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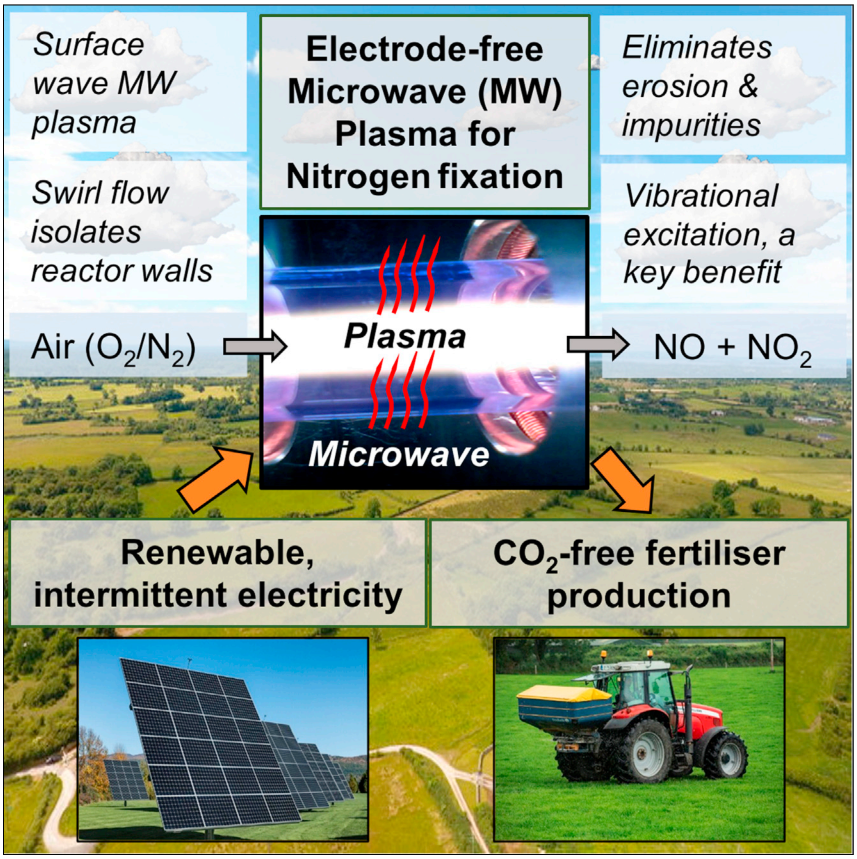

Artificial nitrogen fixation (NF), a cornerstone of civilization, sustains over 40% of the world population. However, the activity is a large contributor to anthropogenic climate change. Plasma technology, famous for enabling the semiconductor revolution of the last decades, shows much promise to aid contemporary efforts using renewable electricity to decarbonize fossil-fuel-based chemical processes. In this article, CO_2-free fertilizer production using a microwave air plasma is discovered as an efficient and environmentally benign candidate to succeed the Haber-Bosch (H-B) process.

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Highlights

Microwave plasma-based oxidation of N_2 by enhanced Zeldovich mechanism

Combination of high flow and high power shows efficient NO_x production

Promising metric: 0.77 L/min NO_x (3.8% relative conversion) at energy cost 2 MJ/mol

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Nitrogen fixation in an electrode-free microwave plasma

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SUMMARY

Plasma-based gas conversion has great potential for enabling carbon-free fertilizer production powered by renewable electricity. Sustaining an energy-efficient plasma process without eroding the containment vessel is currently a significant challenge, limiting scaling to higher powers and throughputs. Isolation of the plasma from contact with any solid surfaces is an advantage, which both limits energy loss to the walls and prevents material erosion that could lead to disastrous soil contamination. This paper presents highly energy-efficient nitrogen fixation from air into NO_x by microwave plasma, with the plasma filament isolated at the center of a quartz tube using a vortex gas flow. NO_x production is found to scale very efficiently when increasing both gas flow rate and absorbed power. The lowest energy cost recorded of ~2 MJ/mol, for a total NO_x production of ~3.8%, is the lowest reported up to now for atmospheric pressure plasmas.

INTRODUCTION

Higher global temperatures and increasing extreme weather events have brought the societal and economic perils of anthropogenic climate change to the fore in recent years. In this context, plasma technology is garnering increasing research interest.[1,2] Plasma-based gas conversion has great potential for enabling carbon-free fertilizer production in the agri-food sector.[3] These efforts are particularly timely and necessary, as economies face the challenge of transitioning to sustainable architectures based on eliminating anthropogenic greenhouse gases.[4]

The increasing availability of renewables provides a ''clean'' electricity source, ideally suited to plasma generation. Industrial scale nitrogen fixation (NF) via the Haber-Bosch (H-B) process dominates artificial fertilizer production, enabling crop yield enhancements, which at present nourish over 40% of the world population.[5] Owing to the exceptional stability of molecular nitrogen's triple bond, the H-B process is an energy-intensive chemical process, which accounts for 1%–2% of the world's energy consumption, consumes 2%–3% of the global natural gas output and emits more than 300 million tons of CO_2 annually.[5] In light of an increasing population (and fertilizer demand) coupled with an urgency to reduce CO_2 emissions, efforts to find alternative technologies for NF, that offer the potential of reduced energy usage while minimizing greenhouse gas emissions, have accelerated. The fast ignition of plasma reactors (within the order of ~1 s) provides for a highly adaptable chemical process in the context of emerging renewable energy-dominated electricity grids. This is in contrast to ''traditional'' chemical processes, such as H-B, which require significant lead times (on the order of hours[6]) to schedule production and hence cannot benefit directly (i.e., without energy storage) from the cost savings available by exploiting cheap ''peak-shaved'' renewable electricity.[5,7]

Context & scale

Industrial-scale nitrogen fixation (NF) via the Haber-Bosch (H-B) process dominates artificial fertilizer production, enabling crop yields that feed over 40% of the world population. However, the H-B process consumes nearly 3% of the global natural gas output and emits more than 300 million tons of CO_2 per annum worldwide. We present plasma-based NF, an electrically powered and CO_2-free process, using air as feedstock, and readily compatible with coupling to renewable electricity. However, the readiness of plasma technology is currently lacking. Future industry deployment requires a process that is efficient, scalable, and free of impurities. For this purpose, we report on a microwave plasma using a swirling flow as a very promising candidate. Favorable conditions are found when scaling higher power with higher throughput. The use of a swirl flow enables an electrode-free reactor, a unique advantage, removing risks of impurities, such as heavy metals entering the food chain.

The Birkeland-Eyde (B-E) process to produce nitric acid was first developed in the early twentieth century.[8–10] The B-E process converted air to NO_x in an electric arc formed inside an electromagnet. Excess heat (i.e., not used in the enthalpy of formation) was partially reclaimed to heat boilers using the arc exhaust, followed by an oxidation stage where the remaining NO is converted to NO_2 in settling tanks (i.e., this relatively slow reaction is preferable at reduced temperatures). This stage is followed by NO_2 hydrolysis in large water absorption towers packed with quartz segments, eventually producing a solution of HNO_3. The industrialized B-E process produced ~2% NO_x and had an energy consumption for the NO_x plasma synthesis stage of 2.4–3.1 MJ/mol with the absorption stages adding approximately 30%–40% additional overhead.[5,7,9]

Although recent advances suggest that the energy cost and capital expenditure of the absorption stage could be significantly reduced, both in size and energy requirements (e.g., using modern NO_x absorbents, such as BaO[11,12] in combination with temperature/pressure swing absorption),[7] the critical energy hurdle of the plasma conversion stage still remains an open research challenge. The technological advances of the last century (such as the success of MW surface-wave plasmas in recent decades and the emergence of solid-state MW technology in recent years, which are of particular relevance here) have motivated a revival of plasma-based NF in a contemporary context characterized by climate challenges and the emergence of renewable electricity.

Microwave (MW) generated plasmas offer desirable characteristics[13] of high ionization fraction (i.e., electron density) coupled with relatively low mean electron energies (in the range ~1–3 eV). The electric field generated by the applied MW power selectively heats the electrons, due to their small mass. Furthermore, the electron energy of 1–3 eV, combined with high electron density, gives rise to efficient vibrational excitation, which can, in turn, significantly promote dissociation routes in gases, such as N_2.[14] Investigations in the early 1980s conducted by Asisov et al.,[15,16] employing a low pressure (10–100 Torr) Electron Cyclotron Resonance (ECR) MW discharge in N_2/O_2 mixes, reported spectacular NO_x production levels of 14% at energy costs of 0.3 MJ/mol.[15,16] However, many modern efforts have focused on (near) atmospheric pressure discharges[7] (see state-of-the-art in Table 1; in NO_x production and energy cost). This is due to the high additional energy overhead associated with the use of vacuum pumps required to sustain low pressure conditions. Note that this cost was not accounted for in the low-pressure ECR plasma mentioned earlier. Such extra energy costs typically eclipse any potential gains in conversion and efficiency available from operating at low pressures. For example, to reach ~100 Torr pressure (i.e., 13% of atmospheric pressure) at a gas flow rate <10 L/min would require at least the employment of a standard vacuum pump (e.g., rotary vane), which requires ~400 W power for operation.[17] This additional power requirement is similar to the typical power used to generate the plasma, indicating a doubling in energy cost when accounting for the use of a vacuum pump. Furthermore, the above spectacular NO_x production levels and energy costs reported for low-pressure ECR MW plasmas[15,16] have never been reproduced since then.

