

DARE2X

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

D5.2 – Summary of Experiments WP5

Lead beneficiary: UoL

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Abstract: This report summarizes the experiments of work package 5 (WP5). WP5's objectives were to investigate the plasma-sorption configuration with higher efficiency towards NH_3 synthesis and to validate the sorption-enhanced plasma-catalytic concept for improved energy efficiency. Non-sorption-enhanced NH_3 plasma catalysis. This was demonstrated in a multicell reactor using a single-stage configuration that simultaneously produce and separate NH_3 , with both sorption and catalyst materials in the plasma-catalytic zone. Additionally, different plasma parameters are explored, including power, plasma zone temperature, and 'constant-versus-pulsed' plasma configurations. A microkinetic model was developed to include the effects of plasma on ammonia production, which shows an increase in catalytic performance and a shift of the best performing materials towards less strongly bound nitrogen (instead of Ru, best performers are Co and Ni).

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² PU: Public, fully open; SEN: Sensitive.



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ABBREVIATIONS AND ACRONYMS

NiOCat Refers to catalyst powder developed in WP2 ZeoSorp Refers to sorption material from deliverable 3.2

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1. Introduction

The DARE2X project is investigating a power-to-x technology for decentralized ammonia based on sorption-enhanced, non-thermal, plasma catalysis. Previously, it was demonstrated that non-sorption-enhanced NH_3 plasma catalysis was not competitive (D5.1). The 50:50 (NiOCat: Al_2O_3) extrudate achieved <1% energy efficiency ($2260 \text{ kWh} \cdot \text{kg}_{\text{NH}_3}^{-1}$), where the benchmark has been set to ~40% energy efficiency ($<20 \text{ kWh} \cdot \text{kg}_{\text{NH}_3}^{-1}$). This is likely due to the stability of NH_3 in plasma being very poor.¹ Therefore, further investigations were conducted on the single-stage configuration to maximize the sorption-enhancement benefits, where both the NH_3 synthesis and NH_3 sorption occur in the plasma-catalytic zone (T5.1).

It is hypothesized that NH_3 throughputs can be enhanced by mitigating plasma-induced degradation. This can be achieved if NH_3 is adsorbed to a material, but this sorption-enhanced effect remains to be realized in a meaningful way. The 25:25:50 (ZeoSorp:NiOCat: Al_2O_3) extrudate has an expected capacity of roughly $\sim 20 \text{ mg}_{\text{NH}_3}$ (from D3.2 result of $44 \text{ mg}_{\text{NH}_3}$ per $1 \text{ g}_{\text{ZeoSorp-extrudate}}$), but we have only measured $\sim 1.5 \text{ mg}_{\text{NH}_3}$ post-plasma (from D5.1 result of $\sim 3.0 \text{ mg}_{\text{NH}_3}$ minus $\sim 1.5 \text{ mg}_{\text{NH}_3}$ from empty tube). This sorption-enhancement may not have been viable because the catalyst powder reaches temperatures that directly inhibits NH_3 adsorption. UoL demonstrated that the plasma zone could be reaching temperatures above $100 \text{ }^\circ\text{C}$, while HB has shown the ZeoSorp's NH_3 capacity is compromised at $100 \text{ }^\circ\text{C}$ (down to $7 \text{ mg}_{\text{NH}_3}$ per $1 \text{ g}_{\text{ZeoSorp-extrudate}}$). Therefore, understanding the actual temperature in the plasma zone will be important. In addition, it will be important to understand the fraction of input power is being converted to plasma, and when the diminishing returns of NH_3 output from our power inputs become apparent.

Another possibility is that the NH_3 adsorption kinetics are not fast enough to compete with plasma radicals that would degrade the NH_3 . There are numerous factors that affect the kinetics of these two processes, and therefore it can quickly get complex. The NH_3 adsorption is likely on a scale of microseconds (10^{-6}), depending on the sorbent properties (surface area, pore size distribution) and the localized NH_3 concentration (presumably nanoscale distances). The hydrogen and nitrogen plasma radicals responsible for degradation can be on a scale of microseconds to nanoseconds (10^{-6} to 10^{-9}) where nitrogen radicals are very reactive with H_2O .² Given that NH_3 is generally considered more reactive than H_2O , it is possible that the degradation of NH_3 via plasma radicals outcompete NH_3 adsorption by several orders of magnitude. This could suggest that the sorption properties would be negligible in such circumstances because if the catalyst site needs nitrogen radicals, then the resulting NH_3 will have to be exposed to nitrogen radicals (whether it is on or leaving the catalyst site). Nevertheless, these kinetics remain unclear, so a catalyst sample where Ni is directly dispersed onto the sorption material (50:50 NiOZeoSorp: Al_2O_3) can potentially provide insights and/or throughput improvements.

With these reasons in mind, temperature measurements were conducted in the plasma zone at different plasma settings: plasma power ($150\text{-}400 \text{ W}_{\text{input}}$), and comparing constant plasma versus 5/5 pulsed plasma (5 seconds on, 5 seconds off). Since the losses of the power to plasma are unclear, a power versus NH_3 output will be conducted with the 25:25:50 (ZeoSorp:NiOCat: Al_2O_3) extrudate to see when we start getting diminishing returns on our

power input. With better understandings of temperature and power inputs, the optimal configurations will be tested using the 25:25:50 (ZeoSorp:NiOCat:Al₂O₃) extrudate and a 50:50 (NiOZeoSorp:Al₂O₃) to see if the sorption-enhanced effect can be meaningfully realized.

2. Pilot scale set-up

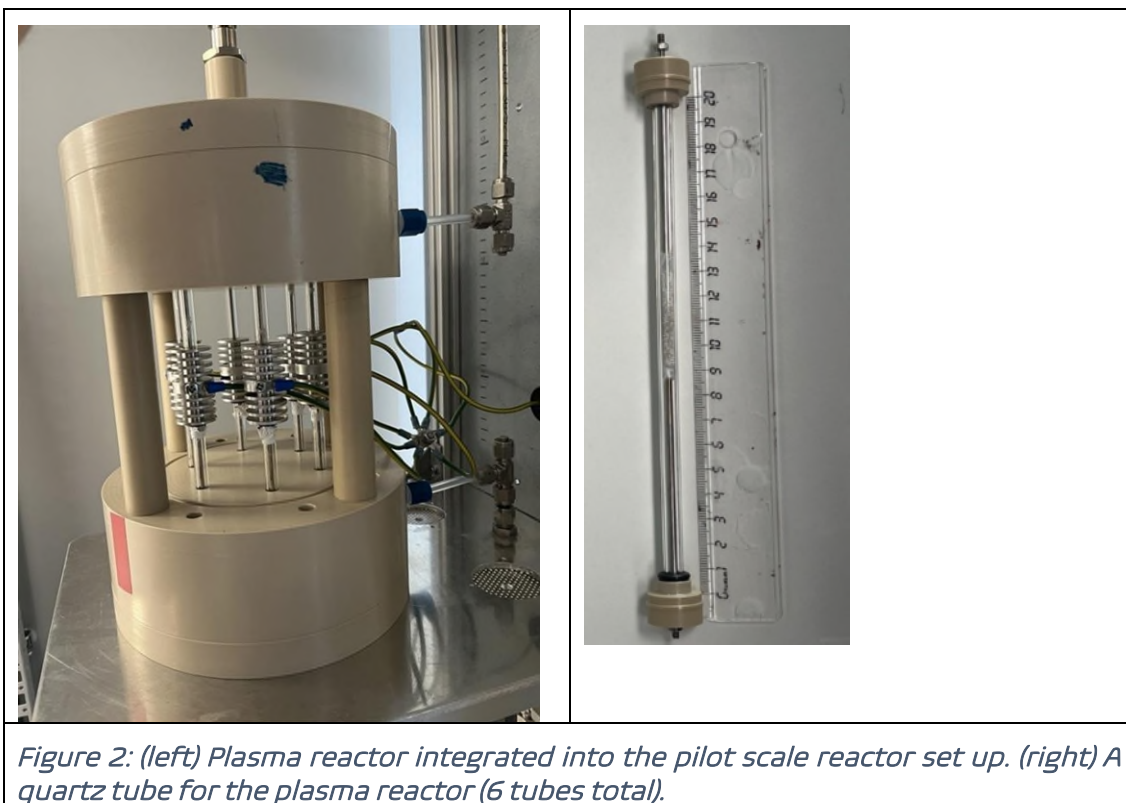
The pilot scale set-up is the same as D5.1 and is summarized in Figure 1. The plasma generator (A) was supplied by AFS Plasma corona perforators (G05F generator). Brooks Mass Flow Controllers (B) were used to control the flow of gases (GF040CXXC-1036002L-T2PNS4-XXXXAX-00X, GF040CXXC-0136020L-T2PBS4-XXXXAX-00C). The plasma reactor was built in-house (C), with the capacity for 6 quartz tubes supplied by Mirit Glas (diameter: 8 mm, wall size: 1.5 mm, length: 200 mm). The faradaic cage (D) was built in-house (aluminium). The stainless steel tubing and valves (EFHIK) were supplied by Swagelok (Part turn actuator EN ISO 5211). The vacuum pump (G) was supplied KNF (N922STE EX). The sorption unit was supplied by Hulteberg Chemistry and Engineering from WP3 and D3.2 (J) with a heating coil added to it. The sample gas to the analysis unit (L) is quantified by an FTIR spectrometer (Thermo Fisher). The sample gas from the analysis unit (M) is diluted with air (B) before being introduced to a catalytic burner, which burns excess H₂ and NH₃ to avoid releasing them in the exhaust.



