Fuel Processing Technology 208 (2020) 106521

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Plasma-enhanced NO_x remediation using nanosecond pulsed discharges in a water aerosol matrix

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ARTICLE INFO

Keywords:
Nitrogen oxide
Dioxide
Diesel
Marine
Transient plasma

ABSTRACT

We report nitrogen oxides remediation using a transient pulsed plasma discharge in a water aerosol gas matrix using nanosecond high voltage pulses. While there have been many studies showing highly efficient conversion of NO to NO_2 using plasma-driven processes, the total removal of NO_x (i.e., NO plus NO_2) is severely limited by the backreaction of NO_2 to NO, which is also driven by the highly reactive radical species in the plasma. By injecting water aerosol into the gas matrix, we are able to selectively drive a plasma-based reaction which minimizes the backreaction of NO_2 to NO. Here, the synergistic effect of the water aerosol and plasma discharge enables enhanced NO_x removal by creating OH radicals which, in turn, drive NO_2 to HNO_3, which is highly soluble in water. In the presence of water aerosol, the plasma discharge results in a 100% reduction in NO and a 98% reduction in total NO_x. Spectroscopic evidence of the short-lived, highly reactive OH radical is obtained through plasma emission spectroscopy and the vibrational signatures of the NO_2^- and NO_3^- intermediates are observed using SERS-enhanced Raman spectroscopy. We show that the NO_x remediation increases with plasma power density demonstrating the scalability of this general approach.

1. Introduction

In the combustion of fossil fuels, NO and NO_2 are produced as harmful pollutants giving rise to smog and acid rain. Several research groups (including our own) have shown effective NO_x (i.e., NO, NO_2) remediation using various plasma treatment approaches [1–4]. However, the detailed chemical pathways associated with these plasma-based process are complex and not fully understood. Fig. S1 of the Supplemental Document illustrates the multitude of the possible chemical pathways in this remediation process. Here, the major products are NO_2, N_2O, N_2O_5, N_2, HNO_2, HNO_3 (indicated in boxes in Fig. S1), and the radicals assisting each reaction include various excited states of O, O_3, OH, N, NO, and HO_2 (shown next to the corresponding arrow in Fig. S1) [5–7]. The reaction of NO with oxygen radicals are believed to be the dominant reactions for plasma-based remediation. The back reaction of N with NO_2 and the reaction of O_3 with NO_2 both replenish NO. While RF-based plasma reactors have been investigated for pollution remediation for several decades, transient plasmas produced by high voltage nanosecond pulses consume far less energy in the creation of the plasma than conventional RF sources [8].The transient nature of the plasma necessitates that very little current is drawn in creating the plasma. That is, once the streamer is created, the applied field collapses before a substantial amount of current (and hence electric power) can flow. Because of its transient nature, this is a cold plasma in which the electron energies are extremely high, while the vibrational modes of the molecules remain close to room temperature [9–11]. These "hot" electrons enable new chemical pathways to be explored in the formation of energetic intermediate species that are otherwise not possible to make through standard equilibrium chemistry.

While many groups have shown that plasma treatment can convert NO to NO_2 extremely efficiently, this approach generally is not effective in removing NO_2 [12–15]. In a comparison by Matsumoto, the NO removal efficiency of nanosecond pulse discharges can be as high as 0.75 mol/kWh, which is considerably higher than that obtained with (microsecond) pulsed corona discharges (0.35 mol/kWh) and dielectric barrier discharge (DBD) reactors (0.2 mol/kWh) [13]. Huiskamp et al.

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https://doi.org/10.1016/j.fuproc.2020.106521
Received 7 April 2020; Received in revised form 1 July 2020; Accepted 1 July 2020

