

DARE2X

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

D3.2 – Deliver a sorption unit for validation

Lead beneficiary: Hulteberg Chemistry and Engineering AB

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Abstract: This report summarizes the upscaled sorption unit that was delivered to DTI and subsequently validated in their system.

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ABBREVIATIONS AND ACRONYMS

EC	European Commission	GA	Grant Agreement
HB	Hulteberg Chemistry and Engineering	DTI	Danish Technological Institute



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1. Introduction

A new Power-to-X technology for decentralized ammonia production based on sorption-enhanced, non-thermal, plasma catalysis is being investigated for the DARE2X project. Using the findings from D3.1 [1], a sorption material was selected and information obtained about its adsorption behaviour and capacity was translated into the design and construction of the sorption unit. This sorption unit was sent to DTI for validation with the ready-to-use sorption material: zeolite extrudates.

This report summarizes the design of the sorption unit and the experimental work related to the initial validation. It confirms similar adsorption and desorption capacities reported in D3.1 for the chosen zeolite.

2. System design

The design of the sorption unit used the data obtained during adsorption tests in Work Package 3 as well as from the plasma reactor tests together with assumptions based on well-accepted rules of thumb. In Table 1, the data used for the design and dimensioning of the adsorption unit is listed.

Table 1. The data used for the design of the sorption unit for the pilot demonstrator.

<i>Parameter</i>	<i>Value</i>	<i>Unit</i>
<i>NH₃ concentration</i>	2.0	mol%
<i>Energy yield plasma</i>	1.2	g NH ₃ / kWh
<i>Adsorption capacity zeolite [1]</i>	48	mg NH ₃ /g ads
<i>Density (bulk)</i>	0.5	g/cm ³
<i>Power supply max</i>	0.5	kW
<i>Cycle time</i>	4	h
<i>Ratio height/width</i>	35	
<i>Adsorber extra dimension factor</i>	50%	

The amount of ammonia in the inlet of the adsorption column is decided by the energy yield of the plasma together with the capacity of the power supply. A high energy yield and the maximum capacity of the power supply were used to calculate the maximum amount of ammonia to be adsorbed. The concentration of ammonia was estimated based on current plasma reactor test results and this was used to determine the total flow rate in the unit.

The adsorption capacity was based on the results from the dynamic adsorption tests performed in Work Package 3 with the chosen zeolite at 30°C, 1000 ppm NH₃ and 5/1 bar pressure swing. The adsorption capacity is dependent on the pressure, temperature and inlet concentration of ammonia and will therefore most likely differ slightly depending on the yield of the plasma reactor, but the listed adsorption capacity is believed to be a good estimation.

The cycle time was set to 4 hours to be able to complete an adsorption cycle during a workday and was used together with the estimated bulk density of the adsorbent to calculate the volume needed for the column to be saturated after the set cycle time. Meanwhile, the ratio between the height and width of the column was set using rule of thumb combined with technical expertise to obtain dimensions that fit the demonstrator unit and available commercial piping dimensions. Finally, an extra 50% was added to the size of the adsorber column to have the possibility to increase as well as decrease the adsorbent volume depending on the yield of the plasma reactor and the efficiency of the adsorption.

Using the above-mentioned data and assumptions, the resulting flows, volumes and dimensions are listed in Table 2. The total inlet flow rate is estimated to be 40 nL/h, of which 0.79 nL/h is ammonia, corresponding to 0.60g NH₃/h. This requires 50 g zeolite for the set cycle time, which equals 100 mL. With the added dimension factor this yields a column volume of 150 mL, with the optimal dimensions being 1.8 cm in width and 62 cm in height. The width of the column determines the maximum particle size to guarantee good packing of the adsorbent bed and minimize wall effects, i.e. 1.8 mm.

Table 2. Calculated values of flow, volume and dimensions of the sorption unit for the pilot demonstrator.

Parameter	Value	Unit
Total flow	39.5	nL/h
Ammonia flow	0.79	L/h
Molar flow NH ₃	0.035	mol NH ₃ /h
Mass flow NH ₃	0.60	g/h
Mass adsorbent/cycle	50.0	g
Volume adsorbent	100	mL
Volume adsorber	150	mL
Width column	1.8	cm
Height column	62	cm
Particle size max	1.8	mm

The calculated volumes and its resulting dimensions were used for the final design specification of the sorption unit, listed in Table 3. For the construction, a 70 cm long 1" tube of stainless steel was used. The tube can hold up to 150 ml of adsorbent, in this case 1.6mm zeolite extrudates.

Table 3. Final design parameters of the sorption unit for the pilot demonstrator.

