

https://dx.doi.org/10.21577/0103-5053.20240009

J. Braz. Chem. Soc. 2024, 35, 7, e-20240009, 1-19 ©2024 Sociedade Brasileira de Química

Exploring Energy-Efficient Techniques and Chemical Kinetics in Reactive Nitrogen Species Production with Ambient Air Plasma for Plasma-Activated Water

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This study investigates the chemical kinetics of reactive nitrogen species (RNS) formation in plasma-activated water (PAW) using ambient air and evaluates its energy efficiency. A singular plasma/liquid reactor was used, with discharge power varying between 16.4 to 27.0 W and agitation speeds set at 0 and 750 rpm. The reactor operated across temperatures from 5.00 to 35.00 °C during a consistent 180 min plasma activation. Analysis encompassed ionic strength effects, hydronium activity, conductivity, and iodide as a redox indicator for PAW. Findings suggest reactive species predominantly originate in the gas phase and move to the liquid through the gas-liquid interface. HNO₃ production in PAW demonstrated a zero-order, temperature-dependent reaction. From activation parameters and ionic strength effects, a determinant step for aqueous HNO₃ production was associated with heightened rates due to increased mass transfer and electric field strength. The research highlighted a trade-off between energy efficiency and nitrate production rate, emphasizing an efficiency peak of 72.33 nmol J⁻¹ in PAW, pivotal for cost and operational benefits.

Keywords: plasma-activated water, reactive nitrogen species, activation parameters, energy efficiency

Introduction

The growing demand for food and the pursuit of sustainable agriculture have led to increased interest in innovative crop production methods.¹ One key challenge is the rising demand for nitrogen fertilizer and the escalating costs of traditional nitrogen sources.² Geopolitical tensions, such as the conflict between Ukraine and Russia, have further exacerbated the issue by disrupting the global supply of nitrogen fertilizer.³ Consequently, there is an urgent need to explore alternative solutions for crop nutrition.

A recent study by Menegat *et al.*⁴ underscores the environmental impact of synthetic nitrogen fertilizers throughout their supply chain. In 2018, emissions associated with synthetic nitrogen fertilizer amounted to 1.13 GtCO₂e, accounting for 10.6% of agricultural emissions and 2.1% of global greenhouse emissions. Of these emissions, 38.8% were attributed to synthetic nitrogen fertilizer production, 58.6% to field emissions, and the remaining 2.6% to transportation. This highlights

*e-mail: pericles@professores.utfpr.edu.br Editor handled this article: Fernando C. Giacomelli (Associate) the importance of considering the entire supply chain when evaluating the environmental impact of synthetic nitrogen fertilizers.

Plasma activated water (PAW) has emerged as a potential solution for enhancing plant growth and productivity.⁵ Produced by exposing water to both thermal and non-thermal plasmas, PAW contains reactive nitrogen species (RNS), reactive oxygen species (ROS), and other active chemical species.⁶ Nitrogen is an essential nutrient for plant growth, and RNS, in particular, have been shown to improve plant growth and root development, ultimately leading to increased crop productivity.⁷

Compared to traditional nitrogen fertilizer fixation methods like the Haber-Bosch process, PAW is a more sustainable alternative. The Haber-Bosch process is highly energy-intensive, consuming 1-2% of the world's total electricity generation, and contributes to 1.4% of global carbon dioxide emissions.² In contrast, PAW production is less energy intensive and generates fewer emissions, offering a greener solution for crop nutrition.

Several companies worldwide are working on commercializing this technology. PAW has been studied for various agronomic applications, including seed disinfection, crop protection, pH control, and soil amendment.⁸ However, much remains to be understood about the chemical kinetics of reactive oxygen and nitrogen species (RONS) produced in PAW during the plasma activation time and its relationship with energy efficiency, aiming to optimize PAW production.

The field of PAW has been a focal point for many researchers over the past decade,⁹⁻³⁹ particularly the production and characteristics of RONS.⁴⁰⁻⁴³ Notwithstanding, experimental investigations specifically focused on the chemical kinetics of RONS in the aqueous phase of PAW during the plasma activation time are limited.⁴⁴⁻⁴⁸

Previous studies, such as the pivotal work by Lukes *et al.*,⁴⁴ demonstrated that during a 30 min pulsed electrical air discharge activation interacting with the water surface, H_2O_2 , NO_3^- , and NO_2^- each adhered to a zero-order production in a buffered solution (pH = 6.9, T = 18 °C). A subsequent post-discharge chemical kinetic study further showed a strong fit with the pseudo-second-order reaction between H_2O_2 and NO_2^- . However, after this report, the field has seen a scarcity of experimental studies further investigating the aqueous chemical kinetics of RONS.

Addressing this gap, our study presents a novel examination of the activation parameters governing RNS production in PAW during the plasma activation time. To the best of our knowledge, these parameters remain undetermined in the literature. Determining these parameters is critical in elucidating the reaction mechanisms of the species produced in solution and identifying the ratedetermining step, i.e., the step involving the highest-energy transition state (TS).

In this research, we probe into the chemical kinetics of the primary RNS produced in PAW, specifically HNO_3 and HNO_2 . The derived activation parameters and the observed effects of ionic strength led us to propose the determining step for the formation of the $HNO_{3(aq)}$ transition state.

Beyond the scope of previous research, we quantified the energy efficiency of HNO_3 and HNO_2 as a function of specific input energy, an important factor in evaluating the cost-effectiveness of RNS production and the broader cost implications of PAW in agronomic applications. We compared the peak values with those found in previous studies for different plasma treatments. In a significant novel contribution, our study is the first to investigate and report the relationship between energy efficiency and reaction rate for aqueous RNS.

To complement our research, we used iodide as a chemical probe to trace the origin of the reactive species, and we also conducted a thorough analysis of PAW's pH and conductivity for comprehensive chemical characterization. Hence, our study offers significant new insights, strengthening the knowledge foundation for the future exploration of PAW's chemical kinetics.

Experimental

Setup and electrical characterization of plasma reactor system

The experimental apparatus used in this study is schematically shown in Figure 1. A thermostatic circulating bath (Microquímica, MQB1, Palhoça, Brazil) was employed to maintain a constant temperature (± 0.01 °C) in the plasma reactor during each experiment. The kinetic study of species generated by plasma was conducted at four different temperatures: 5.00, 15.00, 25.00, and 35.00 °C. The jacketed borosilicate plasma reactor has a total internal volume of 185 mL and was filled with 100 mL of ultrapure water (Milli-Q) for each experimental condition. The dielectric upper cover of the plasma reactor is made of polytetrafluoroethylene (PTFE) and houses two tungsten electrodes (diameter (\emptyset) = 2.4 mm, 2% La, Energyarc, São Paulo, Brazil). The high voltage (HV) electrode is concentric to the reactor, and its distance from the water surface (discharge gap) was maintained at 5 mm for experiments without stirring and at 8 mm with stirring. The ground electrode, parallel to the HV electrode, is positioned at an 8 mm distance from it. In contrast to the HV electrode, the ground electrode is immersed in the water to a depth of 5 cm. Ambient air (from the surrounding atmosphere) was used as the plasma gas, and gas exchange between the reactor and the atmosphere occurred freely through the holes ($\emptyset = 4 \text{ mm}$) in the upper cover. Experiments were conducted under ambient pressure conditions. For experiments involving vortex generation in the plasma reactor, a digital magnetic stirrer (Novainstruments, NI 1111, Piracicaba, Brazil) with rotation speed control was utilized. The effect of stirring the solution was evaluated by operating each power supply without (0 rpm) and with (750 rpm) stirring.