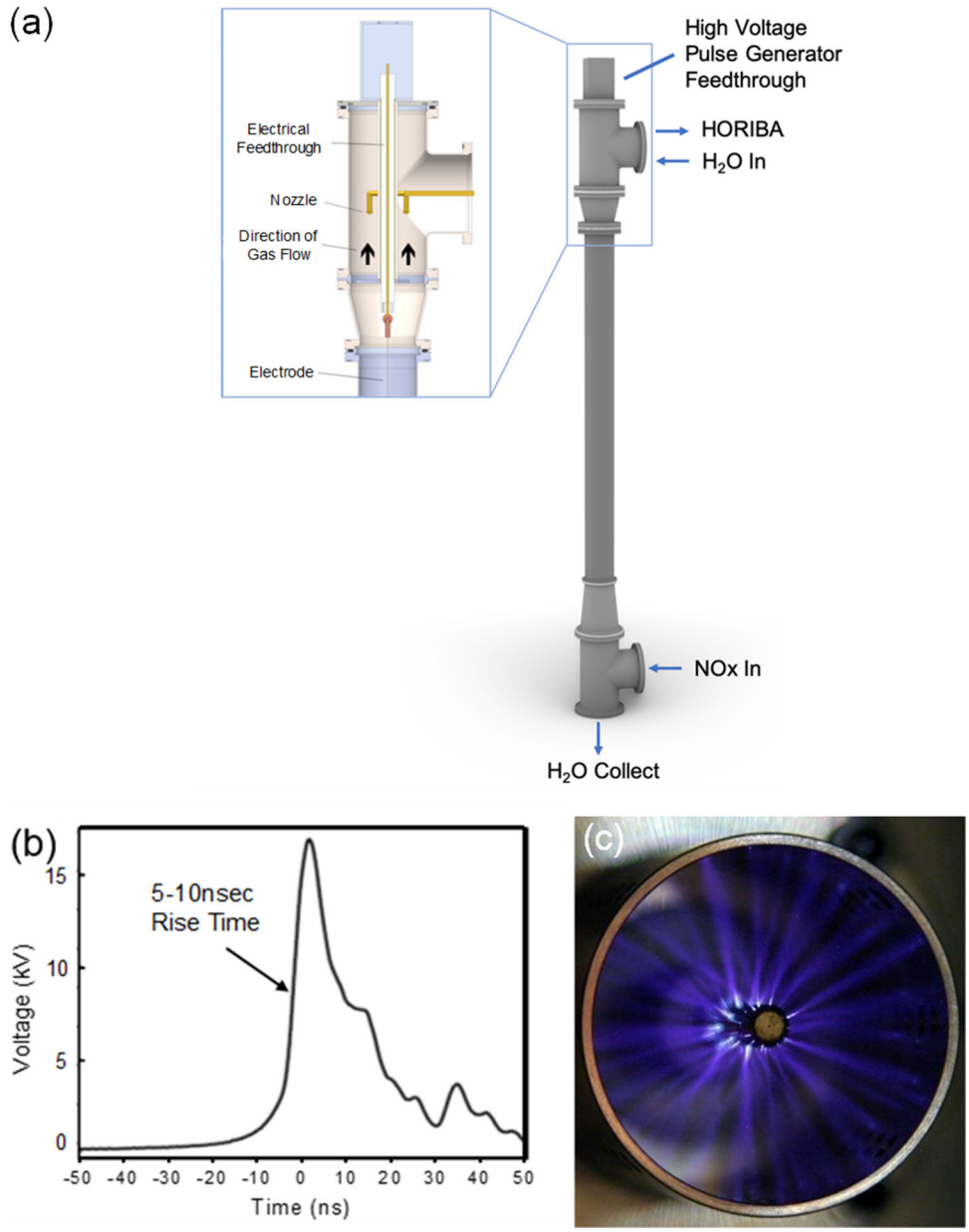

Fig. 1. (a) Schematic diagram of the experimental setup used to test the transient pulsed plasma reactor. (b) Typical output characteristics of nanosecond high voltage pulse generator. (c) Photograph of the transient plasma (hot electron, low-temperature plasma) formed by the high voltage nanosecond pulse approach.

reported NO removal using sub-nanosecond transient plasma with an efficiency of 2.5 mol/kWh when starting conditions of the synthetic gas matrix, a crucial parameter affecting remediation outcomes, included no measurable quantity of NO_2 [16]. Aside from this work by Huiskamp, a handful of papers report NO_x remediation values (i.e., NO $+NO_2$), however, these papers do not discuss reaction pathways or report any spectroscopic evidence of the reaction intermediates [17–25]. Khacef et al. reported a NO_x reduction pathway involving C_3H_6, which reacts with O_2 to yield peroxy radicals (HO_2) that efficiently converts NO to NO_2 [17,18].

