled water was saturated with oxygen for over 24 hours prior before experiment to reduce the amount of dissolved nitrogen in the solution. The average initial pH and conductivity of the oxygen-bubbled distilled water were 6.0 and 1.6 $\mu\text{S}/\text{cm}$, respectively.

Collected plasma acid samples were drawn through a 0.45 μm pore polymer filter via syringe and divided into 10 ml samples in sealed plastic test tubes. Within 5 minutes of sample collection, pH and conductivity were measured with a Sanxin Lab pH/conductivity meter.

III. RESULTS AND DISCUSSION

A. Measurement of pH

The main indications of plasma acid production is pH and conductivity changes of treated solutions. In Fig. 2, the pH of plasma acid generated in air and oxygen carrier gases can be seen as a function of the specific residence time of 1 mL of distilled water in the system, which is the inverse of the water flow rate. Lower pH readings were consistently measured from plasma acid generated in air compared with oxygen with the variation of water flow rate. This is most likely due to the generation of NO_x species solely in an air carrier gas treatment, which also has been reported in other gliding arc systems.^[1,9,11,13]

The measured pH was 2.6 pH units in air and 3.7 pH units in oxygen, which corresponds to theoretical hydrogen ion (H^+) concentrations of $2.51 \times 10^3 \text{ M}$ and $2.00 \times$

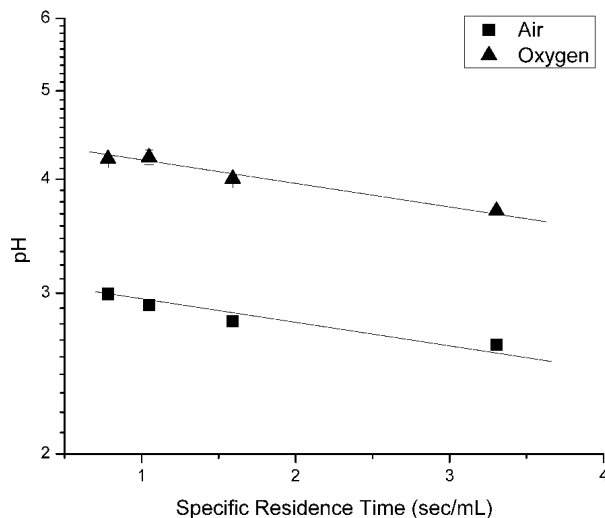


FIG. 2. Plasma acid pH when treated with a gliding arc plasmatron at various water flow rates.

10^{-4} M, respectively. If, in the case of air, this H^+ concentration was assumed to be completely due to nitric acid, the concentration in solution would be 2.51×10^3 M. Since this is most likely not the case, nitrous acid and hydrogen peroxide concentrations also were calculated using Eq. (1) and acid dissociation constant (K_a) values obtained from the 94th edition of the *CRC Handbook*^[14] (Table 1). If only nitrous acid is present in air produced samples, the concentration in solution would be 13.7×10^{-3} M. Expecting hydrogen peroxide to be the primary contributor of the H^+ concentration is unrealistic because of its very weak acidic nature.

$$[HONO] = \frac{[H^+][ONO^-]}{K_a} + [H^+] \quad (1)$$

TABLE 1: Acid Dissociation Constants of Various Acids

Acid	K_a (M)	pK_A	Source
Hydroperoxy, HO_2	1.59×10^{-5}	4.8	Bielski et al. (1985)
Hydrogen peroxide, H_2O_2	2.4×10^{-12}	11.62	Haynes
Nitrous acid, HONO	5.62×10^{-4}	3.25	Haynes

While the lack of nitrogen in oxygen carrier gas treatments seems to exclude the appearance of NO_x species, the H^+ concentration remains unlikely to be solely due to hydrogen peroxide, and hence hydroperoxy was considered. For oxygen carrier gas treatment resulting in a pH of 3.7, hydroperoxy, HO_2 , concentration could be 2.72×10^{-3} M when calculated using a K_a value of 1.59×10^{-5} M.^[15] The lowest pH values for both experimental atmospheres were observed when the water flow rate was lowest or at the highest specific residence time. This suggests that a longer residence time, specifically in the gliding arc plasma region of the system, produces more species, resulting in solutions with higher acidity.

Compared with other gliding arc systems treating water sprays,^[9,11,13] the GAP performs similarly in measured pH and conductivity, κ , of plasma acid samples produced in air and oxygen under similar gas and water flow rates. A comparison of the GAP and other reactors is shown in Table 2. Having similar gas flow rates, Q_g , it can be seen that a lesser water injection flow rate, Q_w , results in a lower pH in air and in oxygen. With a similar Q_w and a higher Q_g , the pH is slightly higher in both air and oxygen.

B. Measurement of Conductivity

The conductivity of the samples measured as a function of specific residence time can be seen in Fig. 3. As is typical of acidic solutions, Figure 3 indicates that the conductivity of the solutions increases with a decrease in the pH. The conductivity of plasma acid in air carrier gas ranged from 440 to 1060 $\mu\text{S}/\text{cm}$ and in oxygen ranged from 25 to 100 $\mu\text{S}/\text{cm}$. These values show an increasing conductivity with decreasing water injection flow rates.

