

Reducing nitric oxide into nitrogen via a radio-frequency discharge

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Abstract

NO/N₂/O₂/H₂O mixtures are usually converted into HNO₃ and/or NO₂ using different discharge approaches. In this study, a radio-frequency discharge was successfully used to reduce NO mainly into N₂ at a low pressure (4 kPa). The influences of experimental parameters, including carrier gas, inlet concentration of NO, O₂, steam, and applied power, are discussed. At least 95.7% of the total N atoms converted from NO into N₂. Other traces of byproducts were N₂O and HNO₂, but neither HNO₃ nor NO₂ were detected. In addition, conversion of NO apparently increased with elevated applied power or decreased inlet concentration of O₂, reaching 92.8% and 74.2% for the NO/N₂/O₂ (2%) and NO/N₂/O₂ (6%)/H₂O (10%) mixtures, respectively, at 120 W. In addition, from the optical emission spectra, a large amount of N₂ (first positive band and second positive band) and NO (γ system) were observed, and the important reactions for NO removal and N₂ formation are proposed.

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1. Introduction

NO_x, the precursor of photochemistry products and acid smog, is mainly emitted from industrial processes or mobile sources. NO_x is harmful to the human health and the ecosystem, damages vegetation and degrades or corrodes materials through acid deposition [1]. Many emissions control strategies have been implemented, such as selective catalytic reduction, selective noncatalytic reduction, and direct thermal decomposition. However, the typical operating temperature of these is relatively high, ranging between 300 and 1000 °C [2,3].

Hence, nonthermal plasma approaches, which can be free of high temperature control and avoid the problems of catalyst poisons and deactivities, have been developed to remove NO. Several kinds of plasma technologies have been demonstrated that can be operated at room temperature and be proceeded in dry or wet process, such as dielectric barrier discharge, corona discharge, and microwave discharge [4–8].

However, higher oxidized nitrogen compounds, such as NO₂ and/or HNO₃, are commonly formed when converting the NO/N₂/O₂/H₂O mixtures [6,9–11]. Although NO₂ and HNO₃ are water soluble and can be removed with scrubbers, to reduce NO into N₂ seems a better choice because it does not need further treatment of acidic wastewater and sludge. Hence, a dry, single-stage, noncatalytic radio-frequency (rf) discharge approach, which has previously not been tried to remove NO, is successfully demonstrated to reduce NO mainly into N₂ in this study. The 13.56 MHz rf plasma is commonly used in industry for IC manufacture and surface modification, as well as being used to recover sulfur from SO₂ and convert methane into syngas [12,13].

In addition, high concentrations of NO_x are yielded from nitric acid plants, the high ovens of heat treating automotive catalysts, and automobile exhaust gases. The NO_x can reach a concentration of 2000 or up to 10,000 ppm [3,14], which is fed into the rf discharge reactor in this study.

In the discharge zone, electrons interact with N₂, NO, and O₂ to generate initiating species for the overall reaction chains [15]. In addition to electron-impact dissociation and ionization reactions, Penning ionization and charge-transfer processes take

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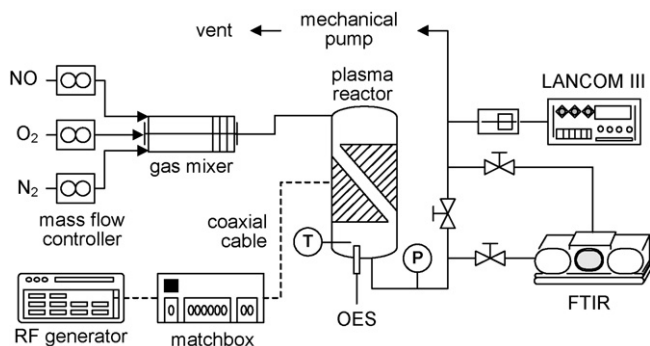
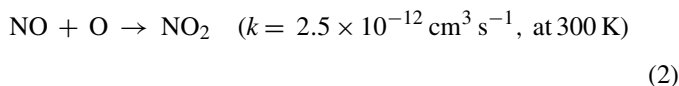
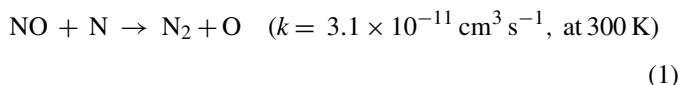