Figure 1: The pilot scale reactor set-up with its components: plasma generator (A), mass flow controllers for gases N_2 H_2 and air (B), plasma reactor (C), faradaic cage (D), valve from plasma reactor to analysis unit (E), valve from plasma reactor to vacuum pump (F), vacuum pump (G), valve from vacuum pump to sorption unit (H), valve from pump to analysis unit (I), sorption unit (J), valve from sorption unit to analysis unit (K), sample gas to analysis unit (L), sample gas from analysis unit to exhaust (M).

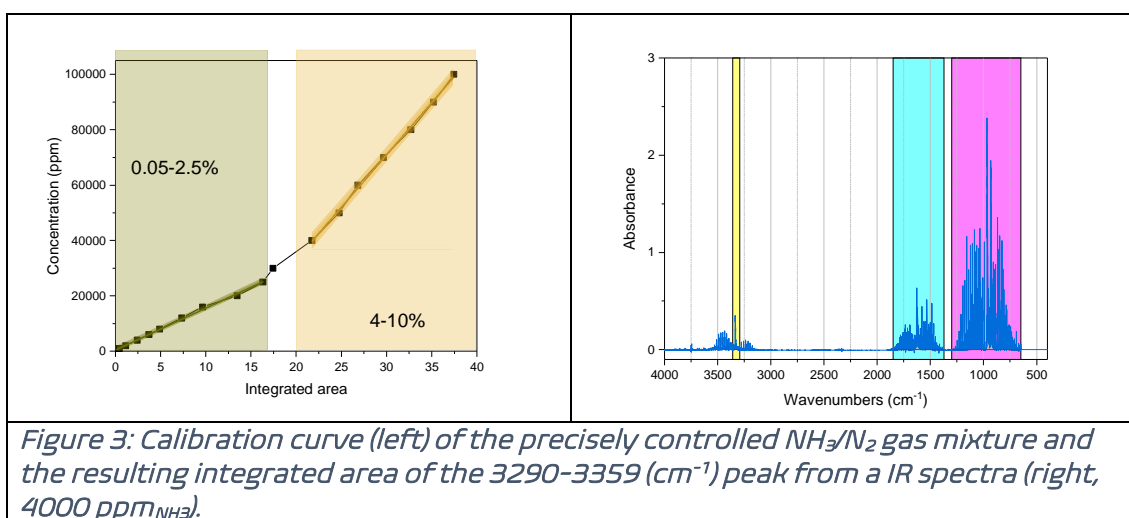
2.1 Plasma Reactor

The plasma reactor is the same as D5.1. It has a reactor body comprised of PEEK (polyether ether ketone) outer electrodes (aluminum) were designed and manufactured in-house (Figure 2 left). It hold 6 quartz tubes that can be loaded with catalyst (Figure 2, right). The quartz tubes (diameter: 8 mm, wall size: 1.5 mm, length: 200 mm) for the plasma reactor have an inner electrode (steel rod, diameter: 3 mm, length: 240 mm) and end pieces comprised of PEEK (polyether ether ketone). Each quartz tube is loaded with glass wool at the ~90 mm mark, to support the extrudate material (particle size: 100–315 μm) until the ~130 mm mark resulting in a mass loading around 280-330 mg per tube (Figure 2, right). Plasma power losses were estimated to be around 60% based on the Lissajous figure method, which were used for the $\text{kWh} \cdot \text{kg}_{\text{NH}_3}^{-1}$ calculations.



2.2 FTIR

Fourier Transform infrared spectroscopy (FTIR) was calibrated using precisely controlled mixes of NH_3 and N_2 gases via mass flow controllers. The calibration was based on the NH_3 peak occurring in the $3290\text{--}3359\text{ cm}^{-1}$ region because it had minimal interferences and noise (Figure 3, right). A linear calibration curve was used to quantify the concentrations of up to $25000\text{ ppm}_{\text{NH}_3}$ (Figure 3, left).



2.3 Materials

The catalyst used in the plasma reactor was nickel-based and supported on zeolites (different from sorption zeolite) developed in WP2. The synthesised catalyst powder (NiOCat) had a Ni loading of 3 ± 1 (wt.%). The catalyst powder (NiOCat) was extruded using a boehmite binder based on methods found in literature.³ The 25:25:50 (ZeoSorp:NiOCat:Al₂O₃) and 50:50 (ZeoSorp:Al₂O₃) extrudates were prepared exactly as described in D5.1. They were prepared by dry mixing 4 g zeolite powder (2:2 g or 4:0 g ZeoSorp:NiOCat), 160 mg (hydroxypropyl)methyl cellulose (sigma aldrich), and 4.8 g Disperal P2 (pseudo-boehmite from Sasol). Once the mixture was thoroughly homogenized, deionized water (10-11 ml) was added dropwise while continuously mixing to obtain a dough ready for extrusion. The dough was then transferred to a hand extruder (DAS Smart metal clay extruder) for shaping through a 1.6 mm diameter die. The resulting green extrudates were transferred to a muffle oven where they were dried at 323 K for 2 h, then 363 K for 12h, and finally calcined at 823 K for 4 h at with a heating rate of 5 K/min. The calcined extrudates were then gently crushed, sieved and the 100–315 μm fraction was retained. The 50:50 (NiOZeoSorp:Al₂O₃) extrudate was achieved via wetness impregnation of the resulting 50:50 (ZeoSorp:Al₂O₃) extrudate fraction (100–315 μm). Both extrudate's Ni loadings were validated with EDX analysis (Table 1).

Table 1: EDX analysis of the extrudate samples.

Spectrum Label	O	Na	Al	Si	K	Ni
25:25:50 (ZeoSorp:NiOCat:Al ₂ O ₃)	50,0 \pm 0,2	2,3 \pm 0,1	21,3 \pm 0,3	24,9 \pm 0,2	0,1 \pm 0,0	1,5 \pm 0,1
50:50 (NiOZeoSorp:Al ₂ O ₃).	46,3 \pm 0,2	8,5 \pm 0,2	30,7 \pm 0,8	10,9 \pm 0,2	0,3 \pm 0,0	3,4 \pm 0,5

Samples of catalyst supports and catalyst were provided in extrudate form by HB, as described in Table 2.

Table 2: Extrudate samples provided by HB.

Sample name
50:50 (ZeoSorp:Al ₂ O ₃)
50:50 (USY500:Al ₂ O ₃)
50:50 (NiO/USY500:Al ₂ O ₃)
25:25:50 (ZeoSorp:USY500:Al ₂ O ₃)
50:50 (Ca-ZeoSorp:Al ₂ O ₃)

3. Determining optimal plasma parameters

Optimal plasma parameters are needed to enable meaningful sorption enhancement. This means a power input that provides high throughputs while still maintaining ambient temperatures of at least $<100\text{ }^{\circ}\text{C}$ (preferably $<50\text{ }^{\circ}\text{C}$). Lower temperatures should facilitate NH_3 adsorption and hopefully mitigate NH_3 degradation (i.e. sorption enhancement). In addition to applying a constant plasma, pulsed plasma (5-10 seconds on, and 5-10 seconds off) is also explored to see if this improves temperature and throughputs. It has also been demonstrated that higher power inputs result in diminishing returns of NH_3 throughput. Investigating when this occurs will help determine which power inputs are most practical, particularly in the pulsed plasma settings.

3.1 Temperature

A temperature transmitter (ODENSA, FTX-300-LUX+) with a fiber optic temperature probe (ODENSA, PRB-G40) was used to measure the temperature. The fiber optic temperature probe was placed into the plasma zone of one of quartz tubes through the bottom of the reactor. This was achieved by removing the bottom lid of the reactor, making the downstream gas flow unavailable for analysis and higher pressures not possible. This meant that the downstream gas would collect inside the cabinet, and therefore not suitable for higher concentrations of H_2 and/or NH_3 . Therefore, these temperature experiments used a reactor flow of $540\text{ ml}_{\text{N}_2}/\text{min}$ and $0\text{ ml}_{\text{H}_2}/\text{min}$ at 0 bar. Plasma inputs were controlled by setting DC-voltage to better control the pulsed plasma. Air cooling was always active on the outer alumina electrodes unless specified otherwise. Initial testing (Figure 4), showed that a constant $200\text{ W}_{\text{input}}$ plasma (200 W power, 6.8 kV high voltage, 65 V DC-voltage) and a constant $100\text{ W}_{\text{input}}$ plasma (100 W power, 5.2 kV high voltage, 36 V DC-voltage) resulted in equilibrated temperatures (after ~ 4 minutes) of $170\text{ }^{\circ}\text{C}$ and $115\text{ }^{\circ}\text{C}$, respectively. Pulsing the plasma for 10 seconds on, and then 10 seconds off (10/10 pulse plasma) halves the power output (over time). Interestingly, a 10/10 pulse $200\text{ W}_{\text{input}}$ plasma (100 W power, 6.8 kV high voltage, 65 V DC-voltage) and a 10/10 pulse $100\text{ W}_{\text{input}}$ plasma (50 W power, 5.2 kV high voltage, 36 V DC-voltage) resulted in equilibrated temperatures of $105\text{ }^{\circ}\text{C}$ ($\pm 20\text{ }^{\circ}\text{C}$) and $75\text{ }^{\circ}\text{C}$ ($\pm 15\text{ }^{\circ}\text{C}$) respectively. A 5/5 pulse $100\text{ W}_{\text{input}}$ plasma had a similar temperature to the 10/10 pulse $100\text{ W}_{\text{input}}$ plasma, with just a narrower temperature range $75\text{ }^{\circ}\text{C}$ ($\pm 8\text{ }^{\circ}\text{C}$).

