Contributions of increased pressure on the above-atmospheric plasma-driven synthesis of ammonia via dual-polarity nanosecond power delivery

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Abstract: In developing of an energy efficient alternative to the Haber-Bosch process, above-atmospheric non-thermal plasma ammonia synthesis can offer insight into the bulk mechanisms of plasma-catalytic processes. Experiments were performed from 1-3 bar_{abs} using fast rise-time nanosecond pulse discharges between pin electrodes. Emission spectra were monitored to passively characterize the plasma qualitatively. Ammonia concentrations up to 700 ppmV were observed at raised pressures without a catalyst.

Keywords: Plasma processing, plasma catalysis, nanosecond pulsed power, ammonia synthesis.

1. Introduction

The demand for clean, carbon-free synthesis of value-added fuels is increasing as the world transitions towards integrating hydrogen-centred energy storage strategies. Plasma-assisted catalytic synthesis of ammonia and methane have drawn attention due to the utilization of similar operating conditions to the production of green hydrogen through electrolysis [1]. Previous experimental investigations into plasma chemistry demonstrated that the decrease in overall collisions between heavy particles in a vacuum limits the required number of useful collisions to initiate rate-limiting reaction steps in the bulk plasma [2].

Based on this understanding, most plasma-assisted catalytic ammonia synthesis research has been conducted using dielectric barrier discharges (DBDs) at ambient conditions or raised gas temperatures. DBD reactor setups and associated alternating current (AC) and pulsed AC power deliveries are flexible, simple-to-monitor systems that have given insight into the mechanisms of nitrogen dissociation in the ammonia production pathway [3].

The first pathway of interest in this work involves the electronic excitation of ground N_2 to its metastable state (N_2 ($A^3\sum_u^+$)) and the subsequent catalytic surface dissociation [4]. Another mechanism of interest requires the plasma-phase dissociation or ionization of N_2 and collisions with hydrogen gas. The required power delivery to the plasma differs depending on the dominant pathway desired and the gas conditions of the reactor.

Previous work in has avoided increases in reactor pressure above atmospheric, limiting the thermodynamic equilibrium conversion of mixed N_2-H_2 systems to ammonia. These harsher conditions restrict on reactor designs and increase the breakdown voltage required to ignite the plasma phase. Through simplified reactor geometry and nanosecond pulse generation, these engineering constraints have been overcome to identify the synergistic and antagonistic contributions that increased pressures exhibit for plasma-driven synthesis of ammonia.

2. Experimental Design

Raised pressure experiments were conducted in a pin-to-pin reactor cell rated for pressures up to 10 bar_{abs}. The interelectrode distance for these pins was fixed at 2 mm, and pressures in the system varied from 1-3 bar_{abs}, the latter being the upper range of ignition conditions for the power delivery device. Gas was delivered through the system at a total flow rate of 60 SCCM set by mass flow controllers (Brooks Instruments) for N_2 and H_2 delivery. Volumetric feed ratios were selected between 5:1 N_2:H_2 to 1:3 N_2:H_2, and the system pressure was held by a pneumatic back pressure regulator (Equilibar).

Power was delivered to the reactor cell through a custom-made high voltage power supply internal to the Catalytic and Plasma Process Engineering group at McGill University [5]. The power supply provides two synchronized 4.0-8.5 kV pulses with rise times ranging from 20-40 ns at frequencies of 1000-5000 Hz. Electrical diagnostics of these pulses were obtained through two passive 1000X high-voltage probes (Tektronix) and a wideband current transformer (Pearson Electronics) and processed through a digital oscilloscope (Picoscope).

The plasmas (Fig. 1) were monitored through a flat optical port at the front of the reactor by a UV-Vis spectrometer (OceanInsight). The spectra were obtained for 15-minute experiments using an integration time of 10 seconds to continuously monitor the relative emission spectra.

The concentration of NH_3 produced from plasma phase reaction mechanisms was monitored using a calibrated on-line mass spectrometer (Pfeiffer GSD301).

