

Example of an outstanding review

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Journal: *Plasma Sources Science and Technology*

Manuscript ID: [REDACTED]

Authors: [REDACTED]

Title: [REDACTED]

blue, italic – author's text

The manuscript presents a study on plasma-based air nitrogen fixation into nitrites (NO₂⁻) and nitrates (NO₃⁻) by a combination of arc discharge plasma combined with a commercial ozone generator. It contains many interesting results, although their presentation is not ideal, sometimes confusing, incomplete or inconsistent. I think clarification of certain results is required in a way to improve the readability of the manuscript and also to acknowledge the importance of the data presented.

I have several comments and questions:

General Question 1: According to 10.1016/j.cep.2015.02.004 the theoretical limit of the energy consumption for non-thermal plasma nitrogen fixation is approximately 0.2 MJ/mol, i.e. more than 2.5 times lower than that of the Haber–Bosch process. How far is the development of non-thermal plasma methods away from this minimum? Is non-thermal plasma fixation processes feasible to be able to compete with other conventional methods used for nitrogen fixation? Can you comment it a little more in the manuscript.

General Question 2: A brief reference to other non-thermal plasma systems used for nitrogen fixation [13–19] is presented in *Introduction*. In many of these works nitrogen fixation was not actually a main goal, but only a way to support e.g. bio-decontamination or plant growth. The goal was not to maximize NO₃⁻ concentration in water, rather to achieve a good composition of various reactive nitrogen and oxygen species in plasma treated water to achieve a given goal. Nevertheless, can you provide more information on the existing studies dealing with a nitrogen fixation in the liquid in the form of NO_x⁻ as it is was in your case, mainly those where the main objective was to maximize NO_x⁻ yield (e.g. 10.1109/TPS.2008.2007585, 10.1088/1009-0630/9/3/08e, etc)? A table summarizing the main condition and parameters of these studies, as well as achieved NO_x⁻ concentrations and energy consumption would be nice to have. I think a reader would be pleased with such comparison to give a credit to your work and achievements.

Page 4, Line 20: *Using this hybrid system, almost all gaseous NO_x was converted into NO₃⁻ in water, which significantly reduced gaseous NO_x and ozone emissions to approximately zero.*

Zero NO_x⁻ and O₃ emissions are reported and it is explained that all gaseous NO_x and O₃ reacted and formed NO_x⁻ in water. Can you evaluate/calculate a 'nitrogen balance' and prove the total concentration of NO_x⁻ in water fully correspond to concentration on NO_x produced by the discharge within 5 minutes and dissolved completely into water?

Your system is equipped with cold traps. Is it possible that some compounds (e.g. NO_x converted into HNO_x) escaped from a water tank and condensed farther in water traps and your gas analysis was fooled? Here again 'nitrogen balance' evaluation would help.

Page 5, Fig.2a: Commercial ozone generator in figure looks like Ozone Tech LAB-Series LAB-II. According to the specification it is DBD based, not corona based ozone generator. Please check.

Page 5, Fig.2a: What is 'gas outlet' used for? Is it's a purge? During 5 minutes experiment did all gas leaving the water tank pass through the traps or not? Or only a gas that was analyzed. How did you do sample the gas toward the gas analyzing systems, by using additional pump? Please explain the details of the experiment, where and how did you measure concentrations of O₃, NO_x. What was detection limit for NO, NO₂ and O₃ in gas phase?

Page 6, Fig.2a: Can you provide a figure with a secondary horizontal axis with the values of stabilized values ozone concentration (ppm) corresponding to the given power (40–100 W)? Or replace the Y axis with ozone concentration in (ppm)?

Page 6, Line 38: *The outlet gases from the air arc plasma reactor (mainly NO_x, O₂, and N₂) and the ozone generator (O₃ and O₂) were premixed and reacted with each other before passing through a tap water bottle (4.5 L).* Specify the volume of the mixing chamber. Have you measured concentrations of NO, NO₂, O₃, eventually other species before and after the mixing chamber? Can you present these values in the paper?

Page 6, Line 40: Specify what species have been monitored and their concentrations evaluated using gas emission analyzer and Fourier transform infrared (FTIR). Using FTIR have you found any other than NO, NO₂ species in the spectra (N₂O, N_xO_y, HNO_x)?

Page 8, Figure 3a: With respect to the topic of the manuscript the figure is not necessary. The effect of gas swirl is not discussed in the paper anyway. Also, the scale is invisible and it is not explained.