Fig. 1. Sketch of the rf discharge system.

part in the NO decomposition [16]. The previous studies indicated that the major removal channels of NO were through reduction reaction (Eq. (1)) and/or oxidation reaction (Eq. (2)) [17–19]. However, long-lived excited N_2 in plasma jets did not play an important role in NO destruction via reaction of $NO + N_2 \rightarrow N_2 + N + O$ [20]:



In addition, the decomposition of NO via electron impact dissociation ($e + NO \rightarrow N + O + e$) also yields a large amount of N and O. However, the rate of electron impact rate is dependent on discharge types owing to their different electron mean energy and plasma density. In order to infer the important mechanisms, plasma diagnostic technology, like optical emission spectroscopy, is often used [19] to examine the major active species in this rf discharge process.

2. Experimental section

A laboratory-scale rf discharge system is shown in Fig. 1. NO (4.8%, N_2 balanced), and high purity O_2 (99.95%) and N_2 (99.995%) were supplied from compressed gas cylinders and their flow rate was adjusted with a calibrated mass flow controller. The reactants were introduced into a gas mixer, and then entered a vertical, cylindrical glass reactor. A 13.56 MHz rf generator (PFG 600, Fritz Huttinger Elektronik GmbH) coupled with a matching network (Matchbox PFM) was used to apply the power. The power was delivered to the plasma reactor that wrapped two outer copper electrodes, as well as to generate an inductively coupled glow discharge. The net power to the discharge was determined by obtaining an optimum match via reading the difference between the forward and reflected power. However, the reflected power is usually zero via the matchbox auto-matching the capacitance and inductance. Before the experiment, a mechanical vacuum pump was used to exhaust the effluents and to remove contaminants. For each experimental run the system was kept at working pressure until the effluents had been measured.

The qualitative and quantitative analyses of reactants and effluents were performed by an on-line Fourier transform infrared (FTIR) spectrometer (Nicolet, Avator 370, with a gas cell of 2.3 L and light path length of 9.6 m). Calibration of gaseous reactants and products was made by withdrawing unreacted gases and by going directly through the sampling line connected to the FTIR. Furthermore, the accuracy of the concentration of NO_x was also checked by a commercially available analyzer (Land, Lancom III). Studies of optical emission spectra were carried out by using an optical spectrometer (Ocean Optics, Model HR 4000CG). The emission light was collected through an optical fiber, which was put in the rear part of the plasma and analyzed via a scanning monochromator.

The gas sampling lines, including the gas cell of FTIR are heated and kept at about 330 K by wrapping a heated belt coupling with a temperature controller in order to measure HNO_2 and HNO_3 . Moreover, the boiling point decreases apparently with the decreased operating pressure, such as the boiling point of HNO_3 is about 315 K, hence, HNO_2 and HNO_3 can vapor in the overall close system (reactor, sampling lines, and gas cell are at the same pressure) until pumping out.

The main operational parameters and conditions were as follows: applied rf power = 30–120 W, inlet concentration of NO ($[NO]_{in}$) = 2400 or 10,000 ppm, inlet oxygen concentration ($[O_2]$) = 0–10%, inlet H_2O concentration = 0 or 10 vol.%, carrier gas = N_2 , and total flow rate = 200 sccm (standard ml min^{-1}). In addition, the feeds were at room temperature and the pressure was operated at 4 kPa in order to start the discharge easily and keep the discharge was in a stable state. The gas temperature of effluents was measured by a thermocouple that was put at the rear of discharge zone in the reactor.

The temperature was in the range of 420–800 K and the gas mean residence times in the physical discharge zone was ranged between 0.2 and 0.4 s for all runs. Part of the forward power that supplied by the rf generator was consumed by the reflected power, heating electrodes, and the electron temperature, hence, the gas temperature was not very high.