Plasma-based NF can be carried out in pure N_2 gas streams (with subsequent reaction to produce NO_x or NH_3) or in N_2/O_2 or N_2/H_2 or N_2/H_2O mixes, where both gaseous and liquid H_2O can be employed.[3,14,18–21] In recent years, various studies have investigated the use of atmospheric pressure plasma for NF using air mixtures (N_2/O_2) (see state-of-the-art in Table 1 in NO_x production and energy cost). Kim et al.[22] studied the use of a low-powered MW plasma at pressures specified as "slightly below atmospheric." The authors used a titanium pin to aid ignition of

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Table 1. State-of-the-art for plasma-based NO_x formation

Plasma type	NO_x %	Energy cost	Flow rate [L/min]	Pressure [atm]	Ref.
Electrode-free MW plasma—swirling flow and surface wave mode	3.8 %	2 MJ mol^{-1} NO_x	20	~1	this work
Microwave (MW) plasma—electron cyclotron resonance	14%	0.28 MJ mol^{-1}	-	0.01	Asisov et al.[15,16] and Rusanov and Fridman[65]
MW plasma with catalyst	6%	0.84 MJ mol^{-1} NO	0.33	0.07	Mutel et al.[66]
MW plasma with pin—low power	0.6%	3.76 MJ mol^{-1} NO_x	6	~1	Kim et al.[22]
Birkeland-Eyde process: plasma arc with magnetic field	2%	2.0 – 3.28 MJ mol^{-1} HNO_3	-	~1	Birkeland[8] and Eyde[10]
Gliding arc plasmatron (GAP)	1.5%	3.6 MJ mol^{-1} NO_x	10	~1	Vervloessem et al.[23]
Rotating gliding arc (RGA)	5.5 %	2.5 MJ mol^{-1} NO_x	2	~1	Jardali et al.[24]
Pin-to-pin DC glow discharge	0.7%	2.8 MJ mol^{-1} NO_x	10	~1	Pei et al. [67]
Packed DBD with catalyst	0.5%	18 MJ mol^{-1} NO_x	1	~1	Patil et al.[68]
DBD, spark, glow, propeller arc	0.6%	56–140 MJ mol^{-1} NO_x	1	~1	Pei et al.[69]

In various plasma types, reporting the obtained NO_x concentration and energy cost, as well as flow rate and pressure are used. Our best results are listed in the first row along with other notable MW reports. Non-MW reports are detailed in the bottom rows. This table serves as an abridged list of reactors given in Figure 2 (see Rouwenhorst et al.[7] for further details), with equivalent NO_x % given here (i.e., 10,000 ppm = 1%)

the discharge at very modest powers from 60-90 W, achieving ~0.6% NO_x at an energy cost of ~4 MJ/mol.

Non-MW plasma approaches of interest include gliding-arc (GA)-type discharges[14,23–28] where a heated and (typically) dynamic plasma arc is sustained using metallic electrodes with direct or alternating current (kHz) power sources.[14,25] Indeed, the GA approach has the best conversion and energy efficiency reported to-date for atmospheric pressure plasma-based NF (up to 5.5% NOx production at <3 MJ/mol energy cost[24]). Similar to MW plasmas, GA plasmas under atmospheric pressure are typically categorized as "warm" plasmas (i.e., average gas temperatures ranging ~1,000–3,000 K), where significant gas heating offers the benefits of both non-thermal and thermal plasma conditions. However, the ability to scale this achievement to higher powers (i.e., >500 W) and flow rates (i.e., >10 L/min), a key requirement for future industrial deployment, is unclear.

Three-dimensional implementations of the GA concept, including the gliding arc plasmatron (GAP)[23,29] or the rotating gliding arc (RGA),[24,25,28,30] often employ a swirling flow. This typically results in a dynamic plasma filament, which has benefited conversion metrics over earlier 2D GA designs (i.e., by expanding the intersection of the plasma and transiting gas). However, another key aspect of this design is that it limits the plasma interaction with the metallic electrodes and containment walls. The strategy hopes to prevent the high current density arcs typical at atmospheric pressure from repeatedly anchoring or rooting to small surface areas or spot(s). This anchoring leads to undesirable metal vaporization and electrode erosion.[31,32] Despite limiting the plasma-wall interaction, this design characteristic cannot be eliminated due to the necessity of current transfer between the electrodes to sustain the plasma. Indeed, GA designs often rely on metallic wall interaction for enhancement via thermionic emission,[33] with stationary arc configurations recently shown to favorably boost "cost-conversion" metrics.[24] Recent reports by Böddeker et al.[31] have investigated the formation of plasma "spots" resulting from material erosion and metal vaporization in a 3D GA plasma reactor. The authors showed that plasma-wall erosion can occur even at relatively low current levels (i.e., ~0.1 A) due to the particulars of the plasma dynamics. Indeed, many laboratory scale GA designs already operate at current levels around 300 mA[23,24,34], which is above the threshold of several atmospheric plasma jet designs utilized in the deposition of metal films.[35,36] Therefore, the viability of scaling the GA approach to higher power densities without significantly increasing electrode erosion remains questionable. Indeed, modern day implementations of high-powered arcs at atmospheric pressure are synonymous with metallurgical applications, such as welding.[37–39]

In the context of NF, anchoring a relatively high current arc to a metal surface,[37] even intermittently, poses a significant risk of contaminating the produced NO_x with common soil hazardous metals, such as copper and chromium (i.e., stainless steel).[40] Of course, there is also the considerable issue of severely limiting the reactor longevity due to frequent electrode damage.[31,34] Heavy metals, even in trace levels, manifest as a very damaging pollutant of soil, a non-renewable resource.[41] Effluents from arc welding are known to contain both micron and sub-micron size metal dust particulates.[42–44] Removal of metal dust from GA plasma reactors would likely require downstream filtration systems, increasing the cost and complexity of any plasma-based NF process. Cold-trapping or water washing of metallic fragments is particularly complicated by the presence of NO_2, which has a relatively high boiling point (i.e., will condense in a cold trap) and has a high affinity to hydrolyze (a fact that is exploited in producing HNO_3 from gas phase NO_x). Therefore, approaches that can sustain an electrode-free (i.e., metal free) ignition at higher powers and flow rates, where the plasma is also isolated from its containment, would provide a significant advantage for plasma-based NF.

Swirling or vortex gas flows can also be employed to stabilize MW plasmas under atmospheric conditions without the need for (metallic) electrodes.[45–49] This is achieved using the unique surface wave sustained discharge mode of MW plasmas.[50–52] The latter offers a distinct advantage of the plasma being located in the vortex center (i.e., tube center), completely removed from interacting with the container walls, unlike typical (gliding) arc plasmas where discharge currents interact with walls and electrode materials. The surface wave mode is also inherently scalable, with ignition possible above atmospheric pressures, i.e., up to several bars.[51] Therefore, such over-pressure conditions can support the high gas throughputs needed for future industrial deployment. MW plasmas have shown utility for pollution abatement,[3,53,54] including the destruction of NO_x species in gas streams,[3,55–58] an application, which, to-date, has achieved a relatively high technology readiness level.[59] However, the use of MW plasmas at atmospheric pressure for NO_x production rather than destruction has received little scrutiny to-date. In light of recent efforts to find alternative CO_2-free means of NF, coupled with recent advances in solid-state MW technology (allowing exceptional control of discharge conditions), MW-sustained plasma presents an interesting prospect for NF. The potential for an electrode-free and hence contamination-free plasma-based NO_x production process is particularly alluring given the need to avoid inadvertent impacts on soil and ecosystems, while at the same time ensuring reactor longevity.

In light of this, here, we report a surface-wave sustained MW plasma in air (and N_2/O_2 mixtures at various mixing ratios) for NO_x production. We combine plasma imaging and exhaust diagnostics (measuring NO and NO_2) with quasi-1D chemical kinetics modeling, to give a detailed account of the total NO_x formation and the underlying mechanisms.

RESULTS AND DISCUSSION

The aim of our work is to discover the key conditions affecting NO_x production for an atmospheric pressure MW plasma sustained within a vortex flow in a surface wave sustained mode. This includes flow dependence, power dependence, and plasma ignition with O_2-enriched air mixtures (i.e., various N_2/O_2 ratios). In NO_x production and energy cost, we present our experimental findings in terms of total NO_x production and energy cost in underlying mechanisms revealed by the quasi-1D modeling, we provide more insight in the underlying mechanisms, based on the quasi-1D numerical analysis, while in conclusions, a conclusion is given.

NO_x production and energy cost

The MW surface wave mode allows relatively long plasma filaments to be maintained along the axis of a plasma tube at atmospheric pressure, where the plasma acts as one half of its own coaxial waveguide (the other side being the quartz container). In this scenario, the plasma column is sustained far beyond its ignition point within a tapered waveguide (e.g., using a surfatron or surfaguide applicator[50,57]) where the applied MWs are propagated perpendicularly (relative to the ignition waveguide) along the plasma column, producing a typically warm plasma (under atmospheric pressure). Periodic exchange of the energy in the wave field heats electrons within the skin depth of the contracted plasma filament[49,60,61] where the axial extent (i.e., length) of the plasma column corresponds to the point at which the wave energy is fully absorbed.

Plasma-based conversion of inert molecules, such as N_2, provides unique reaction pathways not available in thermal conversion. Electrons cause excitation toward the lowest vibrational levels in N_2 and O_2, followed by further vibrational-vibrational (V-V) collisions, which enable a "ladder-climbing" process, gradually populating higher vibrational levels (i.e., $N_2(v)$, $O_2(v)$). Therefore, maintenance of relatively homogeneous mean electron energies near the vibrational excitation threshold of N_2 and O_2 (~1–3 eV) can enable considerable energy coupling to vibrational populations in air mixtures. However, vibrationally excited molecules are strongly affected by high gas heating, causing vibrational-translational (V-T) relaxation and destruction of vibrational species. Therefore, excessive gas temperatures should be limited in order to fully exploit the benefits of vibrational excitation as the most efficient gas conversion process.[14,62,63] Indeed, V-T relaxation, which depopulates the vibrational levels upon collision with ground-state gas molecules, is more efficient at higher gas temperatures.