TABLE 2: Comparison of plasma acid pH and conductivity produced from gliding arc reactors and experimental parameters

Gas	Q_g (L/min)	Q_w (mL/min)	pH	κ ($\mu\text{S}/\text{cm}$)	Source
Air	28	18	2.6	1060	Current study
Air	28	28	2.8	610	Burlica et al. (2006)
Air	2	1	4.0	700	Burlica et al. (2010)
Air	2	25	2.5	1900	Porter et al. (2007)
Oxygen	28	18	3.7	100	current study
Oxygen	28	28	4.9	10	Burlica et al. (2006)
Oxygen	2	25	3.4	200	Porter et al. (2007)

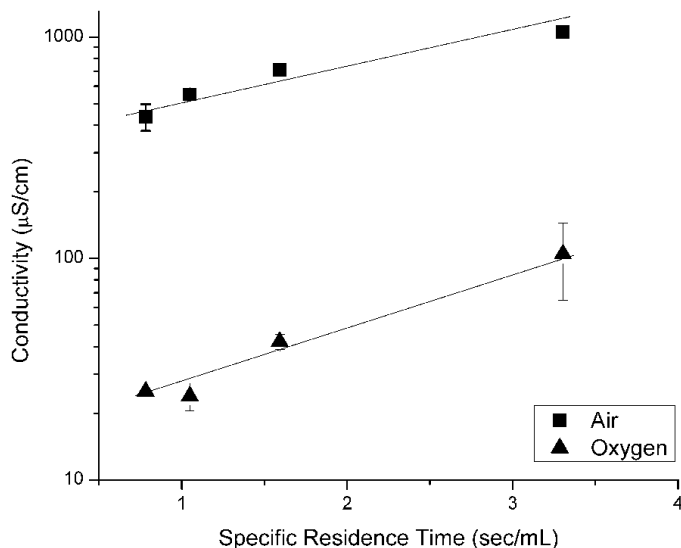


FIG. 3. Plasma acid conductivity when treated with a gliding arc plasmatron at various water flow rates.

C. Temporal Stability of pH

Several groups observed a transient nature of the pH increasing after treatment, which was attributed to the instability of nitrous acid in solution, converting to nitric acid.^[10] The transient characteristics of plasma acid pH would lend to its functional application as an oxidizer, where the excess oxidizing species would naturally deteriorate to safer (pH neutral) solutions. However, these studies were plasma acid samples treated with air carrier gas. It was of interest to see whether the absence of nitrogen in the carrier gas would also result in a solution instability. To collect these results, a similar experimental setup was utilized. The plasmatron had a smaller diameter and the water was injected via an atomizer supplied by a more precise pump at lower flow rates. See Fig. 4 for pH measurements of plasma acid after treatment with the GAP.

An oxygen carrier gas experiment with a modification of the methods described; was conducted where the power and gas flow rate (41 L/min) were held constant whereas the water flow rate varied from 3 to 12.8 g/min. Samples collected were sealed in a vessel with less than 5 m/L of head space for approximately 45 m/L of liquid. Figure 4 indicates

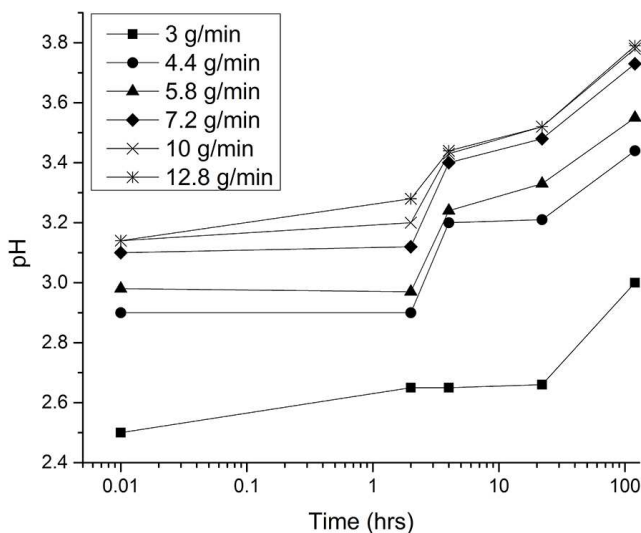


FIG. 4. Transient pH plasma acid samples measured after production from oxygen carrier gas at various water flow rates.

that there is a loss or redistribution of the H^+ in solution over an extended period after treatment with the GAP. Within 4 hours of treatment, a consistent initial increase of approximately 0.3 pH units occurred across all of the samples, excluding the sample collected from the experiment using a 3 g/min water flow rate, which was 0.15 pH units. The remaining slow pH increase continued over several more days, resulting in 0.5 to 1.0 pH increase from original measurements immediately after treatment. The variation of water flow rate results also show a consistent decrease in the plasma acid pH with decreasing water flow rate.

IV. CONCLUSIONS

Development of the GAP for water treatment builds off of the data from other studies with the key advantage of continuous treatment of flowing water and scalability. The GAP is capable of being scaled up for larger flow rates and higher power that could be more applicable to industry needs.

A GAP was used to treat water in air and oxygen carrier gases and successfully produced plasma acid. The pH and conductivity of the produced solution were measured

to verify plasma acid production and quantify the strength. Plasma acid pH in air was significantly lower than in oxygen; 2.6 and 3.7, respectively. Also, the conductivity of plasma acid generated in air was higher than in oxygen; 1060 and 100 $\mu\text{S}/\text{cm}$, respectively. Nitrogen-containing species such as nitric acid was suggested as a possible contributor to the pH decrease in samples from an air carrier gas, whereas the mechanisms of the observed pH decrease from an oxygen carrier gas is still under investigation. When compared with other gliding arc and water spray systems, the concentrations of plasma acid produced in this GAP are very similar. The transient instability of plasma acid pH seen in air carrier gas produced by other studies was observed in oxygen carrier gases, with an initial pH change of approximately 0.5 in 4 hours and up to 1.0 after several days.

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