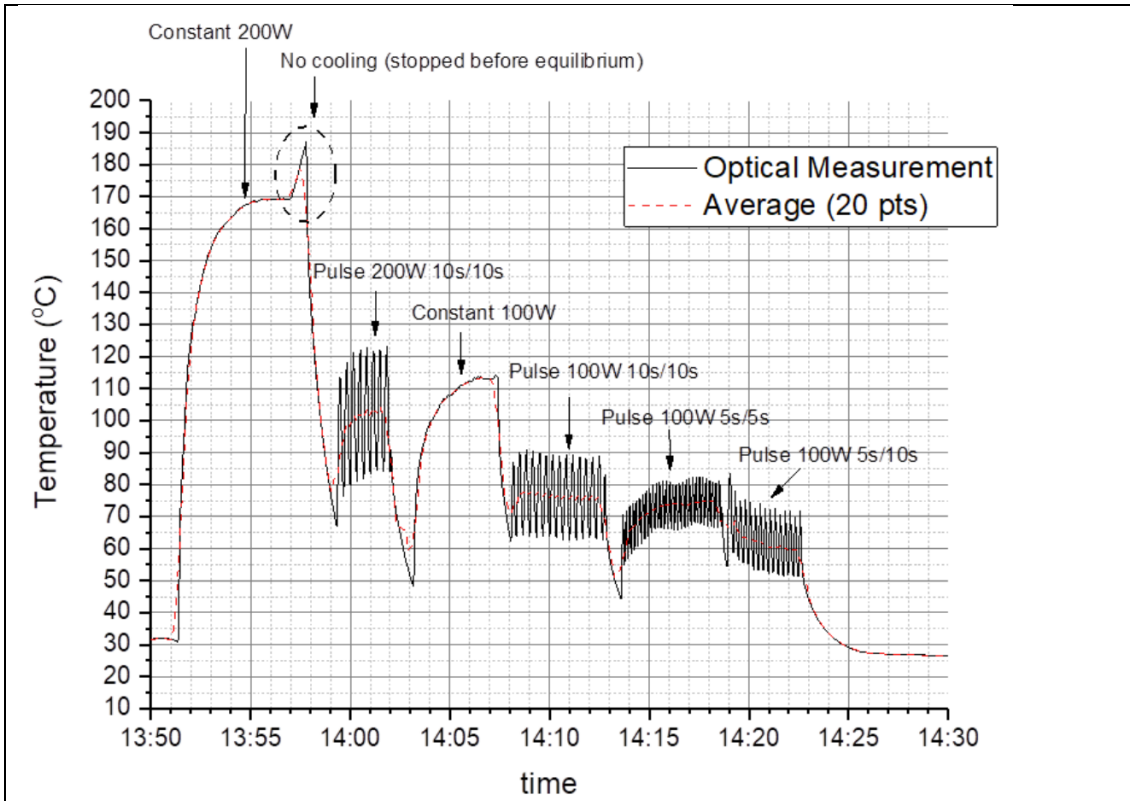
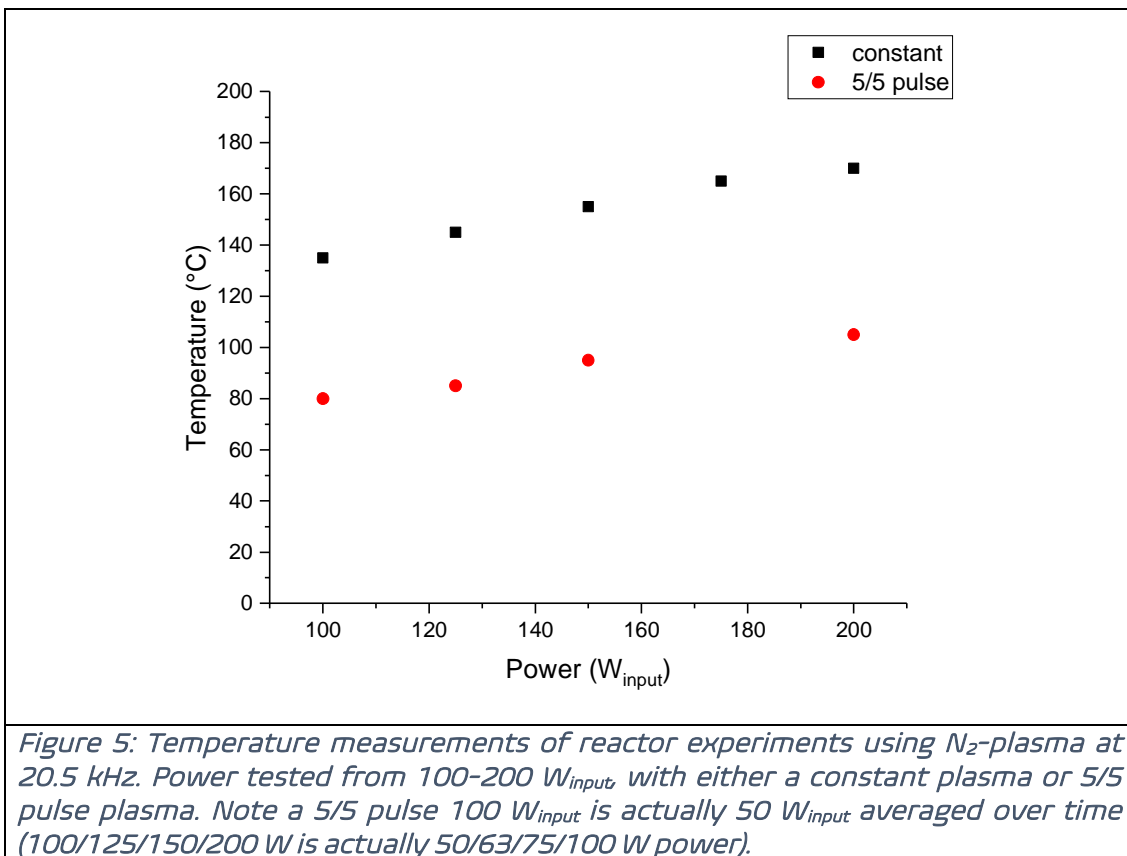


Figure 4: Temperature measurements of reactor experiments using N_2 -plasma at 20.5 kHz. From 13:51–13:58: constant 200 W_{input} (200 W power, 6.8 kV high voltage, 65 V DC-voltage). From 13:59–14:02: 10/10 pulse 200 W_{input} (100 W power, 6.8 kV high voltage, 65 V DC-voltage). From 14:03–14:07: constant 100 W_{input} (100 W power, 5.2 kV high voltage, 36 V DC-voltage). From 14:08–14:13: 10/10 pulse 100 W_{input} (50 W power, 5.2 kV high voltage, 36 V DC-voltage). From 14:14–14:18: 5/5 pulse 100 W_{input} (50 W power, 5.2 kV high voltage, 36 V DC-voltage). From 14:19–14:23: 5/10 pulse 100 W_{input} (33 W power, 5.2 kV high voltage, 36 V DC-voltage).

Further testing (Figure 5) confirms that the 5/5 pulse generally results in lower temperatures by about 55–60 °C. An additional observation is that even with similar power inputs, the constant 100 W_{input} (100 W power, 5.2 kV high voltage, 36 V DC-voltage) results in a higher temperature (135 °C) than the 5/5 pulse 200 W_{input} (100 W power, 6.8 kV high voltage, 65 V DC-voltage) temperature (105 °C). While each plasma pulse requires ~1 second to equilibrate to the correct power, even correcting for this cannot account for this temperature difference. This suggests that there is an advantage to using 5/5 pulsed plasma over constant plasma for lower temperatures at similar power inputs.



3.2 Power curve

Throughout the DARE2X project, the lab scale plasma reactor had demonstrated diminishing returns of NH_3 throughput per watt at higher power inputs. One such example is presented in Table 3 using 50:50 ($NiOCat:Al_2O_3$) (from D5.1). As a result, different power inputs were tested in the demonstration system to determine the optimal power input for further investigations.

Table 3: UoL demonstrating that higher power inputs result in diminishing returns of NH_3 throughput in single tube experiment, with power-loss corrected plasma.

	Power ($W_{\text{corrected}}$)	ppm_{NH_3} in $40 \text{ ml} \cdot \text{min}^{-1}$	$\text{ppm}_{\text{NH}_3} \cdot W_{\text{corrected}}^{-1}$
Empty tube	4	680	170
Empty tube	8	1210	150
Empty tube	12	1550	130
Empty tube	16	1840	115
50:50 (NiOCat:Al ₂ O ₃)	4	3430	860
50:50 (NiOCat:Al ₂ O ₃)	8	6140	770
50:50 (NiOCat:Al ₂ O ₃)	12	7430	620
50:50 (NiOCat:Al ₂ O ₃)	16	8490	530

For these power curve experiments, the plasma reactor (6 quartz tubes) was loaded with the 25:25:50 (ZeoSorp:NiOCat:Al₂O₃) extrudate previously used in D5.1. All experiments used a reactor flow of $360 \text{ ml}_{\text{N}_2}/\text{min}$ and $180 \text{ ml}_{\text{H}_2}/\text{min}$ at 2.5 bar. In each experiment, a constant plasma was applied for 20 minutes, and then turned off. Once the plasma was turned off, the H_2 flow was set to $180 \text{ ml}_{\text{H}_2}/\text{min}$ and pumping vacuum in the reactor zone (dynamic operation). Figure 5 shows the stabilized concentration (left, ppm_{NH_3} in $540 \text{ ml} \cdot \text{min}^{-1}$, after ~ 10 minutes of plasma) and this stabilized concentration per watt (right, $\text{ppm}_{\text{NH}_3} \cdot W^{-1}$ normalized to $40 \text{ ml} \cdot \text{min}^{-1}$). The stabilized concentration per watt was normalized (or upconcentrated) to the same flow that was used in UoL's single reactor tube experiments for easier comparisons.