In the work presented here, we demonstrate a synergistic effect of injecting water aerosol with a transient plasma discharge to push this reaction to HNO_3 via the creation of OH radicals. Here, we perform a comparative study of plasma discharge with (i.e., "wet") and without (i.e., "dry") injection of water aerosol, systematically at different plasma densities. Plasma emission spectra and Raman scattering spectra are taken in order to verify the OH and NO_3^- intermediates.

2. Experimental details

Here, a transient plasma is created using a nanosecond pulse discharge in a coaxial reactor consisting of a 3 ft. (0.9 m) long, 2 in. (5 cm) diameter stainless steel cylindrical anode with a single-wire cathode center electrode, as depicted in Fig. 1. A Transient Plasma Systems Model 20× pulse generator is operated with a peak output voltage of 17 kV (Fig. 1b) at pulse repetition rates up to 2 kHz and continuous powers up to 0.8 kW. Fig. 1b shows a plot of a typical pulse waveform generated using this system. Fig. 1c shows a single pulse image of the transient plasma discharge in a similar co-axial reactor. Radio frequency (RF)-based plasmas have demonstrated remediation of diesel exhaust for several decades [26–32], including a large effort at the Ford Motor Corporation using conventional RF plasmas. However, the recent availability of solid-state nanosecond high voltage pulse generators, which consume less energy than conventional RF plasmas, opens up the possibly of driving these NO_x remediation processes more efficiently. At a peak voltage 17 kV, this system delivers a peak power of 4.76 MW.

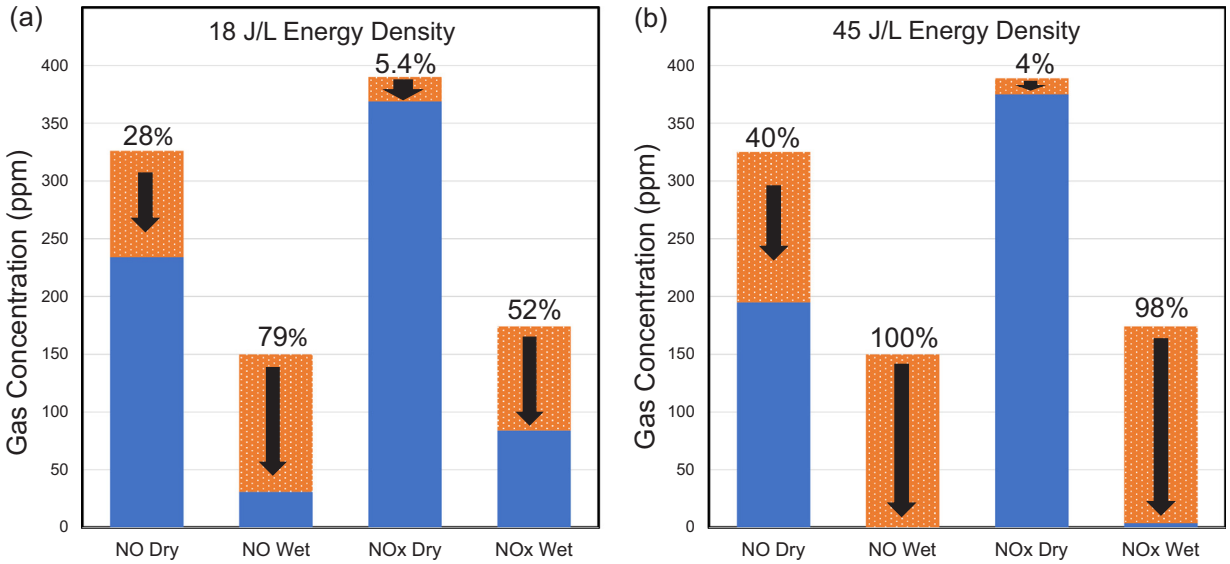

Fig. 2. NO and NO_x gas concentrations with and without the plasma discharge under both "dry" (i.e., without water aerosol) and "wet" (i.e., water aerosol) conditions. (a) low plasma density and (b) high plasma density.

