Non-equilibrium high flow rate plasma reactor for nitrogen fixation

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Abstract: Plasma-based nitrogen fixation is gaining significant attention due to the increased demand in finding alternative solutions to the carbon-intensive fossil fuel based Haber-Bosch process. In this work we present a novel low current (150 mA – 1100 mA) plasma reactor operating in a flow range of 100 – 300 ln/min at atmospheric pressure, for the production of NO and NO_2. The reactor has the potential to combine the non-equilibrium effects of low current discharges with very high flow rates in order to optimize the process.

Keywords: plasma, non-equilibrium, low current, high flow rate, nitrogen fixation.

1. Introduction

The Haber-Bosch (HB) process currently used for industrial artificial fertilizer production is responsible for the emission of more than 300 million tons of CO_2 annually [1]. The transition to a carbon-free economy creates the urgent need for finding an alternative way for the production of chemical fertilizers. Plasma-based nitrogen fixation has attracted significant interest in the past years due to its compatibility with renewable electricity and its turn-key capabilities. The HB process has been significantly optimized, leading to a very low energy cost (EC) for nitrogen fixation into NH_3 (0.5 MJ/mol) [2]. This also presents the biggest challenge for the plasma-based nitrogen fixation: the energy cost of the process experiences a reverse correlation between EC and production rate (PR). Furthermore, plasma-based nitrogen fixation is feasible mostly when the target product is NO_x ($NO + NO_2$) rather than NH_3. Vervloessem et al. showed that in a pulsed spark discharge, the EC of NO_x production from air can drop to a mere 0.4 MJ/mol, at the expense of the PR, which was 0.3 g/h [3]. Jardali et. al. performed studies with a rotating gliding arc plasma, achieving an EC of 2.5 MJ/mol with an appreciable PR of 7 g/h in oxygen-enriched air [4]. This result was further improved by the application of an effusion nozzle by Van Alphen et al,, yielding 2.1 MJ/mol and 7.4 g/h [5]. Significantly better results were achieved by Kelly et al., where a microwave discharge with oxygen-enriched air gave an EC of 2.0 MJ/mol with PR of 85.9 g/h [6]. Very recently, we have shown that increasing the pressure of the plasma process leads to a significant performance improvement in a gliding arc reactor, with EC as low as 1.8 MJ/mol and PR of 68.9 g/h in oxygen-enriched air and a pressure of 3 barg [7].

In the present work, we developed a novel reactor employing a different strategy to the problem. We use a low current, high flow rate reactor with the aim of increasing the PR and decreasing the EC. The high flow rates of the plasma feed gas provide higher PRs: even at low concentrations of NO_x produced, a high flow rate enables a high PR. This effect in combination with elevated pressure can potentially bring plasma-based nitrogen fixation towards industrial applications.

2. Experimental setup

The reactor operates in a pin-to-pin configuration, and the plasma is stabilised by a swirling flow. A schematic of the experimental setup is presented in Figure 1.

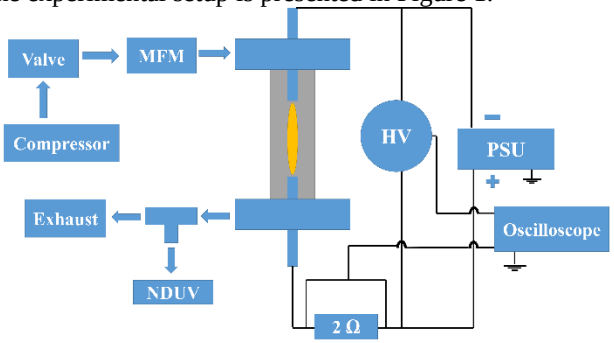

Figure 1. Schematic of the experimental setup.

An air compressor is connected to a control valve, which in turn is connected to the reactor through a mass flow meter (MFM) (IFM SD6500). The voltage is measured with a high voltage probe (HV) (Tektronix P6015A) and the current is obtained by measuring the voltage drop across a shunt resistor with 2 Ω resistance. Both signals are recorded with a two channel oscilloscope (Keysight InfiniiVision DSOX1102A). The DC current is supplied with a current-controlled power supply unit (PSU) (Technix SR12KV-10KW) with negative output polarity. The current was varied between 0.15 A and 1.1 A, and the flow rate of air between 100 ln/min and 300 ln/min. The NO and NO_2 concentrations are measured by non-dispersive ultraviolet spectroscopy (NDUV) using WiTec ULTRA-Sens NOx AK100 TBH gas analyzer.

