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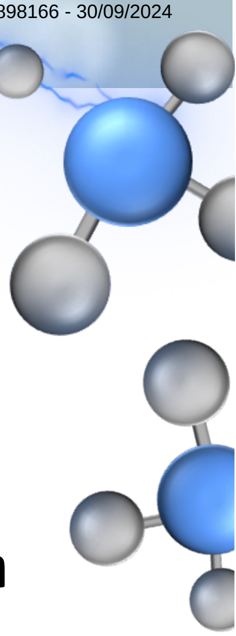

DARE2X

Decentralised Ammonia production from Renewable Energy utilising novel sorption-enhanced plasma-catalytic Power-to-X technology

D4.1 - Report on non-thermal plasma reactor and optimum parameters

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Abstract: Recent advancements in plasma catalysis, where catalysts are incorporated into the plasma, have demonstrated significant improvements in ammonia production efficiency. This deliverable focuses on the design and optimization of plasma reactors for ammonia synthesis, with the goal of reducing energy consumption. Specifically, Work Package 4 (WP4) is tasked with developing a scalable plasma-catalytic system, accelerating catalyst evaluation, and enhancing plasma-catalyst interactions. To achieve this, a dielectric barrier discharge (DBD) reactor has been designed, incorporating innovative features such as a sawtooth-shaped electrode, frosted dielectric surfaces, and water cooling. Additionally, the direct placement of catalysts within the reactor is explored to further improve efficiency. Key operational parameters, including gas composition, discharge power, flow rate, temperature, and pressure, have also been investigated to identify optimal conditions for maximizing ammonia yield while minimizing energy requirements.

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[1] R: Document, report; DEM: Demonstrator, pilot, prototype; DEC: Website, video etc., DATA: Data sets; DMP: Data management plan; ETHICS; SECURITY; Other: Software, technical diagram, algorithms, models etc.

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ABBREVIATIONS AND ACRONYMS

NTP	Non-thermal plasma	FTIR	Fourier transform infrared
AC	Alternating current	SEI	Specific energy input
DBD	Dielectric barrier discharge	OES	Optical emission spectrometry

TABLE OF CONTENTS

1. Introduction

Non-thermal plasma (NTP) assisted ammonia production has emerged as an attractive approach because of its mild operating conditions and can be coupled with renewable electricity resources as plasma can be easily turned on and off. High energy electrons produced in NTP can activate inert N_2, allowing the ammonia production reaction to proceed at mild conditions that are unattainable in thermal catalysis, which requires high temperatures to break the triple bond of N_2. Recent efforts have shown that packing catalysts into NTP, as known as plasma catalysis, can improve ammonia production performance. In this deliverable, we will report on plasma reactor design and optimum parameters for plasma-catalytic ammonia production, aiming at reducing the energy consumption of ammonia production.

Specifically, WP4 is dedicated to developing a scalable plasma system for plasma-catalytic ammonia production, with the goal of accelerating catalyst evaluation in Task 4.2. To support this, a single-cell dielectric barrier discharge (DBD) reactor was specifically designed for Task 4.3.

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The project also explores innovative reactor designs aimed at improving plasma-catalyst interactions and enhancing energy efficiency. These designs include a) incorporating a sawtooth-shaped inner electrode and a frosted dielectric surface to fine-tune the electric field; b) utilizing a water-cooled DBD reactor; and c) placing a catalyst directly within the reactor to further enhance plasma-catalyst interactions and overall energy efficiency.

In addition to reactor design innovations, the impact of key operating parameters, such as gas composition, discharge power, flow rate, temperature, packing method, and pressure, on ammonia production has been investigated. This research aims to identify the optimal conditions for maximizing ammonia yield.

2. Scalable plasma system for ammonia production

The schematic diagram of the plasma-catalytic ammonia production system is presented in Figure 1. A coaxial DBD reactor was employed as the plasma source, which is particularly well-suited for integration with catalysts. Two distinct DBD reactor designs were developed for this system.

The first design, referred to as the standard DBD reactor, utilized a quartz tube with an inner diameter of 4 mm and a wall thickness of 1 mm as the dielectric barrier. A stainless-steel mesh wire, 20 mm in length, was wrapped around the outer surface of the quartz tube, serving as the ground electrode. Inside the quartz tube, a stainless-steel rod with a diameter of 2 mm acted as the high-voltage electrode, creating a 1 mm discharge gap between the rod and the quartz tube.