3. Results and discussion

The conversion of NO (η_{NO}) and the fraction of total N atoms converted from NO into N_2 (F_{N_2}) are calculated by the following equations:

$$\eta_{NO} = \frac{\text{NO converted}}{\text{NO fed to the reactor}} \times 100\%,$$

$$F_{N_2} = \frac{2 \times N_2 \text{ yielded from decomposed NO}}{\text{NO converted}} \times 100\%$$

where NO and N_2 are the moles of compounds NO and N_2 , respectively. The amounts of N_2 converted from inlet NO were calculated based on the mass balance of N atoms by quantifying all N-species detected, including NO, NO_2 , N_2O , HNO_2 , and HNO_3 .

Table 1

The fraction of total N atoms converted from NO into N₂ (F_{N_2}) for various mixtures (N₂ or Ar balance, [NO]_{in} = 10,000 ppm, applied power = 30–120 W)

Mixtures	F_{N_2} (%)
NO/N ₂	>97.7
NO/Ar	>98.8
NO/N ₂ /O ₂ (2%)	>98.2
NO/N ₂ /O ₂ (6%)	>97.5
NO/N ₂ /O ₂ (6%)/H ₂ O (10%)	>95.7

3.1. Fractions of total N atoms converted from NO into N₂

Table 1 shows that F_{N_2} was very high and reached at least 95.7% (in the NO/N₂/O₂/H₂O mixtures) when the power supply was in the range of 30–120 W for different operating conditions, including carrier gas (N₂ or Ar), inlet [O₂] (0–6%), inlet [H₂O] (0 or 10%). Besides N₂, the other trace amounts of N-species were N₂O and HNO₂. Hence, the rf discharge approach can reduce NO mainly into N₂, as well as minimize the formation of higher oxidized nitrogen compounds when converting the NO/N₂/O₂/H₂O mixtures.

F_{N_2} increased from 97.7% and 98.8% for the NO/N₂ and NO/Ar mixtures, respectively, to almost 100% when power was raised from 30 to 120 W (Table 1). Besides N₂, several to tens ppm of N₂O were detected, but no NO₂. Similar products were obtained by using microwave discharge [16,21]. When oxygen was added, it did not change F_{N_2} significantly. F_{N_2} still kept in the range of 98.2–100% and 97.5–100% for [O₂] = 2% and 6%, respectively (Table 1). The results of analyses of byproducts revealed that a little more N₂O (several tens ppm) was yielded in the O₂-added environment.

With conditions of steam (10 vol.%) no HNO₃ and NO₂ could be identified, though they were usually produced in the other discharge reactors. Several to tens ppm of HNO₂ and N₂O led the F_{N_2} to reduce slightly, but F_{N_2} was still greater than 95.7% (Table 1). The addition of H₂O would yield OH radicals to promote the formation of HNO₂ via the NO + OH + M → HNO₂ + M reaction [6,22]. The yield of N₂O was primarily through the reaction of 2NO → N₂O + O [11]. Very little N₂O was produced to demonstrate that N₂O could decompose easily into N₂ and O from the weak N–O bond (binding dissociation energy, $D_0 = 161.3$ kJ/mol) [18]. NO₂ cannot be detected because it maybe caused by the lower rate of NO₂ formation (NO + O + M → NO₂ + M) [17], as well as NO₂ would be re-dissociated owing to its weaker binding energies ($D_0 = 301.6$ kJ/mol). As a result, no HNO₃ was detected because there was no NO₂ as the precursor to form HNO₃ via NO₂ + OH → HNO₃.

NO₃ and N₂O₅ are possible intermediates during the process of plasma de-NO_x in air. However, they were not found in the FTIR spectra. So, their concentration should be relatively very low compared to the NO concentration. In addition, NO₃ fast reacts with NO (NO₃ + NO = 2NO₂, $k = 1.57E+13$ cm³/(mol s) at 273 K) [23]. N₂O₅ is slowly formed by reaction of NO₂ and NO₃ ($k = 3.95E+8$ cm³/(mol s) at 273 K) [24] and self-decomposes to form NO₂ and NO₃ (N₂O₅ = NO₂ + NO₃, $k = 0.0691$ s⁻¹) [23].