The dominant chemistry for NO_x production in atmospheric pressure air plasmas proceeds via a vibrationally enhanced Zeldovich mechanism[14,25,64] consisting of the following reactions:

$$O + N_2/N_2(v) \leftrightarrow N + NO \qquad \text{(Equation 1)}$$

$$N + O_2/O_2(v) \leftrightarrow O + NO \qquad \text{(Equation 2)}$$

The two reactions mentioned earlier are typically rate limited by Equation 1. The mechanism is significantly different from the thermal Zeldovich mechanism (i.e., involving only ground-state N_2 and O_2) due to the presence of vibrationally excited N_2 and O_2 molecules, uniquely available in plasmas. The vibrationally excited N_2 molecules lower the dissociation threshold required to break the strong N_2 triple bond (~10 eV) through colliding with O atoms (Equation 1). The N atoms formed in Equation 1 can then further react with both ground-state and vibrationally excited O_2 molecules (Equation 2) to produce another NO. Equation 2 also produces an additional O atom, which can again react with ground-state and vibrationally excited N_2 molecules (i.e., Equation 1), providing a tightly coupled reaction loop. The NO formed in both steps can be oxidized to produce NO_2 via further interaction with O atoms:

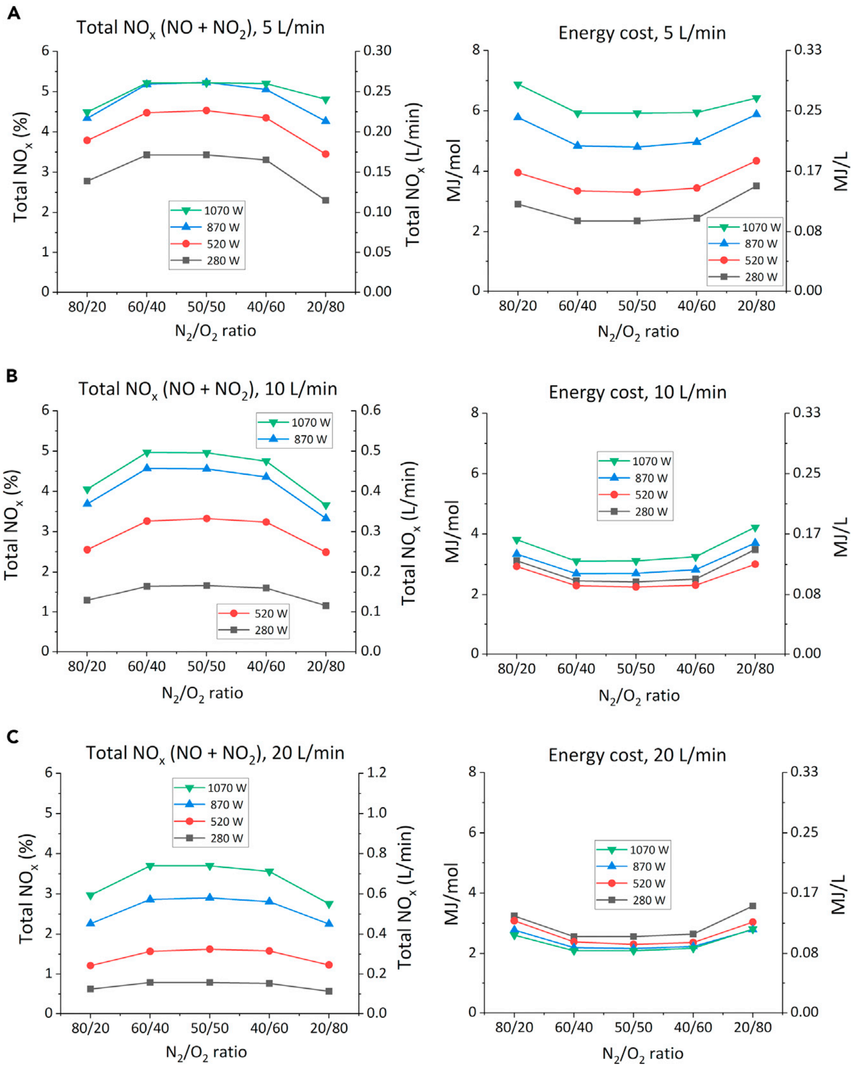

Figure 1. Experimental results for MW plasma in air and N_2/O_2 mixtures at atmospheric pressure

Total NO_x concentration (% and L/min on right-hand axis) and associated energy cost (MJ/mol and MJ/L) for a range of absorbed MW powers and mixture ratios, at flow rates of (A) 5 L/min, b) 10 L/min, and c) 20 L/min. All measurements were performed in triplicate, but the errors bars are too small to be visible. The measured data for this figure are provided in section S3.3 and Table S2.

$$NO + O \rightarrow NO_2 \quad \text{(Equation 3)}$$

Figure 1 presents the total NO_x production and corresponding energy cost for a range of absorbed power and flow rates in our surface wave sustained atmospheric pressure MW plasma, in N_2/O_2 mixtures at different ratios. Data are collected in triplicate, with the average shown. Due to the high stability of the solid-state power supply, the variation in the collected data are found to be typically less than 3% of the absolute NO_x concentrations; hence, error bars are not visible in Figure 1. The absolute NO_x production in units of (normal) liters per minute along with the equivalent energy cost normalized to the inlet gas flow rate (i.e., units of MJ/L) are shown on the right-hand y axes in Figure 1. For the lowest air (i.e., N_2/O_2 80/20 mix) flow rates investigated, i.e., 5 L/min (see Figure 1A), a peak NO_x production of ~4.3% is measured at the highest absorbed MW powers (i.e., 870 W and 1.07 kW), with an energy cost in the range of 6–7 MJ/mol. In terms of absolute NO_x production, this corresponds to a peak production of 0.22 L/min with an energy cost in the range of 0.24–0.29 MJ/L. At the lower powers (i.e., 520 and 280 W), both energy cost and NO_x production are reduced. This is attributed to the reduced gas heating, which promotes higher vibrational populations (i.e., larger V-T non-equilibrium), yielding more energy-efficient NO_x production.[14,23,24,63,70]

The relatively high energy costs found at 5 L/min (Figure 1A) correlate to the visual observation of a plasma filament with significant fluctuations (both radially and laterally). Excessive heating at low mass flow rates results in buoyancy-driven fluctuations (i.e., "natural" convective cooling). The relatively low intensity of the vortex flow at this flow rate is unable to overcome, via advective cooling, the high gas heating rate typical in "warm" contracted atmospheric pressure molecular plasmas.[49,70] Indeed, ignitions for flow rates <5 L/min were typically too unstable and oscillatory in behavior; therefore, they could cause damage to the quartz tube walls.

Enriching the air feed with O_2 to near-stoichiometric mixtures is known to significantly enhance NO_x production in both thermal and plasma-based processes.[14,25,64] Figure 1A indeed reveals that N_2/O_2 ratios between 60/40 and 40/60 result in higher NO_x production and lower energy costs. This trend continues across all flow rates and powers shown in Figure 1, although it is less pronounced at higher flow rates. The highest NO_x values at 5 L/min (Figure 1A) are found to be ~5.2% or 0.26 L/min with an energy cost of ~4.8 MJ/mol (0.2 MJ/L) at 870 W. The observed benefits of O_2 enrichment to near-stoichiometric ratios are consistent with earlier reports in gliding arc plasmas.[23,24,28] The addition of O_2 promotes greater utilization of the N atoms (produced in Equation 1 of the Zeldovich mechanism) via Equation 2 and also increases the availability of O atoms for reaction with N_2 molecules (i.e., Equation 1), as discussed earlier; therefore, it enhances the overall Zeldovich mechanism.

Upon doubling the mass flow rate from 5 to 10 L/min (Figure 1B), we find a drop in the % NO_x produced (explained by the shorter gas residence time), but this is only marginal, whereas a considerable drop in the energy cost is obvious for all powers. Typical energy costs are clearly <4 MJ/mol. The highest NO_x concentrations at 10 L/min reach ~5% or 0.5 L/min for an energy cost of ~3.1 MJ/mol (0.13 MJ/L) in a 50/50 mix at 1.07 kW. Unlike at 5 L/min, the lowest energy cost does not correlate with the lowest power. For 520 W absorbed power we find total NO_x concentration reaching ~3.3% (0.33 L/min) with an energy cost of 2.3 MJ/mol (0.09 MJ/L), whereas for 280 W a total NO_x % of ~1.7% (0.17 L/min) requires 2.4 MJ/mol (0.1 MJ/L).

The efficiency gains found when doubling the gas flow rate (without a large drop in % NO_x production) indicate a considerable benefit in the utilization of relatively high gas flow rates and hence short gas residence times in the plasma (see explanation in underlying mechanisms revealed by the quasi-1D modeling). Visually, the plasma is found to have a more stable operation at 10 L/min compared with 5 L/min. The recorded plasma width is typically similar for increasing flow rates and widens somewhat at higher powers. The plasma length typically increases upon increasing power (up to ~1 kW). This is consistent with the surface-wave mode behavior,[51] where MW power is absorbed as it propagates in the region between the plasma filament and the quartz tube, elongating until the wave power is fully absorbed. The plasma elongation results in longer residence times for gas species inside the plasma. However, by also increasing the gas flow rate, the overall residence time in the plasma is reduced because the rise in flow rate is higher than the rise in plasma length upon increasing power, and we find a net benefit in terms of the energy cost.

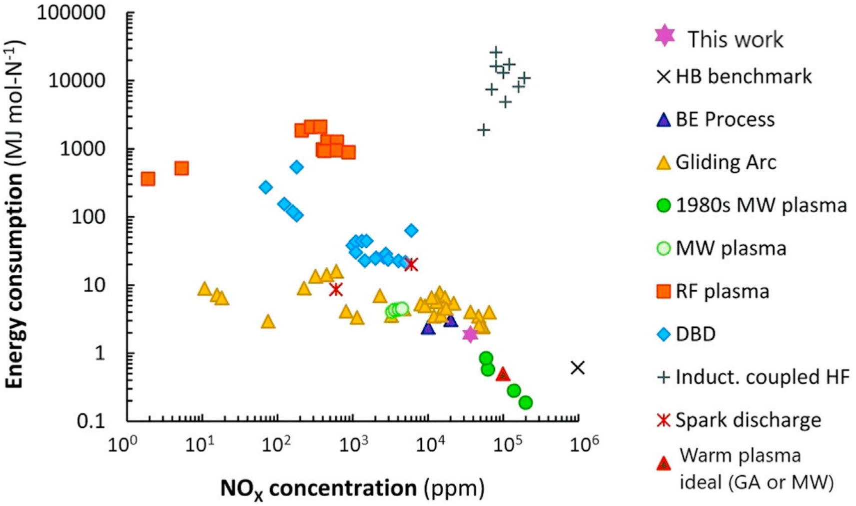

Figure 2. State-of-the-art for plasma-based NO_x formation (and HB benchmark)

Plotting energy consumption versus NO_x concentration. This figure is reproduced from Rouwenhorst et al.[7] to which our best results (i.e., ~3.8 % NOx at ~2 MJ/mol; see star legend) are added.

Upon further doubling the mass flow rate from 10 to 20 L/min (Figure 1C), we see again a drop in energy costs. Interestingly, the highest power (i.e., 1.07 kW) is now the most efficient condition, with the highest NO_x concentration at the lowest energy cost. This extends from the trend at lower powers for 10 L/min (see Figure 1B) where the most efficient conversion occurred at 520 W rather than 280 W. At an absorbed MW power of 1.07 kW, ~3.8% total NO_x concentration is measured for a 50/50 N_2/O_2 mix, with a corresponding energy cost of ~2 MJ/mol, the lowest achieved in our study. This promising metric is exemplified by considering the absolute NO_x production achieved at ~0.77 L/min for an energy cost of ~0.08 MJ/L.

The trend in gas flow rate presented here shows a very interesting avenue to drive higher efficiencies, by increasing gas flow rate in combination with higher MW powers. This would be highly beneficial for the high throughput required in future commercial realization. The limited gas residence time inside the plasma likely limits back reactions of the formed NO with N (the reverse of Equation 1 mentioned earlier).[14] Further discussion of the underlying reaction mechanisms is given in underlying mechanisms revealed by the quasi-1D modeling further on.