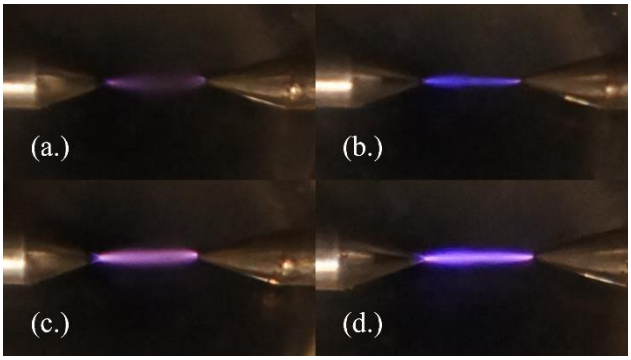

Fig. 1: Images of the plasma formed between two pin electrodes at atmospheric pressure (p=1 bar_{abs}). The diffuse 1:1 N_2:H_2 mixture (a.) and pure N_2 (b.) plasmas were produced at lower voltages than the sparking 1:1 N_2:H_2 mixture (c.) and pure N_2 (d.) plasmas.

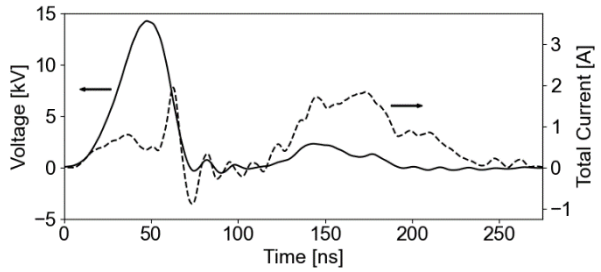

Fig. 2: Pulse characterization of the nanosecond pulser and corresponding current discharge of a 1:1 N_2:H_2 gas mixture at p=3 bar_{abs} and d=2 mm.

3. Methodology

The electrical instantaneous power input (P) into the plasma was calculated through equation 1 using the instantaneous voltage (V) and current (I) readings.

$$P(t) = I(t)V(t) \quad (1)$$

Using the calculated power, the cumulative energy input (E_c) at any time (t_1) into the plasma was calculated as the area underneath the instantaneous power curve.

$$E_c = \int_0^{t_1} I(t)V(t)dt \quad (2)$$

Evaluating this energy value from the onset of a pulse to the end of the pulse results in the energy per pulse (E_p), which can then be related to an overall power delivery ($\bar{P}_{plasma}$) by multiplying with the pulse frequency.

$$\bar{P}_{plasma} = E_p f \quad (3)$$

The ammonia concentration (c_{NH3}) in the outlet was calculated using the 16 m/q signal (I_{16}), Argon's 40 m/q signal (I_{40}) as a standard, and a calibration factor (CF_{NH3}) obtained.

$$c_{NH_3} = CF_{NH_3} \frac{I_{16}}{I_{40}} c_{Ar} \quad (4)$$

The energy efficiency of ammonia synthesis (EE_{NH3}) was defined as the ratio of the mass production rate of ammonia ($\dot{m}_{NH_3}$) divided by the plasma power. We report these values in units of g_{NH3} kWh^{-1}.

$$EE_{NH_3} = \frac{\dot{m}_{NH_3}}{\bar{P}_{plasma}} \quad (5)$$

4. Results and Discussion

The uniform waveforms produced from the pulsers can sustain processing plasmas up to 3 bar_{abs} at an interelectrode distance of 2 mm. While these pulsers can form both diffuse and spark regimes at standard conditions [6], the higher pressure increased the rate of thermalization, preventing diffuse regimes. Electrical diagnostics of the pulser in operation at 3 bar_{abs} is displayed as Fig. 2.

The total current measurements contain a high capacitive current that resulted from the sharp rise time of the pulser. After reaching the peak voltage of the pulser, a streamer formed between the two pin electrodes. This bridged a conductive channel in which a large instantaneous current passed between the two electrodes. This was followed by a secondary streamer which was sustained longer than the primary streamer and delivers additional energy to the plasma, extending the lifetime of the species of interest.