Two AC high voltage power supplies (Neon Ena, max. output 8 kV_{RMS}, 30 mA_{RMS}, 60 Hz, São Paulo, Brazil) and (Neon Ena, max. output 17 kV_{RMS}, 30 mA_{RMS}, 60 Hz, São Paulo, Brazil) were individually employed, denoted as PS1 and PS2, respectively. The effect of average discharge power was studied by using each power supply separately at 220 V (primary) while operating the power supply at its maximum output power for the given plasma reactor. Electrical characterization of the plasma discharge was performed using a two-channel oscilloscope (Tektronix TDS 2012C, 100 MHz, Shanghai, China). The first channel was connected to a 1000:1 high voltage probe



Figure 1. Schematic of the apparatus for producing plasma-activated water.

(Caltest CT4028, 220 MHz, New Taipei, Taiwan) for voltage waveform measurement, and a wideband current transformer (Pearson 411, 0.1 V/A, 20 MHz, Palo Alto, USA) was connected to the second channel for current waveform measurement. The average discharge power (P) was calculated using equation 1, which represents the mean value over a period (T) of the current, I(t), multiplied by the voltage, U(t):

$$P = \frac{1}{T} \int_{0}^{T} U(t) \times I(t) dt$$
(1)

Five power measurements were taken for each condition set, and the average value and its standard deviation were determined. To avoid any electromagnetic interference in the electrical measurements, the plasma system was enclosed in a Faraday cage.

Analysis of plasma-activated water samples

Plasma activation and sample collection

For each experimental condition, the plasma activation time was set at 180 min. During the activation, 700 μ L samples were collected in pre-determined time intervals, transferred to microtubes (Axygen, MCT-150-C, Union City, USA), and immediately analyzed.

pH and electrical conductivity measurements

The pH and electrical conductivity (EC) of the samples were measured using a two-channel meter (OHAUS, 3100M, Parsippany, USA) equipped with a micro pH combination electrode (Sigma-Aldrich, length (L) = 55 mm, St. Louis, USA) and a micro conductivity cell (Mettler Toledo, InLab 751-4 mm, Columbus, USA), both previously calibrated. To account for the temperature dependence of electrical conductivity, the micro conductivity cell was integrated with a temperature probe, and the EC meter was calibrated with a temperature correction coefficient option, allowing for automatic adjustment of the displayed EC value.

Nitric and nitrous acid concentration determination

The concentrations of nitric and nitrous acids were determined spectrophotometrically (Shimadzu, UV-1800, Kyoto, Japan) in quartz microcuvettes (Hellma, 700 μ L, 10 mm optical path, Jena, Germany). Calibration curves for HNO₃ (10.0-100.0 mM) and HNO₂ (2.5-50.0 mM) were prepared, and the standardization of the HNO₃ stock solution was performed through volumetric analysis using Na₂CO_{3(s)} (Vetec, 99.5%, Duque de Caxias, Brazil) as the primary standard. The primary standard preparation and subsequent analyses were carried out in triplicate.

Preparation of HNO₃ and HNO₂ stock solutions

The HNO₃ stock solution (1 M) was prepared by diluting 5.96 mL of concentrated acid (Anidrol, 70%, Diadema, Brazil) in 100 mL of ultrapure water. The HNO₂ stock solution (0.1 M) was prepared by mixing equimolar quantities of two separate solutions: a hydrochloric acid solution (0.2 M) and a NaNO_{2(s)} solution (Neon, 97.0%, Suzano, Brazil).

Role of ionic strength

Considering a reaction where two ions, identified as A^{zA} (possessing a charge z_A) and B^{zB} (carrying a charge z_B), interact to form a transition state:

$$A^{zA} + B^{zB} \rightarrow [AB^{zA+zB}]^{\ddagger}$$
⁽²⁾

This reaction features charged reactants, electrolytes, and takes place under conditions that are non-ideal, a circumstance predicted by Debye-Hückel theory. The observed rate constant manifests a correlation with the ionic strength, which is demonstrated in equation 3 when accounting for low ionic strength values:⁴⁹

$$\log k_{\text{non-ideal}} = \log k_{\text{ideal}} + 1.018 z_A z_B \sqrt{I}$$
(3)

In equation 3, I denotes the ionic strength, and k_{ideal} signifies the rate constant when extrapolated to a scenario where I equals zero. The concept of ionic strength is encapsulated by equation 4, where c_i is used to denote the

concentration of the ion species, while z_i is representative of the charge carried by the ion.⁴⁹

$$I = \frac{1}{2} \sum_{i} (c_i z_i^2) \tag{4}$$

The influence of ionic strength was investigated across a spectrum from 0.00163 to 0.21330 mol L⁻¹, achieved by the inclusion of suitable volumes of a 1 mol L⁻¹ MgCl₂ stock solution. In order to examine the effect of ionic strength, the temperature was consistently held at 15.00 °C, and no stirring was applied.

Detection of oxidant species and hydrogen peroxide

A 10% potassium iodide (KI, Dinâmica, 99.0%, Indaiatuba, Brazil) solution was used to react non-selectively with oxidant species produced by plasma activation of water, generating triiodide ion (I_3^-). To detect hydrogen peroxide spectrophotometrically, an aqueous and acidic solution of titanium oxysulfate was employed, which reacts with H₂O₂ to produce a yellow peroxotitanium complex Ti(O₂)OH(H₂O)₃. The absorbance peak of the complex was found at 409 nm, and its stability was confirmed for at least 6 h. The intensity of the complex's coloration is directly proportional to the concentration of H₂O₂, with a molar extinction coefficient of $\varepsilon = 6.89 \times 10^2$ L mol⁻¹ cm⁻¹. The reaction is specific to H₂O₂ and does not show interference from other compounds present in water, especially under strongly acidic conditions.

Results and Discussion

Origin of reactive species and mass transfer in the plasma reactor

To investigate the production of reactive species and mass transfer in the plasma reactor, a redox indicator, potassium iodide (KI, 10% m/v), was employed. Aqueous iodide, $I_{(aq)}^-$, reacts with oxidizing species to form triiodide (I_3^-), resulting in a color change from colorless to yellow or brown, depending on the I_3^- concentration, in accordance with the half-reaction 5 (E° is the standard reduction potential):

$$I_3^- + 2e \rightleftharpoons 3I^- E^\circ = 0.536 V \tag{5}$$

In this manner, any chemical species with a higher standard reduction potential will spontaneously react, oxidizing the colorless iodide solution to a brownish triiodide. The standard reduction potentials of reactive nitrogen and oxygen species in acidic media, which are reportedly produced in air plasmas and can react spontaneously with iodide, are listed below (reactions 6-18).⁵⁰

$N_2O + 2H^+ + 2e \rightleftharpoons N_2 + H_2O$	E° =1.766 V	(6)
$2NO + 2H^+ + 2e \rightleftharpoons N_2O + H_2O$	$E^{o} = 1.591 V$	(7)
$N_2O_4 + 4H^+ + 4e \rightleftharpoons 2NO + 2H_2O$	E° = 1.035	(8)
$HNO_2 + H^+ + e \rightleftharpoons NO + H_2O$	$E^{\circ} = 0.983 V$	(9)
$2HNO_2 + 4H^+ + 4e \rightleftharpoons N_2O + 3H_2O$	E° = 1.297 V	(10)
$NO_3^- + 3H^+ + 2e \rightleftharpoons HNO_2 + H_2O$	$E^{\circ} = 0.934 V$	(11)
$2 \text{ NO}_3^- + 4 \text{ H}^+ + 3e \rightleftharpoons \text{NO} + \text{H}_2\text{O}$	$E^{o} = 0.957 V$	(12)
$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$	$E^{o} = 1.776 V$	(13)
$O_3 + 2H^+ + 2e \rightleftharpoons O_2 + H_2O$	$E^{\circ} = 2.076 V$	(14)
$O_2 + 4H + 4e \rightleftharpoons 2 H_2O$	$E^{o} = 1.229 V$	(15)
$O_2 + 2H^+ + 2e \rightleftharpoons H_2O_2$	$E^{\circ} = 0.695 V$	(16)
$O_{(g)} + 2H^+ + 2e \rightleftharpoons H_2O$	$E^{\circ} = 2.421 V$	(17)
$ONOO^- + 2H^+ + 2e \rightarrow NO_2^- + H_2O$	$E^{o} = 1.20 V$	(18)

The final equation (equation 18) highlights the reduction potential of peroxynitrite (ONOO⁻),⁵¹ which is a transient and highly reactive species generated in PAW. Peroxynitrite is of particular importance in certain PAW applications, as it demonstrates effectiveness in neutralizing fungi, bacteria, and viruses.^{18,44,52} Additionally, the formation of peroxynitrite was identified through a pseudo-second-order post-discharge interaction between H₂O₂ and HNO₂, as supported by their chemical kinetics investigation.⁵²

Figure 2 displays the time-dependent color changes of the KI solution during 20 min of plasma activation in air without stirring (0 rpm).