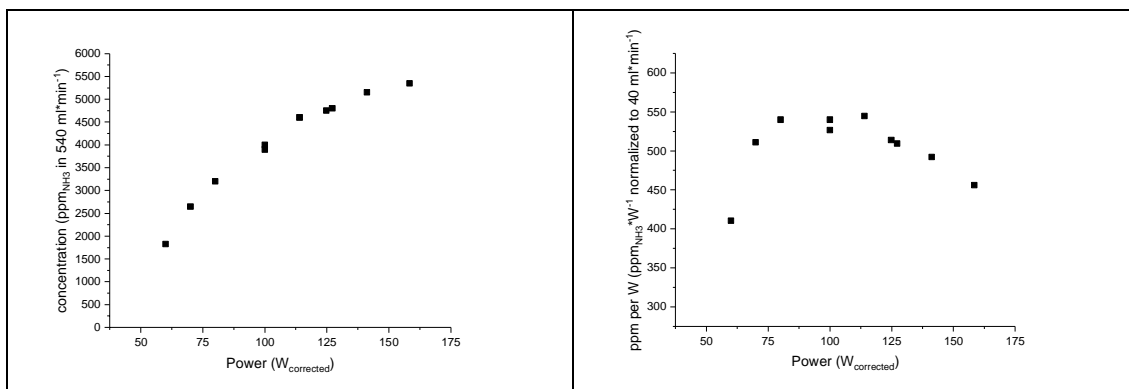


Figure 6: Demonstrator plasma reactor experiments using 25:25:50 (Sorption:NiOCat:Al₂O₃) extrudate across corrected Power ($W_{\text{corrected}} = 0,4 \cdot W_{\text{input}}$). Stabilized concentration (ppm_{NH_3} in $540 \text{ ml} \cdot \text{min}^{-1}$) after 10 minutes of plasma (left). Stabilized concentration per power applied ($\text{ppm}_{\text{NH}_3} \cdot W_{\text{corrected}}^{-1}$ normalized to $40 \text{ ml} \cdot \text{min}^{-1}$) (right).

A range of 150-400 W_{input} was applied on 6 tubes (25-67 W_{input} per tube) which equates to a range of 60-160 $W_{\text{corrected}}$ on 6 tubes (10-27 $W_{\text{corrected}}$ per tube) (Figure 6, left). Based on UoL's single tube experiments (Table 3), lower $\text{ppm}_{\text{NH}_3} \cdot W_{\text{corrected}}^{-1}$ is expected from $>60 \text{ } W_{\text{corrected}}$.

However, UoL's experiments were able to in-situ measure the actual power of their plasma through power-loss correction from their system, while on the demonstration reactor power loss correction (60%) was based on ex-situ measurement. Making some assumptions, $\sim 33 W_{\text{input}}$ per tube ($13 W_{\text{corrected}}$) has yielded similar NH_3 concentrations (per tube) with 50:50 (NiOCat:Al₂O₃) (6200 ppm_{NH₃}, D5.1) as UoL's $8 W_{\text{corrected}}$ experiments. Without correcting for flow or pressure (which is complicated), this assumes a 75% power loss, which isn't far from our 60% measurement. We would therefore expect lower in ppm_{NH₃}*W⁻¹ from $>25 W_{\text{input}}$ ($>6-10 W_{\text{corrected}}$), and it is surprising that we have the lowest outputs at $60 W_{\text{corrected}}$ ($10 W_{\text{corrected}}$ per tube). However, diminishing ppm_{NH₃}*W⁻¹ only begins at $120 W_{\text{corrected}}$ ($20 W_{\text{corrected}}$ per tube) (Figure 6, right).

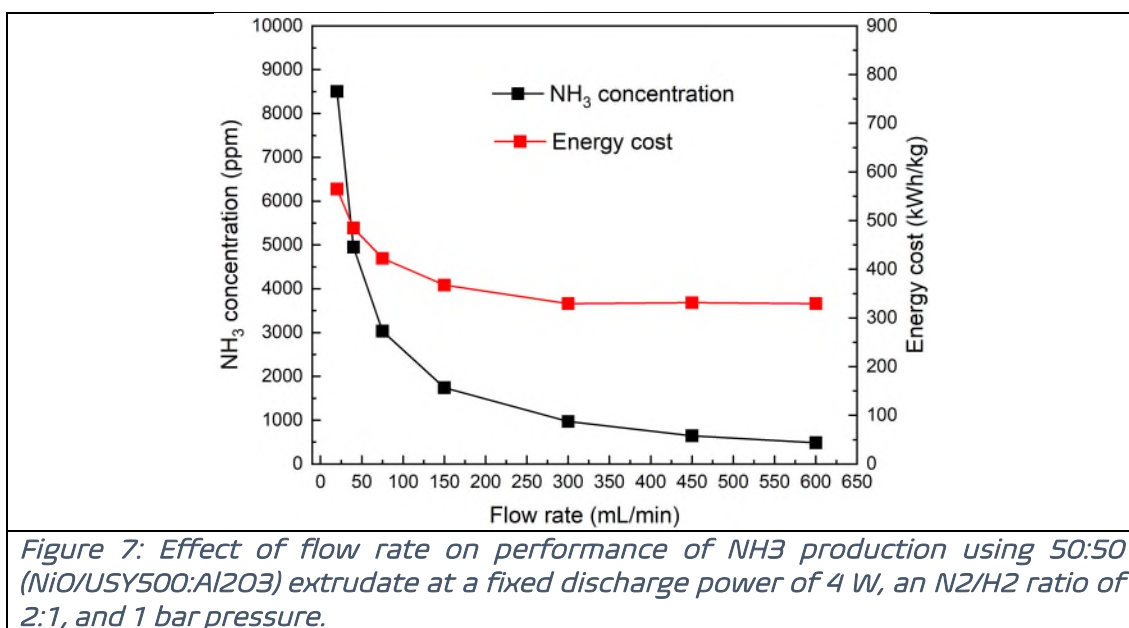
Initial 5/5 pulse plasma experiments at 2.5 bar (not shown) have determined that plasma doesn't reliably form in all tubes (randomly) with only 150-175 W_{input} (25-29 W_{input} per tube). As a result, the compromise between temperature and power per watt became 5/5 pulse plasma around 200-225 W_{input} ($\sim 33-38 W_{\text{input}}$ per tube).

3.3 Flow rate curve

Throughout the DARE2X project, it was observed that increasing the plasma power led to higher NH_3 concentrations, but also resulted in higher energy costs. In general, high NH_3 concentrations are beneficial for downstream separation. However, if a sorption process is applied downstream of the plasma process, a lower NH_3 concentration is not a limitation. Therefore, to make the process more competitive, further reduction of the energy cost is crucial. To address this, experiments were performed by UoL to investigate the optimum flow rate for NH_3 production.

For the flow rate experiments, the plasma reactor (single quartz tube) was loaded with the 50:50 (NiO/USY500:Al₂O₃) extrudate previously used in Deliverable D5.1. All experiments were carried out at a discharge power of $4 W_{\text{corrected}}$, an N₂/H₂ ratio of 2:1, and 1 bar pressure. In each experiment, a constant flow rate was applied, and the NH_3 concentration was measured by FTIR. Figure 7 shows the stabilized NH_3 concentration at different flow rates, and also compares the corresponding energy costs.

When the flow rate was increased from 20 mL/min to 600 mL/min (single tube), the NH_3 concentration decreased from 8503 ppm to 485.7 ppm. At the same time, the energy cost dropped rapidly from 565 kWh/kg NH_3 to 330 kWh/kg NH_3 . Above 300 mL/min, the energy cost remained nearly constant at $\sim 330 \text{ kWh/kg}_{\text{NH}_3}$. These results indicate a key trade-off between NH_3 concentration and energy efficiency. At low flow rates, higher NH_3 concentrations are achieved, which would favor conventional downstream separation. However, this comes at a steep energy penalty. By contrast, higher flow rates reduce NH_3 concentration but significantly improve energy efficiency. Since a sorption-based downstream process can accommodate lower NH_3 concentrations, operating at higher flow rates appears to be the most competitive option. Thus, the optimal regime for process development lies in the high-flow region ($>300 \text{ mL/min/tube}$), where energy cost is minimized and stabilized without further losses in efficiency.



4. Testing extrudates with optimal plasma parameters.

The optimal plasma configurations (5/5 pulse plasma 200-225 W_{input} (100-112 W power, 50 V DC-voltage, 8-9 kV high voltage, 20.5 kHz resonance frequency)) were tested on sorption-containing extrudates (25:25:50 (ZeoSorp:NiOCat:Al₂O₃) and 50:50 (NiOZeoSorp:Al₂O₃)) to see if a sorption-enhanced effect can be meaningfully realized. Constant 200-225 W_{input} plasma configurations were also investigated as control experiments (200-225 W power, ~8-9 kV high voltage 50 V DC-voltage).

All experiments used a reactor flow of 360 ml_{N₂}/min and 180 ml_{H₂}/min at 2.5 bar where the plasma was turned on at 0 minutes. In each experiment after plasma is turned off, the reactor flow is adjusted to 360 ml_{N₂}/min and 0 ml_{H₂}/min and the MFC pump is turned on to achieve ~0.8 bar (after ~10 minutes) for NH₃ desorption. The NH₃ desorption continued until the NH₃ concentration was negligible (ideally <20 ppm_{NH₃}). The resulting data (NH₃ concentration over time) was integrated and converted into NH₃ mass (ppm_{NH₃} x flow x time).

It is hypothesized that the post-plasma NH₃ measured in the previous experiments of D5.1 saturated well before 20 minute duration of plasma was completed. If this 1-3 mg_{NH₃} can be measured after smaller plasma durations, then we can demonstrate a potential sorption enhanced effect. Therefore, varying the plasma duration was investigated.

