NO_x production from N_2 by means of a 3D gliding arc plasmatron

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Abstract: Low-temperature plasmas are gaining a lot of interest for environmental and energy applications. A large research field in these applications is the conversion of atmospheric nitrogen into valuable compounds, that is, so-called nitrogen fixation, which is gaining increased interest, owing to the essential role in the nitrogen cycle of the biosphere. Plasma technology, and more specifically gliding arc plasma, has great potential in this area. Since N_2 is a very stable molecule, two key performance indicators for the research on plasma-based N_2 fixation are the NO_x yield and the energy efficiency. We employ here a novel type of gliding arc plasma reactor, the gliding arc plasmatron (GAP), and we measured the NO and NO_2 yields and the corresponding energy efficiency for different N_2/O_2 ratios. Moreover, in order to get insight in the underlying mechanisms, we developed a detailed chemical kinetics model for the GAP operating at atmospheric pressure for NO_x synthesis. Based on the underlying chemistry, the model allows us to propose solutions on how to further improve the NO_x formation by gliding arc technology.

Keywords: Nitrogen fixation, gliding arc, plasma technology, environmental and agricultural applications.

1. Introduction

Green chemistry and sustainability are high on the agenda to cope with future environmental challenges, including the production of fertilizers. Nitrogen is an essential component for all forms of life, because it is required to biosynthesize basic building blocks of plants and living organisms. The latter can consume nitrogen in a usable form, obtained by chemical reaction with oxygen or hydrogen or carbon. Therefore, we find nitrogen compounds in plant cells, amino acids, proteins and nucleic acids. Although 78.08% of air is composed of molecular nitrogen, this most abundant nitrogen source is not available to the majority of living organisms because it is extremely difficult to break its triple bond, which makes almost any first reaction step of the conversion very energy demanding. As a result, nitrogen fixation (NF), which converts nitrogen molecules into simple nitrogen compounds, such as ammonia or nitric oxide that can be further used as precursors for the (bio)synthesis of more complex molecules, is very significant. However, it is the most challenging step of nitrogen utilization by living organisms [1].

Currently, the most significant process to produce fertilizers is the Haber–Bosch (H–B) process, i.e., the binding of nitrogen with hydrogen to produce ammonia at high pressure and temperature [2]. From an energy point of view, industrial ammonia synthesis is the most energy intensive chemical process. The H–B process consumes 1–2% of the world's total energy production and utilizes 2–3% of the total natural gas output. Furthermore, it emits more than 300 million metric tons of carbon dioxide [3,4]. Indeed, the high energy intensity and environmental concerns triggered by industrial NF, it becomes imperative to develop and integrate more sustainable processes [5,6]. Several alternative (non-conventional) technologies are being investigated, such as biological NF and NF with metallocomplex homogeneous catalysts under ambient pressure [7-9], but also plasma technology. Plasma technology is considered as a "green" technology with great potential for reducing the environmental impact and improving the energy efficiency of NF, as the dependency on fossil fuels during this process is greatly reduced and no greenhouse gas emissions take place.

For N_2 fixation, either thermal or non-thermal plasma can be used. However, atmospheric non-thermal plasmas offer a higher efficiency, because of their capacity to induce chemical reactions within gases with a limited energy cost at ambient pressure and temperature. Gliding arc plasmas are among the most effective and promising plasmas for gas conversion [10] because they offer benefits of both thermal and non-thermal discharges. They are typically considered as "warm" discharges, and vibrational excitation of the molecules is seen as the most efficient way to assist the conversion or synthesis [11]. Although the gliding arc discharge seems a good match for NF, only limited studies have been performed [refs in 10]. Moreover, most of these studies are performed with classical gliding arc reactors. The latter configuration, however, has a few disadvantages. Indeed, it is incompatible with industrial systems because of its 2D geometry, the gas treatment is non-uniform because only a limited fraction of the gas passes through the arc, and the residence time inside the plasma is quite short. To overcome these drawbacks, a 3D gliding arc reactor with specific gas-flow configuration, also called gliding arc plasmatron (GAP), was recently developed [12]. This reactor design is very promising because it can be implemented in industry and the specific gas flow configuration ensures the gas treatment to be more uniform, and it forces a longer residence time inside the arc plasma. Therefore, in this study we performed a detailed, combined experimental and computational study, to explore the possibilities of the GAP for N_2 fixation. We studied in detail the effect of the total flow rate, gas composition, i.e., feed ratios of N_2/O_2, current, pressure and anode length, on the NO_x yield and corresponding energy cost and energy efficiency of the process. Furthermore, the experiments are supported by chemical kinetics simulations and by simulations of the gas flow and the arc plasma movement, to obtain in-depth knowledge on the underlying mechanisms.