The plasma power was calculated by averaging the instantaneous power measurements as:

$$P\,[W] = \frac{1}{n}\sum_{i=1}^{n} V_i \times I_i = \frac{1}{n}\sum_{i=1}^{n} V_{plasma_i} \times \frac{V_{shunt_i}}{R_{shunt}} \quad (1)$$

Where V_{plasma_i} is the voltage drop across the plasma discharge, V_{shunt_i} is the voltage drop across the shunt resistor and R_{shunt} is the resistance of the shunt resistor. The EC is calculated as:

$$EC\ \left[\frac{MJ}{mol}\right] = \frac{P\,[W] * 22.4\left(\frac{Ln}{mol}\right) * 60\left(\frac{s}{min}\right)}{Total\ NO_x[\%] * Flow\ rate\ [ln/min]} \times 10^{-6}\left[\frac{MJ}{J}\right] (2)$$

The PR is calculated as follows:

$$PR_{NO_x}\left[\frac{g}{h}\right] = \frac{\left(NO[\%] * 30\left[\frac{g}{mol}\right] + NO_2[\%] * 46\left[\frac{g}{mol}\right]\right) * flow\ rate\ [ln/min]}{22.4\left[\frac{Ln}{mol}\right]} * 60\left[\frac{min}{h}\right] \quad (3)$$

In eqs. 2 and 3, the change of the volume due to the stoichiometry of NO_x formation is neglected because the main product is NO, while NO_2 is formed at very low amounts. In order to calculate the power, three scopes are taken and then averaged for each of the experimental conditions. The NO_x concentration was measured after the reactor has achieved steady state, and there are no changes in concentration as function of time. In addition, each of the experiments was also conducted three times in order to reduce the uncertainty. The experiments were conducted for two distances between the electrodes: d = 7 cm and d = 14 cm.

3. Results and discussion

Under all experimental conditions, relatively low concentrations of NO_x were achieved as function of the current, gas flow, and electrode distance. The results for the NO_x concentration as function of the current for different flow rates are presented in Figure 2. The maximal NO_x concentration does not exceed 0.25 % (Figure 2 a, 14 cm, 1100 mA, 100 ln/min) and the minimal was 0.06 % (Figure 2b, 7 cm, 150 mA, 300 ln/min). Under all conditions, the NO_x concentration increases nearly linearly as a function of the current, and decreases as a function of the flow rate. There is also a significant decrease in the NO_x concentration as a function of decreasing distance between the electrodes. As mentioned above, the maximum concentration (0.25 %) is achieved for 100 ln/min at 1100 mA for d=14 cm, while the same parameters at d=7 cm yielded only about half of this value (0.13 %). This observation can be explained by the effect of the residence time on the conversion process: shorter distances between electrodes reduce the residence time of the gas in the reactive part of the plasma.

In turn, at a given distance, increasing the gas flow rate also reduces the residence time of the gas in the reactive region of the plasma, leading to an additional reduction in NO_x concentration. As the current is increased, the temperature inside the reactor also increases, and as a result the conversion is also increased.

