Modelling the Chemistry of a N_2/O_2 Plasma in a Gliding Arc Plasmatron

E. Vervloessem, F. Jardali, M. Aghaei, A. Bogaerts.

Department of Chemistry, Research group PLASMANT, University of Antwerp, Universiteitsplein 1, 2610 Antwerp (Belgium)

Abstract: Modern environmental and economical standards demand a more sustainable way for the production of nitrogen-fixated species. Plasma-based nitrogen fixation has potential in this field. There is, however, a lack of fundamental knowledge about the underlying chemistry. In order to elucidate this, we present an experimentally validated zero-dimensional chemical kinetics model, describing the NO_x formation pathways of an N_2/O_2 mixture in a gliding arc plasmatron (GAP) reactor operating at atmospheric pressure.

Keywords: plasma-based nitrogen fixation, gliding arc plasmatron, kinetic modelling

1. Introduction

Nitrogen is an essential building block for all living organisms [1]. In order to make it available, nitrogen is fixed on hydrogen or oxygen through naturally occurring high energy processes and specialized organisms [2]. However, the still growing population demands more fixated nitrogen than the earth can provide. As a response, the Haber-Bosch (HB) process for synthetic nitrogen fixation was developed, supporting 40 % of the world population [2]. However, the increasing demand of fertilizers, and the high energy intensity and environmental concerns of the current industrial HB process have started a wave of research for alternative ways to fix nitrogen on an industrial scale [3,4]. Plasma-based nitrogen fixation has potential in this field [4–6]. There is, however, a lack of fundamental knowledge about the underlying chemistry [1]. In order to elucidate this, we present a zero-dimensional chemical kinetics model, describing an N_2/O_2-mixture in a gliding arc plasmatron (GAP) reactor (Fig. 1.: left) operating at atmospheric pressure.

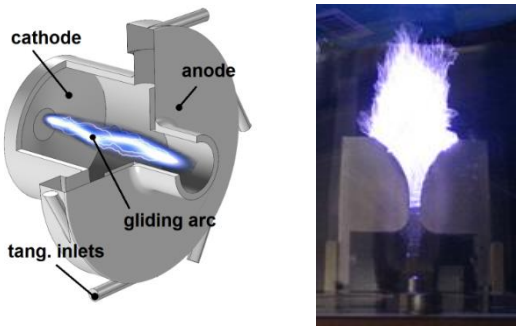

Fig. 1. Schematic view of the gliding arc plasmatron (left) and a picture of a classical gliding arc (right).

The gliding arc plasmatron (GAP), developed at Drexel University by Nunnally, Rabinovich et. al. [7], has shown to be a promising reactor for plasma-based gas conversion [7,8]. In gliding arc reactors, a discharge is created between two electrodes (anode and cathode) by applying a potential difference. This discharge glides along the electrodes dragged by a gas flow (Fig. 1). For the GAP used here, the cylindrical reactor body is the cathode and the outlet the anode. This is in contrast to the classical gliding arc (GA) that has a flat configuration [9] (Fig. 1: right) and therefore only has a fraction of the inlet gas passing through the arc. The GAP, on the other hand, has 6 tangential inlets, creating a reverse vortex flow, which results in better mixing, a longer residence time and thermal insulation, which reduces heat losses and prolongs the life of the electrodes [10]. It is expected that the GAP exhibits good energy efficiency for gas conversion at atmospheric pressure, due to the active contribution of nitrogen and oxygen vibrational levels in the dissociation process. It has indeed shown good results for CO_2 conversion [8], dry reforming of methane [11] and CO_2 conversion in a CO_2/N_2 mixture but has not yet been applied for NO_x formation in an N_2/O_2 gas mixture. To our knowledge, the best results for plasma-based nitrogen fixation in literature were achieved in a milliscale classical gliding arc (ca. 1-2 % NO_x) [9]. To investigate whether the GAP could produce similar results, more insight in the underlying physics and chemistry is needed, which we try to obtain with this zero-dimensional chemical kinetics model.

2. Model

The chemistry is described by a zero-dimensional chemical kinetics model, ZDPlaskin [12]. It calculates the number densities of species as a function of time in a given volume by numerically solving a set of continuity equations (equation 1) for all individual species included in the model, based on production and loss rates.

$$\frac{dn_i}{dt} = \sum_j \left[\left(a_{ij}^R - a_{ij}^L \right) k_j \prod_i n_l^L \right] \qquad (1)$$

n_I is the density of species, a_{ij}^R and a_{ij}^L are the left and right stoichiometric coefficients for the following general reaction:

$$aA + bB \xrightarrow{k_j} cC + dD\ (+\delta\varepsilon) \qquad (2)$$

With species i for reaction j. Here A, B, C and D are the different species and a, b, c and d their respective stoichiometric coefficients. $\delta\varepsilon$ represents the potential energy change. The reaction rate constants k_j are taken from literature for heavy particle reactions, while for most electron impact reactions, they are calculated by a Boltzmann solver, BOLSIG+, built into ZDPlasKin, for which cross sections are also taken from literature.

