Non-equilibrium NO formation in plasma reactors: the role of transport, excitation and radicals

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Abstract: Plasma-based NO synthesis from N_2-O_2 mixtures offers a sustainable route for electrified nitrogen fixation. Modelling and experiments reveal that limiting oxygen dissociation by tailoring the gas heating profile allows one to surpass thermodynamic limits by enhancing NO yield, reducing energy costs to 1.5 MJ/mol. Decoupling O_2 injection from the pure N_2 plasma extends the chemical non-equilibrium time windows.

1. Introduction

Plasma-based direct synthesis of nitric oxide (NO) from N_2-O_2 mixtures offers a promising approach to electrified nitrogen fixation, a crucial step in decarbonizing the fertilizer industry [1]. Since the development of the Birkeland-Eyde process in the early 1900s, the efficiency of plasma reactors has been constrained by the challenges of thermal equilibrium.

Current benchmarks at atmospheric pressure show energy demands of around 2.0–2.4 MJ per mole of NO [2-4], with NO concentrations ranging from 1% to 6%. Significant improvements in NO yield from the plasma process could dramatically reduce energy consumption, positioning it as a competitive alternative to traditional fertilizer production methods.

The formation of nitric oxide has been shown to be dependent on flow velocity, deposited power and nitrogen vibrational excitation [5,6]. Optimization of the process therefore relies on models capable of describing and pinpointing the most influential physical and chemical processes at play in the reactor.

2. Methods

A 0D model including thermal chemical kinetics for the main species involved in NO formation is used to pinpoint NO and O creation and destruction kinetics. The same model is then used to optimize NO production by tailoring the gas heating profile.

In-situ Raman spectroscopy is used to obtain temperature and concentration maps of NO, O, N_2 and O_2 with the aim of validating the mechanisms described in the models.

0D models including also N_2 vibrational kinetics are then developed to explore the possibilities of nitrogen activation and subsequent oxygen injection for enhanced NO production.

3. Results and Discussion

0D thermal models of N_2-O_2 mixtures reveal a much longer timescale for oxygen dissociation than for NO formation via the Zel'dovich mechanism. This creates a window of time where NO concentration reaches a maximum (up to 20%mol) before being destroyed by collisions with atoms. This is accompanied by a reduction in NO energy cost down to 1.5 MJ/mol. The duration of this time window for optimal performance is inversely proportional to both temperature and pressure.

In experiments at 180 mbar, the gas flow limits the residence time of the gas within the high temperature (4500 K) plasma region to around 500 µs, thereby promoting NO concentrations higher than thermal chemical equilibrium.

These results show that limiting O radicals creation while accelerating the Zel'dovich is the key to obtain NO yields above thermal equilibrium. This can be improved by separating the oxygen injection from the pure N_2 plasma. Simulations reveal that nitrogen radicals transported from the plasma region quickly react with the injected oxygen, starting the Zel'dovich mechanism. Part of those radicals recombines to vibrational levels above $v = 20$, for which the reaction $\mathrm{N_2}(v) + \mathrm{O} \rightarrow \mathrm{NO} + \mathrm{N}$ is exothermic. This further enhances NO formation.

For relatively low downstream temperature (below 2000 K), oxygen dissociation proceeds slowly. This means that the nitric oxide formed thanks to the nitrogen radicals formed in the plasma region is only destroyed after hundreds of milliseconds, making the non-equilibrium window much longer that the one achieved with pre-mixing of N_2 and O_2.

References

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