The total NO_x concentration obtained here (Figure 1) is comparable with the best performing plasmas reported for NO_x production to-date (see Table 1; Figure 2), including the recent record values reported for a 3D rotating gliding arc plasma by Jardali et al.[24] It must be noted that the low energy values for 1980's MW plasma shown in Table 1; Figure 2 did not include the large energy associated with using a vacuum pump. Such energy costs, in fact, are comparable with the energy needed to generate the plasma in the first instance, making the approach unfeasible. Our lowest energy cost of ~2 MJ/mol (Figure 1C) ignited with relatively high gas flow rates of 20 L/min, giving 3.8% total NO_x concentration is, to the best of our knowledge, one of the most efficient performances for NO_x production demonstrated in plasma-based NF at atmospheric pressure to-date.[5,7,10,23–25] Indeed, the record values of Jardali et al.[24] for gliding arc plasma have an absolute production of ~0.11 L/min NO_x compared with ~0.77 L/min found here at our lowest energy cost of ~2 MJ/mol (~0.08 MJ/L) and highest flow rate of 20 L/min. Therefore, the most promising trend observed here is that future investigation of higher flow rates with higher powers could lead to further improvement on this "conversion-cost" metric with benefits to scaling plasma-based NO_x production. Unfortunately, higher power and flow rate conditions were not possible in our current reactor configuration due to the limits of the power supply (i.e., ~1 kW) and reactor configuration (i.e., limitations of the gas connections at high flow rates and safety limitations in our current lab relating to ventilation of high NO_x levels), but this will be the subject of future work.

Despite the exciting progress to-date, plasma-based NF is currently still not competitive to the highly optimized and mature H-B process fixing >10% N into NH_3 for an energy cost of ~0.5 MJ/mol.[6] However, as recently underlined by Rouwenhorst et al.,[7] a more suitable comparison for state-of-the-art NF into NO_x would be an electrolysis-based H-B process combined with the Ostwald process (oxidizing NH_3 into NO_x with eventual dissolution in water, forming HNO_3). Notably, in contrast to the traditional H-B process producing H_2 using steam reforming of methane, electrolysis-based H-B offers an environmentally benign alternative based on (water) electrolysis to produce H_2 without a CO_2 by-product. In this context, the authors provide a revised target of ~0.7 MJ/mol[7] (i.e., lifting the target from ~0.5 MJ/mol of the traditional H-B process) for future plasma-based NF processes to be highly competitive with this electrolysis-based H-B benchmark, although it must be realized that this electrolysis-based H-B process is not yet the standard in the industry. Our MW discharge configuration discussed here shows much promise to achieve such a target, given its low technology readiness level at present. Critically, the results presented here show that stable plasma operation with relatively high gas throughput is possible without the filament touching its container, which contrasts to other plasma reactor configurations. Optimal conditions in gliding arc plasmas, for instance, are presently limited to relatively low mass flow rates and powers[23,24] and therefore present a considerable challenge for scale-up. The high gas throughput and production rates of MW plasmas, as demonstrated here, will offer greater flexibility for plasma-based NF, powered by intermittent renewable electricity sources, such as solar and wind[7,71] while also offering a promising avenue for further reducing energy costs. The electrode-free ignition, discussed in this work, provides a significant advantage, given the reduced energy losses to the walls, which limits damage, especially at higher powers, and has the key benefit of a prolonged reactor lifetime with no metal contamination (potentially detrimental to soil and ecosystems) during NO_x production.

Future avenues for reducing the energy cost of the plasma-based NF could include the use of downstream catalysts,[59] particularly if they could effectively utilize the high population of vibrationally activated species and the heated gas available in the vicinity of the plasma (see underlying mechanisms revealed by the quasi-1D modeling and section S3.2). Further, innovations to limit back reactions (which include the findings of this report) or downstream cooling of the plasma exhaust could also prove beneficial to lowering energy costs. Indeed, the absorbed energy is dissipated primarily to gas heating in the present process. Only a minority fraction of the coupled energy is converted to chemical energy due to enthalpy of formation requirements for nitrogen oxidation. The "warm" plasma discharge provides the activation levels necessary for both thermal and (critically) vibrationally induced nitrogen oxidation. The unused vibrational populations are eventually returned as heat in the exhausted gas downstream (i.e., V-T relaxation). The theoretical "ideal value" for the chemical energy coupling in warm plasmas, such as MW or GA reactors of 0.5 MJ/mol has been suggested recently by Rouwenhorst et al.[7] (see red triangle in Figure 2). Based on the best metrics found in this report (i.e., 3.8% NO_x at 2 MJ/mol) this would result in circa 1.5 MJ/mol lost as heat energy. This underlines the importance of recovering heat energy as a key component to driving efficient implementation of this process. Modern waste heat recovery technologies (e.g., gas-liquid plate exchangers[72] for high-grade waste heat (>300 C) or contemporary Stirling engine designs[73] for lower grade waste heat ~50–300 C) could offer significant improvements in heat recovery compared with the state-of-the-art technologies available a century ago to Birkeland and Eyde.

As mentioned in introduction earlier, given its relatively high cost in the original B-E process, the energy overhead of the NO_2 absorption stage will also need particular attention to develop the technology readiness of plasma-based NF. Modern advancements of NO_x trapping technologies commonly used in automotive applications employing absorbents such as BaO[11,12] in combination with temperature/pressure swing absorption techniques could be promising in this regard.[7]

Although pre-compressed dry gases (Air Liquide 99.999% purity N_2 and O_2 cylinders) are utilized in this work due to our laboratory infrastructure, on-demand compression of ambient air would be a more energy-efficient supply infrastructure (notably, the original B-E process used air blowers[8,74]). Tankless membrane air compressors, for instance, have an energy rating of about ~1 W per L/min flow rate.[75] Therefore, low-cost compressors would represent a relatively small overhead compared with the MW energy input (i.e., ~300–1,000 W) at typically <<5% of the absorbed plasma power. We estimated the cost of using pre-compressed air bottles (as per our laboratory infrastructure) at several orders of magnitude higher per liter compared with the cost of using such a tankless (i.e., on-demand) air compressor. Of course, integrated processes that can recirculate the compressed gas could help lower this energy overhead even more. Further to this, the use of high gas flow rates (as shown to be beneficial in this work) will not include a large energy burden compared with the cost of nitrogen oxidation in the plasma or downstream processes used to produce nitric acid.

Advancing the technology readiness of MW plasma-based NF will also depend on the architecture of power delivery. The beneficial characteristics of using solid-state MW amplifiers over magnetrons will be important in this regard. Solid state is inherently modular in contrast to magnetrons, which require large DC power supplies and enlarged magnetron cavities for scale-up, whereas the superior frequency stability and power control of solid-state amplifiers allow mixing with low losses. This modularity will be key for the "decentralized scalability" requirements of utilizing intermittent electricity powered NF processes. Further, this modular format allows low voltage (and hence low-cost) DC power supplies, limiting capital expenditure. Solid-state amplifiers also have a considerably enhanced longevity (~x10) compared with Magnetron technology. These characteristics will enable collections of amplifiers and mixers to be deployed in flexible reactor arrangements, allowing both multiple parallel reactors and/or in a smaller number of higher power plasma reactors. The efficiencies of solid-state MW power amplifiers are already typically ~50% and are set to exceed magnetrons in the coming years (currently at ~70% efficiency from "plug to load"). Indeed, solid-state MW power transmission already likely supersedes low frequency ~kHz and DC powered plasma reactor designs of current research interest (e.g., GA's and dielectric barrier discharges [DBD's]) as these sources typically sacrifice a large fraction of the transmitted power in high resistance components used to ballast/stabilize the dynamic arc conditions. Current

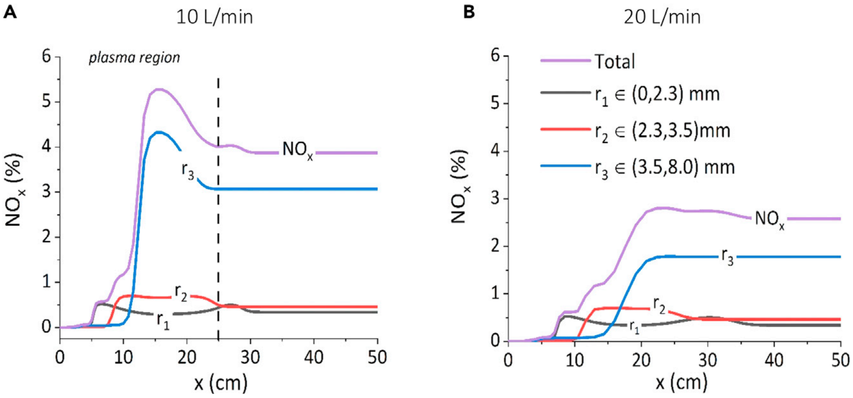

Figure 3. Quasi-1D modeling results of total NO_x concentration [%]

(A and B) At 870 W and N_2/O_2 ratio of 80/20 (dry air), for (A) 10 L/min and (B) 20 L/min mass flow rate, along the lateral (x) and radial (r) extent of the gas inside the quartz tube (inner radius 8 mm). The total NO_x concentration is the summation of the contributions from each radial section (i.e., r_1, r_2, and r_3); see supplemental information for modeling details. The vertical dashed line at x = 25 cm indicates the end of the plasma.

state-of-the-art solid-state high-powered MW amplifiers use laterally diffused-metal-oxide-semiconductors (LDMOS; as employed in this report). The emergence of high-powered gallium nitride (GaN) amplifiers will likely drive significant efficiency improvements.[76]

Underlying mechanisms revealed by the quasi-1D modeling

In order to better understand the benefits of higher flow rates on the NO_x production efficiency, presented in NO_x production and energy cost, we applied a quasi-1D model (see quasi-1D chemical kinetics modeling) to our conditions. In Figure 3 we present the simulated NO_x concentrations for an N_2/O_2 ratio of 80/20 (dry air) at 870 W and two different flow rates (10 and 20 L/min) for the feed gas passing through the plasma length ($0 < x < 25$ cm) and continuing "downstream," where a steady state is eventually reached in terms of total NO_x concentration (at $x > 35$ cm). It must be noted that the converted mix is found to be primarily NO and NO_2, with other N_xO_y species found to be negligible in quantity. Indeed, this is consistent with our experimental findings of NO_x production and energy cost, where NO and also NO_2 are the only measurable outputs. Notably, the ratio of NO_2 to NO will increase downstream as NO is slowly oxidized to NO_2 (i.e., as the gas cools and the relatively slow NO oxidization reaction proceeds). However, comparison of the total NO_x at its steady state just outside the plasma region (as defined by the model) with a NDIR/UV gas sample taken downstream will be equivalent (as the total NO_x remains unchanged once a steady state is reached outside the plasma). The total NO_x concentration shown in Figure 3 (i.e., NO and NO_2) is a summation of the contributions for three sections, which simulate the gas transiting through two inner (i.e., $0 < r_1 < 2.3$ mm and $2.3 < r_2 < 3.5$ mm) and an outer region (i.e., $3.5 < r_3 < 8$ mm) of the plasma filament, centered within the gas plug inside a quartz tube of inner radius 8 mm (see quasi-1D chemical kinetics modeling and section S2.2 for the model details). This partition serves as a proxy to study the distribution in plasma power density that different gas molecules will "feel" when transiting different sections of the gas plug.