2. Experimental setup

The experiments were performed with a GAP, as developed recently by Nunnally et al. [12]. A schematic drawing of the GAP is illustrated in figure 1. This three-dimensional gliding arc reactor is making use of forward and/or reverse vortex flow. The gas flows in the reactor through tangential inlets. An arc is formed between both electrodes (purple in figure 1). In the case of a reverse vortex flow, the cold gas first flows upwards close to the walls (solid spiral in figure 1), creating an isolating and cooling effect, and then flows downwards (in a reverse vortex; dashed spiral in figure 1) where it mixes with the arc plasma, resulting in more energy-efficient reactions. For these experiments, we used four different stainless steel electrodes, i.e. a high voltage electrode and three grounded electrodes. The high voltage electrode, which acts as the cathode, has a length of 20.30 mm and a diameter of 17.50 mm. All grounded electrodes, acting as anode, have the same length (16.30 mm) but their diameter is 7.08, 14.20, and 17.50 mm, respectively. There is a 3 mm gap between the cathode and anode. A mixture of N_2 and O_2 is used as feed gas.

A photograph and diagram of the entire experimental system is shown in figure 2. Two mass-flow controllers (Bronkhorst) were used to feed N_2 and O_2 (with a purity of 99.9%) into the GAP and no preheating of the gas was applied.

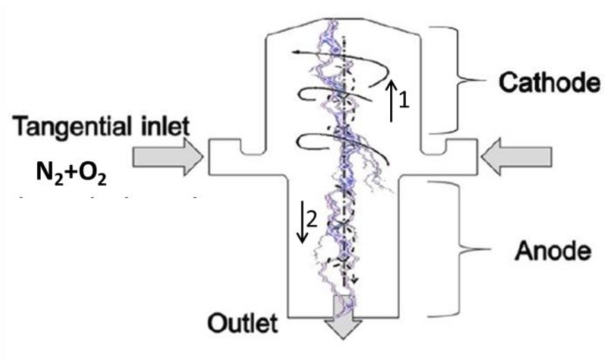

Fig. 1. Schematic picture of the gliding arc plasmatron in reverse vortex flow configuration. Both the forward and reverse vortex flows are indicated (with full and dashed spirals, respectively). This vortex flow configuration stabilizes the arc discharge (indicated in purple) in the center of the reactor and forces the reverse gas flow to go through the plasma.

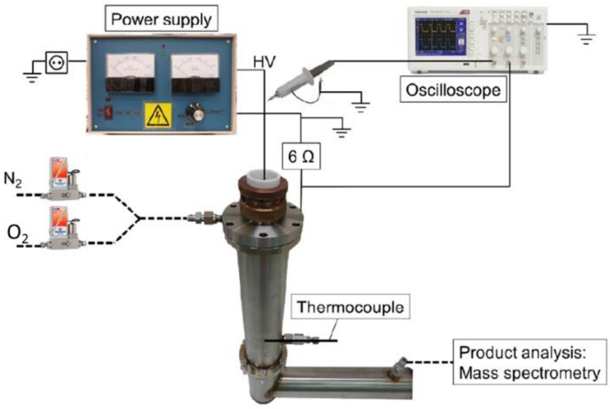

Fig. 2. Schematics of the entire experimental system.