Figure 2. Visualization of gas-liquid mass transfer in water during 20 min of plasma activation under atmospheric pressure conditions ($P = 20.4 \pm 0.1$ W, 0 rpm, T = 25.0 °C).

During the first two minutes of plasma activation, a yellow layer was observed near the gas-liquid interface,

indicating the redox reaction of aqueous iodide and the production of triiodide ions. This initial thin layer subsequently extended into the aqueous solution, forming a diffusion front at 2 and 3 min. However, after this initial diffusion, additional gradients were observed, which may be attributed to particle size and subsequent aggregation. This resulted in initially homogeneous diffusion fronts becoming inhomogeneous, leading to droplet and structure formation over the period of 3 to 20 min.⁵³

It is important to note that triiodide is a heavy anion with a molecular weight of 380.71 g mol⁻¹. Consequently, precipitation of triiodide was observed in the reactor between 4 and 20 min, accumulating from the bottom-up over the course of 10 to 20 min.

In summary, these observations suggest that the formation and diffusion of triiodide during plasma activation is a complex process involving both initial diffusion fronts and subsequent aggregation-induced inhomogeneities. Based on the observations made in this study, it can be concluded that the reactive species induced by plasma are primarily produced in the gas phase and subsequently absorbed in the liquid phase through the gasliquid interface. The reactive species then diffuse through the liquid phase and accumulate over time. These findings suggest that the Henry's constant for gas dissolution is likely to play a crucial role in the air plasma-water interface chemistry.

Production of nitrogen species in air plasma

Nonthermal N_2/O_2 plasmas have been shown to generate NO at bulk gas temperatures much lower than those required for thermal N_2 oxidation. In fact, the concentration of NO produced by these plasmas can exceed the levels expected based on bulk thermodynamic equilibrium.⁵⁴ The Zeldovich mechanism is the accepted chain mechanism for NO production in both combustion and plasma processes. In this mechanism, the breaking of the strong bond in the N_2 molecule (bond order = 3) is the determining step. This bond is broken very efficiently in reactions involving vibrationally excited nitrogen molecules (reaction 19).⁵⁵

$$O + N_2^* \to NO + N \tag{19}$$

The above step is followed by the exothermic process (reaction 20):

$$N + O_2 \rightarrow NO + O \tag{20}$$

The sum of the two reactions of chain propagation gives the overall reaction (reaction 21):

$$N_2 + O_2 \rightarrow 2NO \tag{21}$$

In general, NO synthesis through electronic excitation in plasma is mostly due to the dissociation of molecular nitrogen by direct electron impact (reaction 22):

$$N_2 + e \to N + N + e \tag{22}$$

After dissociation of N_2 , NO synthesis takes place by the second step in the Zeldovich mechanism (reaction 20). When NO is already formed, it can be further oxidized in plasma to NO₂ and other nitrogen oxides through the following reactions (reactions 23 and 24):

$$NO + O + M \rightarrow NO_2 + M$$
(23)
$$NO + O_3 \rightleftharpoons NO_2 + O_2$$
(24)

The acceleration of Zeldovich chain reactions can be achieved by increasing the degree of ionization and atomization. In addition, dissociative recombination of O_2^+ and N_2^+ ions with electrons can also enhance the production of atomic •N and •O (reactions 25 and 26).²⁸

$$e + O_2^+ \to \bullet O + O ((^1D) \text{ ca. } 40\%, (^1S) \text{ ca. } 5\%)$$
(25)
$$e + N_2^+ \to \bullet N + N ((^2D) \text{ ca. } 45\%, (^2P) \text{ ca. } 5\%)$$
(26)

In this study, a direct air plasma discharge was applied to the surface of water, resulting in the evaporation of the liquid and the production of water vapor at the plasma/ gas-liquid interface. As plasma typically transfers heat to the liquid surface,⁴² the gas phase contains water in a concentration determined by its vapor pressure in air. Furthermore, plasma-induced gas-phase reactions generate hydroxyl radicals (•OH), which are highly reactive species (reactions 27 and 28):

$$e + H_2O \rightarrow e + \bullet OH + \bullet H$$
(27)
$$O(^{1}D) + H_2O \rightarrow \bullet OH + \bullet OH$$
(28)

The •OH radical can further react with itself and with other species produced in air by the plasma discharge and form ROS such as H_2O_2 , HO_2 (reactions 29 and 30):

•OH + •OH + M
$$\rightarrow$$
 H₂O₂ + M (29)
•OH + O₃ \rightarrow HO•₂ + O₂ (30)

RNS such as HNO_2 and HNO_3 are rapidly produced in the presence of the hydroxyl radical (reactions 31 and 32):

- •OH + NO + M \rightarrow HNO₂ + M (31)
- $\bullet OH + NO_2 + M \to HNO_3 + M$ (32)

Hydroxyl radicals can further decrease HNO_2 concentration in the gas phase through the reaction 33.⁵⁵

$$\bullet OH + HNO_2 \rightarrow NO_2 + H_2O \tag{33}$$

Electrical characteristics of the discharge

Figure 3 displays the AC discharge voltage and current waveforms obtained at a temperature of 25 °C, a stirring rate of 750 rpm, and an average discharge power of 27.2 W. The current waveform exhibits a non-sinusoidal shape, with an additional current pulse coinciding with the peak voltage of both positive and negative amplitudes for each half-cycle. The distortion in the current waveform can be attributed to the superimposition of higher harmonics on the sine wave.⁵⁶



Figure 3. AC waveforms of voltage (channel 1) and current (channel 2) recorded at a discharge power of 27.2 W, T = 25 °C, and a stirring speed of 750 rpm.

Magnetic stirring at a rate of 750 rpm increased the average discharge power under the same power supply. Specifically, the average discharge power increased from 16.4 ± 0.1 to 21.3 ± 0.9 W and from 20.4 ± 0.1 to 27.0 ± 1.0 W for power supplies PS1 and PS2, respectively. As expected, a higher maximum output power (PS2) led to a higher average discharge power. The discharge gap (d_g) increased from 5 to 8 mm due to vortex formation, causing the plasma discharge to be randomly distributed over a larger area. This may have contributed to the higher standard deviations observed in the average discharge power when stirring. The vortex formation increased the discharge gap, which allowed the plasma to cover a larger surface area and increased the overall power while maintaining discharge stability.