The second design, the water-cooled DBD reactor, is depicted in Figure 1(b). In this configuration, water at a temperature of 20 °C was used as the ground electrode, while the other parameters remained identical to those of the standard DBD reactor. The addition of water cooling was intended to enhance the reactor's performance by maintaining a stable temperature during operation.

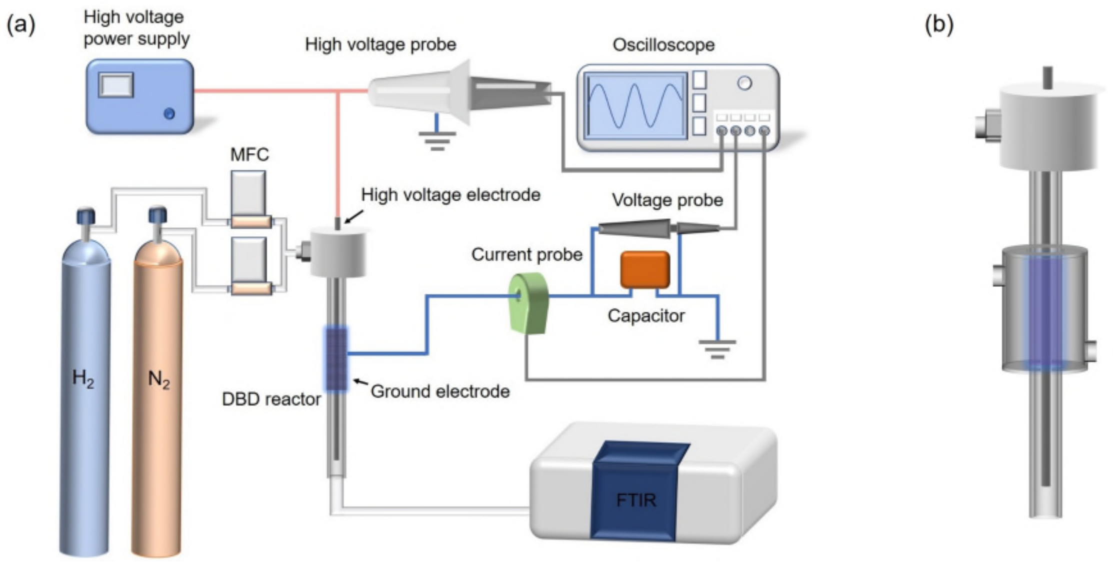

Figure 1. Schematic diagram of (a) the plasma-catalytic ammonia production system, and (b) water-cooling DBD reactor.

An alternating current (AC) sinusoidal high-voltage power supply, with a peak-to-peak voltage of 30 kV and a frequency of 11 kHz, was used to generate plasma in the discharge gap. The applied voltage was monitored using a high-voltage probe (Tektronix P6015A), while the voltage across the external capacitor was measured with another voltage probe (Tektronix TPP0101). Current measurements were taken using a current monitor (Pearson 2877). These electrical signals were recorded using a four-channel digital oscilloscope (Tektronix MDO 3054, 500 MHz, 2.5 GS/s) to ensure accurate data capture. Power consumption during the discharge process was calculated using the Q-U Lissajous method.

Optical emission spectrometry (OES) diagnostics were performed with an optical fiber connected to a spectrometer (Andor SR750), equipped with a 2400 g/mm grating, to analyze the discharge within a wavelength range of 200-800 nm. Pure nitrogen (N_2) and hydrogen (H_2) were introduced into the discharge gap as feed gases, with a total flow rate of 40 mL/min and an N_2/H_2 ratio of 1:3, unless otherwise specified. Ammonia concentration was measured using a Fourier transform infrared (FTIR) spectrometer (Jasco FT/IR-4200).

Figure 2 compares the performance of the two plasma reactor designs. These experiments were conducted without packing any catalysts. The ammonia concentration achieved in the water-cooled DBD reactor was approximately 40% lower than that of the normal DBD reactor. For instance, at a discharge power of 8 W, the ammonia concentration in the normal DBD reactor reached 1000 ppm, whereas the water-cooled DBD reactor produced only about 600 ppm. Despite this, increasing the discharge power resulted in higher ammonia concentrations in both reactor types. However, it was also observed that the energy yield of ammonia decreased as discharge power increased. The highest energy yield (0.26 g/kWh) without a catalyst was obtained in the normal DBD reactor at a discharge power of 4 W.