The individual gas flow rates were varied between 1 and 22 L/min, providing a total gas flow rate between 8 and 30 L/min. The reactor was powered by a DC current source type power supply (APS-Advanced Plasma Solutions). The plasma voltage and current were measured by a high-voltage probe (Tektronix P6015A) and a current sense resistor of 10 W, respectively. The electrical signals were sampled by a two-channel digital storage oscilloscope (Tektronix TDS2012C). The current was varied between 0.2 and 0.4 A.

In the reactor tube, which was placed after the GAP, a thermocouple was inserted to measure the temperature of the effluent stream. The output gas composition was analyzed online by mass spectrometry (Hiden Analytical Limited). NO and NO_2 were the detected products and their concentrations were determined using a series of calibration gas mixtures (QGA Pro v1.6).

3. Description of the modeling work

To elucidate the underlying mechanisms of the gliding arc assisted NO_x synthesis, we developed a 0D plasma chemistry model, which allows describing the behavior of a large number of species, and incorporating a large number of chemical reactions, with limited computational effort. In this 0D chemical kinetics model, called ZDPlaskin, balance equations were used to calculate the time-evolution of the species densities, taking into account the various production and loss terms by chemical reactions. From these species densities, the NO_x yield can be obtained, and in combination with the plasma power and gas flow rate (and thus the specific energy input; SEI), this also yields the energy cost and energy efficiency. Besides that, the model also calculates the gas temperature, the electron density, and electron temperature. Moreover, a 3D gas flow pattern in the reactor setup is calculated, with COMSOL Multiphysics Simulation Software, based on solving the Navier–Stokes equations, assuming a turbulent flow.

4. Results and discussions

In figure 3 the performance of the GAP was investigated at a constant total flow rate of 10 L/min, and by varying the N_2 fraction from 10% to 90%, corresponding to an N_2/O_2 ratio of 0.11 to 9. All experiments were performed three times and averages of at least 100 voltage–current (V–I) cycles were used to obtain the final power consumption value. The NO and NO_2 concentration in ppm are shown in the left and right axis, respectively. The concentration of NO increases with increasing N_2 fraction up to 80% (N_2/O_2 ratio of 4), after which the NO concentration declines. In fact, the decrease in NO concentration is due to the reduced oxygen flow. Indeed, both nitrogen and oxygen are needed for NO formation. The NO_2 concentration attains its peak at a feed ratio of 50% N_2, and above that value, the NO_2 concentration steadily declines, because of the reduced availability of oxygen molecules surrounding NO, for its further oxidation to NO_2. Note that at higher currents, the maximum NO_2 concentration occurs at 40% N_2. This can be explained by our modeling work, showing that different reactions are dominant at different conditions. The effect of the total gas flow rate on the NO_x concentration is illustrated in Figure 4. The experiments were performed at 80% nitrogen fraction. The NO concentration increases with total flow rate up to 12 L/min, after which it decreases. On the other hand, the NO_2 concentration decreases upon higher gas flow rate. The highest total NOx concentration in our setup is reached at a N2 fraction of 70 %, with a total flow rate of 10 L/min, and has a value of 1.5 % (or 15,288 ppm); yielding 1.3 % and 0.19 % for NO and NO2, respectively. Patil et al. investigated NOx formation in a pulsed power milli-scale classical (planar) gliding arc reactor [13,14], and they reported the highest NOx concentration (at a flow rate of 1 L/min and a 1/1 N2/O2 ratio) of 2 %, with about 0.9 % NO and 1 % NO2. The formation of NO2 from dry air in a classical gliding arc plasma was investigated by Bo et al [15]. The highest amount of NO2 produced was 0.7 %. Compared to the above studies, the NOx yield obtained in our GAP is very competitive. Further enhancement might be possible by improving the reactor design.