Adsorber unit specifications	
Volume	150 mL
Width column	1" OD
Height column	70 cm
Material	SS-316
Temperature span	Approx. -73 – 600 °C
Pressure span	0-40 bar
Adsorbent	Zeolite extrudate
Particle size	1.6 mm

3. Validation of sorption unit

3.1. Experimental

The sorption unit, Figure 1, was first validated without any sorption material added and then validated with the loaded sorption material. The sorption material was loaded as delivered directly from the vacuum sealed bag (Zeolite extrudates, 125 g, 150 ml, dried at 120 °C). Gases used were 2% NH₃/N₂ (1036-2%NH₃/N₂) and N₂ (13-N₂). Brooks Mass Flow Controllers were used to control the flow of gases (GF040CXXC-1036002L-T2PNS4-XXXXAX-00C and GF040CXXC-0013020L-T2PBS4-XXXXAX-00C respectively).

Excess ammonia was trapped in 500 ml de-ionized water using a bubbler (Simax) with a Por.4 filter (robu-glass). The trapped ammonia was quantified using a UV-Vis spectrometer (Macherey-Nagel Nanocolor-Vis 2) with its corresponding test kits (Nanocolor Ammonium 100 Ref: 985008 and Nanocolor Ammonium 2000 Ref: 985002). All experiments were conducted at room temperature (20-25 °C).



Figure 1. Summary of the experimental set-up with the sorption unit, water trap and mass flow controllers (not pictured).

3.1.1. Validation of experimental set-up

The experimental set-up was initially validated with an empty sorption unit, Table 1. Experiments #1 and #4 were expected to have less NH₃ because the system still needed to saturate with NH₃ during that first hour (labelled 'Initial' in comments). Disregarding these initial experiments, an average of 87.3 mg (± 4.8) NH₃ was measured, which accounts for >95% of the ammonia input with a relative error of around 5%.

Table 4. Validation of experimental set-up.

Exp #	Gas (NH ₃ ppm)	Gas (ml/min)	Time (h)	Pressure (bar)	Input (NH ₃ mg)	Measured (NH ₃ mg)	Comment
1	20000	100	1	1.5	90	75 (±2)	Initial
2	20000	100	1	1.5	90	90 (±1)	
3	20000	100	1	1.5	90	80 (±3)	
4	20000	100	1	1.5	90	82 (±2)	Initial
5	20000	100	1	1.5	90	90 (±3)	
6	20000	100	1	1.5	90	89 (±4)	

3.1.2. Validation of sorption unit

The Zeolite extrudates (125 g) were loaded directly into the sorption unit without any pre-treatment. Experiments were performed in 3 cycles (Exp # 1.x, 2.x, 3.x) where each cycle had sub steps measuring either excess NH₃ during adsorption (gas NH₃ 20000 ppm, 3.5 bar) or released NH₃ during desorption (gas NH₃ 0 ppm, 1.5 bar). Net adsorbed NH₃ was calculated based on NH₃ input (Gas NH₃ ppm x flow x time), and NH₃ measured in the water trap (bubbler, 500 ml D.I.), Table 5,

Table 5. Validation of the sorption unit.

Exp #	Gas (NH ₃ ppm)	Gas (ml/min)	Time (h)	Pressure (bar)	Input (NH ₃ mg)	Measured (NH ₃ mg)	Adsorbed (NH ₃ mg)
1.1	20000	1500	4.5	3.5	6075	930 (±2)	5145
1.2	20000	200	0.5	3.5	90	74 (±1)	5160
1.3	20000	200	0.5	3.5	90	71 (±1)	5170
1.4	0	200	0.25	1.5	0	40 (±1)	5130
1.5	0	200	16.5	1.5	0	1745 (±34)	3385
2.1	20000	1500	2	3.5	2700	667 (±30)	5420
2.2	0	200	0.25	1.5	0	93	5325
2.3	0	200	0.5	1.5	0	235	5090
3.1	20000	1500	1.5	3.5	2025	1467	5650
3.2	0	200	0.75	1.5	0	331 (±3)	5320
3.3	0	200	18.5	1.5	0	1477 (±7)	3840

3.2. Results and Discussion

For these initial validations, it was important to account for most of the ammonia being inputted into the system. Validating the experimental set-up, Table 4, meant that most of the ammonia (>95%) was accounted for and no doubts could arise whether the ammonia had been adsorbed or blown through our water trap (bubbler).

When validating the sorption unit, the experiments run in D3.1 [1] were used as basis. It had PSA experiments (5/1 bar, 30 °C, 10000 ppm NH₃) where the 1st cycle had a breakthrough time of roughly 38 minutes, and the subsequent cycles had a breakthrough time of 22 minutes. This translates to roughly 55-60% of the ammonia being desorbed when swinging from 5 bar down

to 1 bar, which can roughly be translated to the attainable physisorbed ammonia. The remaining 35-40% is the more strongly bound chemisorbed ammonia that is too impractical to desorb and can be thought of as a one-time sunk cost. Given that the pressure swings in the validation were from 3.5 bar down to 1.5 bar, less than 55-60% of our ammonia was expected to be desorbed.