In general, NO₃ and N₂O₅ concentrations are not significant in plasma de-NO_x processes.

In this study, the pressure was operated at 4 kPa in order to start the discharge easily and keep the discharge was in a stable state with a lower mean electron temperature and lower gas temperature. The reaction kinetics will be different for atmospheric pressure application, because three body collision reactions have rates strongly increasing with pressure; quenching rates of excited species change drastically; the mean electron temperature and gas temperature vary with the type of discharges, etc.

3.2. Effects of carrier gas, [NO]_{in} and pressure on NO conversion

Adding different carrier gas into NO showed that η_{NO} increased from 97.1% to 99.4% for Ar-balanced mixture, while from only 57.6% to 97.2% for N₂-balanced gases, when the power was increased from 30 to 120 W (Fig. 2). The higher η_{NO} for using Ar as carrier gas was obtained because Ar efficiently transferred the energies which it gained from the energetic species to decompose NO [16]. Conversely, besides excitation, N₂ molecules used some of the power for the process of self-dissociation and recombination. Especially at lower power with a lower plasma density, most of the energetic species impacted with N₂ to lose their energies, resulting in a larger gap of η_{NO} when compared with Ar-balance mixture.

At a lower [NO]_{in} (2400 ppm) in N₂, η_{NO} was higher than at a higher [NO]_{in} and increased from 78.3% to 98.6% as the power rose from 30 to 120 W (Fig. 2). Because a lower [NO]_{in} means fewer NO molecules need to be converted than at a higher [NO]_{in} under a fixed power with a fixed plasma density. The high η_{NO} for either higher or lower [NO]_{in} can be performed to reveal that the rf discharge approach is feasible for a wide range of [NO]_{in}.

Operating pressure was found to influence the η_{NO} . At 1.33 kPa, a higher η_{NO} (71.3–89.7%) than that of at 4 kPa ($\eta_{NO} = 57.6$ –85.3%) was found at 30–60 W in the NO/N₂

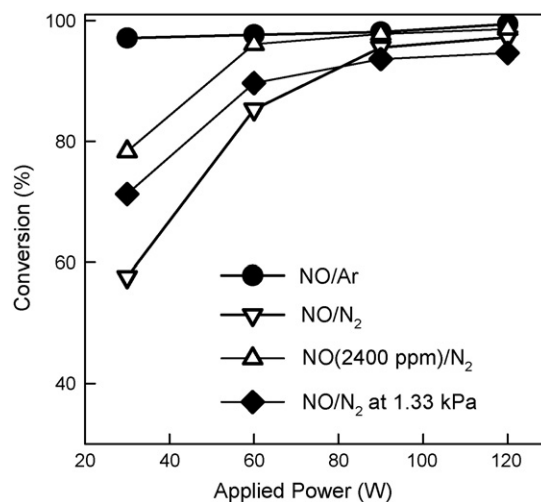


Fig. 2. Conversions of NO for different carrier gas, [NO]_{in}, and pressure ([NO]_{in} = 10,000 ppm, 4 kPa, N₂ balance without O₂, except when otherwise stated) at various applied powers.

mixtures (Fig. 2). Due to at a lower pressure, electrons with a higher kinetic energy could elevate the probability of impact-dissociation. However, a lower pressure with a shorter residence time of NO molecules in the discharge zone reduced the probability of collisions. Moreover, O₂ formed from the removal of NO would excited or dissociated into atomic O again at a higher power with a larger plasma density, leading to an increase in the rate of NO recombination. Hence, instead of a higher conversion, η_{NO} was 93.6% (at 90 W) and 94.6% (at 120 W), 2–2.6% less at 1.33 kPa than at 4 kPa (Fig. 2).