The plasma reactor temperature did not affect the average discharge power. In our examination of the effects of average discharge power within a fixed discharge gap, we observe that an increase in this power leads to a proportionate rise in the electric field (E), as defined by equation 34:

$$E = \frac{U_g}{d_g}$$
(34)

where, U_g is the gas voltage and d_g represents the discharge gap distance.⁵⁵⁻⁵⁷ A stronger electric field consequently results in higher values of both the reduced electric field (E/n₀, the ratio of the electric field to neutral gas concentration) and the mean electron energy. This elevation in electron energy is critical for enhancing electron impact dissociation of air molecules, facilitating more effective production of atomic oxygen and nitrogen, essential for forming NO via the Zeldovich mechanism.

Furthermore, our study includes an analysis of the Townsend ionization coefficient (α), which is a crucial factor in the ionization process of non-equilibrium electrical discharges. The relationship between α and the electric field is captured by equation 35:

$$\frac{\alpha}{p} = 15e^{-\frac{365}{\frac{E}{p}}}$$
(35)

In this equation, p represents the gas pressure in Torr. The constants in this expression, $A = 15 \text{ cm}^{-1} \text{ Torr}^{-1}$ and $B = 365 \text{ V cm}^{-1} \text{ Torr}^{-1}$, are specific to air within the electric field to pressure ratio (E/p) range of 30-500 V cm⁻¹ Torr^{-1}.⁵⁵ As the discharge power increases, α also increases, reflecting a rise in electron production *per* unit length of plasma discharge. This amplification in ionization consequently leads to an enhanced generation of reactive species.

The modulation of discharge power was achieved by adjusting the applied voltage. This adjustment not only strengthened the electric field but also increased the mean electron energy. These changes significantly impact the energy-dependent reaction rates for NO production and enhance the Townsend ionization coefficient (α), providing more electrons for electron-induced reactions. The enhancement in α correlates with the increased rates of NO₃⁻ reactions, as elaborated in the "Kinetic study of NO₃⁻ production by plasma activation" sub-section.

In order to provide a more detailed analysis, we will discuss the impact of average discharge power on various parameters, including HNO₃ kinetic study, HNO₂ concentration, pH, conductivity, and RNS energy efficiencies in subsequent sections. This will allow us to gain a more comprehensive understanding of the relationship between discharge power and these key variables.

In summary, the formation of a vortex due to magnetic stirring at a rate of 750 rpm increased the discharge gap, allowing the plasma to cover a larger surface area. This led to an increase in the overall power while maintaining discharge stability. Additionally, the increase in average discharge

power had significant effects on the ionization process, leading to the generation of a greater number of reactive species and impacting energy-dependent reaction rates.

Characterization of reactive nitrogen species in solution

Figure 4 presents the UV-Vis scanning spectra illustrating the effect of plasma activation time on pristine plasmaactivated water. The spectra indicates that nitrate (NO₃⁻) exhibits a single absorption maximum at 302 nm, with a molar extinction coefficient (ϵ) of 7.1 L mol⁻¹ cm⁻¹. In contrast, nitrous acid (HNO₂) displays multiple absorption maxima at 336, 346, 357, 371, and 386 nm. Among these maxima, the 371 nm peak demonstrates the highest absorption (ϵ = 45.77 L mol⁻¹ cm⁻¹) and is thus optimal for quantification purposes due to its enhanced sensitivity. The identities of each species were further confirmed by the UV-Vis scanning spectra obtained from samples used for calibration curves.

Chemical kinetics in solution

Kinetic study of NO₃⁻ production by plasma activation The production of NO₃⁻ in plasma-activated water



Figure 4. UV-Vis absorbance spectra of pristine plasma-activated water recorded at various plasma activation times (in min) under the conditions of T = 5 °C and P = 27.0 ± 1.0 W.

exhibited a zero-order reaction under all experimental conditions, with its concentration increasing linearly as plasma activation time increased, as depicted in Figure 5 for different temperatures at fixed average power and agitation conditions.

As nitrate concentration followed a zero-order equation 36:



Figure 5. Kinetic profile of NO₃⁻ generation via plasma activation, for different initial water temperature across different average discharge power and agitation parameters: (a) P = 16.4 ± 0.1 W, 0 rpm, (b) P = 21.3 ± 0.9 W, 750 rpm, (c) P = 20.4 ± 0.1 W, 0 rpm, (d) P = 27.0 ± 0.1 W, 750 rpm.

$$\frac{d[NO_3^-]}{dt} = k_{obs}$$
(36)

The observed rate constant (k_{obs} , in units of mol L⁻¹ min⁻¹) was determined by calculating the slope of the plot of $[NO_3^-]$ *versus* time. As a zero-order reaction was observed, the rate of NO_3^- production remained constant ($v = k_{obs}$), regardless of changes in the concentration of the species. This finding aligns with our previous research⁴⁶ and with the work of Lukes *et al.*,⁴⁴ who also observed zero-order production of NO_3^- in plasma-activated water using a gasphase pulsed discharge in contact with the water surface to generate RONS.

Our results demonstrated that, across all tested average discharge power and agitation speeds, a decrease in temperature led to an increase in the observed rate constant (k_{obs}) for NO₃⁻ production. For example, at 750 rpm and 27.0 ± 1.0 W, k_{obs} increased from 0.42 mM min⁻¹ at 35 °C to 0.80 mM min⁻¹ at 5 °C. These findings are consistent with our previous work.⁴⁵

An increase in temperature is known to elevate water vapor pressure,⁵⁸ thereby enhancing the humidity of the gas/plasma phase. In their research, Nakagawa *et al.*⁵⁹ demonstrated that within an atmospheric-pressure pulsed corona discharge, the density of OH radicals rises in correlation with increased humidity. This augmentation in OH radical concentration at higher temperatures can subsequently lead to a decrease in HNO₃ concentration through reaction 37:⁶⁰

$$HNO_3 + OH \rightarrow H_2O + NO_3 \tag{37}$$

As a consequence, the reduced availability of HNO₃ would subsequently result in a lower concentration of nitrates in the aqueous phase.

The results from k_{obs} (equation 36) conformed to both Arrhenius (equation 38) and Eyring (equation 39) linearized equations, and the activation parameters were obtained:

$$\ln k = -\frac{Ea}{RT} + \ln A \tag{38}$$

$$\ln\frac{k}{T} = -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} + \frac{\ln k_{B}}{h}$$
(39)

where T is the temperature, R is the ideal gas constant, E_a is the activation energy, A is the pre-exponential factor, ΔH^{\ddagger} is the enthalpy of activation, ΔS^{\ddagger} is the entropy of activation, k_B is the Boltzmann constant, and h is the Planck constant. Arrhenius and Eyring plots are shown in Figures 6a and 6b, respectively. The calculated activation parameters are summarized in Table 1.



Figure 6. (a) Arrhenius plot and (b) Eyring plot for NO₃⁻ production in PAW for different conditions of average discharge power and stirring speeds.

Table 1. Activation parameters for HNO3 production in PAW

	Conditions			
Activation parameter	$P = 16.4 \pm 0.1 W,$ 0 rpm (PS1)	$P = 21.3 \pm 0.9 W,$ 750 rpm (PS1)	$P = 20.4 \pm 0.1 W,$ 0 rpm (PS2)	$P = 27.0 \pm 1.0 W,$ 750 rpm (PS2)
E _a / (kJ mol ⁻¹)	-21.72	-18.41	-19.42	-14.10
$\Delta H^{\ddagger} / (kJ \text{ mol}^{-1})$	-24.17	-20.85	-21.86	-17.79
$\Delta S^{\ddagger} / (J \ K^{-1} \ mol^{-1})$	-332.90	-319.13	-321.39	-306.82
$\Delta G^{\ddagger} / (kJ mol^{-1})$	+73.42	+72.70	+72.36	+72.16

 ΔG^{\ddagger} calculated at T = 293.15 K; E_a: activation energy; ΔH^{\ddagger} : enthalpy of activation; ΔS^{\ddagger} : entropy of activation; ΔG^{\ddagger} : Gibbs energy of activation; PS1: power supply 1; PS2: power supply 2.