The reported adsorption capacities in D3.1 and sorption unit validation experiments are summarized in Table 6. It is important to note that adsorption capacity is highly dependent on the NH₃ gas concentration (ppm) and gas flow speed (ml/min) during the adsorption step. These were markedly higher in the validation experiments time, 2% NH₃ instead of 1000 ppm and 1500 ml/min instead of 300 ml/min.

Table 6. Summary of adsorption capacity for the zeolite in each cycle.

Experiment	Cycle	Adsorption capacity (mg _{NH3} /g _{adsorbent})	NH ₃ desorbed (%)
D3.1 (PSA exp 10)*	1	79	-
	2	48	-
	3	44	-
Validation	1	41	35
	2	43	-
	3	45	35

* It was not possible to calculate the amount of NH₃ desorbed in these experiments since the measured NH₃ concentration during desorption was above the limit for the analysis equipment used.

The first experiment (#1.1) started with an input of 6075 mg_{NH3} (1500 ml/min, 4.5 h), and measured an excess of 930 mg_{NH3}, suggesting breakthrough had occurred. Two subsequent experiments (#1.2, #1.3) verified that most of the ammonia input (90 mg_{NH3}, 200 ml/min, 0.5h) resulted in the water trap (71-74 mg_{NH3}). A pressure swing desorption was performed (#1.4) with N₂ gas (200 ml/min, 0.25 h, 1.5 bar) but was largely ineffective due to the flow limitations of the water trap (200 ml). Therefore, the system was purged overnight (#1.5) with N₂ gas (200 ml/min, 16.5 h, 1.5 bar) and resulted in a desorption of 1785 mg_{NH3}. This concluded the first cycle, suggesting an adsorbent capacity of 41 mg_{NH3}/g_{adsorbent}, with 35% of the ammonia desorbed.

The second cycle started (#2.1) with an input of 2700 mg_{NH3} (1500 ml/min, 2.0 h), and measured an excess of 667 mg_{NH3}, suggesting breakthrough had occurred. The subsequent pressure swing desorption (#2.2) with N₂ gas (200 ml/min, 0.25 h, 1.5 bar) had similar results (93 mg_{NH3}), and was followed by a brief purging period (#2.3) with N₂ gas (200 ml/min, 0.5 h, 1.5 bar) resulting in 235 mg_{NH3}. This concluded the second cycle, suggesting an adsorbent capacity of 43 mg_{NH3}/g_{adsorbent} but without enough time to fully desorb the physisorbed ammonia, which was estimated to take roughly 7-8 hours (200 ml/min, 1.5 bar) or 1 hour (1500 ml/min, 1.5 bar).

The third cycle started (#3.1) with an input of 2025 mg_{NH3} (1500 ml/min, 2.0 h), and measured an excess of 1467 mg_{NH3}, suggesting breakthrough had occurred. The subsequent pressure swing and brief purging period were combined (#3.2) with N₂ gas flow (200 ml/min, 0.75 h, 1.5 bar) and resulted in 331 mg_{NH3}, which matched very well with the ammonia measured in #2.2 and #2.3 (331 mg_{NH3}). The system was purged overnight (#3.3) with N₂ gas (200 ml/min, 18.5 h, 1.5

bar) and resulted in a total desorption of 1811 mg_{NH₃}. This concluded the third cycle, suggesting an adsorbent capacity of 45 mg_{NH₃}/g_{adsorbent}, with 35% of the ammonia desorbed.

4. Conclusions

The sorption unit was designed based on input from D3.1 and delivered for validation. The validation tests show similar adsorption capacities as the previously measured. The rising adsorbent capacities across cycle 1-3 suggest the sorbent material was not entirely saturated but the consistent desorption values suggest proximity to saturation. The total desorption of cycle 1 and cycle 3 match very closely, with 35% ammonia desorption when swinging from 3.5 to 1.5 bar. This also aligns with D3.1 where it achieved 55-60% desorption but with a larger pressure swing from 5 to 1 bar. The limitation of the water trap means that the desorption step could not be as aggressive and fast as would be intended with realistic operations, but it still gave us values within reasonable expectations.

The sorption unit functions as devised and is ready for operation together with the plasma unit in the two-stage process.

5. References

- [1] B. Rolim, J. Digné and C. Hulteberg, "D3.1 - Summary of experiments WP3," 2024.