Comparing the total calculated NO_x concentrations with the experiments at the same N_2/O_2 ratio (80/20), power (870 W) and flow rates, we find agreement of about

~15% between the model and experiment. Given the required assumptions of the quasi-1D modeling, this is deemed sufficient agreement to enable insight into the primary chemical trends. Indeed, to describe the detailed chemistry within reasonable calculation time, the model must simplify the physics (see quasi-1D chemical kinetics modeling). In future work, it would be interesting to develop more sophisticated higher-dimensional models, to reach better agreement with experiments, but this is only feasible upon increasing computational power. At $x > 35$ cm in Figure 3, corresponding to downstream the MW plasma, the simulated total NO_x concentration is ~3.9% for 10 L/min, whereas our NDIR/UV analysis at the same conditions (N_2/O_2 ratio and power; Figure 1) indicates a total NO_x concentration of ~3.6%. Increasing the flow rate to 20 L/min, the modeling predicts a total NO_x concentration of ~2.6%, whereas our experiments reveal a value of ~2.2%. The doubling in gas flow rate from 10 to 20 L/min results in a drop in the total calculated NO_x concentration by only ~33% (i.e., from 3.9% to 2.6%) (Figure 3), with a similar drop found in our experiments of ~39% (i.e., from 3.6% to 2.2%). This is a reasonable quantitative agreement, given the approximations of the quasi-1D modeling, and indicates the capabilities of the model for predicting the general trends with regard to flow rate behavior, which is of particular interest here. Similar agreement was reached at the other N_2/O_2 ratio and powers investigated in Figure 1.

Analysis of the main production avenues for NO shows that the Zeldovich mechanism (reactions 1 and 2 of NO_x production and energy cost) dominates, in agreement with literature for GA plasmas.[14,23,24,63,70] At 10 L/min the thermal Zeldovich mechanism (i.e., involving ground-state N_2) accounts for 28% of NO production, whereas the vibrationally enhanced Zeldovich mechanism (i.e., involving $N_2(v)$) accounts for the remaining 72%. At 20 L/min we see a similar breakdown, with the thermal and vibrationally enhanced Zeldovich mechanisms accounting for 26% and 74% of NO production, respectively.

The rate-limiting step in the (vibrationally enhanced) Zeldovich mechanism is $O + N_2/N_2(v) \leftrightarrow N + NO$ (Equation 1 of NO_x production and energy cost) with both $N_2(v)$ and O concentrations as potential limiting factors to NO production. The second part of the Zeldovich mechanism, i.e., $N + O_2/O_2(v) \leftrightarrow O + NO$ (Equation 2 in NO_x production and energy cost) involves (vibrationally excited) O_2 and N atoms (primarily produced by Equation 1). However, the N atoms also play a pivotal role in NO loss (back Equation 1).[14] In Figure 3 we see the major contribution from the outer region of the filament ($3.5 < r_3 < 8$ mm) in terms of overall NO_x production, as this covers a much wider region (i.e., accounting for 81% of the gas plug volume here, see section S2.2). Therefore, in the following, we will focus on this region to gain further insight into the underlying mechanisms, given its dominance on the total NO_x produced.

In Figure 3A, at a flow rate of 10 L/min, we see the calculated peak NO_x concentration is reached inside the plasma region (at x~15 cm). In Figure 3B, at a flow rate of 20 L/min, the peak NO_x concentration shifts to the end of the plasma region (~20 cm). Notably, the peak NO_x concentration reached at 20 L/min (~2.7%) is virtually sustained outside the plasma region (to ~2.6% at steady state; $x > 35$ cm), whereas the NO_x concentration for 10 L/min falls from a peak of ~5.3% (at ~15 cm) to ~3.9% ($x > 35$ cm). This difference is attributed to the different impact of the back reactions at 10 L/min versus 20 L/min, as explained in the next sections.

The calculated total NO_x production rate in the region $3.5 < r_3 < 8$ mm is plotted in Figure 4. At 10 L/min, the peak production (Figure 4A) corresponds to the sharp

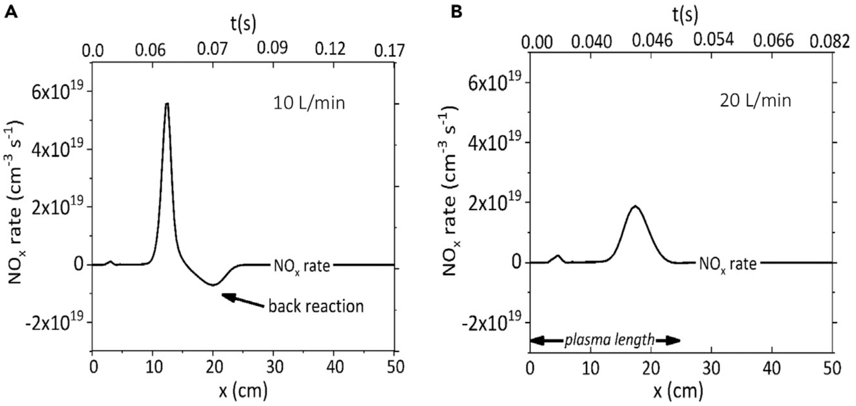

Figure 4. Quasi-1D modeling results of the total NO_x production rate

(A and B) [cm^{-3} s^{-1}] at 870 W, for (A) 10 and (B) 20 L/min, in the interval $3.5 < r_3 < 8$ mm. The negative rate results in NO_x loss due to back reactions (i.e., reverse Equation 1). The equivalent residence time t[s] is shown on the top x axis: note the time tick marks correlate to the position axis at the specified times only and the spacing on the time axis is non-uniform due to the non-linear relationship between the position and residence time, given the dynamic gas velocity (see section S.2.1).

increase in NO_x population (seen in Figure 3A), for x > 10 cm. However, at x ~12 cm, the NO_x production slows down and eventually turns negative (corresponding to NO_x destruction) at x~15 cm. The back reaction (reverse Zeldovich Equation 1) becomes dominant here, as indicated in Figure 4A. The comparatively longer residence time in the plasma at 10 L/min (~0.077 s) results in lowering the peak NO_x concentration due to this back reaction occurring during the gas transit through the latter half of the plasma region. In contrast, at 20 L/min, as shown in Figure 4B, the peak production is shifted to the end of the plasma region. The shortening of the residence time (only ~0.049 s for transiting the plasma region) suppresses the back reaction, with peak NO_x values sustained as the gas leaves the discharge region. Although a higher gas flow rate leads to a drop in NO_x production, both our experimental and calculation results show a drop of only 33 (or 39)% in overall NO_x produced, despite a 100% change in flow rate (i.e., from 10 L/min to 20 L/min). Therefore, the higher gas flow rate yields somewhat less conversion (for similar power conditions), but this is largely compensated by the more energy-efficient production, because of the lack of back reactions.

When comparing Figures 4A and 4B, we see that the back reactions contribute less; therefore, the energy use in the reactions is more efficient at 20 L/min. It is clear that the peak NO_x production rate is lower at 20 L/min than at 10 L/min (although the peak is clearly broader; therefore, the overall production is not so much lower, especially because no NO_x destruction occurs, as explained earlier). Therefore, both conditions show a similar energy cost. In addition, despite the NO_x percentage yielded being lower at the higher flow rate, the absolute production of NO_x (i.e., in L/min) is actually larger at the higher flow rate of 20 L/min. This manifests as ~0.54 L/min NO_x outflow at 20 L/min versus ~0.39 L/min NO_x at 10 L/min gas flow rate. This is consistent with the experimental trends discussed in NO_x production and energy cost earlier. The lower peak production rate at 20 L/min can be explained by the lower gas temperature and vibrational temperature predicted by our model, as plotted in Figure 5. For a flow rate of 10 L/min, a peak in calculated bulk gas temperature of ~3,100 K is reached at x~15 cm (in the outer filament region $3.5 < r_3 < 8$ mm), whereas at 20 L/min, the calculated peak bulk gas temperature in the same outer

