Specific energy cost for nitrogen fixation as NO\textsubscript{x} using DC glow discharge in air

Xuekai Pei\textsuperscript{©}, Dogan Gidon\textsuperscript{©} and David B Graves\textsuperscript{©}

Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, United States of America

E-mail: graves@berkeley.edu

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Abstract
We report on factors influencing the specific energy costs of producing NO\textsubscript{x} from pin-to-pin DC glow discharges in air at atmospheric pressure. Discharge current, gap distance, gas flowrate, exterior tube wall temperature and the presence of activated Al\textsubscript{2}O\textsubscript{3} catalyst powder were examined. The presence of heated catalyst adjacent to the plasma zone improved energy efficiency by as much as 20\% at low flows, but the most energy efficient conditions were found at the highest flowrates that allowed a stable discharge (about 10–15 l min\textsuperscript{-1}). Under these conditions, the catalyst had no effect on efficiency in the present study. The lowest specific energy cost was observed to be between about 200–250 GJ/tN. The transport of active chemical species and energy are likely key factors controlling the specific energy costs of NO\textsubscript{x} production in the presence of a catalyst. Air plasma device design and operating conditions must ensure that plasma-generated active intermediate chemical species transport is optimally coupled with catalytically active surfaces.

Keywords: nitrogen fixation, atmospheric pressure air plasma, NO\textsubscript{x} production, energy cost

1. Introduction
Nitrogen fixation, i.e. converting unreactive molecular nitrogen (N\textsubscript{2}) into more reactive forms of nitrogen (N\textsubscript{r}), is fundamental in the manufacture of nitrogen-based fertilizers. The dominant process currently is the high temperature and high-pressure catalytic formation of NH\textsubscript{3} from N\textsubscript{2} and H\textsubscript{2}, commonly known as the Haber–Bosch (HB) process, named after its early 20th century inventors [1–3]. Although the process of making NH\textsubscript{3} via the HB process is energetically efficient, the resulting system of fertilizer application is quite inefficient, resulting in a serious perturbation to the worldwide geochemical N cycle. N\textsubscript{r} losses to both water and air are significant challenges to worldwide agriculture and alternatives are needed to supply the required N-based fertilizers with less impact on the environment [4–7].

One strategy is to capture and recycle some of the N\textsubscript{r} lost to the environment in agriculture. For example, organic waste from livestock contains considerable quantities of nitrogen, but much of this N\textsubscript{r} is lost in the form of volatile NH\textsubscript{3} as the waste is bacterially degraded [8, 9]. This NH\textsubscript{3} lost to the atmosphere is a serious pollutant and it considerably reduces the N-content (and therefore the fertilizer value) of the resulting organic fertilizer. It has been known since the early 19th century [10] that lowering pH by adding acid to the decaying waste will significantly reduce losses of NH\textsubscript{3} by converting volatile NH\textsubscript{3} into involatile NH\textsubscript{4}\textsuperscript{+}. Indeed, sulfuric acid is currently used as an additive to organic waste in Northern Europe for this purpose, and it is known to be effective [11]. But it is also possible to acidify aqueous waste using nitric acid created by combining air plasma-generated NO\textsubscript{x} with water.

Although this technology has been shown to work in initial field trials (e.g. Ingels, 2019), the relative energy inefficiency of the air plasma is a challenge in order to make the technology commercially attractive for farmers. The question of the factors controlling NO\textsubscript{x} generation energy efficiency in
atmospheric pressure air plasma is the focus of the present article.

The question of specific energy costs associated with NOx production in natural lightning discharges has received considerable attention in the atmospheric chemistry literature since NOx can have major effects, especially in the upper atmosphere [12–14]. Most of the studies related to lightning report specific energy costs of about 400 GJ/tN (gigajoules expended per metric ton nitrogen produced), or equivalently about 1017 molecules J−1. One simulated lightning study reported relatively low specific energy costs. Wang et al [15] found the specific energy cost for high current pulsed discharges might be as low as about 100 GJ/tN, albeit with a large error range.