4.1 25:25:50 (ZeoSorp:NiOCat:Al₂O₃)

As mentioned in D5.1, testing the 25:25:50 (ZeoSorp:NiOCat:Al₂O₃) extrudate in the plasma reactor (~290 mg per tube, ~1740 mg per reactor) should demonstrate a sorption-enhanced effect where roughly 440 mg of the sorption material should have the capacity of roughly ~20 mg_{NH₃} (from D3.2 result of 44 mg_{NH₃} per 1 g_{ZeoSorp-extrudate}). After verifying the temperature of 5/5 pulse ~225 W_{input} (~90 W_{corrected}) to be around ~100 °C, we can expect a capacity of ~3 mg_{NH₃} (from 7 mg_{NH₃} per 1 g_{ZeoSorp-extrudate}). This capacity would be even less with a constant ~225 W_{input} (~90 W_{corrected}) plasma reaching >170 °C.

Initial tests measured the NH₃ throughput of constant ~225 W_{input} plasma at 20 minutes and 5 minutes (Figure 8). While the NH₃ measured post-plasma is an imperfect measurement because of the dwell volume, it should still provide a notion of how much plasma is being desorbed. In other words, this error will be negligible if the NH₃ desorption is significant enough to demonstrate meaningful sorption-enhancement.

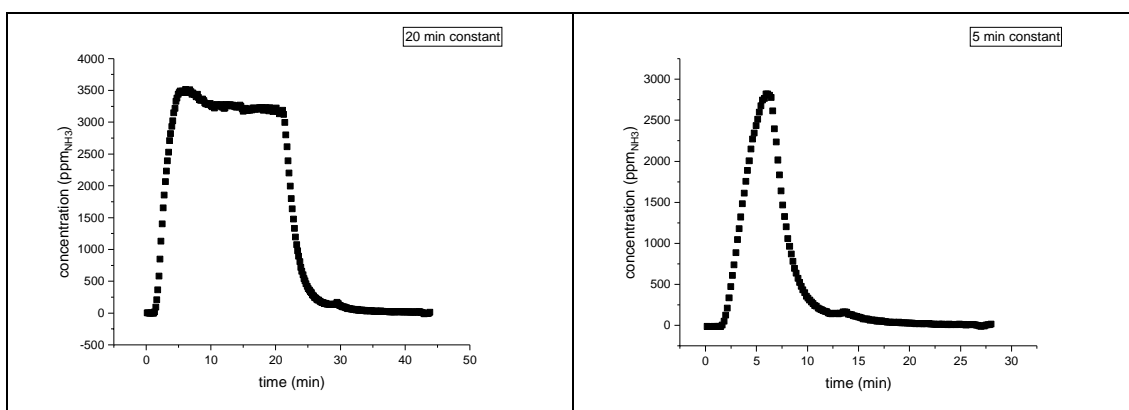


Figure 8: Demonstrator plasma reactor experiments using 25:25:50 (Sorption:NiOCat:Al₂O₃) extrudate. Constant plasma 216 W_{input} (216 W power, 8.1 kV high voltage, 50 V DC-voltage) (left). Constant plasma 217 W_{input} (217 W power, 8.0 kV high voltage, 50 V DC-voltage) (right).

The constant plasma experiments showed an interesting phenomenon, where the NH₃ measured post-plasma remained similar despite the different plasma durations (Table 4). However, this post-plasma remains a smaller fraction of the total NH₃ throughput. This can be due to the higher temperatures at constant plasma, and therefore a negligible NH₃ capacity that saturates very early. It is also apparent that our process efficiency (>1000 kWh per kg_{NH₃}) is very far from competitive (<20 kWh per kg_{NH₃}). If this NH₃ capacity is saturated almost immediately (after a few pulses of plasma), then the process efficiency would look much more promising (<500 kWh per kg_{NH₃}).

Table 4: Ammonia output of the 25:25:50 (Sorption:NiOCat:Al₂O₃) constant plasma experiments.

	Total mg _{NH3}	plasma mg _{NH3}	post-plasma mg _{NH3}	kW _{corrected} h per kg _{NH3}
constant 50V 20 min	26,9	22,6	4,3	1100
constant 50V 5 min	5,3	1,6	3,7	1400

The subsequent experiments used 5/5 pulse plasma (5 s on, 5 s off) at varying durations (20, 5, 2, and 1 minutes) to see if the lower temperature improves NH₃ capacity (higher post-plasma mg_{NH3}), and the shortest duration required to saturate this NH₃ capacity (Figure 9).

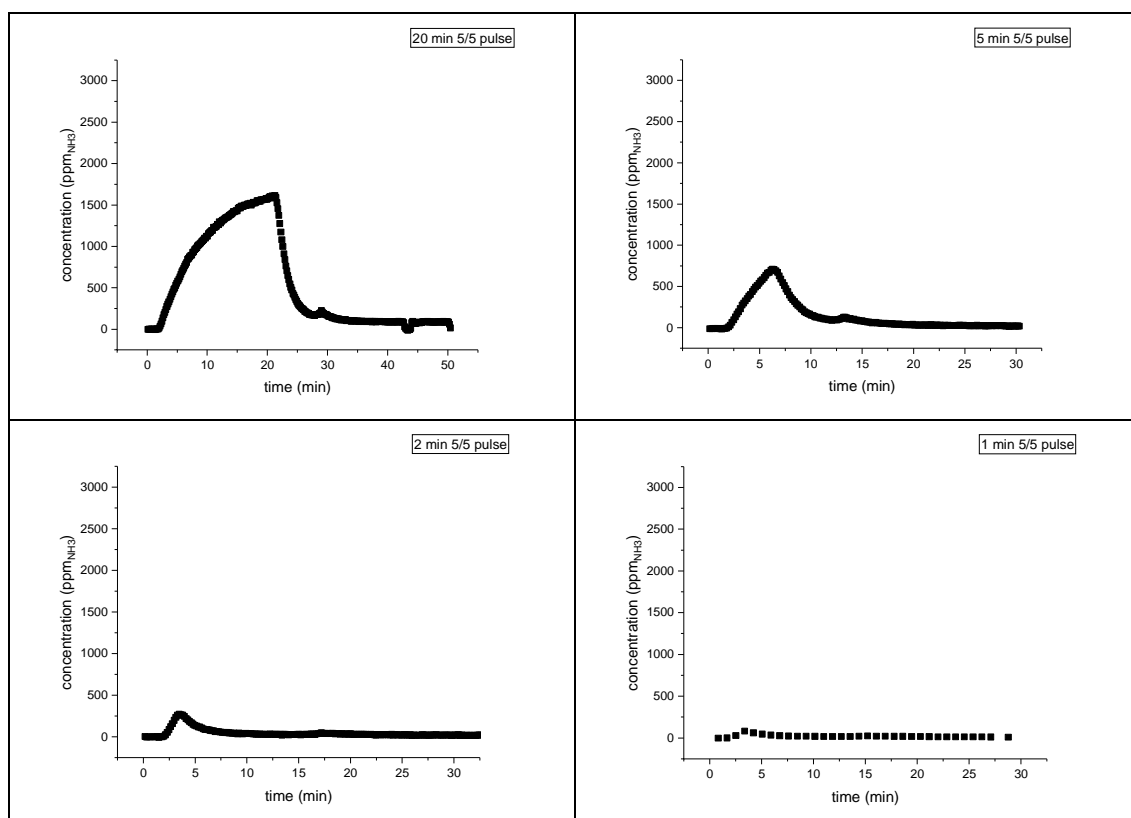


Figure 9: Demonstrator plasma reactor experiments using 25:25:50 (Sorption:NiOCat:Al₂O₃) extrudate. 5/5 pulse plasma 225 W_{input} (113 W power, 8.2 kV high voltage, 50 V DC-voltage) (top left). 5/5 pulse plasma 230 W_{input} (115 W power, 8.5 kV high voltage, 50 V DC-voltage) (top right). 5/5 pulse plasma 225 W_{input} (113 W power, 8.7 kV high voltage, 50 V DC-voltage) (bottom left). 5/5 pulse plasma 225 W_{input} (113 W power, 8.5 kV high voltage, 50 V DC-voltage) (bottom right).

With a 5/5 pulse plasma experiment, the power input is effectively halved compared to a constant plasma experiment of the same duration. Interestingly, the 5/5 pulse with a 20 minute duration (Figure 9, top left) had a similar post-plasma throughput as both the constant plasma experiments at 20 and 5 minutes (Figure 9). However, the 5/5 pulse experiments at lower

durations have lower post-plasma throughputs (Table 5). The experiments with 1, 2 and 5 minute durations show a linear trend in post-plasma throughput, which debunks any hope for saturating the extrudate’s NH₃ capacity very quickly (i.e. after a few pulses).

Table 5: Ammonia output of the 50:50 (NiOZeoSorp:Al₂O₃) 5/5 pulse plasma experiments.

	Total mg _{NH3}	plasma mg _{NH3}	post-plasma mg _{NH3}	kW _{corrected} h per kg _{NH3}
5/5 pulse 50V 20 min	11,7	7,8	3,9	1300
5/5 pulse 50V 5 min	2,0	0,3	1,7	1900
5/5 pulse 50V 2 min	0,7	0,0	0,7	2200
5/5 pulse 50V 1 min	0,4	0,0	0,4	2100

4.2 50:50 (NiOZeoSorp:Al₂O₃)

The 50:50 (NiOZeoSorp:Al₂O₃) extrudate was tested in the plasma reactor (~300 mg per tube, ~1800 mg per reactor) to see if the sorption-enhanced effect required closer proximities between the catalyst (NiO) and the sorption material. The plasma experiments are summarized in Figure 10.