The results in Table 1 reveal that the activation energy was negative for all conditions, indicating that the reaction rate increases with decreasing temperature.⁶¹ This finding is consistent with Henry's law, which predicts that the solubility of most gases increases at lower temperatures. The negative activation energy can be attributed to the enhanced solubility of the reactants at lower temperatures, leading to a higher concentration of the reactants in the solubility of species is likely to play a critical role in controlling the rate of NO₃⁻ production in this system.

The entropy of activation was negative for all conditions, indicating that the transition state for aqueous nitrate production by air plasma occurs via an associative step. This process involves two or more species combining to produce a single species, resulting in a decrease in ΔS^* . The negative entropy of activation implies that the reactants have a more ordered arrangement in the transition state compared to the initial state, which can be explained by the formation of stronger and more specific interactions between the reactants during the reaction.

The enthalpy of activation for all conditions was exothermic, consistent with an associative step in the formation of the transition state⁴⁹ for aqueous nitrate production by air plasma. The formation of chemical bonds during this step releases heat, leading to a decrease in ΔH^{\ddagger} . Furthermore, according to Le Chatelier's principle, an exothermic reaction shifts towards the products as the temperature decreases. This observation supports the idea that the transition state formation involves an associative step. In general, the dissolution of a gas is an exothermic process, which can also contribute to the exothermic nature of the enthalpy of activation observed in this study. Overall, the exothermic nature of the enthalpy of activation aligns with the associative mechanism for the transition state formation during aqueous nitrate production by air plasma.

The Gibbs energy of activation (ΔG^{\ddagger}) was calculated using equation 40:

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \Delta S^{\ddagger} \tag{40}$$

at an average temperature of 293.15 K (20 °C), which corresponds to the average temperature between 5 and 35 °C in the experimental range. Table 1 shows that the values of ΔG^{\ddagger} for all conditions are positive, ranging from +72.16 to +73.42 kJ mol⁻¹. This indicates that the transition state formation is an endoergic process requiring energy input to proceed. The value of ΔG^{\ddagger} decreases slightly when the plasma reactor is agitated. This decrease in ΔG^{\ddagger} suggests that the agitation of the plasma reactor leads to a more favorable reaction pathway for the production of the transition state. Overall, the positive values for ΔG^{\dagger} indicate that the transition state formation is an endoergic step requiring energy input (as work) from the surroundings, which is provided by the plasma discharge.

Nitrites and nitrates can be produced in PAW from the dissolved gases NO ($k_{\rm H} = 1.9 \times 10^{-5} \text{ mol m}^{-3} \text{ Pa}^{-1}$) and NO₂ ($k_{\rm H} = 1.2 \times 10^{-4} \text{ mol m}^{-3} \text{ Pa}^{-1}$), through the following reactions (41-42):

$$2NO_{2} + H_{2}O_{(1)} \rightarrow HNO_{2(aq)} + HNO_{3(aq)}$$
(41)
$$NO_{(aq)} + NO_{2(aq)} + H_{2}O_{(1)} \rightarrow 2HNO_{2(aq)}$$
(42)

However, these reactions are limited by the low values of the Henry's constants and contribute only a small fraction of the total nitrate and nitrite produced. In contrast, HNO_3 readily dissolves in the aqueous phase due to its large Henry's law constant (2.1×10^3 mol m⁻³ Pa⁻¹).

Figure 7 shows the influence of ionic strength on the rate of nitrate production in PAW. A slight decline in the rate constant ($k_{obs} = k_{non-ideal}$) can be observed with the rise in ionic strength, which is reflected by the parameter $z_A.z_B = 0.27$, derived from the slope of the graph. The relatively low correlation coefficient ($r^2 = 0.68$) might be indicative of the reaction not being confined solely to the aqueous phase, contrary to the assumption of equation 3. These findings can be related to the salting out principle, which correlates an increase in salinity, or salt concentration, with a reduction in gas solubility.⁶²



Figure 7. Effect of the ionic strength on k_{obs} for nitrate production in PAW at 15.0 °C, without stirring.

In a more detailed analysis, the introduction of solute ions to a nonelectrolyte solution incites a competition for bonding with water molecules. Due to their ionic properties, these solutes are able to draw polar H_2O molecules through electrostatic Coulombic interactions. This advantage allows the solute ions to outpace nonelectrolytes in their interaction with H_2O molecules. As a result, H_2O molecules predominantly align with the solute ions, leading to the creation of a hydration shell-a systematic alignment of water molecules that envelop the ions.⁶³

Based on the analysis of the plasma-gas-liquid interphase, the activation parameters, and the ionic strength effect, we propose the following step for the formation of the transition state for $HNO_{3(aq)}$ production:

$$HNO_{3(g)} + H_2O_{(l, interface)} \rightarrow HNO_{3(aq)}$$
(43)

This process involves the absorption of gas into the liquid phase, accompanied by a zero-order chemical reaction. This step is identified as the limiting factor, primarily because the rate constants for nitrogen species production in the air/plasma phase are significantly higher than the observed rate constant in the aqueous solution. For instance, consider the process that precedes the first step in the Zeldovich mechanism: the formation of highly vibrationally excited dinitrogen molecules (N₂*), induced by electron impact. The reaction rate coefficient for this process, denoted as k_{ev} , is approximately 10^{-8} cm³ s⁻¹ when the electron temperature (T_e) is 1 eV.⁵⁵ This rate translates to 6.02×10^{10} M⁻¹ s⁻¹. However, it is important to note that despite the difference in reaction order, the fastest reaction observed in this study is characterized by a rate constant $k_{obs} = 1.33 \times 10^{-5} \text{ M s}^{-1}$, occurring at a temperature of 5 °C and an average power of 27.0 ± 1.0 W.

Additionally, the dissolution of $HNO_{3(g)}$ is an exothermic, associative reaction that is enhanced by lower temperatures, with a standard enthalpy change ($\Delta_r H^\circ$) of $-33.3 \text{ kJ mol}^{-1}$.

Effect of average discharge power and agitation on NO_3^- production

The production of NO_3^- was found to increase with agitation due to simultaneous increases in average discharge power and enhanced mass transfer. The increased power amplifies the electric field and Townsend ionization coefficient, leading to more electrons contributing to electron impact reactions and intermediate production of NO through the Zeldovich mechanism. A study conducted by Douat *et al.*⁶⁴ demonstrated that enhanced plasma power generates a greater number of NO_x species within the plasma region. In particular, the densities of both NO and N_2O escalated as a function of the absorbed power in a micro plasma jet. Furthermore, agitation improves the mass transfer of species from the gas phase to the liquid phase, as HNO₃ has a high Henry's constant (2.1 × 10³ mol m⁻³ Pa⁻¹) and readily dissolves in water.

Agitation resulted in an increase in k_{obs} when compared to the same temperature and power supply. For example, using PS2 at 5 °C, k_{obs} increased by 3.3%, from 0.77395 ± 0.0235 mM min⁻¹ (0 rpm) to 0.7994 ± 0.01347 mM min⁻¹ (750 rpm). The final average nitrate concentration was only slightly higher (1.7%) with agitation, going from 126.6 ± 8.2 to 128.7 ± 7.6 mM under the same conditions.

Production of H₂O₂ by plasma activation

In all conditions of average power, temperature, and agitation, the concentration of H_2O_2 was found to be below the limit of detection (LOD) of the peroxotitanium method. This observation is in line with the findings of Hoeben *et al.*,³⁰ who reported that plasma-water interactions at low energy densities were insufficient to produce significant concentrations of hydrogen peroxide in PAW. Furthermore, higher energy densities led to peroxide degradation due to thermal effects, even when cooling the RF plasma reactor, within the energy density range of 45-450 kJ L⁻¹. Considering the present work employed longer plasma activation times of up to 180 min, leading to energy densities of up to 3000 kJ L⁻¹, it is plausible that thermal decomposition of H₂O₂ contributed to its concentration falling below the LOD.