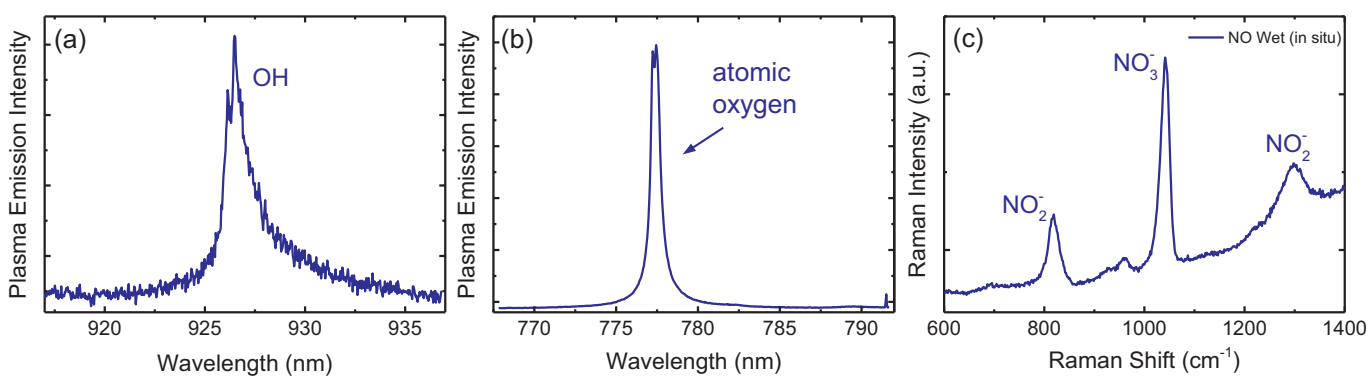

Fig. 3. (a) Plasma emission spectra of (a) OH radicals and (b) atomic oxygen observed from high voltage discharge in aqueous solution. (c) SERS-enhanced spectrum of NO-plasma exposed Ag nanoparticles.

Fig. 1a illustrates the reactor configuration in which a water aerosol (i.e., approximately 100 nm diameter nanoparticles) is injected into the reactor using an ultrasonic nozzle in the direction counter to the flow of NO_x to be treated. At the output of this reactor, NO and NO_x concentrations are measured using a portable gas analyzer (Horiba Model PGA-350), which samples at a flow rate of 0.5 L/min. In the experiments reported here, our synthetic gas mixture was prepared by mixing neat NO gas with compressed dried air at 500 PPM by volume. This model of gas analyzer detects NO and NO_x using chemiluminescence detection with a measurement repeatability of 0.5% relative to the full measurement scale of 500 ppmV or ± 2.5 ppmV absolute.

3. Results and discussion

Fig. 2 shows a plot of the NO and NO_x concentrations taken with ("wet") and without ("dry") water aerosol injection. Fig. 2a and b show the results obtained at plasma energy densities of 18 J/L and 45 J/L, respectively. The starting NO concentrations ranged from approximately 150 to 325 ppmV, while the starting NO_x concentrations ranged from approximately 160 to 390 ppmV. Here, we observe relatively little plasma-induced remediation in the dry gas mixtures: 40% for ΔNO and only 4% for ΔNO_x. However, a dramatic increase in NO and NO_x remediation is observed the presence of water aerosol injection: 100% for ΔNO and 98% for ΔNO_x. These remediation values correspond to 0.54 and 1.1 mol/kWh for the wet reactor and 0.45 and 0.81 mol/kWh under dry conditions. This marked improvement in remediation efficacy demonstrates the synergistic effects of adding water together with plasma discharge, which increases the availably of OH radicals far beyond that attained with the plasma alone or the water aerosol alone. This plasma-enhanced remediation mechanism is comprised of a two-step process, in which the NO is converted to NO_2 by atomic oxygen radicals in the plasma followed by the rapid conversion of NO_2 to HNO_3 via the OH radicals created by discharging the plasma in the presence of water aerosol. This second step minimizes the backreaction of NO_2 to NO, greatly improving the efficacy of this approach. The resulting HNO_3 is highly soluble in the water aerosol matrix is captured with near unity efficiencies and subsequently titrated. We would like to point out that our initial NO concentrations in Fig. 2 are somewhat different under dry and wet conditions. Huiskamp et al. observed a strong dependence on the initial concentrations of NO, however, these data were taken under mildly moist conditions and they observe an increase in NO_2 at these energy densities. Nevertheless, we observe a clear enhancement in NO_x remediation with water aerosol injection [16].