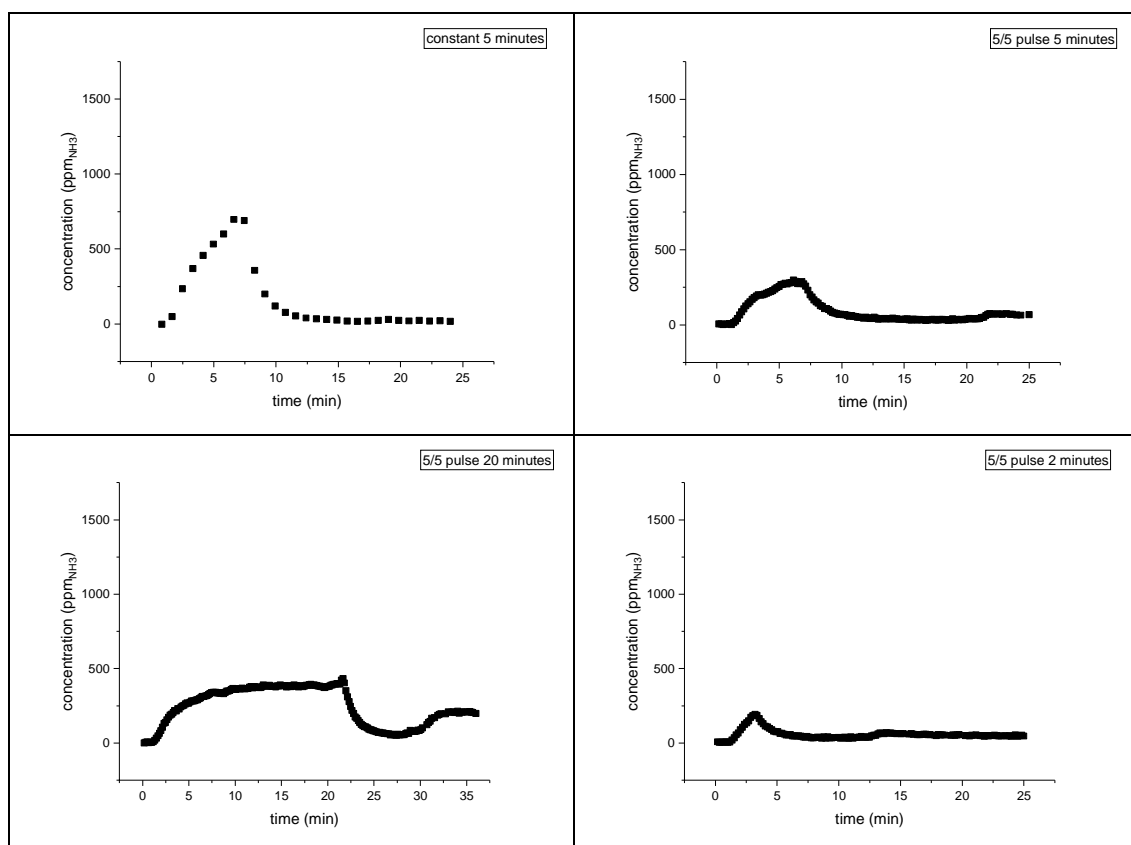


Figure 100: Plasma reactor experiments using 50:50 (NiOZeoSorp:Al₂O₃) extrudate. Constant plasma 214 W_{input} (214 W power, 8.5 kV high voltage, 50 V DC-voltage) (top left). 5/5 pulse plasma 230 W_{input} (115 W power, 8.9 kV high voltage, 50 V DC-voltage) (top right). 5/5 pulse plasma 236 W_{input} (118 W power, 9.2 kV high voltage, 50 V DC-voltage) (bottom left). 5/5 pulse plasma 238 W_{input} (119 W power, 8.9 kV high voltage, 50 V DC-voltage) (bottom right).

This extrudate has twice the amount of sorption material, therefore 6 mg_{NH₃} capacity (at ~100 °C) would be expected. Both constant and 5/5 pulse plasma was tested at a duration of 5 minutes, where there doesn't seem to be a significant difference between plasma throughputs when accounting for the half power input in the 5/5 pulse plasma (Table 6). However, there is a significant difference in post-plasma throughput, with the 5/5 pulse plasma yielding the same as the constant plasma despite half the power input. This significantly improves the catalysts performance from 4500 to 2500 (kW_{corrected}h per kg_{NH₃}). Additionally, both 20 and 2 minute durations were tested with the 5/5 pulse plasma, showing that shorter durations does not linearly decrease the post-plasma throughput. At 2 minutes, the catalyst still manages to yield a total 1,2 mg_{NH₃} (achieving 1800 kW_{corrected}h per kg_{NH₃}).

Table 6: Ammonia outputs of the 50:50 (NiOZeoSorp:Al₂O₃) plasma experiments.

	Total mg _{NH₃}	plasma mg _{NH₃}	post-plasma mg _{NH₃}	kW _{corrected} h per kg _{NH₃}
constant 50V 5 min	1,6	0,4	1,2	4500
5/5 pulse 50V 5 min	1,5	0,2	1,3	2500
5/5 pulse 50V 20 min	5,0	2,4	2,6	3200
5/5 pulse 50V 2 min	0,9	0,1	0,8	1800

The constant plasma yields are lower compared to the 5/5 plasma yields mainly due to lower post-plasma yields. This suggests that temperature affects these experiments via sorption-enhancement. In addition, the improvement of kWh per kg_{NH₃} with shorter plasma durations suggests better efficiencies because NH₃ sorption capacity quickly saturates resulting in diminishing returns for longer duration tests. As a result, a quick modification to the plasma reactor was applied to see if it was possible to further improve the cooling. The reactor was enclosed and cooled with a flow of cold N₂ gas (Figure 11). A temperature transmitter (ODENSA, FTX-300-LUX+) with a fiber optic temperature probe (ODENSA, PRB-G40) was used to measure the temperature of the enclosure (but not the actual plasma zone).

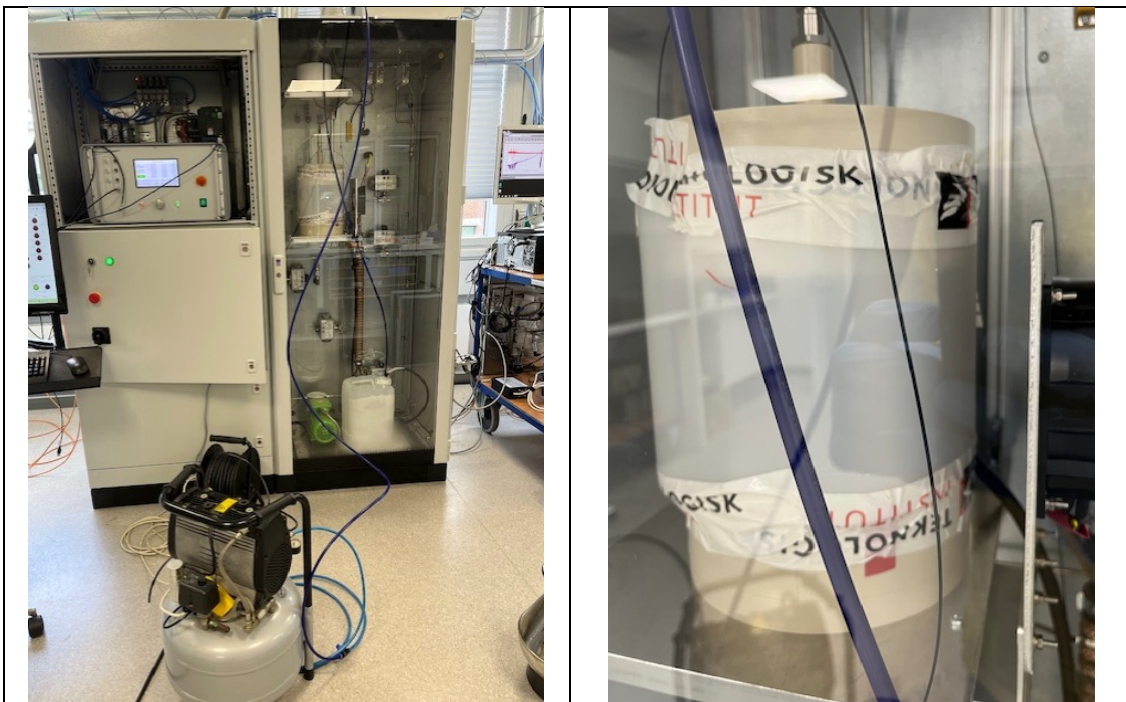


Figure 11: Plasma reactor experiments using 50:50 (NiOZeoSorp:Al₂O₃) extrudate replacing air cooling with liquid N₂ cooling. An air compressor pumps air into the liquid N₂ reservoir (left) which forces the cooled N₂ gas to evaporate through the enclosed reactor with a fiber optic temperature probe inside the enclosed space (right).

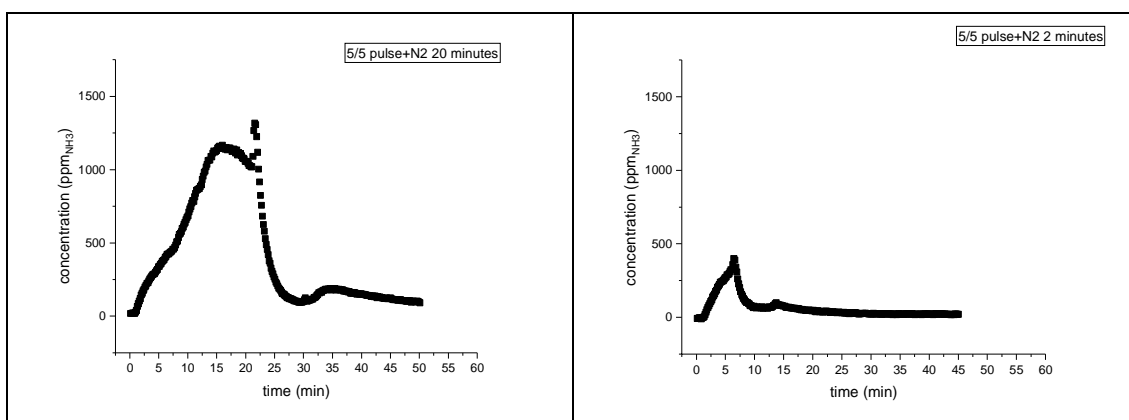


Figure 12: Plasma reactor experiments using using 50:50 (NiOZeoSorp:Al₂O₃) extrudate with N₂ gas cooling. 5/5 pulsed plasma 220 W_{input} (110 W power, 9.0 kV high voltage, 50 V DC-voltage) (left). 5/5 pulsed plasma 224 W_{input} (112 W power, 8.8 kV high voltage, 50 V DC-voltage) (right).