Additionally, it is important to consider the chemical interactions that could further influence the concentration of H₂O₂ in PAW. Specifically, the presence of nitrite ions in the water could lead to reactions with H₂O₂. It is wellrecognized that HNO₂, formed from the protonation of nitrite, is prone to react with oxidant species such as H_2O_2 and O_3 . This reaction pathway results in the production of HNO₃, a more stable nitrogenous species. Therefore, in addition to the factors of energy density and thermal decomposition, the interaction between H₂O₂ and NO₂⁻ (leading to the formation of HNO₃) could significantly contribute to the lower detectable levels of H₂O₂. This aspect underscores the complexity of chemical dynamics in PAW systems and suggests that multiple mechanisms might be responsible for the observed concentrations of hydrogen peroxide. The detailed mechanisms of these reactions and their implications will be further discussed in the following section, providing a more comprehensive understanding of the factors influencing H_2O_2 concentration in these systems.

HNO₂ production by plasma activation

Figures 8a-8d depict the concentration profiles of HNO_2 during plasma activation for different temperatures at fixed average power and agitation conditions. Although the HNO_2 concentration increased over time, determining

its reaction order was not possible using integrated rate expressions of 0, 1, 2, 3, 1/2, and 3/2 orders. This challenge may arise from the instability of HNO_2 , which is prone to react with oxidant species such as O_3 and H_2O_2 in both gas and liquid phases, producing HNO_3 (reactions 44-45):

$$HNO_{2(aq)} + O_{3(g)} \rightarrow HNO_{3(aq)} + O_{2(g)}$$
(44)

$$HNO_{2(aq)} + H_2O_{2(aq)} \rightarrow HNO_{3(aq)} + H_2O_{(1)}$$
(45)

In these reactions, nitrous acid serves as an oxidizing agent, accepting electrons from ozone or hydrogen peroxide and consequently converting into nitric acid.

Although hydrogen peroxide was undetected in PAW using the peroxotitanium method in this study, trace amounts might still be present in water due to dissolution, as suggested by its relatively high Henry's law constant ($k_{\rm H}$ ca. 9 × 10² mol m⁻³ Pa⁻¹).^{28,65} Conversely, ozone is less soluble due to its relatively low Henry's law constant ($k_{\rm H}$ ca. 10⁻⁴ mol m⁻³ Pa⁻¹),^{28,65} but it can still dissolve in limited quantities. A KI solution imbibed in filter paper detected oxidant species in the reactor's gas phase, as reported in our previous study.⁴⁶

It is crucial to note that hydrogen peroxide and ozone both react non-selectively with iodide, resulting in triiodide formation through the following reactions 46-47:

$$\begin{aligned} H_2 O_{2(aq)} + 2I_{aq)}^- + 2H_{(aq)}^+ \rightarrow I_{3(aq)}^- + 2H_2 O_{(l)} \\ O_{3(aq)} + 2I^- + 2H_{(aq)}^+ \rightarrow I_{3(aq)}^- + O_2 + H_2 O_{(l)} \end{aligned}$$
(46) (46)

 HNO_2 decomposition in aqueous solution occurs through the reversible reaction 48:

$$2HNO_{2(aq)} = \frac{k48}{k-48} NO_{2(aq)} + NO_{(aq)} + H_2O_{(l)}$$
(48)

In reaction 48, k_{48} and k_{-48} represent the forward and reverse rate constants, respectively. The resulting NO₂ further undergoes hydrolysis to produce HNO₃ and HNO₂ according to reaction 41, where k_{41} is the forward rate constant.

Figure 8 demonstrates that the rate of nitrite production and nitrite concentration increased with decreasing temperature for all conditions. Several factors contribute to the rise in $\text{HNO}_{2(aq)}$ concentration with decreasing temperature. First, the temperature dependence of Henry's law coefficient for nitrous acid, which increases from



Figure 8. Kinetic profile of HNO_2 generation via plasma activation, for different initial water temperature across different average discharge power and agitation parameters: (a) P = 16.4 ± 0.1 W, 0 rpm, (b) P = 21.3 ± 0.9 W, 750 rpm, (c) P = 20.4 ± 0.1 W, 0 rpm, (d) P = 27.0 ± 0.1 W, 750 rpm.

38 ± 2 M atm⁻¹ at T = 30 ± 0.1 °C to 223 ± 11 M atm⁻¹ at T = 0.2 ± 0.1 °C.⁶⁶ Second, the rate constant for the forward reversible (k₄₈) HNO₂ decomposition to nitric oxide and nitrogen dioxide decreases from 28.6 M⁻¹ s⁻¹ at 30.0 °C to 3.46 M⁻¹ s⁻¹ at 10.0 °C.⁶⁶ Third, the rate constant for the reverse reversible HNO₂ (k₋₄₈) decomposition increases from $1.67 \times 10^8 \, \text{M}^{-1} \, \text{s}^{-1}$ at 30.0 °C to $1.98 \times 10^8 \, \text{M}^{-1} \, \text{s}^{-1}$ at 10.0 °C.⁶⁶ Finally, the rate constant for HNO₂ production from aqueous nitrogen dioxide (k₄₁) increases from $7.76 \times 10^7 \, \text{M}^{-1} \, \text{s}^{-1}$ at 30.0 °C to $14.7 \times 10^7 \, \text{M}^{-1} \, \text{s}^{-1}$ at 10.0 °C.⁶⁶

In summary, the rate constant for HNO_2 decomposition decreases, while the rate constants contributing to HNO_2 production increase at lower temperatures, resulting in a higher aqueous HNO_2 concentration and stability at lower temperatures.

Considering the plasma/gas phase chemistry, it is evident that condensed water vapor forms on the plasma reactor walls from the onset of plasma activation. This phenomenon occurs because the plasma discharge is directed towards the water surface, causing water evaporation and increased air humidity. The humid air enhances OH• production through reactions 27-28. The decrease in HNO₂ concentration with increasing temperature can be attributed to the exponential increase in water vapor pressure with temperature.⁵⁸ This increase in water vapor pressure enhances hydroxyl radical formation in the gas/plasma phase, which in turn promotes reaction 33 and reduces HNO_{2(g)} concentration.

Contrary to nitrous acid, which can be reverted back to nitrogen monoxide through the process of reaction 33 followed by reaction 49, nitric acid does not possess any back reaction.¹⁰ This distinction provides further clarity as to why HNO₃ exhibits a zero-order production in PAW, while the production order for HNO₂ remains undetermined.

$$NO_2 + O \bullet \to \bullet NO + O_2 \tag{49}$$

Effect of average discharge power and agitation on $\ensuremath{\text{NO}_2}\xspace^-$ production

The influence of average discharge power and agitation on NO_2^- production was examined. At a constant temperature, elevating the average discharge power resulted in a higher HNO_2 concentration due to increased electron impact dissociation within the Zeldovich mechanism. This process generates the primary intermediate species, NO (reactions 19-20). Agitating the plasma reactor also raised the HNO_2 concentration at a consistent temperature (refer to Figure 8). This effect can likely be attributed to improved mass transfer between the plasma/gas region in the reactor as a consequence of agitation. Concurrently increasing the average discharge power and agitation augmented both the

electric field and Townsend ionization coefficient (refer to "Electrical Characteristics of the Discharge" sub-section), which led to more electrons participating in electron impact reactions that produce RNS intermediates (Zeldovich mechanism).