This topic has also received considerable attention from researchers in the plasma chemistry literature in recent years [2, 16–33]. For example, Janda et al [16] reported a pin-to-plane atmospheric air transient spark discharge, driven by a DC power supply, to generate NOx. They reported a specific energy cost of about 600 GJ/tN for NOx production in air. Hao et al [17] investigated an air operated non-thermal plasma jet in a microhollow cathode discharge geometry to generate NOx. The lowest specific energy cost was also reported to be about 600 GJ/tN under stable discharge conditions. Patil et al [18] reported a milli-scale gliding arc reactor operating at atmospheric pressure for nitrogen oxides synthesis. These authors observed the lowest energy cost for NOx formation of about 103 GJ/tN (equivalently, about 28.7 kWh kg−1 of fixed N2). This value was later reported to be about 300 GJ/tN [28].

Previous studies on NOx generation energy costs in our laboratory have focused on the use of various classes of atmospheric pressure air discharges, including a surface microdischarge (SMD) plasma, a nanosecond pulsed pin-to-plane discharge and a device we termed the ‘propeller arc’ [34, 35]. The most energy efficient of these devices for NOx production is the propeller arc, with the lowest value observed to be about 250 GJ/tN.

Other researchers have reported attempts to improve plasma energy efficiency for nitrogen fixation by adding heterogeneous catalysts [24, 31, 36, 37]. For example, Iwamoto et al [31] investigated ammonia synthesis from N2-H2 precursors using an atmospheric pressure DBD (dielectric barrier discharge) plasma with catalyst present. They found the catalysts can have a significant impact on energy efficiency for DBD plasma. Patil et al [24] reported low temperature plasma-catalytic NOx synthesis in a packed bed DBD reactor. The nitrogen fixation efficiency was increased by almost 60% in the presence of catalyst, although the reported specific energy costs for the ‘cold’ DBD-catalyst system are relatively high compared to the results from gliding arc and other ‘warm’ discharges discussed earlier. These results motivated us to attempt to combine warm plasma with catalyst activation for NOx formation from air.

In this paper, we focus on a simple pin-to-pin DC glow discharge in flowing air at atmospheric pressure. We first present the experimental set-up and measurement methods we utilized in the study, followed by results and discussions regarding energy cost of NOx production under different discharge conditions. We investigated the effect of discharge current, gas flow, gap distance, surface temperature and the presence of catalyst on NOx production efficiency.

2. Experimental setup and measurement

2.1. Experimental setup

Figure 1 shows the experimental setup for NOx production by DC glow discharge in this paper. It is a pin-to-pin electrode configuration. Two tungsten pins with diameter 1.6 mm are used as the discharge electrodes (anode and cathode). The electrodes are situated in the center of a quartz tube (ID 10 mm, OD 12 mm) and held by two copper fixtures in the copper tubes (ID 7 mm, OD 10 mm). The copper tubes are also used as the gas flow channel and are fit flush inside the quartz tube. The gap distance (‘d’) between the two electrodes can be adjusted from 0 to 100 mm. A HV (high voltage) DC power supply (Spellman high voltage, SL10PN1200) is used as the power source. A ballast resistor (120 kΩ) stabilizes the discharge current by limiting the discharge current below 10 mA.
120 mA. This is the highest current rated for the DC power supply. We note the ballast resistor is not necessary when the power supply has an over-current protection circuit. In our research, the simple pin-to-pin configuration discharge driven by DC power supply with a ballast resistor is a glow discharge according to most literature \[38-40\].

Air flows into the quartz tube from the cathode (grounded) side and is controlled by a mass flow controller (UNIT INSTRUMENTS, 0–15 slm). The generated NO\(_x\) flows into a standard gas cell (Bruker, A132-2) with 20 cm path-length, placed inside the Fourier transform infrared (FTIR) spectrometer. The FTIR absorption spectrum is collected and recorded after 5 min of stable discharge for each experimental condition. We note that 5 min for stabilizing the system is sufficient for the smallest flow rate (11 l min\(^{-1}\)) during our experiments.