At the beginning of each experiment, the enclosure started around 10 °C. After the 20 and 5 minute plasma durations (Figure 12), the enclosure was 40 °C and 20 °C, respectively. This method seemed to improve the output of the 20 minute experiment, but not the 2 minute experiment (Table 7).

Table 7: Ammonia outputs of the 50:50 (NiOZeoSorp:Al₂O₃) plasma experiments.

	Total mg _{NH3}	plasma mg _{NH3}	post-plasma mg _{NH3}	kW _{corrected} h per kg _{NH3}
5/5 pulse 50V 20 min	9,2	5,4	3,8	1600
5/5 pulse 50V 5 min	1,2	0,2	1,0	3200

4.3 Conclusions on integrated sorption catalytic reactor

These investigations hoped to discover a meaningful sorption-enhancement effect. Meaningful in this case would be a well-performing extrudate (25:25:50 (ZeoSorp:NiOCat:Al₂O₃)) gaining an order of magnitude in NH₃ yield (<500 kWh per kg_{NH3}). This has not been the case. However, some improvements are seen in the poor-performing 50:50 (NiOZeoSorp:Al₂O₃) extrudate with something that could resemble sorption-enhancement. Sorption enhancement have been shown in literature,⁴ but we did not observe as big an effect. An explanation for this could be the lack of precise temperature control in the reactor. The sorption material was optimised for room temperature adsorption, but temperature measurements of the reactor is in the 80-200°C even with active air cooling. When the plasma is active the temperature increases, thereby lowering the NH₃ capacity. Then when the plasma is turned off temperature decreases during the desorption part which is the opposite of the desired operation for the sorption material. Further development of sorption-enhanced reactor will require precise temperature control of the reactor.

5. Including plasma reactions in a kinetic model for catalyst screening

The model conducts NH₃ synthesis catalyst screening using microkinetic simulations that operate within a batch reactor. Two versions of the microkinetic code were developed in Python: 1) a thermal catalysis version focusing on conventional surface catalysed reactions, and 2) a plasma-assisted catalysis version - extended model incorporating plasma generated radicals. Both use ordinary differential equations solved via solve_ivp with LSODA integrator (rtol=1e-13, atol=1e-14), screening grids of adsorption energies from -8 to -1.1 eV for the Nitrogen adsorption energies and -4.2 to -1.35 eV for hydrogen adsorption energies. Time integration spans 0–2 seconds to reach steady state.

Both simulations assume a batch reactor with volume 1.0 m³, temperature 800K, total pressure 10 Mpa, gas composition of 25% N₂/75% H₂ with no initial NH₃. The system distinguishes N-type sites (for N-containing species) and H-type sites (for H-containing species), with separate coverages, which accounts for site specific adsorptions.

The surface features two site types: N-type for nitrogen-containing species (N₂*, N*, NH*, NH₂*, NH₃*, vacant sites Q_vs_N) and H-type for hydrogen-containing species (H₂*, H*, vacant sites

Q_vs_H). This bifurcation accounts for distinct adsorption behaviors, preventing competitive poisoning. Coverages sum to unity per site type.

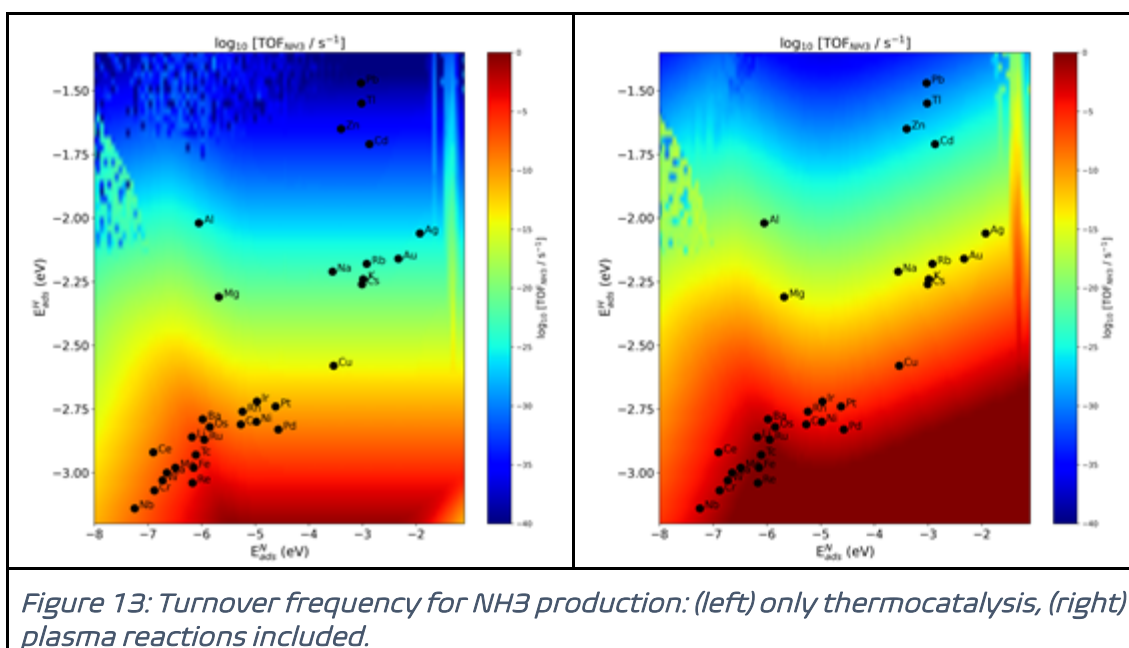
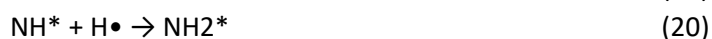
Both versions share common conditions: temperature (800K), total pressure (10 MPa), gas composition (1:3 N₂:H₂ ratio with no initial NH₃), reactor volume (1.0 m³) and active sites (1.0 mol). The system distinguishes N-type sites (for N-containing species) and H-type sites (for H-containing species), with separate coverages. This bifunctional model accounts for site-specific adsorption, common in heterogeneous catalysis where metals may have facets preferring N or H binding. Initial conditions set gas pressures to equilibrium values and surface vacant. Kinetic parameters are descriptor-dependent: Activation energies (E_a) for forward and reverse reactions are calculated via linear scaling relations derived from BEP principles. Performance metrics include maximum TOFs for key steps (N₂ dissociation, NH₃ formation, NH₃ desorption), surface coverages at peak NH₃ production, and overall activity.

Pre-exponential factors include A_{surf} = 2.0e10 s⁻¹·K⁻¹ for surface reactions, A_{N2} = 3.0e4 Pa⁻¹·s⁻¹·K^{0.5} and A_{H2} = 3.0e4 Pa⁻¹·s⁻¹·K^{0.5} for N₂ and H₂ adsorption, and A_{NH3} = 2.5e4 Pa⁻¹·s⁻¹·K^{0.5} for NH₃ re-adsorption. Activation energies (E_a) are derived from BEP relations using descriptors E_{ads}(N) and E_{ads}(H), screened over grids (e.g., -8 to -1.1 eV for N, -4.2 to -1.35 eV for H, 100 points each). Mixed descriptor mix_descNH = 0.07·E_{ads}(N) + 0.93·E_{ads}(H) informs NH_x barriers. Forward E_a are max(linear function, 0); reverse E_a follow thermochemistry.

The thermal catalysis version models a standard Langmuir-Hinshelwood mechanism on the surface, with 8 elementary steps. The reactions are reversible, and rates follow mass-action kinetics. The reaction steps include:



The plasma-assisted catalysis version extends the thermal model with 12 additional steps (9-20), incorporating plasma-phase radicals (N^* , H^* , NH^* , NH_2^*) for non-thermal activation which are also reversible:



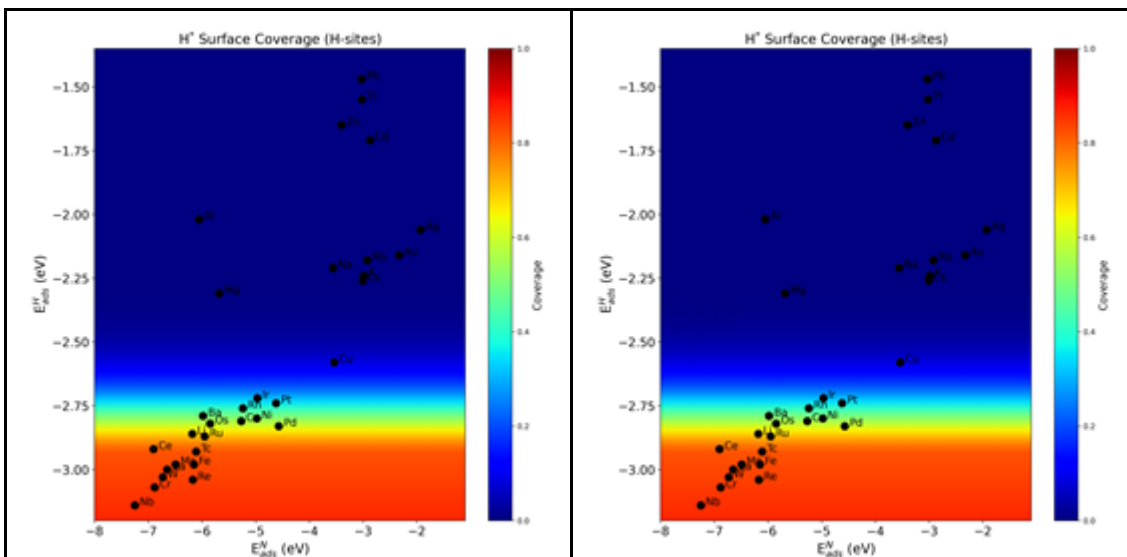


Figure 14: Hydrogen coverage: (left) only thermocatalysis, (right) plasma reactions included.