3.3. Effects of O₂, NO₂ and steam

η_{NO} apparently decreased with increased oxygen content. In the NO/N₂/O₂ rf discharge, η_{NO} reached 92.8% and 77.6% for [O₂] = 2% and 6%, respectively, at 120 W in the NO/N₂/O₂ mixtures (Fig. 3). However, η_{NO} was 4.4–7.9% less at [O₂] = 2% and 12.8–22.3% less at [O₂] = 6% than at no oxygen (NO/N₂) condition at 30–120 W. This is because O₂ molecules attached to the energetic species, resulting in a significant decrease in the vibrational temperature of N₂ [15]. Moreover, the O₂-added can be excited or dissociated into O radicals, which increases the rate of NO recombination.

Interestingly, although the presence of oxygen decreased η_{NO} , the concentration of NO₂ was still under the detection limit. The reason may be the lower rate of NO₂ formation (NO + O + M → NO₂ + M) [17], and NO₂ could be re-dissociated owing to its weaker binding energies.

In the presence of NO₂ in the NO/N₂/O₂ mixtures, NO₂ almost all removed. Moreover, the conversion of NO₂ was always higher than NO, and the η_{NO} was slightly lower than for the gas streams without NO₂. For example, at an inlet molar ratio of [NO]/[NO₂] = 2/1 in the NO/NO₂/N₂/O₂ (6%) mixtures, η_{NO} increased from 43.6% to 83.1% when power was increased from 30 to 120 W, and the conversion of NO₂ reached 100% at a power greater than 60 W (Fig. 3). In addition, the major product was N₂ with only several ppm of N₂O.

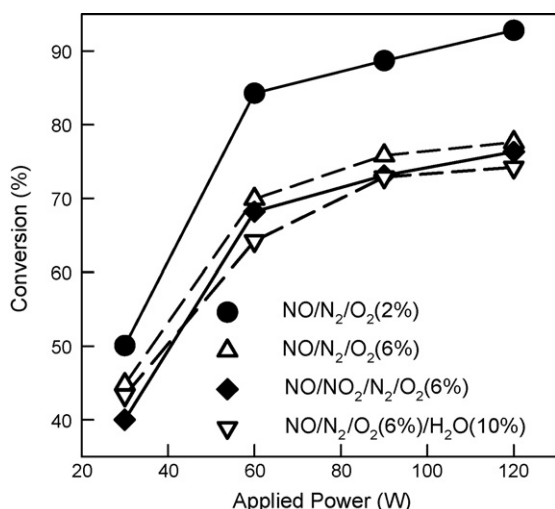


Fig. 3. Conversions of NO affected by [O₂], NO₂ and steam at various applied powers.

In the NO/NO₂/N₂/O₂ mixtures the decrease of η_{NO} was caused by NO₂ molecules reacting with some of the energetic species, resulting in the decrease of concentration of active species. Moreover, the NO₂ removal yielded NO by reacting with the O radicals. The removal of highly toxic NO₂ should occur through the cleavage reaction of NO₂ + e (or M), or the NO₂ + N and NO₂ + O reactions, producing N₂, N₂O, and NO [22]. The easier dissociation of the N–O bond of the NO₂ molecule than with the NO is caused by the lower binding dissociation energy ($D_0 = 301.6$ kJ/mol for NO₂, while $D_0 = 626.8$ kJ/mol for NO) [18].

The addition of steam (10 vol.%) showed that η_{NO} decreased slightly 1.5–5.7% when compared to the steam-free condition. η_{NO} increased from 43.3% to 74.2% as the power increased from 30 to 120 W in the H₂O/NO/N₂/O₂ (6%) mixtures (Fig. 3). Since H₂O is an efficient quencher, it consumes some of the active species. Moreover, H₂O reacts with N or N₂ to form OH and HN, which then further brings about NO recombination through reactions, including N + OH, O + HN, and OH + HN [25,26], leading to the decrease of η_{NO} . Surprisingly, only several to tens ppm of HNO₂ and N₂O, but no HNO₃, were detected. Because there was no NO₂ as the precursor to form HNO₃ via NO₂ + OH → HNO₃, abundant OH radicals could be generated through electron-impact dissociation reaction (H₂O + e → OH + H + e) [11].