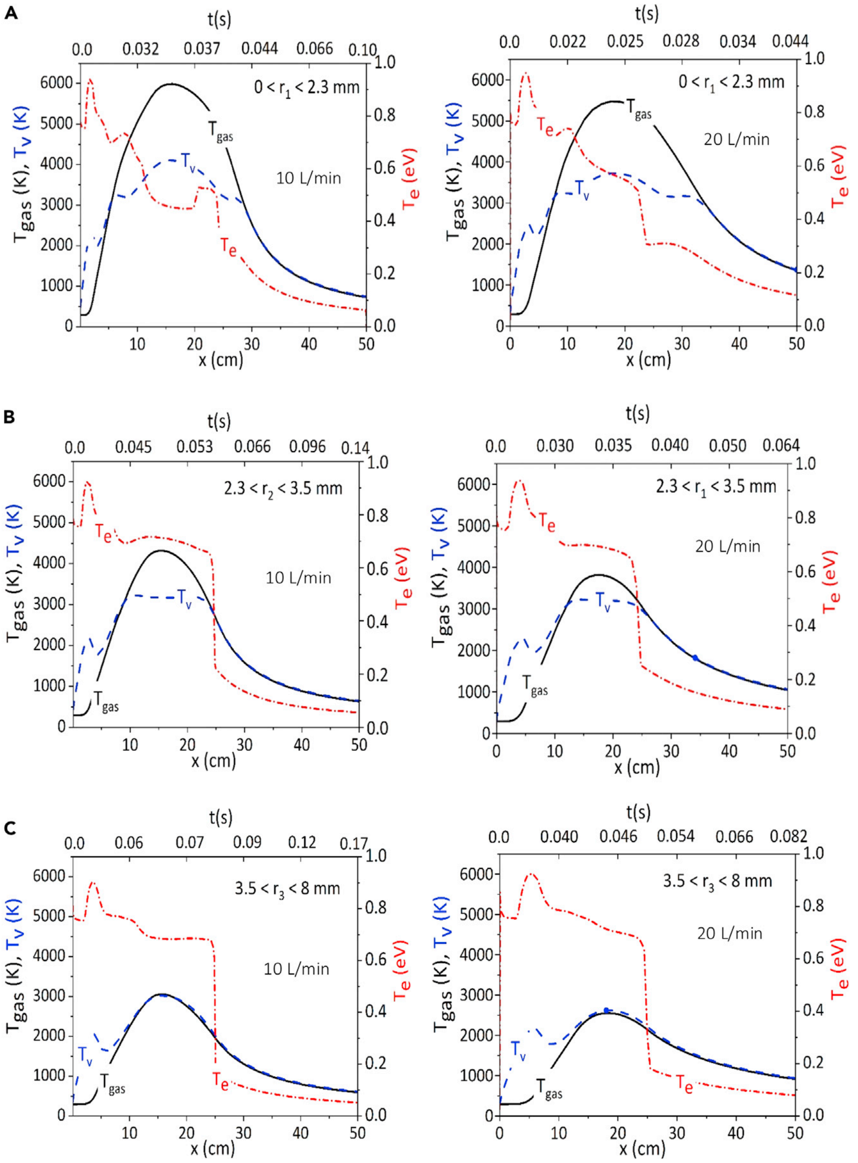

Figure 5. Quasi-1D modeling results of gas temperature

(A–C) (T_{gas} [K]), vibrational temperature of the first N_2 level with respect to ground state (T_v [K]) (left y axis) and electron temperature (T_e [eV]) (right y axis) at 870 W power for flow of 10 L/min (left) and 20 L/min (right), for three different radial regions: (A) $0 < r_1 < 2.3$ mm, (B) $2.3 < r_2 < 3.5$ mm, and (C) $3.5 < r_3 < 8$ mm. The equivalent residence time t[s] is shown on the top x axis; note the time tick marks correlate to the position axis at the specified times only, and the spacing on the time axis is non-uniform due to the non-linear relationship between the position and residence time, given the dynamic gas velocity (see section S.2.1).

region is only ~2,500 K (see Figure 5C). Notably, our model predictions are not corroborated directly by experimental measurements in this report; however, the span of temperatures found here is largely in line with earlier reports using optical diagnostics.[77] Such techniques consider an accuracy of ~10%–30%,[78] an uncertainty range consistent with the accuracy expectations of our simulations.

Gas temperatures in the inner regions of the plasma filament (which account for a combined 19% of the gas plug volume and thus are not so impactful to NO_x

production) are given in Figures 5A and 5B. The gas temperatures are clearly higher in the inner regions, both at 10 and 20 L/min, due to the higher power density, with peak gas temperatures of ~4,300 K (at 10 L/min) and ~3,800 K (at 20 L/min) for $2.3 < r_2 < 3.5$ mm, and even ~6,000 K (at 10 L/min) and ~5,500 K (at 20 L/min) for $0 < r_1 < 2.3$ mm. Hence, at a flow rate of 20 L/min, the calculated peak bulk gas temperatures are clearly lower in all plasma regions (see Figures 5A–5C). In addition, for 20 L/min the peak gas temperature is reached only near the end of the plasma region (x ~20 cm, while it is at x ~15 cm for 10 L/min). Indeed, the gas transiting the plasma region has less time to heat up within the shorter residence time. Combined with the higher advective cooling at 20 L/min, this leads to lower gas temperatures, resulting in somewhat lower NO_x production. However, as discussed earlier, this drop in NO_x production is compensated significantly by the absence of back reactions, leading to lower energy costs for this higher gas flow rate.

The vibrational temperature is also plotted in Figure 5, and applies to the N_2 vibrational levels, and more specifically the population of the first vibrational level with respect to the ground state, i.e., $T_v^{(v=0 \leftarrow v=1)}$ (see section S2.6). We see that the vibrational temperature is clearly higher than the gas temperature in the first part of the plasma in all cases, indicating a strong overpopulation of the N_2 vibrational levels or a strong vibrational-translational (V-T) non-equilibrium. It does not only apply to the first N_2 vibrational level but also to the higher levels, as clearly observed in the calculated vibrational distribution function (VDF), plotted in the section S3.4 and Figures S5 and S6. However, upon rising gas temperature, V-T relaxations (i.e., collisions of the vibrational levels with ground-state molecules) become increasingly important, causing a drop in the vibrational-level populations and hence in the vibrational temperature, which becomes nearly equal to the gas temperature (V-T equilibrium). Hence, this means that the VDF will follow a Boltzmann distribution, dictated by the gas temperature, as is clear from the section S3.4, Figures S5 and S6. Nevertheless, both the gas temperature and the vibrational temperature rise further to a maximum of around x ~ 15 cm (at 10 L/min) or close to x ~ 20 cm (at 20 L/min). At these high values of gas and vibrational temperature, the thermal and especially the vibrationally enhanced Zeldovich mechanism will be very important, explaining the high NO_x production rate (before the back reaction takes over at 10 L/min). Note that in the inner filament regions, the vibrational temperature is somewhat lower than the gas temperature above x ~10 cm, whereas both temperatures are equal to each other in the outer filament region (which accounts for 81% of the volume), indicating that the vibrationally enhanced Zeldovich mechanism will be relatively more important here.

The electron temperature, also presented in Figure 5, is about 0.8 eV (~8,000 K), on an average, in all plasma regions, for both 10 and 20 L/min, with a corresponding (average) reduced electric field calculated to be 22 Td (not shown), which are indeed ideal conditions for strong vibrational excitation.[14] In addition, the electron temperature is clearly higher than the gas and vibrational temperature, especially in the outer region of the filament (i.e., $3.5 < r_3 < 8$ mm), which dominates the overall NO_x production. This indicates that our MW plasma at atmospheric pressure is not thermal but warm plasma. In the afterglow (i.e., x > 25 cm), the electron temperature drops dramatically to very low values, due to the absence of plasma power to heat the electrons, and it approaches the gas temperature; hence, the gas becomes thermalized.

Not only do the N_2 molecules have a high vibrational temperature, the same is true for the O_2 molecules. Indeed, substantial populations of both $N_2(v)$ and $O_2(v)$ are predicted by the model, as shown in Figure 6 for the outer filament region. The

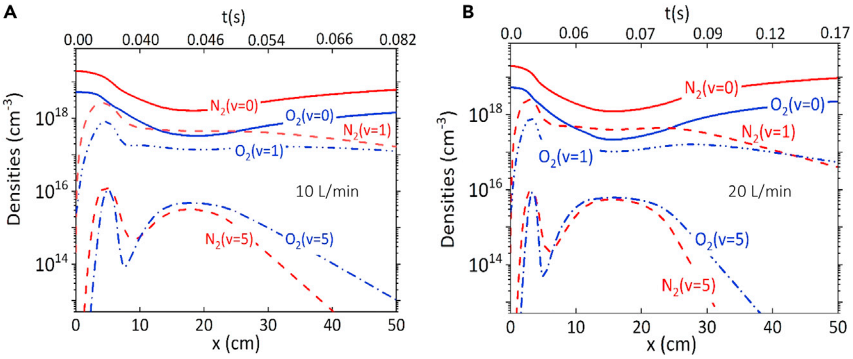

Figure 6. Quasi-1D modeling results of $N_2(v)$ and $O_2(v)$ level populations

(A and B) (For v = 0, 1 and 5, where v = 0 stands for the ground state) [cm^{-3}] at 870 W power, and $3.5 < r_3 < 8$ mm, for (A) 10 L/min and (B) 20 L/min. The equivalent residence time t[s] is shown on the top x axis; note that the time tick marks correlate to the position axis at the specified times only, and the spacing on the time axis is non-uniform due to the non-linear relationship between the position and residence time, given the dynamic gas velocity (see section S.2.1).

relative population of the first N_2 vibrational level (i.e., $N_2[v = 1]$) reaches peak values of 12.3% of the gas mix at 10 L/min, and of 13.2% at 20 L/min. Likewise, for $O_2(v=1)$ the relative population peaks at ~4% of the total gas mix at both 10 and 20 L/min, with an associated peak vibrational temperature $T_v^{(0 \leftarrow 1)}$ of 1,700 K. The entire VDF for both O_2 and N_2, at both 10 and 20 L/min and various positions in the plasma, is given in the supplemental information (Figures S5 and S6). The higher N_2 and O_2 vibrational levels have somewhat lower populations, as indicated in Figure 6 for $N_2(v = 5)$ and $O_2(v = 5)$, and they also drop faster in the afterglow. When comparing 10 and 20 L/min (Figures 6A and 6B), we see that the N_2 and O_2 vibrational populations are retained over a longer distance at 20 L/min than at 10 L/min. This is due to the shorter residence time when doubling the mass flow rate, leading to faster mass transport of the vibrationally excited species. This promotes the forward reactions of the Zeldovich mechanism (reactions 1 and 2) with respect to the back reactions, explaining the more energy-efficient NO_x production at 20 L/min.

In Figure 7 we plot the calculated densities of O and N atoms, and of the electrons, for the outer filament region, throughout the plasma and afterglow. For 10 L/min, in Figure 7A, the O concentration inside the plasma region is found (on an average) to be ~0.2% of the total gas mixture, with peak values reaching ~1.6% in the latter half of the plasma region. This is much lower than the $N_2(v)$ levels, indicating that the O atoms are the limiting factor in the first step of the Zeldovich mechanism (Equation 1 in NO_x production and energy cost). Examination of the fundamental production avenues for O atoms (i.e., excluding Equations 1, 2, and 3, which by oxidation of N_2 results in a net loss for O), we find that 67% of the production is due to the dissociation of vibrationally excited O_2 (up to v=15), upon collision with gas molecules: $O_2(v) + N_2/O_2 + \Delta H \rightarrow O + O + N_2/O_2$. Dissociation of $O_2/O_2(v)$ by electronically excited N_2 molecules (primarily $N_2[B^3\prod_g]$ and the metastable $N_2[A^3\Sigma_u^+]$) contributes to 23%, whereas direct electron impact dissociation of $O_2/O_2(v)$ accounts for just ~6%.