We investigated the effects of air humidity (between 0%–95%) on the energy cost of NO\(_x\) production. However, there was no significant change in either energy cost or NO and NO\(_2\) concentration. The HONO concentration increases only from 10 ppm to 125 ppm (gas flow rate is 3 l min\(^{-1}\), discharge gap is 8 mm) as the humidity increases from 0% to 95% and discharge current increase from 15 mA to 75 mA.

In order to investigate the effect of cooling the external tube surface on the NO\(_x\) production, the quartz tube is placed in a bath of flowing ice water (0 °C) or ice alcohol (−114 °C) as shown in figure 1. Alternatively, an alcohol ‘blast’ burner can be used for heating the outside of the quartz tube to a temperature up to 1000 °C.

In this paper, we also investigated the effects of a catalyst on the NO\(_x\) production during the discharge. The powdered catalysts are placed under the discharge area, with no direct contact with the plasma. The catalyst is positioned using a stainless-steel mesh container as shown in figure 1. The position of the container (length 8 mm) can be moved along the tube to change its position with respect to the plasma zone.

In the present study, we chose to use only a single catalyst: activated Al\(_2\)O\(_3\) (purchased from Spectrum Chemical). The powdered Al\(_2\)O\(_3\) particle size is 200 mesh, or less than about 75 microns in diameter. The mass of Al\(_2\)O\(_3\) used was fixed at 0.2 g. Further details about the catalyst are presented in the following sections.

### 2.2. Measurement and methods

The power consumption of the discharge is calculated by multiplying the discharge voltage (\(V_{\text{dis}}\)) and the discharge current (\(I_{\text{dis}}\)) due to the DC glow discharge. Both discharge voltage and discharge current are time-independent in most cases of our experiments. Two HV probes (Tektronix P6015A) are used to measure the applied voltage (\(V_{\text{a}}\)) and \(V_{\text{dis}}\) as shown in figure 1. The discharge current is measured by the voltage across the ballast resistor (120 kΩ) and also can be read on the power supply panel directly. The two methods of measuring current were always equal within the accuracy of the instruments. The discharge current is controlled by changing the applied voltage after gas breakdown. The HV probes are linked to a 200 MHz digital oscilloscope (Tektronix TDS2024) with a sampling rate up to 2 GHz.

FTIR spectroscopy is performed as an in situ diagnostic for NO\(_x\) concentration. The FTIR absorption spectra are recorded after stabilization of the signal as mentioned in section 2.1. The wavenumber resolution of the measurements is set as 0.5 cm\(^{-1}\); and 32 scans are averaged to create each spectrum. Figure 2 shows a typical FTIR spectrum at a discharge current of 75 mA, with gap distance 8 mm and gas flow rate 31 min\(^{-1}\). The primary species produced by the discharge include NO, NO\(_2\), and HONO. The small quantity of HONO observed is apparently produced by reactions between NO and NO\(_2\) and water vapour in the air. The absolute concentrations of NO\(_x\) (including NO, NO\(_2\), HONO in this paper) are determined by comparing the measurements to calibration data generated by precision calibration gas mixtures (GASCO LLC). Known concentrations of NO and NO\(_2\) in N\(_2\) were added to the standard gas cell for calibration. The FTIR sensitivity to these known gas concentrations was recorded and used to quantify subsequent measurements. In this paper, HONO concentration is only estimated. The absolute concentrations of HONO were estimated by fitting the measured FTIR spectra to spectra simulated using parameters in the HITRAN database (http://hitran.iao.ru/). To generate simulated standard spectra, we used a wavenumber range of 1100–1400 cm\(^{-1}\), a wavenumber computational step of 0.01 cm\(^{-1}\), an optical path of 0.2 m (corresponding to the window-to-window width of the standard gas cell), an assumed Gaussian apparatus function, and an apparatus resolution of 1 cm\(^{-1}\). The species concentration was adjusted to find the best fit with the experimentally measured spectra. In figure 2, the concentrations of NO, NO\(_2\) and HONO are 3117 ppm, 213 ppm and 47 ppm, respectively. We note that N and/or O balance could be established to prove that only NO, NO\(_2\) and HONO are produced in principle. However, the highest concentration of NO\(_x\) during our experiments is about 7000 ppm as the inlet flow of N\(_2\)+O\(_2\).
is 1 l min$^{-1}$. The maximum fraction of the inlet air converted to products is only about 0.7% (and for most cases it is lower than 0.3%). It is a challenge to fully establish the N and/or O balance under our experimental conditions.