The vast majority of the plasma conversion takes place in the column-shaped center of the reactor [13], so we focus our 0D model on this part of the reactor. We can justify the use of a 0D model, since the plasma is confined in the inner vortex of the gas flow, and it can be considered uniform, so we can assume a constant power density applied to the gas, during its residence time. Indeed, the 0D model does not include spatial variations by means of transport. Notwithstanding, the temporal dependence of the species densities can be transformed into a spatial dependence through the gas flow rate; the densities only change axially and not radially, like in a plug flow reactor [14].

Vibrational excitation of N_2 is promoted in the GAP [5] and is advantageous for more energy efficient dissociation of nitrogen, since it can help to overcome the reaction energy barrier of the non-thermal Zeldovich mechanism [15]. With that in mind, we pay special attention to the vibrational levels of nitrogen: 24 vibrational levels for nitrogen and 15 levels for oxygen were implemented in the model. The species taken into account in the model are listed in Table 1. In total, 1233 different electron impact, 423 neutral-neutral, 542 ion-neutral and 258 ion-ion chemical reactions are included, as well as 8937 vibrational-vibrational (VV) exchanges between N_2-N_2, O_2-O_2, N_2-O_2 and 1700 vibrational-translational relaxations between O_2-O_2 and N_2-N_2 (VT), between all vibrational levels.

Table 1. Species included in the model

Nitrogen species	Neutral	N_2
	Ion	N^+, N_2^+, N_3^+, N_4^+
	Vibrationally excited	$N_2(v_1 - v_{24})$
	Electronically excited	$N_2(C^3\Pi_u), N(2D), N(2P), N_2(A^1\Sigma_u)$, $N_2(B^3\Pi_g), N_2(A^3\Sigma_{uv}^4)$
	radical	N
N_xO_y species	$NO, N_2O, NO_2, NO_3, N_2O_5, N_2O_3, N_2O_4$ $NO^+, N_2O^+, NO_2^+, NO^-, N_2O^-, NO_2^-, NO_3^-, O_2^+N_2$	
Oxygen species	Neutral	O_2
	Ion	$O^-, O_2^-, O_3^-, O_4^-, O^+, O_2^+, O_4^+$
	Vibrationally excited	$O_2\ (v_1 - v_{15})$
	Electronically excited	$O\ (1D), O\ (1S), O_2\ (E_1), O_2\ (E_2)$
	radical	O

The model calculates, among others, the NO_x concentration and the energy efficiency and energy cost for NO_x formation. These quantities are compared with experiments performed in our group, for a range of different N_2/O_2 ratios and gas flow rates, and the calculation results agree well with the experiments. Therefore, we can use the model to elucidate the underlying mechanism of NO_x formation in a N_2/O_2 GAP.

3.Results and discussion

Fig. 2. illustrates the chemical pathways for NO_x-formation in the GAP (top), as predicted by our model, in comparison with the mechanisms occurring in a classical gliding arc (bottom) [5]. The GAP show a difference in the dominant formation and loss mechanisms of NO and NO_2, which is attributed to the gas temperature difference. Indeed, the latter greatly influences the reaction rate constants. The classical gliding arc operates at a gas temperature between 1000 – 1500 K [5], while in the GAP the gas temperature rises up to 3100 K [13]. The splitting of nitrogen happens in both cases predominantly (>90%) via vibrationally excited nitrogen, followed by collision with oxygen radicals ($O + N_2(v) \rightarrow N + NO; R1$), demonstrating the importance of the vibrational levels. This process is followed by the second step of the Zeldovich mechanism ($N + O_2 \rightarrow NO + N; R2$). Both processes are the most predominant reactions for the production of NO in both reactors. Whilst in a classical GA the contribution of R1 is larger than R2, the opposite is true in a GAP. In addition, our reaction analysis showed that the NO_2 production and loss reactions were more affected by the rise in gas temperature compared to the NO production. In a classical GA the reactions $O + NO \rightarrow NO_2$ ($R4$) and $NO_3 + NO \rightarrow NO_2 + NO_2$ ($R5$) contribute the most to NO_2 production, while in a GAP, the reaction $NO + O + M \rightarrow NO_2$ ($R3$) has the largest contribution (>99%). As the latter reaction also occurs in the classical GA, but other formation reactions appear even more important, this can explain why in the classical GA the NO_2 concentration at its maximum (± 5000 ppm) is comparable to the NO concentration, while in the GAP the maximum NO_2 concentration is approximatly 10 times lower (815 ppm) than the maximum NO concentration (9222 ppm).

Since the vibrational levels of nitrogen play a significant role in the more energy efficient pathway for NO_x production, by lowering the energy barrier for N_2 splitting, the VDF of N_2 is very important. Therefore, we have investigated the VDF as a function of pressure, N_2/O_2 ratio, gas temperature, flow rate and power.