At 20 L/min, as shown in Figure 7B, the calculated O atom concentration is on an average ~0.03% of the mix, with a peak of only ~0.25%. The reason is the more efficient O atom consumption, in the Zeldovich mechanism (forward Equation 1, as the back Equation 1 is suppressed at 20 L/min) and in oxidation of NO to NO_2 (Equation 3), as well as the more limited O atom production due to the shorter residence time in the plasma (see further on). However, despite the lower O atom

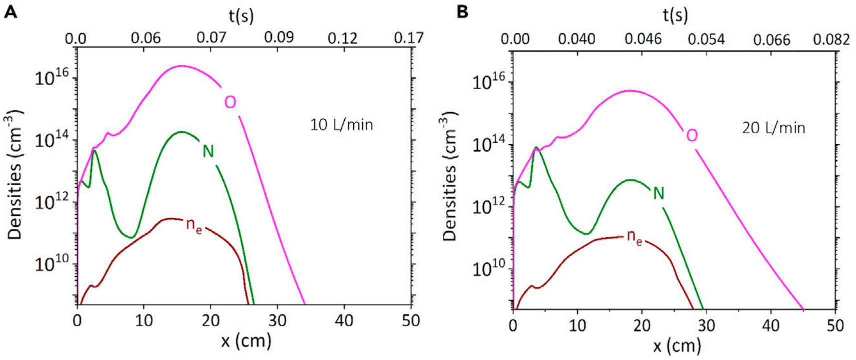

Figure 7. Quasi-1D modeling results of O, N and electron density [cm^{-3}]

(A and B) At 870 W power, 3.5 < r < 8 mm, for (A) 10 L/min and (B) 20 L/min. The equivalent residence time t[s] is shown on the top x axis: note the time tick marks correlate to the position axis at the specified times only, and the spacing on the time axis is non-uniform due to the non-linear relationship between the position and residence time, given the dynamic gas velocity (see section S.2.1).

concentration, the drop in overall NO_x production is limited, exactly due to the absence of the back reactions, as discussed earlier. At 20 L/min, the production of O atoms is found to be dominated by electronically excited N_2 molecules (i.e., $N_2[B^3\prod_g]$ and $N_2[A^3\Sigma_u^+]$) colliding with $O_2/O_2(v)$, accounting for ~76% of the overall O atom production, whereas the reaction of vibrationally excited $O_2(v)$ (i.e., $O_2(v) + N_2/O_2 + \Delta H \rightarrow O + O + N_2/O_2$), which dominated at 10 L/min, contributes only for 6% at 20 L/min. This shift in O atom production chemistry from 10 to 20 L/min is due to the more limited time for vibrational excitation of $O_2(v)$ (i.e., V-V interactions), due to the shorter residence time in the plasma at 20 L/min. This is clear from the O_2 VDF plotted in the section S3.4. Indeed, in Figure S6 we see the relative underpopulation of $O_2(v)$ at 20 L/min compared with 10 L/min. This shift in chemistry also explains the overall lower O atom concentration. Methods (e.g., gas quenching[79]) that can promote higher electronic N_2 excitation or higher vibrational excitation of O_2 under high flow conditions would enhance O atom formation and therefore could provide potential avenues to further increase NO_x production at lower energy costs.

The average N atom concentration at 10 L/min (also shown in Figure 7A), taken over the plasma region (i.e., 0–25 cm), is found to be only ~14 ppm of the gas mix, with the production trend following the NO_x production. The relatively low N atom concentration is due to the tightly coupled Zeldovich mechanism (Equations 1 and 2), where the N atoms play an intermediate role and thus have a short lifetime. However, surplus N atoms play a key role in limiting NO formation, due to the back reaction: $N + NO \rightarrow O + N_2/N_2(v)$ (i.e., back of Equation 1). At 20 L/min, the N atom concentration in the plasma is found to be further reduced to ~1.2 ppm (on an average), as shown in Figure 7B. This very low N atom concentration is consistent with the limited back reaction at 20 L/min, as discussed earlier (see Figure 4B earlier).

Electrons do not play a direct role in NO production (cf. Zeldovich mechanism) but are essential in activating the gas initially, and sustaining the chemistry, mainly by electron impact vibrational excitation of N_2 and O_2. The electron density inside the plasma reaches a peak of ~3 × 10^{11} cm^{-3} at 10 L/min and of ~1 × 10^{11} cm^{-3} at 20 L/min (see Figure 7). However, this has no real impact on NO_x production.

Future numerical investigations would undoubtedly benefit from a more spatially resolved description of the plasma dynamics and chemistry. A necessary prerequisite for this would be the investigation of dominant pathways in fully resolved approaches, such as employed in this work in combination with appropriate sensitivity analysis[80] to enable a smaller subset of chemistry to be derived. Such a reduced chemistry could then allow tractable plasma fluid and computational fluid dynamics studies. The large chemistry of N_2/O_2 employed in this work is largely a result of the resolution of vibrational levels. Therefore, reduction of the plasma chemistry for higher-dimensional modeling will need to verify which vibrational levels can be omitted or assumed via a predefined distribution (e.g., Boltzmann or Treanor[81]) while maintaining the required level of detail.

Conclusions

In this paper, we demonstrate energy-efficient NO_x formation from air and N_2/O_2 mixtures, in a plasma filament isolated at the center of a MW plasma tube, using a vortex gas flow. The electrode-free ignition provides a significant advantage, given the reduced energy losses to the walls, which limits damage, especially at higher powers, with the key benefits of a prolonged reactor lifetime and no metal contamination (which is potentially detrimental to soil and ecosystems for applications in agriculture). NO_x production is found to scale efficiently with gas flow rate and power. For relatively high flow rates (i.e., 20 L/min), increasing MW power (up to ~1 kW) leads to the highest NO_x production (~3.8%), as well as minimum energy cost (~2 MJ/mol), giving the best cost-conversion metric for this work. This energy cost is the lowest reported up to now in literature for atmospheric pressure plasmas. The rising trend in power and flow rate is very beneficial, given the high-volume throughputs required for future industry deployment. Ignition in O_2-enriched air feeds close to stoichiometric N_2/O_2 ratios (i.e., 50/50) is found to benefit NO_x production, reducing energy costs.

Our numerical model offers insight into the fundamental behavior with changing gas flow rate and residence time within the plasma. Doubling the gas flow rate limits the back reactions in the last part of the plasma, due to the shorter gas residence time. At the higher gas flow rate, sufficiently high vibrational-level populations and atomic species densities are retained over a longer distance in the plasma, thus promoting the forward reactions of the Zeldovich mechanism. This leads to a comparatively small drop in NO_x production upon increasing the gas flow rate, despite the shorter residence time, and at a significantly lower energy cost.

Together, our findings demonstrate the benefits of high flow rates (i.e., limited residence time) matched with appropriate power, for energy-efficient NO_x production in atmospheric pressure MW air plasma, in a surface wave sustained mode without electrodes. Future work can consider even higher power and flow combinations to drive efficient conversion for industrial exploitation. Our work underlines the importance of residence time to prevent back reactions, gained at higher flow rates and powers. It also encourages the potential merits of other methods with great potential for reducing back reactions, discussed recently in particular for the related field of plasma-based CO_2 conversion.[82] This includes exhaust gas quenching using nozzles (e.g., Laval nozzle[45]) and using heat exchangers or external coolants[79] in the immediate vicinity of the plasma.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources and materials should be directed to and will be fulfilled by the lead contact, Seán Kelly (sean.kelly@uantwerpen.be).

Materials availability

This study did not generate new unique materials.

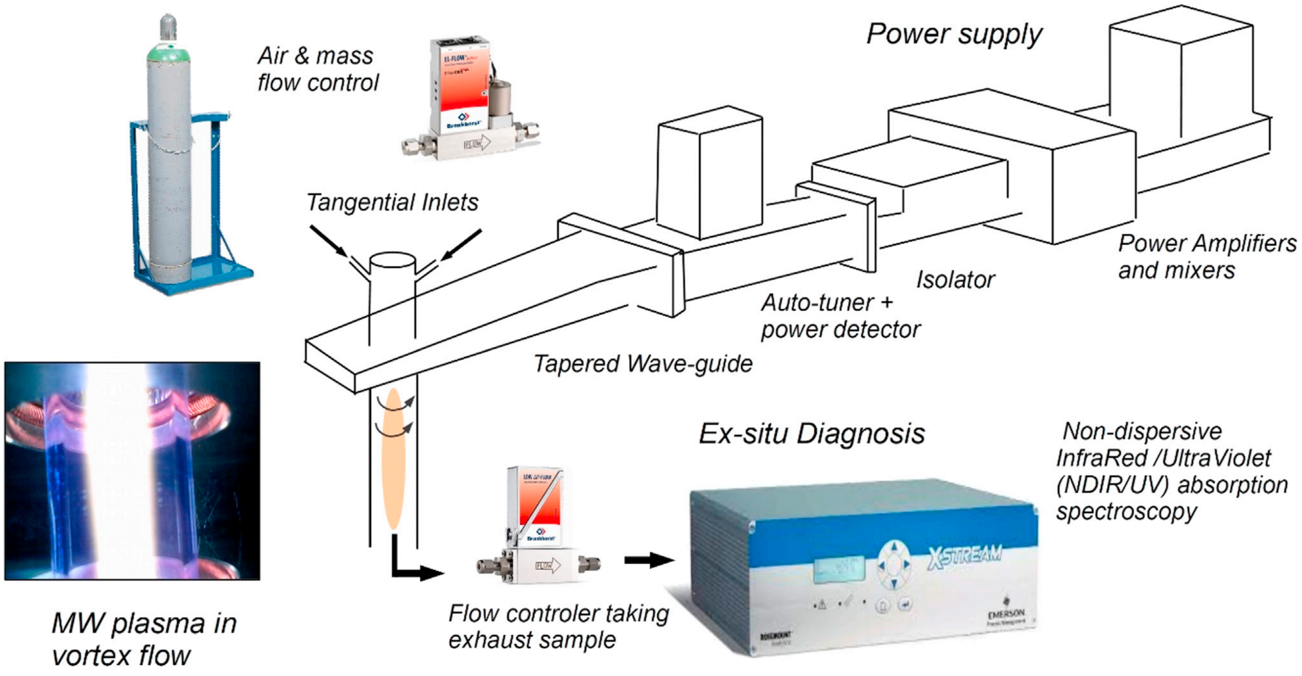

Figure 8. Experimental setup

Of our solid-state MW plasma power supply and tapered waveguide section for plasma ignition, including the exhaust diagnostic arrangement—the inset camera image illustrates the radial extent of the plasma filament inside the waveguide.