Page 8, Figure 3b vs Page 4, line 43: *An AC plasma power supply providing a voltage of up to 12 kV and current of few hundreds of milliamperes (mA) ... is employed to generate stable elongated arcs.* Figure shows amplitudes 2 kV and 2 A. Please explain how they match with 12 kV and mA currents.

Page 8, Results and Discussion: I would find more appropriate first to present the results on gaseous species generated at various power of both ozone generator (40-100 W) and arc discharge plasma (100 W, 160 W) measured before and after the mixing chamber and at the gas output and only then to show concentration of RONS in liquids and confront these values. Please consider reorganizing your manuscript.

Page 8, Line 55: *In this study, we investigated the effect of the distance from the arc discharge to water surface (i.e., Δ , indicated in Fig. 4a) for the first time.* I found it strange that this information is not presented among the objectives in *Introduction* and also not mentioned in *Experimental Setup*. All information about the used experimental system and the main objectives must be explained earlier than in *Results and Discussion*. Nevertheless, what is the practical point to alter the distance Δ ? The objective of the manuscript is nitrogen fixation. To maximize the yield of fixed N, i.e. to maximize the concentration of NO_x- in water. It is almost obvious that the maximum would be reached if the distance between source of NO_x and water was minimal. My opinion is that the whole chapter 3.1 can be omitted and you should mainly concentrate on detailed analysis of gas and water in the system of arc discharge + ozone generator, i.e. chapter 3.2.

Page 9, Line 36: *However, a high concentration of gaseous NO_x emission was detected, approximately 3800 ppm, at 160 W electrical power. This indicates that a significant portion of fixed nitrogen was lost in the form of gaseous NO_x, which is an important air pollutant.*

I assume the concentration was measured at the gas outlet after the gas passed through the water tank. What was the concentration of NO_x before the water tank? Can you check on 'nitrogen balance', i.e. compare inlet and outlet concentrations of NO_x (before and after water tank) and confront it with the concentration of measured NO_x- and find if the balance fits?

Page 10, Fig. 4a: Information about the experimental setup, including figures must be in *Experimental setup*, not in *Results and Discussion*.

Page 10, Fig. 4b: It would be nice to show the concentration of gaseous NO, NO₂ measured before the gas enters the water tank. Or even H₂O₂ concentration in gas phase, if you can measure it. Can you provide any data?

Page 11, Line 24: *A lower arc plasma power condition (e.g., 110 W) shifts the optimized condition to 70 W supplied power of the ozone generator, with a 98 ppm nitrate concentration in 4.5 liters of water with NO_x emission controlled at 35 ppm and no O₃ emission.* What do you consider 'optimized conditions'? When NO₃- concentration is maximal and NO₂- minimal? Why in case of arc discharge power of 160W the NO₂- and H₂O₂ concentrations suddenly decrease for ozone generator power above 40-50W (Fig. 5bc)? On contrary Figure 6 shows continuous and monotonous decrease of both gaseous NO and NO₂ concentrations with the increasing ozone generator power. The pH change could explain it, however it remains fairly constant and drop down only for ozone generator power of 70W and above (Fig. 7a, for 160 W). Can you explain?

Page 13, Fig. 6ab: I think NO and NO₂ absorption spectra (Fig. 6ab) are not necessary to show. I would recommend to present absorbances as concentrations and put these data points in Fig. 6c to have NO, NO₂ and NO_x concentrations plotted against the ozone generator all together. But the way, why data for only arc discharge power of 160W are presented? In case of NO₂-, NO₃- data for both 100 W and 160 W are presented in Fig. 6? It would be nice to have a complete data set for both arc discharge powers (100, 160 W) and explain the details and differences. Have you found any change or NO/NO₂ ratio with a change of arc discharge power (e.g. from 100 to 160 W)?

Page 14, Fig. 7a: With an increase of ozone generator power a sudden decrease of pH is observed (when going from left to right). Why pH drop happens first for arc discharge power of 110 W and only then for 160 W. I would expect the opposite. How many times you measured pH? Can you present error bars?

Page 17, Line 16: The title of the chapter is misleading. It presents only a set of chemical reaction and discusses possible pathways. There is no discussing concerning real reaction kinetics, considering reaction rates of various chemical reactions with respect to temperatures, concentrations, Henry's constants etc.