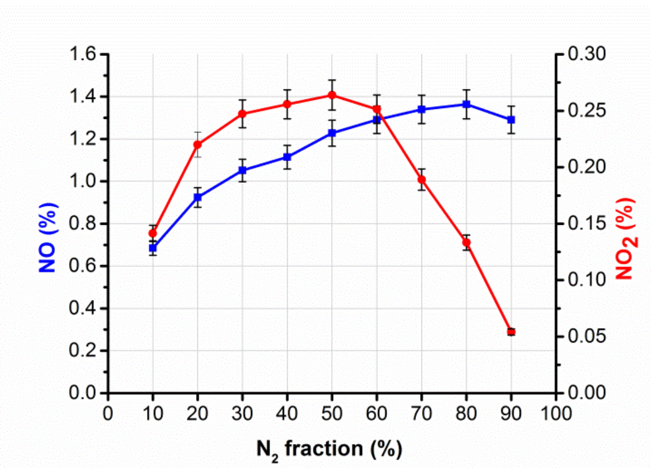

Fig. 3. Concentration of NO and NO_2 for different N_2 fractions in the feed gas, at a total flow rate of 10 L/min.

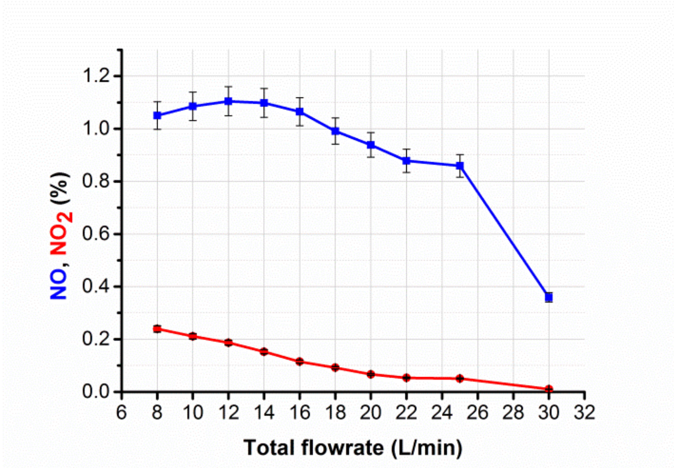

Fig. 4. Concentration of NO and NO_2 at different total flow rates, with N_2 fraction of 80%.

The energy efficiency and energy consumption are shown in figure 5. At the highest total NO_x concentration, i.e., total flow rate of 10 L/min and N_2 fraction of 70 %, the energy efficiency and energy consumption are 2% and 3.3 MJ/mole, respectively.

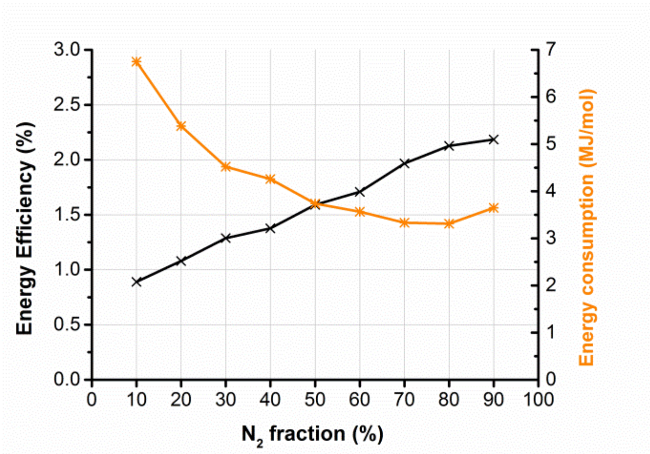

Fig. 5. Energy efficiency and energy consumption for different N_2 fractions in the feed gas, at a total flow rate of 10 L/min.

The results reported in the literature vary a lot among different plasma types [16]. The NO yields are typically in the low % range, with energy consumption values varying from 0.3 up to 1600 MJ/mol. Fore example, DBDs show relatively low NOx yield (0.5%), with relatively high energy cost (18 MJ/mole). Thermal plasmas provide reasonable NOx yields but typically at fairly high energy costs. For example the reported energy cost for arc discharges, laser-produced plasmas, RF discharges, and arc jets are 10.6, 8.96, 11.6 and 4 MJ/mole [16]. Indeed, the energy in a thermal system is distributed over all degrees of freedom, including those not effective for the NOx synthesis.

GA discharges have been applied by Patil et al. [13, 17] with results up to 2% NO_x yield and 2.8 MJ/mole energy consumption. Hence, our first results are quite competitive. We believe that by further exploring our GAP setup, the results will be even more promising.

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