The low Henry's constant value for HNO₂ ($k_{\rm H} = 4.7 \times 10^{-1}$ mol m⁻³ Pa⁻¹) is approximately four orders of magnitude smaller than the Henry's constant for HNO₃ (2.1 × 10³ mol m⁻³ Pa⁻¹). This difference might explain why the final HNO₂ concentration is highly sensitive to agitation. Owing to its relatively low solubility, HNO₂ mass transfer was significantly enhanced by the vortex at the liquid-gas interface, thereby increasing its absorption. When employing PS2, agitation resulted in a 124.5% rise in the final HNO₂ concentration (after 180 min of activation) at 5.00 °C, from 20.0 ± 3.7 to 44.9 ± 1.0 mM. In contrast, the final HNO₃ concentration experienced only a 1.7% increase under the same conditions (refer to "Effect of average discharge power and agitation on NO₃⁻ production" sub-section).

Production of H_3O^+ by plasma activation

Figure 9 demonstrates that the formation of H_3O^+ in plasma-activated water exhibits a zero-order kinetic behavior at all the tested temperatures, while maintaining constant average power and agitation conditions. At the onset of plasma activation, the concentrations of NO_3^- and H_3O^+ were comparable, with the dissociation of the strong acid HNO₃ serving as the primary source of H_3O^+ ions in the solution. In dilute solutions, the activity coefficient (γ_{\pm}) approaches one, and concentration is nearly equivalent to the activity of the species (a_{\pm}) (equation 50), where m_{\pm} represents the molality of the ion:

$$\mathbf{a}_{\pm} = \gamma_{\pm} \mathbf{m}_{\pm} \tag{50}$$

Hydronium ions in PAW are predominantly generated through the dissociation of both HNO₃ and HNO₂. Consequently, hydronium activity exceeded that of nitrate for the same activation duration, resulting in a higher k_{obs} for hydronium production under identical temperature, average power, and agitation conditions. For instance, at 5.00 °C, P = 16.4 ± 0.1 W, and 0 rpm, k_{obs} equaled 0.5936 ± 0.0128 mM min⁻¹ for nitrate and 0.6980 ± 0.0944 mM min⁻¹ for hydronium.

The sole deviation from this pattern occurred when the concentration of produced HNO_2 was at its peak. The combination of a weak acid and its conjugate base (NO_2^{-}) culminates in the formation of a buffer solution, which accounts for the higher k_{obs} for nitrate production compared to k_{obs} for hydronium production at 5.00 °C,



Figure 9. Kinetic profile of H_3O^+ generation via plasma activation, for different initial water temperature across different average discharge power and agitation parameters: (a) P = 16.4 ± 0.1 W, 0 rpm, (b) P = 21.3 ± 0.9 W, 750 rpm, (c) P = 20.4 ± 0.1 W, 0 rpm, (d) P = 27.0 ± 0.1 W, 750 rpm.

 $P = 27.0 \pm 1.0$ W, and 750 rpm. Under these conditions, k_{obs} was 0.7994 \pm 0.0135 mM min⁻¹ for nitrate and 0.7162 \pm 0.0738 mM min⁻¹ for hydronium.

In some experiments at 5 °C, hydronium activity decreased over time instead of increasing linearly (Figures 9b, 9c, and 9d). This can be attributed to the weaker acidity of nitrous acid (HNO₂, $pK_a = 3.15$) compared to nitric acid (HNO₃, $pK_a = -1.4$), causing the nitrite ion (NO₂⁻) to behave as a base. Additionally, the nitrite-to-nitrate disproportionation reaction (reaction 51) is faster at acidic pH levels below 3.5. This reaction consumes hydronium ions, leading to a lower concentration:

$$3NO_2^- + 3H^+ \rightarrow 2 \bullet NO + NO_3^- + H_3O^+$$
 (51)

Elevating the average discharge power led to a higher k_{obs} for hydronium ion production, even when agitation speed and temperature remained unchanged. This outcome can be ascribed to the concurrent increase in both k_{obs} for HNO₃ production and the concentration of HNO₂ over time at higher average power, which in turn accelerates the production rate of hydronium ions.

Electrical conductivity

As shown in Figure 10, the electrical conductivity demonstrated a linear increase with the duration of plasma activation. This trend was observed consistently across all tested temperatures, under conditions of fixed average power and constant agitation. Judée et al.7 also observed a linear increase in electrical conductivity (EC) with plasma activation time when generating PAW in tap water using a dielectric barrier discharge (DBD) without temperature control. In general, as the ion concentration in an electrolyte solution rises, the conductivity of the solution also increases due to the greater availability of ions to contribute to conductivity. HNO3 production in PAW is a dominant zero-order reaction, and HNO3 concentrations consistently exceeded those of HNO₂ (Figures 5 and 7). Consequently, the final conductivity value is heavily influenced by HNO₃ contributions, in accordance with Kohlrausch's law of independent migration of ions, shown in equation 52:

$$\Lambda_{\rm m}^{\rm o} = \nu_+ \lambda_+ + \nu_- \lambda_- \tag{52}$$

where Λ_m^o represents the limiting molar conductivity of



Figure 10. Electrical conductivity profile of plasma-activated water for different initial water temperature across different average discharge power and agitation parameters: (a) $P = 16.4 \pm 0.1$ W, 0 rpm, (b) $P = 21.3 \pm 0.9$ W, 750 rpm, (c) $P = 20.4 \pm 0.1$ W, 0 rpm, (d) $P = 27.0 \pm 0.1$ W, 750 rpm.

the electrolyte solution, λ_+ and λ_- denote the limiting molar conductivity of the cations and anions, and ν_+ and ν_- are the numbers of cations and anions *per* formula unit, respectively.⁵⁸

The limiting molar conductivity is an indicator of the maximum conductivity achievable in an electrolyte solution as the electrolyte concentration increases. Thus, the calculated molar conductivities based on the experimental concentrations of species and their respective limiting molar conductivities were consistently higher than the measured values.

As the concentrations of NO_3^- , H_3O^+ , and HNO_2 increased with the elevation of average discharge power and agitation and the reduction of temperature, the conductivity of the plasma-activated water followed a correlated trend.

Energy efficiency

To calculate the energy density (\in) of the plasma reactor in Joules *per* liter (J L⁻¹), we used the average discharge power (P) in Watts (W), the activation time (Δ t) in seconds (s), and the volume of activated water (V_w) in liters (L), according to equation 53:

$$\in = \frac{P \times \Delta t}{V_{w}}$$
(53)

The energy efficiency values (η) for producing nitrite, nitrate, and their sum in mol *per* Joule (mol J⁻¹) were determined by dividing the observed species concentration by the applied energy density, as given by equation 54:

$$\eta = \frac{[\text{Species}]}{\epsilon} \tag{54}$$

As demonstrated in earlier sections, the highest concentrations of nitrogen species were produced at 5.0 °C. Consequently, the calculations for energy efficiency were based on the amount of nitrogen species generated at this temperature. The energy efficiencies of nitrate and nitrite production, as well as the overall production efficiency in relation to energy density, are depicted in Figures 11a, 11b, and 11c, respectively.

Figures 11a and 11c reveal that higher average power and agitation led to decreased energy efficiency for nitrate and total nitrogen when considering the same energy density. This suggests that increased average power in the



Figure 11. Profiles of energy efficiency for the production of nitrogen species in relation to energy density, examined under various average power and agitation settings: (a) for nitrate, (b) for nitrite, and (c) overall production.

discharge can result in higher power consumption due to heat dissipation and subsequent thermal decomposition of reactive nitrogen species in the discharge, which are highly temperature-sensitive, as demonstrated in earlier sections. Supporting this, Hoeben *et al.*³⁰ reported that non-cooled radio frequency (RF) plasma reactors induced RONS decomposition in PAW once the temperature naturally reached 54 °C.