Using the discharge power and measured NO$_x$ concentration, the energy cost of NO$_x$ production is calculated as follows:

$$E_N = \frac{P_{\text{dis}} \times 60}{24 \text{ l mol}^{-1} \times c_{\text{NO}_x} \times 10^{-6} \times 14 \text{ g mol}^{-1} \times 10^{-3}}.$$  \hspace{1cm} (1)

Here, $E_N$ is energy expended per unit of reactive N$_r$ (including NO, NO$_2$, and HONO) expressed in units of GJ/tN. $P_{\text{dis}}$ is the plasma power consumption (W), 60 is 60 s min$^{-1}$, $Q$ is the gas flow rate (l min$^{-1}$), $c_{\text{NO}_x}$ is the concentration of NO$_x$ (ppm), 24 l mol$^{-1}$ is the molar volume of ideal gas at 1 atm, 293 K, and 14 g mol$^{-1}$ is the molar mass of N atom. The factor of $10^{-3}$ arises from conversion of J g$^{-1}$ to GJ/tN.

In order to characterize the chemical reaction process under different conditions, NO selectivity is defined as

$$\text{NO selectivity} = \frac{c_{\text{NO}}}{c_{\text{NO}} + c_{\text{NO}_2}}.$$  \hspace{1cm} (2)

3. Results and discussion

In this section, we report the effects of different factors on the specific energy cost of NO$_x$ production in the DC glow discharge. These factors include discharge current, gas flow rate, gap distance, surface temperature of the quartz tube and the presence or position of catalyst.

3.1. Effect of gas flow on NO$_x$ production

Figure 3 shows the NO selectivity (figure 3(a)) and discharge power consumption (figure 3(b)) as a function of discharge current at different gas flow rates in the DC glow discharge. The discharge gap distance fixed at 8 mm here.

Figure 3. (a) NO selectivity and (b) power consumption of discharge plotted as a function of discharge current at different gas flow rates in the DC glow discharge. The discharge gap distance fixed at 8 mm here.

is increased from 1 l min$^{-1}$ to 3 l min$^{-1}$. However, above 3 l min$^{-1}$, the NO selectivity is maintained at about 0.95 under all discharge current conditions. This means most of the NO$_x$ species are in the form of NO. For a gas flow of 1 l min$^{-1}$, the NO selectivity decreases from 0.86 to 0.67 with increasing of discharge current.

NO could be oxidized to NO$_2$ by reaction between NO and O$_2$ in the region between the plasma zone and the FTIR spectrometer absorption region, a distance of 30 cm. However, the measurements of NO selectivity changes inside the gas line using the calibration gas of 5000 ppm NO in air showed only about 5% of the NO is oxidized to NO$_2$ by oxygen at a gas flow rate of 1 l min$^{-1}$ and 2% at 3 l min$^{-1}$ in this region. We therefore conclude that this is not a significant factor in our NO$_x$ measurements.

In figure 3(b), the discharge power consumption increases almost linearly with the discharge current at a fixed gas flow rate. For flows between 1 l min$^{-1}$ - 5 l min$^{-1}$, the power consumption values are similarly increased from $\sim$18 W.
to \( \sim 55 \text{ W} \), as the discharge current increases from 15 mA to 75 mA. At a higher gas flow rate, the discharge power consumption will be larger at the same discharge conditions. The discharge could not be sustained at lower discharge currents. For example, at 15 l min\(^{-1}\), the discharge can only be stably operated with a discharge current above about 45 mA.