These findings indicate that using water as the ground electrode had a negative impact on ammonia production. Consequently, all subsequent experiments were performed using the normal DBD reactor. Additionally, modifications such as incorporating a sawtooth-shaped inner electrode and a frosted dielectric surface in the normal reactor did not result in performance improvements and therefore is not discussed here.

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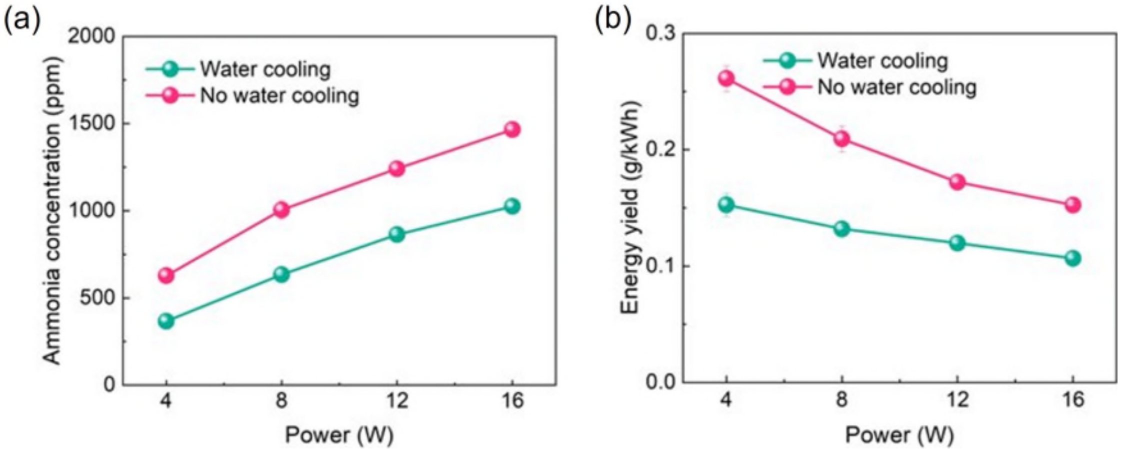

Figure 2. Effect of DBD reactor type on (a) ammonia concentration and (b) energy yield of ammonia production in plasma-assisted ammonia production without a catalyst.

The normal DBD reactor can be easily scaled using a multi-cell approach, where multiple DBD reactors (e.g., three reactors in parallel) share the same power supply. This plasma system strategy, illustrated in Figure 3, enables the simultaneous operation of multiple reactors, increasing the overall efficiency and throughput of the ammonia production process. By implementing this parallel configuration, the system can handle larger volumes and maintain uniform plasma conditions across each reactor, making it a promising method for industrial-scale applications.

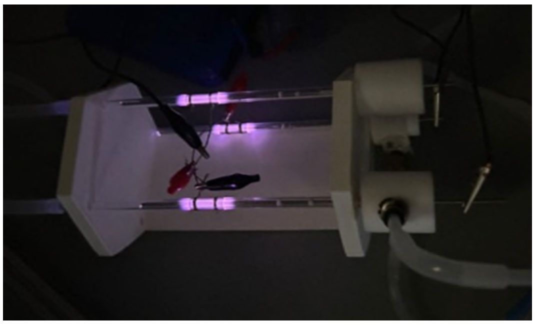

Figure 3. A picture of the multi-cell DBD reactors in parallel shared with the same power supply.

3. Effect of temperature

A previous study demonstrated that the temperature of the DBD reactor can significantly impact plasma-catalytic ammonia production [1]. Here, we explored the effect of temperature on ammonia production by placing the DBD reactor inside a furnace, which was set to 300 °C. Cobalt (Co) supported on alumina (Al_2O_3) with varying loadings was used as the catalyst.

Figure 4 compares the ammonia concentrations achieved under different conditions, both with and without heating the reactor to 300 °C, at a discharge power of 8 W. In all cases, heating the reactor to 300 °C resulted in higher ammonia concentrations. However, the improvement from additional heating was relatively modest. For instance, the ammonia concentration increased from 2400 ppm to 2800 ppm when the reaction was conducted at 300 °C.