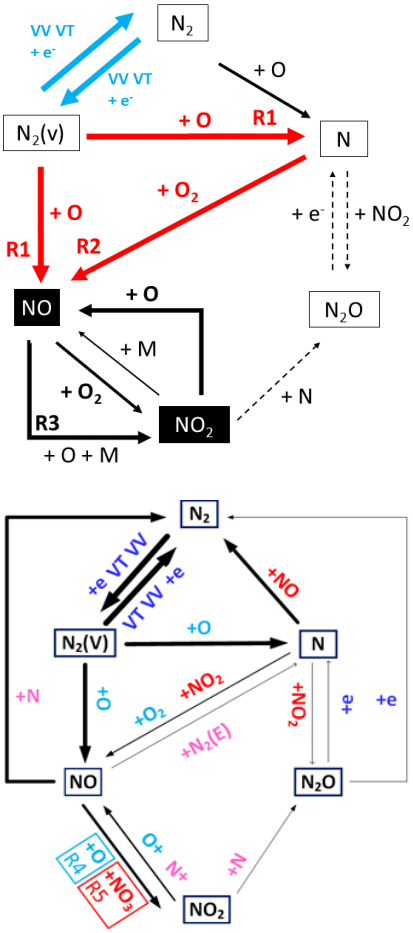

Fig. 2. Dominant formation and loss processes of NO and NO_2 in a GAP (top) and in a classical GA (bottom) [5]. In case of the GAP, a 50/50 O_2/N_2 mixture, a flow rate of 7.5 l/min, 1 bar and a power of 175 W are used, while for the classical GA, a 50/50 O_2/N_2 mixture, a flow rate of 2 l/min, 1 bar and a power of 46 W are used, resulting in the same SEI of 1.4 kJ/L. The thickness of the arrow lines corresponds to the net time-integrated rate of the reaction. The Zeldovich mechanism is indicated in red.

Our model reveals that when the reactor conditions give rise to a non-equilibrium in the vibrational distribution function (VDF), the energy consumption is the lowest and the conversion the highest, indicating that the N_2/O_2 ratio allows for effective use of the vibrationally excited N_2. The simulations show that a lower pressure has a positive impact on the conversion (8.5% at 10 mbar; 1.5% at 1 bar). Nevertheless, working at reduced pressure is less convenient for industrial application.

The optimum simulated (and measured) conversion of N_2 (1.5%) and energy consumption (3.8 MJ/mol) in the GAP are comparable to other reported non-thermal plasma reactors for nitrogen fixation [4] (at 1 bar; 10L/min; 1/1 N_2/O_2; 415 W), but they are not yet competitive with the industrial Haber-Bosch production process. The biggest challenge for the future will be to keep the energy consumption low, while improving the conversion. Insights in the underlying chemistry can redirect our focus on specifically restricting the processes that limit the NO_x production.

The intrinsic potential of GA-based nitrogen fixation is promising, due to its flexibility, capacity to be coupled to sustainable energy sources, non-equilibrium and use of air as inlet gas. By gaining further insight into the underlying processes, we hope to be able to improve plasma-based nitrogen fixation.

4. References

[1] B. S. Patil, Q. Wang, V. Hessel, and J. Lang, Catal. Today **256**, 49 (2015).

[2] M. M. M. Kuypers, H. K. Marchant, and B. Kartal, Nat. Rev. Microbiol. (2018).

[3] B. S. Patil, F. J. J. Peeters, G. J. van Rooij, J. A. Medrano, F. Gallucci, J. Lang, Q. Wang, and V. Hessel, AIChE J. **64**, 526 (2018).

[4] A. Bogaerts and E. C. Neyts, ACS Energy Lett. **3**, 1013 (2018).

[5] W. Wang, B. Patil, S. Heijkers, V. Hessel, and A. Bogaerts, ChemSusChem **10**, 2110 (2017).

[6] B. S. Patil, *Plasma (Catalyst) – Assisted Nitrogen Fixation : Reactor Development for Nitric Oxide and Ammonia Production* (2017).

[7] T. Nunnally, K. Gutsol, A. Rabinovich, A. Fridman, A. Gutsol, and A. Kemoun, J. Phys. D. Appl. Phys. **44**, (2011).

[8] M. Ramakers, G. Trenchev, S. Heijkers, W. Wang, and A. Bogaerts, ChemSusChem **10**, 2642 (2017).

[9] B. S. Patil, J. Rovira Palau, V. Hessel, J. Lang, and Q. Wang, Plasma Chem. Plasma Process. **36**, 241 (2016).

[10] S. C. Kim and Y. N. Chun, Environ. Technol. **35**, 2940 (2016).

[11] E. Cleiren, S. Heijkers, M. Ramakers, and A. Bogaerts, ChemSusChem **10**, 4025 (2017).

[12] L. C. P. S. Pancheshnyi, B. Eismann, G.J.M. Hagelaar, Univ. Toulouse, LAPLACE, CNRS-UPS-INP, Toulouse, Fr. (2008).

[13] G. Trenchev, S. Kolev, W. Wang, M. Ramakers, and A. Bogaerts, J. Phys. Chem. C **121**, 24470 (2017).

[14] R. Bogaerts, A. Kozak, T. van Laer, K. Snoeckx, Faraday Discuss. **183**, (2015).

[15] C. S. Kalra, Y. I. Cho, A. Gutsol, and A. Fridman, **1** (2005).