Figure 4 shows the calculated specific energy cost (GJ/tN) of NO\(_x\) production as a function of discharge current with different gas flow rates. The lowest NO\(_x\) production energy cost always appears at around 40 mA for all the gas flow rate conditions. Additionally, the higher gas flow rate presents the lowest energy cost at the same discharge current in the range from 1 l min\(^{-1}\) to 10 l min\(^{-1}\). For example, the lowest energy cost decreases from 500 GJ/tN to 290 GJ/tN at around 40 mA. From 10 l min\(^{-1}\) to 15 l min\(^{-1}\), the energy costs increase slightly at the same discharge current.

According to our previous study [35], reducing the \( \chi \) factor (the normalized product of average electric field and average gas temperature), while sustaining the discharge, can be a guiding principle for reducing the energy cost of NO\(_x\) production. In the present experiments, the applied electric fields are nearly constant, while the energy cost is reduced considerably as flow is increased at constant current. This is especially true for flows between 1 l min\(^{-1}\) to 5 l min\(^{-1}\). Gas flow will alter species’ residence time in the plasma, and also affects rates of heat transfer from the plasma region, both of which could possibly help account for this observation. For example, more rapid thermal quenching of NO outside the plasma zone may prevent its conversion back to N\(_2\) and O\(_2\). This could lead to the observed higher energy efficiency. Further discussion on this is included in the concluding remarks.

### 3.2. Effect of gap distance on NO\(_x\) production

In this section, we report the effect of gap distance on NO\(_x\) production in the DC glow discharge. We utilized a DC power supply with maximum applied voltage of 10kV. The maximum gap distance which allows breakdown with this power supply is about 8 mm. In order to expand the range of accessible gap distances, we strike a discharge at 2 mm, and then move the ground electrode away from the powered electrode. In this way, a discharge can be maintained with a gap of up to 100 mm.

Figure 5 shows the NO selectivity (figure 5(a)) and power consumption (figure 5(b)) plotted as a function of discharge current at different gap distance. Here the gas flow rate is fixed at 5 l min\(^{-1}\). Figure 5(a) shows that NO selectivity decreases with increasing gap distance at constant current, but decreases slightly with increasing discharge current at same gap distance. These effects might be related to changes in NO residence time in the discharge. It is possible that NO is produced inside the air plasma [41] and this is followed by oxidation with O or O\(_2\) to form NO\(_2\). NO residence time increases with increasing gap distance. This proposed mechanism might be the cause of the observed NO selectivity increase with increasing gas flow rate as illustrated in figure 3(a).

In figure 5(b), we see that discharge power consumption increases almost linearly with current as well as gap distance. The maximum power consumption reaches about 307 W at a discharge current of 75 mA and gap distance of 80 mm.

Figure 6 shows the calculated specific energy cost of NO\(_x\) production as a function of the same parameters as illustrated in figure 5. The energy cost reduces with gap decrease in the range of 2 mm–20 mm at constant discharge current. At a current of 40 mA, NO\(_x\) energy cost decreases from 620 GJ/tN to 240 GJ/tN. Specific energy cost reduced over these conditions by 60%. However, when the gap distance is increased from 20 mm to 80 mm, the energy cost increases at constant current. In addition, the discharge cannot be maintained at low current (lower than 45 mA), if the gap distance exceeds 40 mm.

Figure 7 illustrates specific energy cost and the average electric field (\( V_{\text{avg}}/d \)) plotted versus gap distance. In this case, the discharge current is fixed at 45 mA and gas flow rate is fixed at 5 l min\(^{-1}\). Clearly, there is a similar relation between specific energy cost and average electric field as gap distance is changed. For gaps between 2 mm and 20 mm, both
quantities decrease rapidly with gap distance. Average electric field drops monotonically with gap, whereas energy cost appears to experience a minimum (see figure 6). Average electric field appears to be correlated with specific energy costs in a complex fashion. Figure 8 demonstrates how specific energy cost varies with average electric field for each of the measured gap distances. There appears to be an approximately linear rise with increasing of average electric field (>1 kV cm⁻¹) for currents below about 40 mA. The lowest specific energy cost appears to saturate at about ~240 GJ/tN, irrespective of discharge current or gap distance.