This limited enhancement suggests that external heating of the plasma reactor may not be necessary. Notably, the reactor temperature can naturally reach up to 150 °C at a discharge power of 16 W without any additional heating. Therefore, the benefits of heating beyond this point appear minimal for plasma-catalytic ammonia production.

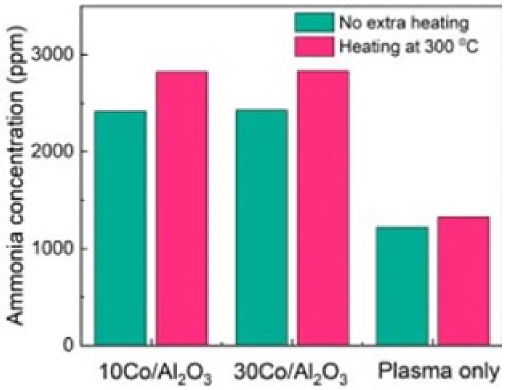

Figure 4. Effect of temperature on plasma-catalytic ammonia production at a discharge power of 8 W and a flow rate of 40 mL/min.

4. Effect of N_2:H_2 feed ratio and flow rate

Figure 5 (a) and (b) illustrate the effect of the N_2:H_2 feed ratio on ammonia production at a constant discharge power of 8 W and a flow rate of 40 mL/min. Increasing the N_2:H_2 ratio from 1:4 to 1:2 resulted in a noticeable rise in both ammonia concentration and energy yield. However, further increasing the N_2:H_2 ratio beyond this point caused a decline in both metrics. This suggests that the optimal N_2:H_2 feed ratio for plasma-catalytic ammonia (NH_3) production is not necessarily the stoichiometric 1:3 ratio, which is based on the conventional reaction ($N_2 + 3H_2 \rightarrow 2NH_3$) [2-3].

In a plasma system, the activation energy required to break the nitrogen (N≡N) and hydrogen (H-H) bonds differs substantially from that in traditional thermal catalysis. Nitrogen, with its strong triple bond (945 kJ/mol) [4], is much harder to dissociate in plasma than hydrogen. Therefore, a higher concentration of nitrogen may be necessary to ensure sufficient dissociation. In our experiments, the optimum N_2:H_2 ratio was found to be 1:2, which produced 10% more ammonia than the stoichiometric ratio of 1:3. However, the optimal ratio may vary if catalysts are incorporated into the plasma system. For this reason, subsequent research still employed the conventional N_2:H_2 ratio of 1:3.

Additionally, increasing the flow rate led to a decrease in ammonia concentration but improved the energy yield. Higher flow rates correspond to a lower specific energy input (SEI), which is known to positively impact plasma-catalytic reactions. Our previous studies also reported increased energy efficiency in NH_3 production at lower SEI levels, irrespective of the catalyst used [5]. This can be explained by the fact that, at lower SEI, while fewer electrons are generated, a greater proportion of them effectively collide with target molecules (N_2 and H_2), reducing energy loss and increasing overall reaction efficiency.