In order to corroborate the hypothesis that OH radicals drive the $NO_2 \rightarrow HNO_3$ step in this NO_x remediation process, in situ plasma emission spectroscopy was performed using nanosecond pulsed plasma discharge with water, as shown in Fig. 3a. Here, a sharp peak is observed at a wavelength around 927 nm, which corresponds to charge neutral OH radicals that are short lived, highly chemically active species, as reported by Sato et al. [33] These OH radical species are known

to produce various oxidizing agents, such as hydrogen peroxide and ozone, as used in water purification and the decomposition of volatile organic compounds (VOCs) [33–43]. Here, however, we believe the OH radicals are used directly to drive NO_2 to HNO_3, as described above. Fig. 3b shows a plasma emission spectrum centered around 777 nm, which corresponds to light originating from atomic oxygen species, responsible for the first step in this remediation process (i.e., NO → NO_2). Fig. 3c shows surface enhanced Raman scattering (SERS)-enhanced vibrational spectra of H_2O/NO_2 plasma exposed Ag nanoparticles. Sharp peaks observed around 822 and 1053 cm^{-1} are in agreement with previous reports of NO_2^- and NO_3^- species, which correspond to the deprotonated HNO_3 reaction intermediate [44–46]. These spectroscopic signatures provide further evidence of the OH-driven reaction pathway proposed for this water aerosol-enhanced, plasma-driven process. This approach circumvents the standard NO(g)/HNO_3^0(aq) equilibria and overcomes the relatively low solubility of NO in water, which is several orders of magnitude lower than the solubility of HNO_3. The HNO_3 is then removed in H_2O with nearly unity capture and subsequently titrated, as is typical done in a wet scrubber configuration. The synergistic effect of OH for NO_x removal has been discussed previously by Huiskamp et al., however, the effect was minimal since only mildly moist air was used and not the aerosols used here [16].

In conclusion, we demonstrate a synergistic effect in the remediation of toxic nitrogen oxide pollutants (i.e., NO and NO_2) by discharging a nanosecond pulsed transient plasma discharge together with injection of a water aerosol into the gas matrix. Previous studies have shown high efficiency conversion of NO to NO_2 via plasma-based processes but poor removal of total NO_x (i.e., NO and NO_2) due to the rapid backreaction of NO_2 back to NO. By comparing the plasma-based remediation with and without injection of water aerosol, we are able to isolate a reaction pathway that minimizes the backreaction of NO_2 to NO by increasing the availability of OH radicals. This results in a two-step process, whereby NO is first converted to NO_2 by atomic oxygen radicals, and then NO_2 is subsequently converted to HNO_3 via OH radicals. Here, the key reactants OH and O are evidenced by plasma emission spectroscopy, while the vibrational signatures of the HNO_3^- intermediate species are observed using SERS spectroscopy. Using this synergistic approach, we observe a 98% reduction in NO and a 100% reduction in total NO_x due to the plasma discharge in the presence of water aerosol. Without the plasma discharge, the NO_x removal efficiency is generally limited by the low solubility of NO and NO_2 in water. Here, we provide a way around this limitation by rapidly driving NO_2 to HNO_3, before it can be converted by the backreaction to NO.

Declaration of competing interests

W. P. Schroeder received research support from the TCC Group through the University of Southern California (USC), Los Angeles, CA, USA. He continues to serve in an advisory capacity as a paid consultant for the TCC Group.

Credit author statement

Christi Schroeder: Conceptualization, Methodology, Investigation, Validation, Writing - original draft, Writing - review & editing; William Schroeder: Conceptualization, Methodology, Investigation; Sisi Yang: Investigation, Data curation; Alec Nystrom: Methodology; Zhi Cai: Investigation, Data curation; Sriram Subramanian: Investigation, Methodology; Shujin Li: Investigation, Data curation; Martin Gundersen: Conceptualization; Stephen B. Cronin: Writing - original draft, Writing - review & editing.

Acknowledgements

This work was supported by the Tai Chong Cheang Steamship Co. (TCC) HongKong, China.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuproc.2020.106521.

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