In a recent previous publication, we demonstrated an empirical relationship between specific energy cost and a dimensionless parameter (χ) that involves the product of average electric field and average gas temperature [35]. We estimate neutral gas temperature (Tg) near the cathode using optical emission spectroscopy (OES) [42, 43]. As shown in figure 9(a), peak rotational temperature (Tr) remains near 1700 K ±300K. Gas temperature estimated by OES is probably the maximum temperature since most emission originates near the region of highest plasma density where we would expect gas temperature to be near its maximum value.

We also measured the quartz tube outside surface temperature in the discharge area using a thermocouple (see figure 9(b)). The tube outer surface temperature should be lower than gas temperature in the discharge area. However, it reflects the variation of the gas temperature near the inner tube surface. We can see, as the discharge current changes from 25 mA to 75 mA, the tube external surface temperature increases from ~400 K(130 °C) to ~550 K(280 °C) when the gas flow rate is 1 l min⁻¹. Higher gas flow rate reduces surface temperature as revealed in figure 9(b). These measurements suggest that the radial gas temperature gradient increases with gas flow rate, approximately independent of current.

It remains to be seen if this increase in gas temperature gradient can be related to the previous scaling result using the χ factor. However, we note that the general trend in energy cost illustrated in figure 8 is in agreement with the previously discussed χ factor scaling since energy cost gradually decline on Vdis/d is reduced.

3.3. Effect of surface temperature on NOx production

In this section, we report the effect of tube external surface temperature on NOx specific energy cost by cooling or heating the quartz tube during discharge operation. We were motivated to explore tube wall temperature effects because if NO production efficiency is in part controlled by rapid quenching of NO after being created in the discharge region, a cooler tube wall region might be more efficient. Conversely, heating the tube wall region might decrease energy efficiency.

Figure 10 shows the specific energy cost for NOx production at different gas flow rates, obtained by cooling (figure 10(a)) or heating (figure 10(b)) the quartz tube. The surface temperatures are maintained near 0 °C, −114 °C and 1000 °C, respectively. In figure 10, the solid lines are the
results shown in figure 4 for reference to the case with no tube heating or cooling. The symbols are the results corresponding to increasing or decreasing tube surface temperature.

We can see in figure 10(a) that specific energy cost is slightly reduced when the surface temperature is maintained at 0 °C, especially for a gas flow rate of 3 l min⁻¹. However, there is little change in energy cost between 0 °C and −114 °C at 5 l min⁻¹. The effect of heating the external quartz tube surface is illustrated in figure 10(b). In these experiments, the surface temperatures are maintained at ∼1000 °C by an alcohol ‘blast’ burner. Heating the surface, even up to 1000 °C, appears to have little or no effect on the energy cost for NOₓ production in the DC glow discharge. It seems that the energy cost reduction by cooling the surface temperatures directly is modest compare with the effects of gas flow rate or gap distance for the conditions we explored.

3.4. Effect of catalyst on NOₓ production

In the final section, we turn to the measurements of specific energy costs associated with adding a heterogeneous catalyst near the discharge region. The metallic oxides (Al₂O₃, MoO₃, WO₃ etc) could be used to catalytically promote NO formation using plasma were reported by some researchers [22–24]. Rapakoulias et al [22] suggested following mechanism: vibrationally excited N₂ dissociatively adsorbs on the catalyst surface and then mobile oxygen which was also vibrationally-excited reacts on the surface to give NO. The reaction of adsorbed nitrogen with mobile oxygen was found
to be the rate determining step. Mutel et al. [23] also suggested that it should be possible to obtain a best energy cost by increasing the specific catalytic surface. Patil et al. [24] found that activated Al$_2$O$_3$($\gamma$-Al$_2$O$_3$) with the smallest particle size gave the highest concentration of NO$_x$ and the lowest specific energy consumption of all their tested materials and particle sizes. Therefore, in this paper we chose to use activated Al$_2$O$_3$ (Spectrum Chemical) coupled with the DC glow discharge to test the effects of catalyst on plasma-generated NO$_x$ production. Future work will address other catalysts as well.