There is a temperature dependence for nitrogen species formation. According to the Zeldovich mechanism, the formation of NO in the second step (reaction 47) is exothermic, and increasing the temperature shifts the equilibrium towards the reactants, leading to a decrease in the overall rate of NO formation due to the decreased availability of N to react with O_2 . Consequently, the energy efficiency of NO synthesis through electronic excitation is constrained by the high energy cost of atomic nitrogen.⁵⁵

In the case of nitrate production, our study identified a clear trade-off between energy efficiency and reaction rate. We observed that although a higher average discharge power of 27.0 ± 1.0 W (with stirring at 750 rpm) did increase the observed rate constant for nitrate production (as illustrated in Figure 5d), it conversely resulted in the lowest energy

efficiency. This can be explained by the fact that a higher average discharge power leads to an increase in energy density (as *per* equation 53), which in turn results in a decrease in energy efficiency (as indicated by equation 54). Our experiment yielded the highest energy efficiency for nitrate production (48.60 nJ mol⁻¹) at an average discharge power (P) of 20.4 ± 0.1 W, with no stirring, and an energy density of 1110 kJ L⁻¹. As far as we are aware, this is the first reported instance of such a trade-off between reaction rate and energy efficiency.

The highest energy efficiency value for nitrite (52.6 nmol J⁻¹) was observed at 16.4 \pm 0.1 W, 0 rpm, and 49 kJ L⁻¹, with peak values observed for the lowest energy densities under all conditions. However, for energy densities higher than 1150 kJ L⁻¹, the highest energy efficiency was observed at P = 21.3 \pm 0.9 W, 750 rpm, followed by 27.0 \pm 1.0 W, 750 rpm, due to the increasing nitrite concentration over time with increasing applied power and agitation (as shown in Figure 11b).

The overall energy efficiency for nitrate and nitrite production was highest (72.33 nmol J⁻¹) at $P = 20.4 \pm 0.1$ W, 0 rpm, and 1110 kJ L⁻¹. This is the same condition for the highest nitrate energy efficiency, indicating its significant

contribution to the overall nitrogen efficiency achieved.

To compare the energy efficiencies obtained in this study with those reported in the literature, we recalculated the maximum energy efficiencies reported in other experiments using equation 54 as needed. The appropriate discharge power, plasma activation time, water volume, and concentration of species were considered for each experiment. The results are presented in Table 2. In cases where the experimental conditions for achieving maximum energy efficiency were the same, the energy efficiency for the production of NO₃⁻ + NO₂⁻ was found to be approximately the sum of the energy efficiencies of the individual species.

 Table 2. Comparison of energy efficiencies in different processes for generating RNS from air and water

Reference	$\begin{array}{c} \eta_{max} \left(NO_{3}^{-} \right) / \\ \left(nmol \; J^{\text{-}1} \right) \end{array}$	$ \begin{array}{c} \eta_{max} \left(NO_{2}^{-} \right) / \\ (nmol \; J^{}) \end{array} $	$ \begin{array}{c} \eta_{max} \left(NO_{3}^{-} + NO_{2}^{-} \right) / \\ (nmol \ J^{-1}) \end{array} $
8	13.01	_	13.01
28	28.95	2.10	31.05
30	9.15	22.7	29.9
14	0.11	0.07	0.18
23	15.51	0.06	15.56
15	2.00	2.00	3.99
17,35	5.49	0.27	5.75
23	20.95	0.85	21.91
67	125.00	-	125.00
This work	58.60	42.56	72.33

 η_{max} : maximum energy efficiency.

All studies in Table 2 used a single plasma reactor for PAW generation, except for Dinh *et al.*,⁶⁷ who employed an additional DBD reactor as an ozone generator to oxidize nitrogen species produced by the arc plasma in the gas phase before absorption by the aqueous phase. This resulted in a higher reported energy efficiency of 125.00 nmol J⁻¹, making it an attractive option for applications where a high NO_3^- selectivity is desired, such as fertilizers. However, the use of an extra DBD reactor and pure oxygen inlet incurs additional costs.

Using a single plasma/liquid reactor for PAW generation, this study achieved an energy efficiency of 72.33 nmol J⁻¹ without the need for gas flow, making it a simple and efficient approach that offers advantages in terms of cost and ease of operation. Subsequently, a lab-scale product was developed, and a patent⁶⁸ was filed along with an industrial design,⁶⁹ thus enabling its potential use in various applications. To evaluate the effectiveness of the produced PAW as a fertilizer, seed germination enhancer, crop protector, and pH controller, further studies are required.

Conclusions

In conclusion, this study has provided a comprehensive understanding of the origin of reactive species, mass transfer processes, and the production of nitrogen species in a plasma reactor. Our findings confirm that reactive species are predominantly generated in the gas phase and subsequently absorbed into the liquid phase through the gas-liquid interface. The role of Henry's constant in the gas dissolution process and the air plasma-water interface chemistry has been emphasized, with the absorption of HNO_{3(g)} into the liquid phase being the limiting step in the HNO_{3(aq)} production.

The Zeldovich mechanism is responsible for the production of nitrogen species in air plasma, with the Townsend ionization coefficient increasing alongside the average discharge power. This increase in ionization results in the generation of a greater number of reactive species, leading to higher production rates of NO_3^- and NO_2^- .

The kinetics of NO_3^- production by plasma activation have been studied, revealing a zero-order reaction and a temperature-dependent relationship with the observed rate constant. The activation energy, entropy, and enthalpy were found to be negative for all conditions, indicating an associative step in the transition state formation and an exothermic reaction that favors product formation at lower temperatures.

The effect of average discharge power and agitation on NO_3^- and NO_2^- production has been investigated, showing that increased agitation and power lead to higher production rates due to enhanced mass transfer and increased electric field strength. The production of H_2O_2 was found to be below the limit of detection under all experimental conditions, while the rate of HNO_2 production and stability increased with decreasing temperature. The influence of average discharge power and agitation on NO_2^- production was examined, with higher HNO_2 concentrations observed at increased power and agitation due to enhanced mass transfer and Zeldovich mechanism processes.

The production of H_3O^+ in plasma-activated water followed a zero-order reaction, with the main source being the dissociation of HNO₃ and HNO₂. The electrical conductivity of the plasma-activated water increased linearly with plasma treatment time, primarily due to the generation of ions, with HNO₃ contributions playing a significant role.

For nitrate production, a trade-off exists between energy efficiency and reaction rate. Although the highest average discharge power of 27.0 \pm 1.0 W with 750 rpm stirring led to increased k_{obs} for nitrate production, this condition corresponded to the lowest energy efficiency. The study has demonstrated a simple and efficient approach for plasma-activated water generation using a single plasma/liquid reactor, with a high reported energy efficiency of 72.33 nmol J⁻¹, offering advantages in terms of cost and ease of operation.

Further research is needed to evaluate the effectiveness of the produced plasma-activated water as a fertilizer, seed germination enhancer, crop protector, and pH controller, among other applications. This study has laid the groundwork for the development of a lab-scale product, with a patent and an industrial design filed, thus enabling its potential use in various fields.

Acknowledgments

The authors gratefully acknowledge the Universidade Tecnológica Federal do Paraná (UTFPR) for providing the necessary resources and facilities to carry out this research work. We also thank Fundação Araucária (FA) for their financial support through the Synapse of Innovation Program (Paraná), grant number SIN2019011000116. This funding was instrumental in enabling us to carry out our research project.

Author Contributions

Péricles I. Khalaf proposed the research, secured the necessary funding, wrote the main manuscript, and prepared all figures; Érica T. Berlatto conducted the experiments and was responsible for the analysis of data. Both authors reviewed and approved the final version of the manuscript.

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Submitted: September 28, 2023 Published online: January 24, 2024