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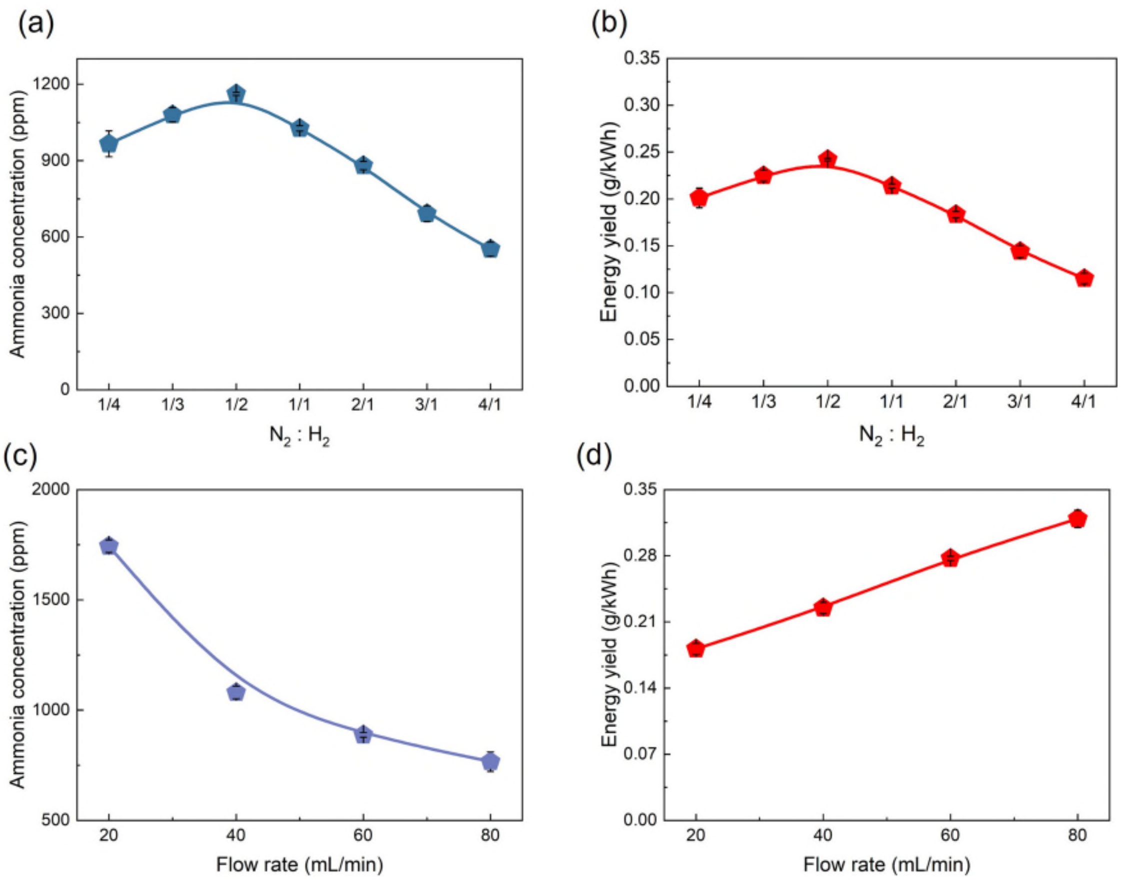

Figure 5. Effect of gas feed ratio on (a) ammonia concentration and (b) energy yield at a discharge power of 8 W and a flow rate of 40 mL/min without a catalyst; effect of flow rate on (c) ammonia concentration and (d) energy yield at a discharge power of 8 W and a N_2:H_2 ratio of 1:2.

5. Effect of packing strategy

The packing strategy of catalysts in a plasma-catalytic system plays a crucial role in its overall performance. Plasma-catalytic ammonia (NH_3) synthesis faces inherent challenges due to plasma-induced reverse reactions, such as NH_3 decomposition. In the plasma discharge, the formed ammonia can undergo electron impact dissociation, leading to NH_3 decomposition, which limits both the achievable ammonia yield and the energy efficiency [6]. A potential solution to mitigate NH_3 decomposition is to optimize the catalyst packing within the plasma reactor.

To explore the effect of packing strategy, a two-stage plasma reactor was developed, allowing for various plasma-catalyst configurations. Figure 6 illustrates the different setups:

Configuration A: A single plasma-only stage with a 20 mm discharge length.

Configuration B: A fully packed plasma-catalyst stage, where highly active Co-5A was incorporated directly within the discharge zone.

Configuration C: A two-stage reactor where the feed gas first passes through a plasma-only stage before entering a plasma-catalyst stage.

Configuration D: Another two-stage reactor, but here, the feed gas first passes through the plasma-catalyst stage before reaching the plasma-only stage.

In both configurations C and D, the stages were separated but connected to the same high-voltage supply. Compared to configurations C and D, configuration B fully packs the discharge zone with catalysts.