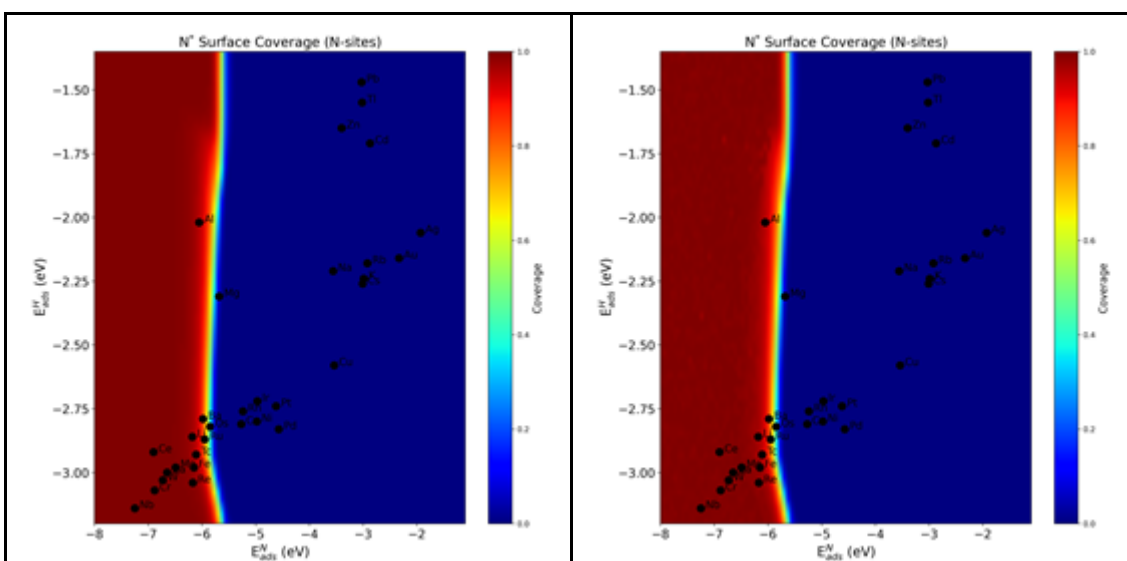


Figure 15: Nitrogen coverage: (left) only thermocatalysis, (right) plasma reactions included.

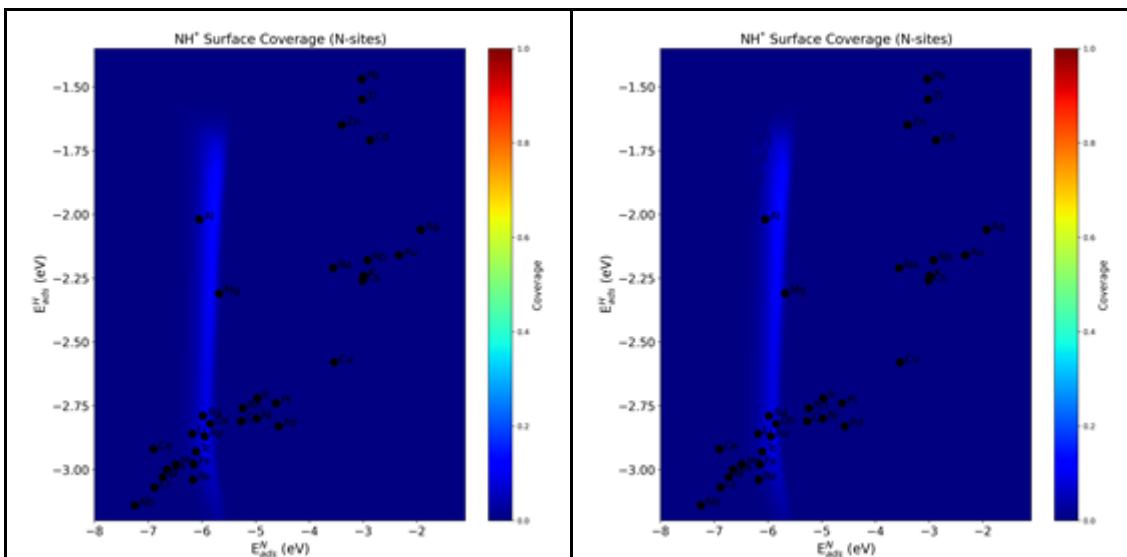


Figure 16: NH intermediate coverage: (left) only thermocatalysis, (right) plasma reactions included.

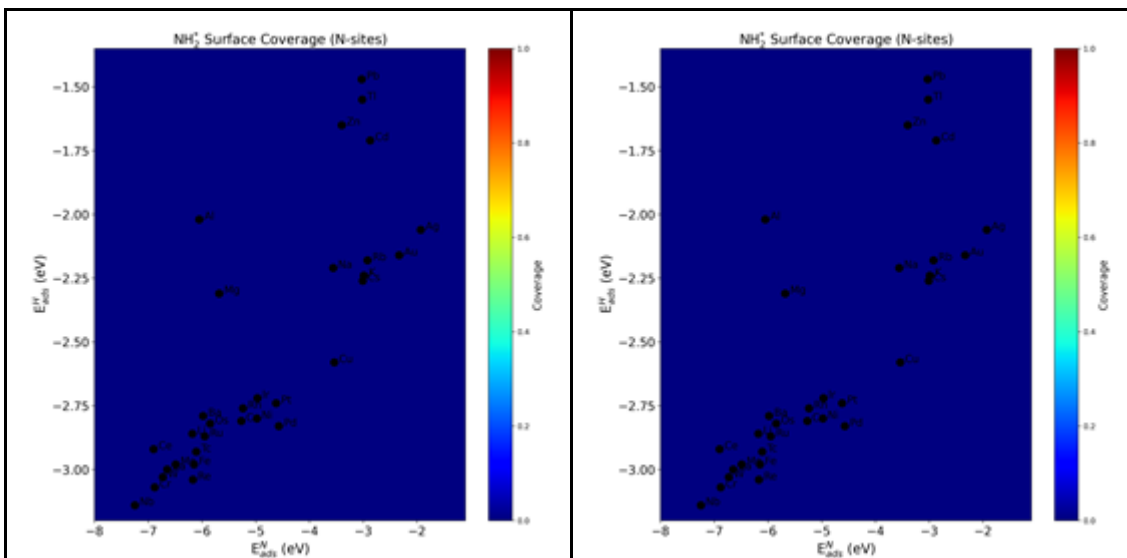


Figure 17: NH₂ intermediate coverage: (left) only thermocatalysis, (right) plasma reactions included.

Modelling showed that reactions occurring in plasma can be modelled with the thermocatalytic mechanism, which is supplemented with additional reactions taking place in plasma. This increases the rate of ammonia production and skews the maximum of the volcano towards catalysts that bind nitrogen slightly less strongly. Thus, ammonia is best produced on Ni and Co, instead of Ru and Fe. Overall, the rates increase.

6. Conclusions

The goal of WP5 was to integrate the catalyst (WP2), sorption material (WP3) and reactor design (WP4) into a lab-scale demonstration unit. This was achieved and this deliverable has summarized the main experiments performed on the unit in comparison reactor and material testing from the other WPs. The catalyst and sorption materials were integrated into an extrudate that yielded $>3000 \mu\text{mol}_{\text{NH}_3} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ and demonstrated a sorption-enhanced effect. In addition, the sorption unit successfully yields concentrations well over $>8 \text{ mol}\% \text{ NH}_3$.

This demonstration unit also successfully exhibits the challenges of upscaling this plasma technology while maintaining competitive energy efficiencies. The DARE2X project aimed to achieve $<10 \text{ kWh per kg}_{\text{NH}_3}$, where the state-of-the-art was understood to be around $55\text{--}60 \text{ kWh per kg}_{\text{NH}_3}$.^{5,6} After building the plasma reactor system, these literature sources were scrutinized in a different lens: it's not entirely clear how energy efficiencies of plasma catalysis are determined with supplemental heat providing higher temperatures. Plasma energy efficiencies of $<60 \text{ kWh per kg}_{\text{NH}_3}$ are achievable when the energy yield (at $250\text{--}300 \text{ }^\circ\text{C}$) is $15\text{--}20$ times than at conditions $<150 \text{ }^\circ\text{C}$.⁵ D2X achieved a total energy efficiency of $<350 \text{ kWh per kg}_{\text{NH}_3}$ (Figure 7), where supplemental heat ($250\text{--}300 \text{ }^\circ\text{C}$) could have possibly achieved a plasma energy efficiency closer to or below literature values. However, optimizing materials for higher temperatures would require more time and a different reactor design. A reactor design that could strictly control the temperature of the plasma zone would enable some interesting investigations. This could include testing several plasma temperatures windows with various catalysts (weak N-binding Ni or Co versus strong N-binding Fe or Ru) and sorption materials (adsorptions across $25\text{--}300 \text{ }^\circ\text{C}$) to further investigate if meaningful sorption-enhancement is possible for NH_3 synthesis via plasma catalysis.

7. References

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