The energy delivery to the plasma can be further explained using the cumulative energy delivered to the plasma over the timespan of a pulse, as shown in Fig. 3. A large portion of the delivered energy is attributable to the capacitive current produced as the voltage rose to ignition. After ignition, the instantaneous power of the pulse rose, resulting in an increased slope of the cumulative energy plot. An additional surge of energy was provided in the secondary streamer, which may have resulted in a large portion of the energy per pulse being delivered into excitation of chemically useful species and vibrational excitation of molecules. The spread of energy per pulse indicates that the amount of conductive current per pulse is variable. The magnitude of the instantaneous current delivered in the primary and secondary streamers may be dependent on memory effects between pulses. Despite this variability, the average energy per pulse may provide an adequate description of the energy deposited for plasma processing.

The optical emission spectra of the plasma at three different pressures, shown in Fig. 4, includes information about the relative concentrations of excited states present. The second positive system of N_2 (SPS) includes a series of peaks, corresponding to the $C^3\Pi_u$-$B^3\Pi_g$ electronic transition. While no direct information about the metastable N_2 ($A^3\sum_u^+$) comes from this peak, the relative concentration of the metastable state can be inferred due to deexcitation pathways from $B^3\Pi_g$-$A^3\sum_u^+$ and calculated average electron energy of the plasma. The dominant band (0-0 transition) of the SPS exists at 337 nm and decreases in relative magnitude to the 656 nm peak as the pressure of the system increases.

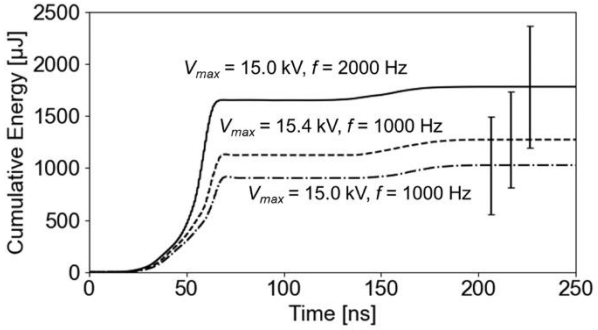

Fig. 3: Cumulative energy per pulse delivered to the plasma from the nanosecond pulser with a 1:1 N_2:H_2 ratio gas flow at p=2.5 bar_{abs} and d=2 mm.

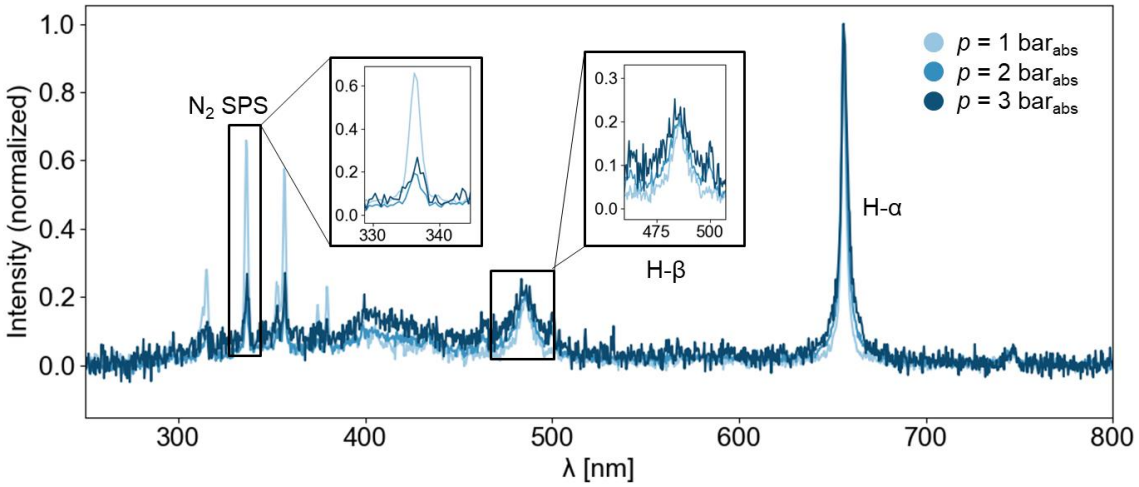

Fig. 4: Emission spectra of a plasma discharge sustained at various pressures at a set pulse frequency (f=1000 Hz) and N_2:H_2 feed ratio (1:1).