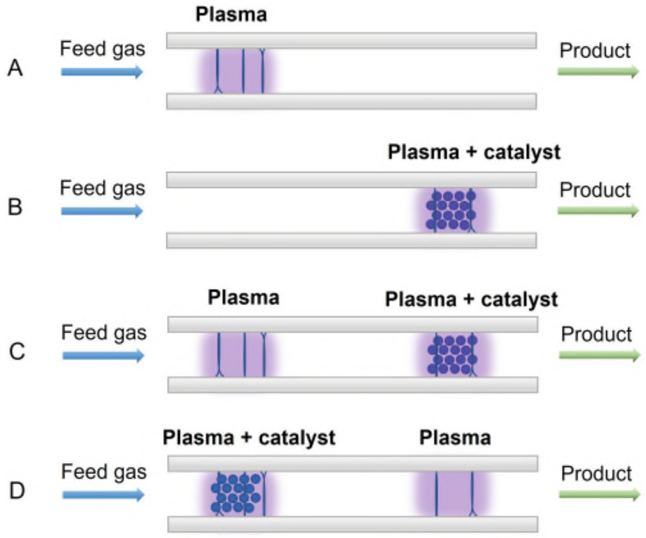

Figure 6 Different packing configurations for ammonia production (A: single plasma, B: single plasma-catalyst, C: plasma stage and plasma-catalyst stage, D: plasma-catalyst stage and plasma stage) at the same flow rate and applied voltage using Co-5A as the catalyst.

Figure 7 shows the ammonia concentrations achieved under these different configurations and operating conditions. At a peak-to-peak voltage of 16 kV and a flow rate of 40 mL/min (with an energy input of 12 kJ/L per stage), configuration C, where the feed gas passed through the plasma-only stage before the plasma-catalyst stage, produced the highest ammonia concentration (8463.6 ppm). In contrast, configuration D, which reversed the order of stages, resulted in a significantly lower ammonia concentration (7257.6 ppm), despite having the same power consumption, underscoring the importance of reactor configuration in plasma-catalytic systems. Interestingly, configuration D still produced slightly more ammonia than configuration B (6811.7 ppm), indicating that the plasma-only stage was driving the production process rather than promoting ammonia decomposition.

The effect of packing strategy was further analyzed at higher specific energy inputs (SEI) by either increasing the applied voltage or reducing the flow rate. At a peak-to-peak voltage of 16 kV and a flow rate of 20 mL/min (24 kJ/L per stage), configuration C again yielded the highest ammonia concentration. In this case, configuration B outperformed configuration D (11907 ppm vs. 11311 ppm), suggesting that, under these conditions, plasma-induced ammonia decomposition was more pronounced in configuration D.

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When SEI was increased by reducing the flow rate and raising the applied voltage, as shown in Figure 7(d), the impact of the packing strategy became even more evident. Configuration D exhibited a significantly lower ammonia concentration (15869.8 ppm) compared to configuration B (20436.3 ppm). This marked difference indicates a strong decomposition effect at high SEIs, likely due to rapid plasma-induced reverse reactions, where higher ammonia concentrations lead to increased NH_3 decomposition in the plasma. These results highlight the critical influence of catalyst packing strategy and reactor configuration on ammonia production and decomposition in plasma-catalytic systems, particularly at high energy inputs.