Data and code availability

Data from this study are available from the lead contact upon reasonable request.

MW plasma reactor and exhaust diagnostics

The experimental layout is schematically shown in Figure 8. An electronic image of the setup is shown in section S3.1, along with an accompanying video (Video S1) showing the reactor operation available for download in supplemental information. It is based on a solid-state 2.45 GHz microwave (MW) power source composed of a collection of LDMOS power amplifiers from which the output powers are combined in a waveguide (WR340). This waveguide is connected via an isolator and an auto-tuner to a tapered waveguide section, including a 16 mm inner diameter quartz tube. The latter is mounted perpendicularly through an 18 mm coupling hole (i.e., <1/4 wavelength in diameter), where the plasma ignition takes place. An auto-tuner, impedance analyzer, and adjustable short are used to tune the electric field to optimal conditions for electrical breakdown and to sustain a continuously powered plasma with minimum reflected power (<<5%). The measurement of the absorbed plasma power, a key variable, is carried out using the Homer series auto-tuner from S-TEAM labs[83] using a six-port-reflectometer (SPR) method.[84] Tangential gas injection ports coupled with a helical insert allow a swirl or vortex flow within the quartz discharge tube. Upon ignition, a surface wave sustained mode[50] is generated, with the plasma filament located at the tube center (see inset in Figure 8). This provides a key benefit by isolating the warm plasma from the quartz tube walls, allowing for elongated plasma column formation along the tube lateral axis.

The oxidation of nitrogen results in the production of gaseous NO and NO_2 via the overall reactions

$$O_2(g) + N_2(g) + 180.5\ kJ/mol \rightarrow 2NO \qquad \text{(Equation 4)}$$

$$2\ O_2(g) + N_2 + 66.36\ kJ/mol \rightarrow 2NO_2 \qquad \text{(Equation 5)}$$

Analysis of the exhausted NO_x species (i.e., NO and NO_2) was performed using infrared and ultra-violet absorption spectrometry (Rosemount X-STREAM XEGP Continuous Gas Analyzer[85]), as explained in detail in the section S1. Sampling was performed once the reactor has reached a steady state in terms of the exhaust temperature, as explained in section S3.2. The energy cost of the conversion from air or N_2/O_2 mixtures was obtained from the measured absorbed power and total% NO_x produced (i.e., the sum of NO and NO_2) from the NDIR/UV as:

$$Energy\ cost\left[MJ\ mol^{-1}\right] = 10^{-6} * \frac{P\left[J\ s^{-1}\right] * 24.05\left[L\ mol^{-1}\right] * 60\left[s/min\right] * 100\left[\%\right]}{total\ NO_x\ [\%] * Flow\ rate\ [nL/min]} \qquad \text{(Equation 6)}$$

where P [W or J/s] is the absorbed MW power and 24.05 [L/mol] represents the molar volume of ideal gas at normal temperature and pressure conditions for which our mass flow controllers (Bronkhorst) are calibrated. The NDIR/UV data used in Figure 1 along with a breakdown for the NO and NO_2 populations have been added to the supporting information in section S3.3 and Table S2.

Quasi-1D chemical kinetics modeling

A quasi-1D model was employed using ZDPlasKin (zero-dimensional plasma kinetics) solver.[86–88] An overview of the simulation scheme is given in Figure 9. The time-evolution of the species densities, including electrons, and various charged and neutral species, is calculated by considering the production and loss terms by chemical reactions:

$$\frac{dn_i}{dt} = \sum_j \left(a_{ij}^R - a_{ij}^L\right).R_j \qquad \text{(Equation 7)}$$

$$a_A\,A + \ a_B B\ (+\varDelta H) \xrightarrow{k_j} a_c C + \ a_D D\ (+\varDelta H) \qquad \text{(Equation 8)}$$

$$R_j = \ k_j \prod_l n_l^L \qquad \text{(Equation 9)}$$

Here, n_i represents the density of species i and a_{ij}^R and a_{ij}^L are the stoichiometric coefficients of species i on the right-hand and left-hand side of reaction j. Reactions have the general form of Equation 8 where A, B, C and D are the species and a_A , a_B, a_c, and a_D their stoichiometric coefficients. ΔH in Equation 8 represents the possible energy change during the reaction. The reaction rate R_j is calculated by Equation 9, where k_j is the reaction rate coefficient of reaction j and $\prod_l n_l^L$ represents the product over left-hand side reactants. At each time step the relation $dx = v\ dt$ advances the gas plug, so that the time dependency is translated into an axial spatial dependency (so-called "quasi-1D"). This assumes that the velocity v is uniform across the tube diameter. Dynamic changes in the gas velocity due to temperature and stoichiometric changes in the gas mixture are updated on each time step (further details in section S2.1 and Figure S1).

The reduced electric field $E/_N$, where N is the neutral gas density, is calculated from a specified power density.

$$E/_N = \frac{\sqrt{P/\sigma}}{N} \qquad \text{(Equation 10)}$$

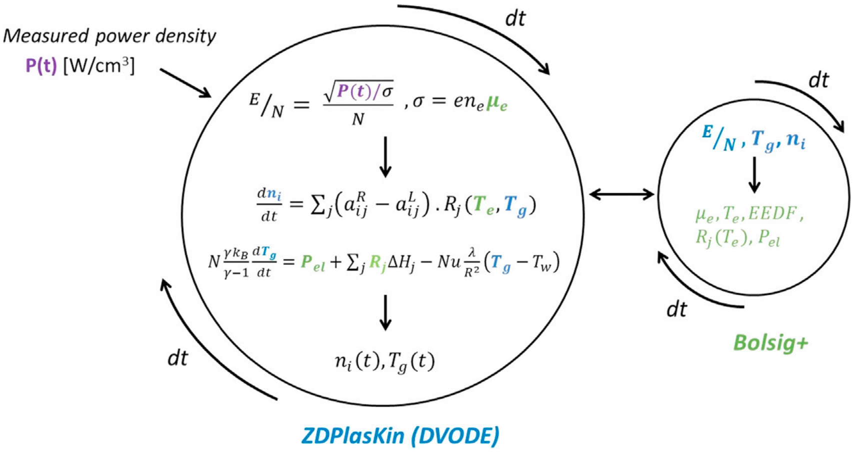

Figure 9. Overview of the numerical solution scheme for the quasi-1D model

Employing the zero-dimensional plasma kinetic solver ZDPlasKin, which incorporates the DVODE ordinary differential solver code for ODE integration and the software BOLSIG+ to solve the Boltzmann equation at each time step. An experimentally determined power density [W/cm^3] is coupled externally to enable solution via the reduced electric field E/N.

Here, σ is the plasma conductivity, which is calculated using the electron mobility $\mu_e\ (E/N)$ (output from the Boltzmann solver[86,88]) via $\sigma = en_e\mu_e$ where e is the electron charge.

The power density $P\left[\frac{W}{cm^3}\right]$ is derived from experimental measurements of the absorbed power (i.e., forward minus reflected power), combined with the approximation of plasma volume via camera imaging inside the tapered section of the waveguide (see Figure 8 inset) and the visual estimation of plasma length. A cylindrical shape is assumed for the plasma volume.[63] This is consistent with vortex-stabilized discharges, where the plasma is contained within the tube inner region, separated from the containment walls by a swirling or vortex flow boundary. The plasma elongates along the direction of the flow (i.e., along the axial extent of the reactor tube), forming a cylindrical shape in its steady state.[48,49,63] The light emission across the radial extent of the plasma filament (shown in Figure 8) is used as a proxy for the plasma width. We solve the quasi-1D model for different radial positions, as explained in the section S2.2. For each of these quasi-1D models a triangular distribution of power density in the lateral extent of the plasma (i.e., along the direction of gas flow) is assumed, in line with the earlier modeling of power dissipation in surface wave sustained MW plasmas.[13,52] Further details of the power density determination are given in the section S2.2 and Figure S2.

Next to the species densities, also the gas temperature is solved in the model at each time step, based on gas heating due to elastic collisions of electrons with the gas molecules, the enthalpy contributions from the chemical reactions between all plasma species (ΔH in Equation 8 earlier), heat losses to the walls, and the dynamic heat capacity, taking an account of the gas mixture. The radially averaged gas temperature T_g (which is assumed to have a parabolic profile) is calculated by considering the time-dependent gas thermal balance equation under isobaric conditions[89,90] as:

$$N\frac{\gamma k_B}{\gamma - 1}\frac{dT_{gas}}{dt} = P_{el} + \sum_j R_j \Delta H_j - Nu\frac{\lambda}{R^2}(T_g - T_w) \qquad \text{(Equation 11)}$$

where γ is the specific heat ratio (i.e., the ratio of the isobaric and isochoric heat capacity,[63] which is the function of temperature and employs data from[91]), k_B is the

Boltzmann constant, P_{el} is the power density due to elastic collisions of electrons with heavy neutrals (an output from the Boltzmann solver[86,88]), R_j is the rate of reaction j with associated enthalpy contribution of ΔH_j, λ is the gas thermal conductivity, T_w is the wall temperature (set to 300 K), and R is the reactor inner radius (taken from the experiments; see MW plasma reactor and exhaust diagnostics). It must be noted that in Equation 11 (LHS) the fluid-related term "$\gamma\ k_B/(\gamma - 1)\ dT_{gas}/dt$" is equivalent to a "$NC_p\ dT_{gas}/dt$" formulation, given by $\gamma = C_p/C_v$. The ratio γ is dynamically updated throughout the (isobaric) simulation based on the changing gas mixture during conversion. Finally, the non-dimensional quantity '*Nu*' in Equation 11 is the Nusselt number, which is defined as the ratio of convective to conductive heat transfer to the tube walls (further details in section S2.3). The mixture fraction along with the gas temperature and the reduced electric field are continually updated in calls to BOLSIG+, as shown in Figure 9 (further details in sections S2.1 and S2.4).

The air chemistry (i.e., N_2/O_2) employed here is detailed in our previous work.[14,63,70] A total of 82 species are included in the model, i.e., the electrons, N_2, and O_2 molecules in ground state and various (vibrational and electronic) excited levels, various radicals and ions, as detailed in the section S2.5. For the heavy particle reactions, the rate coefficients are adopted from earlier work,[14,63,92] whereas the rate coefficients for the electron impact reactions are calculated using the Boltzmann solver BOLSIG+[88] built in ZDPlasKin, as explained in the section S2.4.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.joule.2021.09.009.

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AUTHOR CONTRIBUTIONS

S.K. conducted the experiments and modeling. S.K. and A.B. wrote the paper.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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