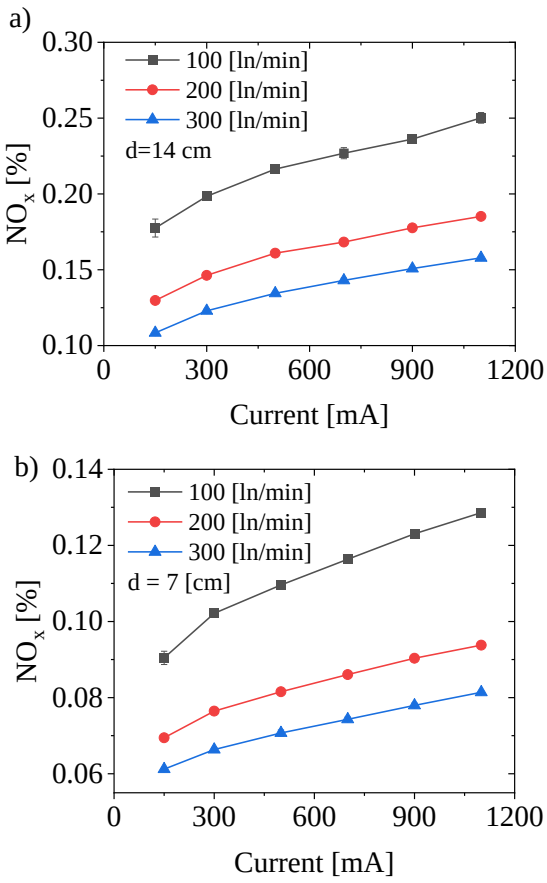

Figure 2. NO_x concentration as function of the current, for different flow rates and for two distances between the electrodes: a) d = 14 cm and b) d = 7cm. Error bars are included, but are too small to be visible

Even though the conversion in the presented process is low, increasing the pressure can significantly improve the performance of plasma-based nitrogen fixation, as shown by Tsonev et al. [7], which can optimize the process in future studies. Combining low currents with high pressure and flow rate can lead to very low EC and significantly increase the PR. Due to the high flow rates, the PR of NO_x is quite high, as compared to literature, despite the low concentrations. The production rate for d = 14 cm as function of the current, for different flow rates, is presented in Figure 3.

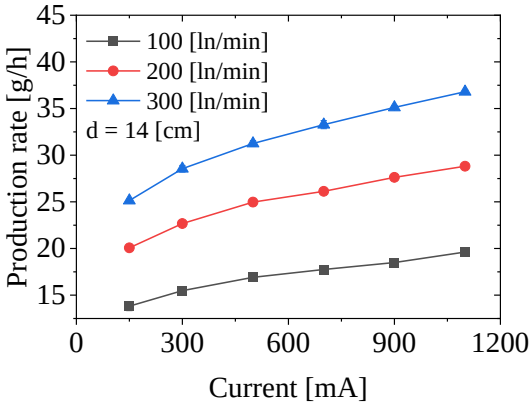

Figure 3. Production rate as function of the current for different flow rates, at a distance between the electrodes of 14 cm. Error bars are included, but are too small to be visible.

We can see that even though the concentration decreases with the flow rate, the PR is significantly increased, reaching nearly 37 g/h at a current of 1100 mA and flow rate of 300 ln/min. Even at concentrations as low as 0.11 % at 150 mA, the PR has an appreciable value of 25 g/h, indicating the importance of operating the plasma reactor in high flow rate regimes. Furthermore, industrial applications usually employ high flow rates, making this reactor appealing for industry.

As mentioned in the introduction, the biggest advantage of the HB process is the low EC. This parameter is also the most essential for the plasma-based nitrogen fixation, as the energy efficiency determines whether the technology can be implemented in the current energy grid. The EC as a function of the current for different flow rates is presented in Figure 4, for a distance between the electrodes of 14 cm (a) and 7 cm (b). Evidently, the EC as a function of the current has significantly different behaviour for the different electrode distances. For the electrode distance of 14 cm (Figure 4 a), the energy cost is nearly constant regardless of the increasing current, while for 7 cm (Figure 4 b) there is a linear trend with a positive slope. For both electrode distances, the EC decreases with increasing flow rate. As we explained earlier, increasing the distance between the electrodes from 7 to 14 cm leads to doubling of the NO_x concentration.