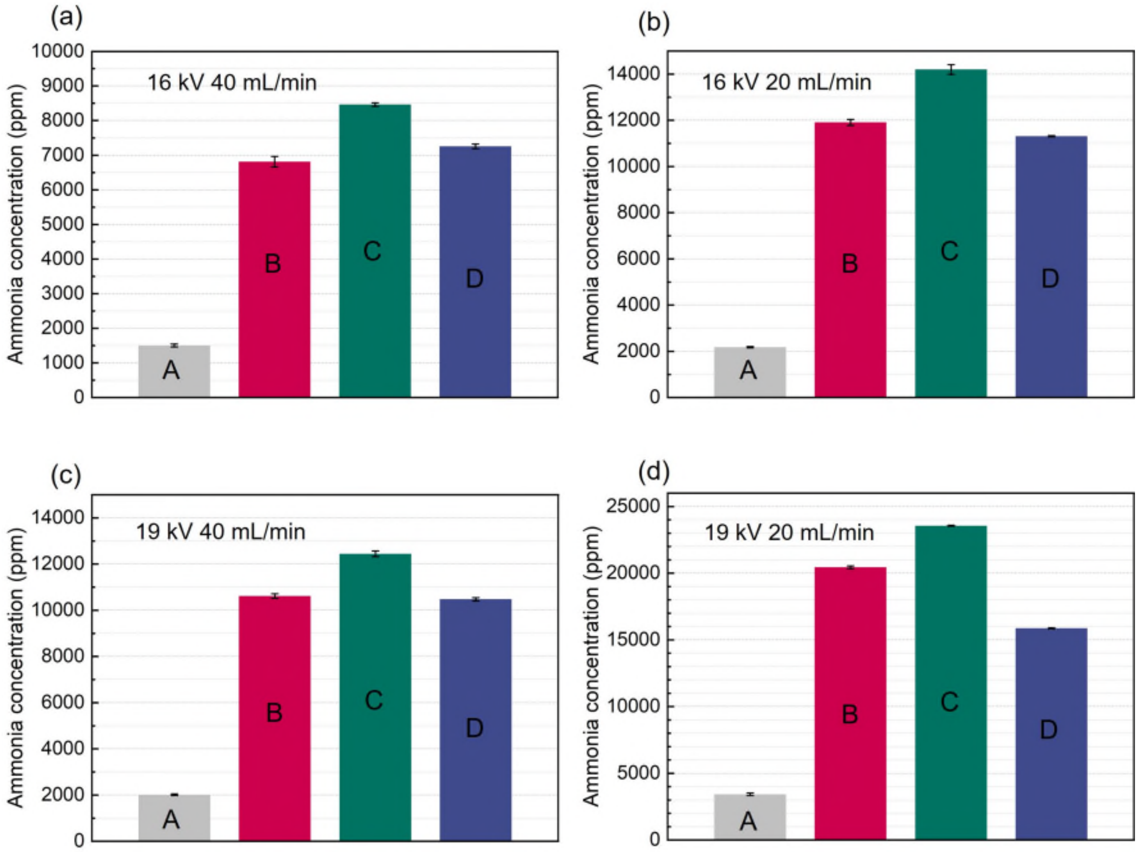

Figure 7 Ammonia concentrations in different packing configurations at the operating conditions of (a) 16 kV and 40 mL/min, (b) 16 kV and 20 mL/min, (c) 19 kV and 40 mL/min, and (d) 19 kV and 20 mL/min, respectively.

Figure 8 illustrates the energy yield of ammonia production across the different configurations. Configuration B demonstrated significantly higher energy yields—1.7 times greater than configuration C and 2.6 times higher than configuration D. This suggests that fully packing the catalyst within the discharge zone can effectively reduce ammonia decomposition and improve energy efficiency, making configuration B the most favorable for optimizing both ammonia production and energy use.

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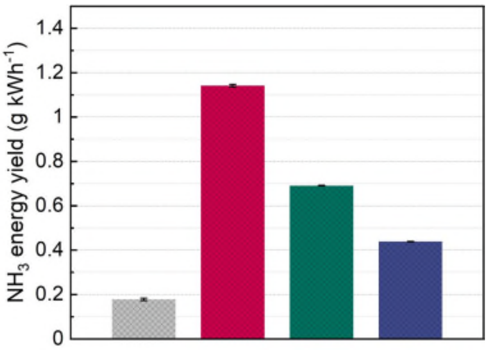

Figure 8 Ammonia energy yield achieved in different configurations at an applied voltage of 19 kV and flow rate of 20 mL/min.

6. Effect of pressure

Figure 9 presents a schematic diagram of the pressure-controlled DBD system, designed to study the effect of pressure on plasma-catalytic ammonia production. This system enables the investigation of ammonia synthesis across a pressure range of 1 to 3 bar, providing valuable insights into how pressure influences both reaction efficiency and ammonia yield.