3.4. Examination of optical emission spectroscopy (OES)

Table 2 lists the relevant optical emission species with the main bands or peak positions [27–30]. The observation of the representative emission spectrum of NO/N₂/O₂ mixtures at 120 W and 4 kPa in this study shows the activated species of the N₂ second positive band, N₂ first positive band (threshold energy, $E_{\text{th}} = 7.4$ eV), and NO (γ system) were mainly observed (Fig. 4). However, N₂⁺ (first negative band) and atomic N or O were difficult to be identified, though they were observed in N₂ rf plasma at 10 Pa (N₂⁺) [27] and in NO/N₂ dielectric barrier discharge at 5 kHz and 12.5 kV (atomic N) [31].

The relative optical emission intensity (I) of active species, including NO (γ -band) and N₂ (second positive), between various conditions was compared with the η_{NO} by assigning I_{NO} and I_{N_2} values as 1 in the NO/N₂/O₂ mixtures at 30 W (Table 3). The results show that in NO/N₂/O₂ mixtures, larger I_{NO} and I_{N_2}

Table 2
Lists of the relevant bands or peaks for optical emission spectrum of NO/N₂/O₂ mixtures discharge

Species (system)	Transition	Band/peak position (nm)
N ₂ (second positive)	C ³ Π → B ³ Σ	337.1, 357.7, 375.5, 380.5, 400, 406
N ₂ (first positive)	B ³ Π → A ³ Σ	550–900
NO (γ -band)	A ² Σ ⁺ → X ² Π	226.9, 237.0, 247.9, 259.6, 271.5, 285.0
N	3s ⁴ P → 3p ⁴ S ⁰ 3d ⁴ P → 3p ⁴ P ⁰	745.2 674.5
N ₂ ⁺ (first negative)	B ² Σ _u ⁺ → X ² Σ _g ⁺	391.4, 427.8
O	³ S ⁰ → ³ P	777.2, 777.4, 844.6

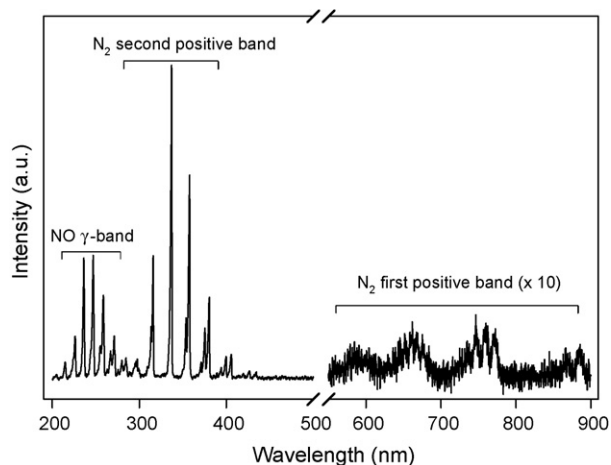


Fig. 4. A typical optical emission spectrum of $\text{NO}/\text{N}_2/\text{O}_2$ (6%) mixtures at 120 W and 4 kPa.

accompanied with a higher η_{NO} were found at 120 W than at 30 W (Table 3). This is because with an increased power supply a higher plasma density provides more energetic electrons, exciting more N_2 , NO and O_2 , which then increases the probability of NO collision and removal.

When at the same power supply (120 W) I_{NO} is much higher with a close value of I_{N_2} in the NO/N_2 mixtures than in the $\text{NO}/\text{N}_2/\text{O}_2$ mixtures (Table 3). Since O_2 is a very efficient quencher [32] that results in some electronically excited species, ionic molecular nitrogen, and atomic N or O cannot be identified in the $\text{NO}/\text{N}_2/\text{O}_2$ mixtures. Moreover, the addition of oxygen decreases the number of atomic N due to the destructive process involving NO and O_2 molecules [32], leading to a decrease in the reaction rate of $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$ and a decrease in η_{NO} .