The 656 nm peak corresponds to the Balmer series transition (3-2) of dissociated hydrogen (H-α). The increase in the relative magnitude of the 656 nm peak may be a function of a higher number density of electrons in the plasma or due to a greater number of dissociation channels for hydrogen, which are proportional to the number of collisions in the plasma. The presence of an upward positive shift in background continuum may indicate Bremsstrahlung radiative processes, which are related to the number density of electrons in the plasma.

Pressure effects on the plasma-phase reaction mechanisms were investigated through varying flow rates of N_2 and H_2 at 2 bar_{abs} in the reactor. The outlet NH_3 concentration from the reactor is shown in relation to this N_2 feed fraction in Fig. 5. It was found that the highest ammonia production occurred with rich H_2 feeds at raised pressures. This may infer a higher involvement of dissociated hydrogen in bulk plasma chemistry, as proposed previously by other groups [7]. Additionally, an increased number density of electrons corresponds with a greater rate of ionization, leading to further deexcitation pathways that may form useful, long-living intermediates. Both mechanisms are supported by spectra results.

At a constant N_2:H_2 feed ratio of 1:1, a lower outlet concentration of ammonia was observed at raised pressures. As shown in Fig. 6, the highest conversion was achieved at atmospheric conditions. It is of note that the energy efficiency increased at higher pressures despite similar outlet concentrations. This is most likely due to a decrease in conductive current, which may be correlated to the decreased conversions.

Further quantification of the number density of electrons is required to properly characterize these plasmas. In addition, nanosecond resolved light emission measurements from the plasma using a photoelectron multiplier can give further insight into the performance of these pulsers at higher pressures.

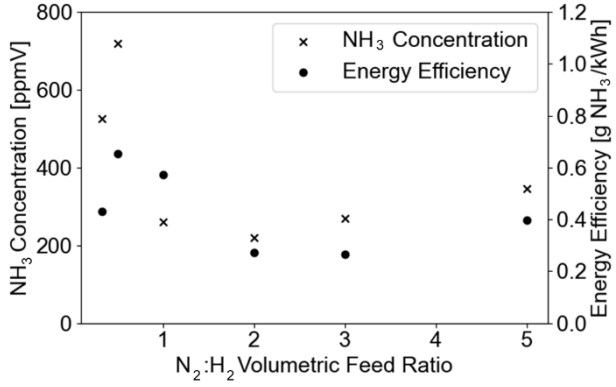

Fig. 5: Ammonia production and energy efficiency related to the feed ratio at a constant standardized flow ($\dot{V}$=60 SCCM), constant pressure (p =2 bar_{abs}), and pulse frequency (f=1000 Hz). Power delivery was calculated to be 2.5 +/- 0.7W, depending on the conductive current.

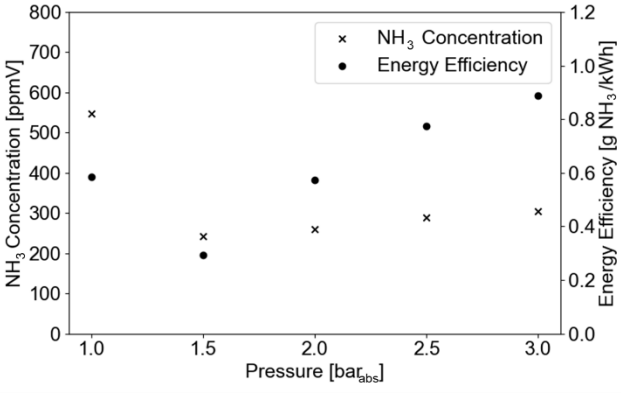

Fig. 6: Ammonia production and energy efficiency at various pressure with a constant standardized flow ($\dot{V}$=60 SCCM), N_2:H_2 volume feed ratio (1:1), and pulse frequency (f=1000 Hz). Power was scaled to reach breakdown conditions.

5. Conclusion

The evolution of plasma chemistry in increasing pressure systems was explored using a pin-to-pin, continuous-flow reactor. High-voltage ignition requirements at pressures up to 3 bar_{abs} were overcome by nanosecond pulses with peak magnitudes above 16 kV. Despite an increase in the number of collisions in the plasma due to the higher number density of heavy species, ammonia production decreased as energy deposition in the plasma may have been limited. A greater contribution of H_2 to plasma-phase pathways for ammonia synthesis is expected as the pressure of the cell rises based on these results.

6. References

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