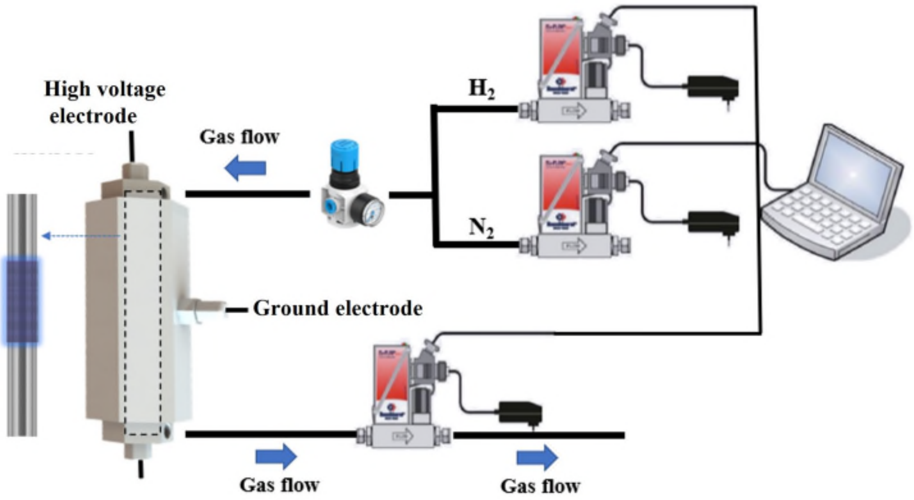

Figure 9. Schematic diagram of the pressure-controlled DBD system

Figure 10 illustrates the effect of pressure on plasma-catalytic ammonia production. Under plasma-only conditions, increasing the pressure had minimal impact on ammonia concentration across all tested discharge powers. However, when a catalyst was introduced into the plasma, higher pressure led to a decrease in ammonia concentration. These findings suggest that increasing reactor pressure offers no significant advantage for plasma-catalytic ammonia synthesis. Consequently, operating the system at lower pressures simplifies the overall design and operation of the plasma system without compromising performance.

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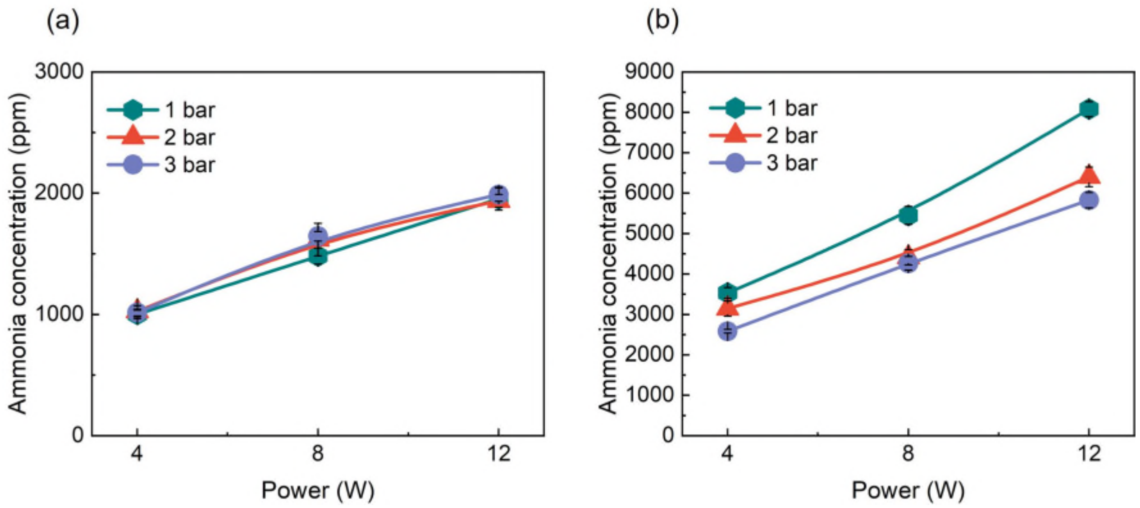

Figure 10. Effect of pressure on ammonia production in (a) plasma only conditions and (b) plasma-catalytic conditions with zeolite 4A + Ca as the catalyst.

7. Conclusions

In conclusion, we demonstrated the development of a scalable plasma-catalytic system for ammonia production, which presents significant potential for enhancing energy efficiency and optimizing process conditions. Our research demonstrated that reactor design, operating parameters, and packing strategies played critical roles in the overall performance of ammonia synthesis. The use of a normal DBD reactor was found to outperform the water-cooling variant in terms of ammonia concentration and energy yield, with temperature effects showing minimal benefits beyond natural reactor heating. The optimization of the N_2:H_2 feed ratio and flow rate further highlighted the importance of tuning gas conditions for enhanced energy yield, with a higher nitrogen ratio proving beneficial. Packing strategies, particularly the configuration of the plasma-catalyst stages, were found to significantly impact ammonia production, with full packing configurations yielding higher concentrations and preventing ammonia decomposition. Lastly, operating pressure was shown to have a limited effect on ammonia production, especially under plasma-only conditions, suggesting that low-pressure systems may be more practical. Overall, this research provides key insights into the effective design and operation of plasma-catalytic systems for ammonia production, laying the groundwork for future optimizations.

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