In rf discharge, the activated species, including N_2 2nd pos. ($E_{\text{th}} = 11.1$ eV), N_2 metastable state ($\text{N}_2(\text{A})$, $E_{\text{th}} = 6.22$ eV) and atomic N ($E_{\text{th}} = 9.76$ eV) were obtained directly via the electron impact. Subsequently, NO γ -band ($\text{NO}(\text{A})$) was excited by the collisions with $\text{N}_2(\text{A})$ through $\text{NO}(\text{X}) + \text{N}_2(\text{A}) \rightarrow \text{NO}(\text{A}) + \text{N}_2(\text{X})$. Compared with the former energy levels of energetic species, NO can be removed by colliding with electrons, excited N_2 or N, due to the lower threshold energy ($E_{\text{th}} = 6.50$ eV) of NO dissociation. Hence, reactions (1) played important roles in NO removal, as well as reaction (1) to reduce NO to N_2 . As for the oxidation of NO via reaction (2) with a lower reaction rate constant, it yields NO_2 , however, NO_2 will be dissociated by reacting with e, N or O to yield N_2 , N_2O , and NO [22]. Hence, almost no NO_2 was detected in the rf discharge.

Table 3
Relative intensities of I_{NO} and I_{N_2} in different discharge mixtures

Mixtures	Power (W)	I_{NO}	I_{N_2}	NO conversion (%)
$\text{NO}/\text{N}_2/\text{O}_2$ (6%)	30	1.0	1.0	44.8
	120	2.1	7.8	77.6
NO/N_2	120	3.5	7.5	97.2

Finally, the energy efficiency of the de-NO rf plasma that represents the NO removed by a unit electrical power (kWh) is calculated based on deposited power [33], excluding the losses of electrodes heating and power transformation/delivery (the losses is about 50% of applied power). The energy efficiencies are 5.6 g NO/kWh (NO/N_2 at 30 W) and 4.2 g NO/kWh ($\text{NO}/\text{N}_2/\text{O}_2$ (6%)/ H_2O (10%) at 30 W), as well as are lower than the typical values of energy efficiencies (g NOx/kWh) in various plasmas, such as 3.7 for microwave, 3.8 for dc plasma, 17 for combined DBD scrubber system, 19 for electron beam, 25 for pulse corona, and 28 for packed-bed DBD [33–38]. Hence, the performance of this rf conversion plasma approach should be improved for elevating the energy efficiency via the adjustment of operating parameters, such as the increase of total inlet flow rate in the future.

4. Conclusion

As much as 95.7–100% of the N atoms converted from NO into N_2 for $\text{NO}/\text{N}_2/(\text{O}_2)/(\text{H}_2\text{O})$ mixtures using the rf discharge approach. The major product was N_2 , with several to tens ppm of HNO_2 and N_2O detected, but no HNO_3 and NO_2 . From the observation of optical emission spectra, a large amount of N_2 and NO were excited, suggesting the $\text{NO} + \text{N}_2 \rightarrow \text{N}_2 + \text{N} + \text{O}$ reaction and then the $\text{NO} + \text{N} \rightarrow \text{N}_2 + \text{O}$ reaction play important roles in the removal of NO and the formation of N_2 . In addition, operating the discharge at a higher power, a lower inlet molar fraction of O_2 or NO, or the addition of steam, could lead to a higher conversion of NO. NO conversion reached 74.2%, 77.6%, 92.8%, and 97.2% for the $\text{NO}/\text{N}_2/\text{O}_2$ (6%)/ H_2O (10%), $\text{NO}/\text{N}_2/\text{O}_2$ (6%), $\text{NO}/\text{N}_2/\text{O}_2$ (2%), and NO/N_2 mixtures, respectively, at 120 W. The results revealed that the gaseous compositions significantly influenced the NO conversion, while they had only a small effect on the fraction of total N atoms converted from NO into N_2 . However, the rf discharge approach is not practical in this stage due to its lower operating pressure and lower energy efficiency. The further research for plasma process operating at atmospheric pressure with a higher flow rate to convert NO mainly into N_2 should be proceeded. In addition, the other atmospheric pressure, lower electron temperature and gas temperature plasmas are also in developing, such as a continuous-wave microwave or low frequency ac plasma for converting NO mainly into N_2 .

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