The powdered Al$_2$O$_3$ particle size is 200 mesh, or about 75 microns in diameter and the mass is fixed at 0.2 g. We recycle the catalyst and repeat the measurements three times at each experimental condition, ensuring that the catalytic material has reproducible effects on measured conversion. After each experiment, we allowed 2–3 h for the discharge tube to cool to room temperature. After this, the next experiment is run.

The peak gas temperature inside the discharge is high enough to melt the highly porous structural features of the activated Al$_2$O$_3$. So, in this work, the catalyst material is placed adjacent to—at least several mm away from—the discharge area. It is important that the catalyst not be in direct contact with the plasma. The powder catalyst is maintained by a stainless-steel mesh container as shown in figure 1. Two positions of the catalysts are investigated: P1 (just beneath the plasma) and P2 (about 1 cm downstream from the plasma) as shown in figure 11.

Figure 12 plots specific energy cost for NO$_x$ production in the presence of activated Al$_2$O$_3$ for catalyst position P1 and P2, in figures 12(a) and (b), respectively. The effect of heating the tube wall when catalyst is present is also shown in figure 12(c)). The solid lines are the reference results in the absence of catalyst, as seen in figure 4. Figure 12(a) illustrates that specific energy cost is reduced significantly when the catalyst is near the plasma, especially at the lowest gas flow rate (eg. 1 L min$^{-1}$). However, at a gas flow rate of 5 L min$^{-1}$, the positive effects of catalyst on energy efficiency seem to be eliminated. This result suggests that if the gas flow transports an active intermediate species too rapidly downstream, it cannot reach the catalyst to form additional NO. We found that increasing the catalyst from 0.2 g to 0.4 g made, at most, a 10% change in energy cost under these conditions. However, we note that the catalyst configuration might have an effect on energy efficiency, and this will be studied in future work. Furthermore, when the catalyst is moved to position P2 as
shown in figure 12(b), it has no effect on the energy cost for NO\textsubscript{x} production at all, regardless of the gas flow rate. These results support the idea that some plasma-generated and relatively short-lived intermediate species are important for whatever the heterogeneous catalyst is doing to increase specific energy efficiency of the discharge. Gicquel et al [37] interpret the results from their low-pressure plasma-catalysis results in a similar manner.

These results are supported by the experiments that involve heating the external tube wall, and therefore the catalyst, shown in figure 12(c). At the lower gas flow rates, the presence of catalyst (position P1) results in a substantial reduction in specific energy cost. However, when gas flow is increased to 5 l min\textsuperscript{−1}, the effect of wall heating is almost eliminated, with a modest improvement seen only at the highest currents.

We also investigated the NO selectivity for NO\textsubscript{x} production in the presence of activated Al\textsubscript{2}O\textsubscript{3}, corresponding to the experimental conditions in figure 12. Although the energy cost could be reduced significantly by the catalyst as shown in figure 12, the NO selectivity is almost the same for different gas flow rates, especially at low discharge current. It seems that the role of catalyst is to produce more NO and not convert NO to NO\textsubscript{x} to reduce the energy cost.