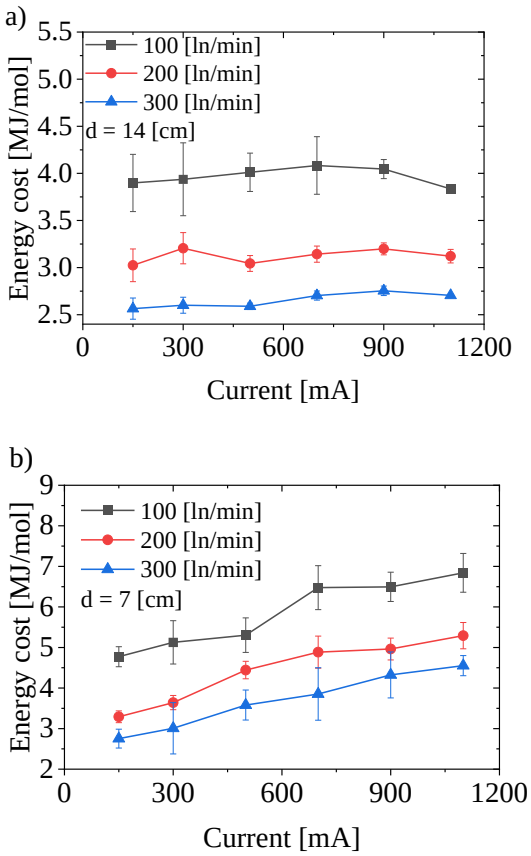

Figure 4. Energy cost as a function of the current for different flow rates, at two distances between the electrodes: a) 14 cm and b) 7cm.

It is interesting to see that this doubling of the concentration does not correlate to a doubling of the power (which increases less than twice). The power as function of current for 300 ln/min and different electrode distance is presented in Figure 5. In both cases nearly linear dependence is observed as function of the current. The largest increase in power as function of the electrode distance is observed in the low current region (> 450 mA) being close to 230 W for 150 mA. For higher current (< 450 mA) the increase in power becomes even smaller being close to 100 W for 1100 mA. This leads to lower EC values for the 14 cm case than the 7 cm one. The power does not increase linearly with distance, which leads to an EC as low as 2.6 MJ/mol for the lowest current at d=14 cm and a flow rate of 300 ln/min (Figure 4 a). This value is comparable with the results in [4] where the experiments were performed in oxygen-enriched air, while the reactor in this work operates in pure air – hence without hidden EC required for enrichment.

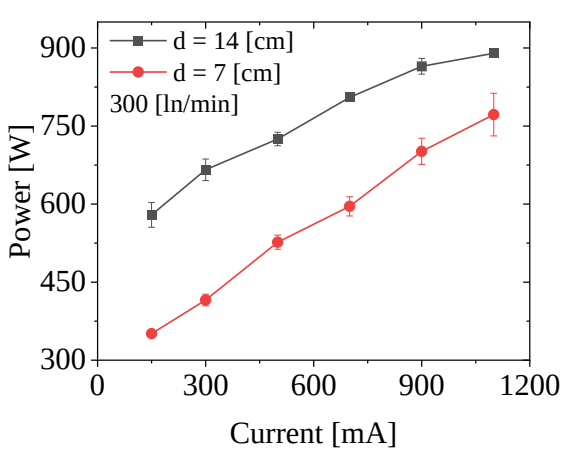

Figure 5. The power as function of current for 300 ln/min and different electrode distance. Error bars are included, but are too small to be visible for some of the points.

The nearly constant EC as a function of the current for the 14 cm case also gives promising results for the scalability in terms of current, because at 1100 mA the energy cost is 2.7 MJ/mol, which is not significantly higher than 2.6 MJ/mol at 150 mA, but coincides with the highest PR obtained in this work.

4. Conclusions

A novel plasma reactor operating at high feed gas flow rates, just using air (100 – 300 ln/min) and low currents (150 – 1100 mA) was developed for nitrogen fixation. The reactor shows promising results for scaling up plasma technology, reaching production rates as high as 37 g/h with energy cost of 2.7 MJ/mol, or energy cost as low as 2.6 MJ/mol with production rate of 27 g/h. The reactor has managed to achieve energy costs as low as the ones previously achieved only with oxygen-enriched feed gas, and with nearly 4 times higher production rate.

The results show that the power does not scale linearly with the distance between the electrodes, while there is a doubling in the NO_x concentration between 14 cm and 7 cm.

We believe that further optimisation of such reactor is relatively simple. Increasing the pressure and further increasing the distance between the electrodes could potentially make plasma-based nitrogen fixation a significant competitor to the Haber-Bosch process.

5. Acknowledgments

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6. References

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