Clearly, heterogeneous catalyst coupled with the DC glow discharge can significantly improve energy efficiency for NO\textsubscript{x} production, at least under some conditions. Proper transport of intermediate species from the plasma to the catalytic surface seems to be important to exploit catalysis. We also note that under optimal conditions of current, gap distance and gas flow, the presence of catalyst did not improve specific energy cost below about 200–250 GJ/tN. The goal of the present study was to better understand the factors involved with NO\textsubscript{x} production energy efficiency and not necessarily to find the most efficient conditions. Nevertheless, it is striking that the lowest specific energy cost observed with the DC glow discharge in this study is close to the optimal value we observed for the propeller arc, a rather different type of discharge [34]. There appears to be a lower limit to specific energy cost for a range of different types of air discharges. Detailed understanding of the controlling factors awaits further study.

4. Concluding remarks

We examined a range of factors that influence specific energy cost of producing NO\textsubscript{x} from DC glow discharges in air at atmospheric pressure. Discharge current between 15 mA and 75 mA affected specific energy cost significantly, with optimal values typically between about 35 mA–45 mA depending on the other factors. The main NO\textsubscript{x} species created (selectivity over 0.95) was NO under most of the conditions in the present study, except at the lowest gas flowrate and higher gap distances (above about 8 mm).

Gap distance was varied between 2 mm and 80 mm and specific energy cost dropped dramatically between 2 mm and 8 mm but was fairly independent of gap distance above 8 mm. Gas flowrate was varied between 1 l min\textsuperscript{−1} and 15 l min\textsuperscript{−1}. Higher flowrate significantly reduced specific energy cost at lower flows, but above 5–10 l min\textsuperscript{−1}, the effect was modest. An important effect of higher flows was that it eliminated any contributions of near-wall effects from influencing specific energy cost. This has implications for the mechanisms of catalysis. We tested the effect of external tube wall temperature, varying this value between −114 °C and 1000 °C in the absence of catalyst. Lowering tube wall temperature had only a modest effect, and then only at a flowrate of about 3 l min\textsuperscript{−1}. Heating the tube wall in the absence of catalyst had virtually no effect.

In the design used in this report, the plasma is mostly confined to a narrow region at the center of the cylindrical tube. Gas flow acts to transport plasma-generated chemical species and heat in the axial direction whereas diffusion acts to transport these quantities in the radial direction. A simple scaling analysis suggests that rates of axial convective transport and radial diffusive transport are comparable at a gas flow of about 1 l min\textsuperscript{−1}. Above this value, axial convection starts to dominate radial diffusion, offering an explanation of the observation that beneficial wall effects (e.g. cooling in the absence of catalyst or heating in the presence of catalyst) are eliminated at gas flows higher than about 3–5 l min\textsuperscript{−1}. A detailed discussion of likely mechanisms contributing to the observed effects reported here is beyond the scope of this report. However, the overall conversion of air to NO\textsubscript{x} is obviously a combination of kinetic processes that both create and destroy NO\textsubscript{x}.

The addition of catalyst powder (activated Al\textsubscript{2}O\textsubscript{3}) improved energy efficiency significantly, most notably when wall temperature was raised to 1000 °C, but only when gas flows were below about 5 l min\textsuperscript{−1}. Furthermore, the catalyst bed needed to be located just beneath the plasma zone in order to be effective. Presumably, active precursors created in the plasma zone were apparently quenched or lost unless the catalytically active surface is within a few mm of the active plasma zone. Even when active, the catalyst had no significant effect on product selectivity. The most energy efficient conditions were found at the highest flowrate that allowed a stable discharge (about 101 l min\textsuperscript{−1}) and under those conditions, catalyst had no effect on efficiency. The lowest specific energy cost was between 200–250 GJ/tN, a value that is close to the most efficient conditions found in previous work with different types of atmospheric pressure air discharges [35].

The importance of gas flow and catalyst location both suggest that transport of chemical species and energy are likely key factors controlling the specific energy cost of NO\textsubscript{x} production from DC glow discharges in air at atmospheric pressure. In order to fully exploit catalysis for this process, it seems that it will be necessary to design the device and operating conditions such that plasma-generated active intermediate chemical species transport is optimally coupled with catalytically active surfaces. The similarity of energy efficiency values seen from the present study of a DC glow and other discharges in air suggests the results may be applicable to other air discharges.
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