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Decentralized production of Nitrogen-based fertilizers

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Samenvatting

De huidige wijze van grootschalige productie van ammoniak is gezien het effect op het klimaat op lange termijn niet houdbaar. Ammoniakproductie kan duurzamer worden gemaakt door fossiele brandstoffen (aardgas) te vervangen door waterstof uit hernieuwbare elektriciteit, die vervolgens reageert met stikstof in het Haber-Bosch proces. Deze nieuwe technologie heet Power2ammonia en biedt ook de mogelijkheid om decentraal te opereren.

Nederlandse boeren zoeken naar mogelijkheden om duurzame elektriciteit, die middels zonnepanelen lokaal wordt gegenereerd, effectief te benutten. Eén van de mogelijkheden is om deze duurzame elektriciteit te gebruiken voor kleinschalige productie van ammoniak.

In dit rapport is het onderzoek naar de haalbaarheid van decentrale productie van duurzame ammoniak in agrarische gebieden, inclusief kansrijke toepassingen van duurzame ammoniak, beschreven. Er zijn drie nieuwe technologieën geëvalueerd in zes verschillende business cases namelijk:

- productie van ammoniak via groene waterstof en het Haber-Bosch proces middels NFUEL technologie en verdere verwerking tot kunstmest (ammoniumnitraat, calcium-ammoniumnitraat, ammoniumfosfaat, en ureum-ammoniumnitraat);
- nitraatproductie via oxidatie van stikstof uit lucht en verdere verwerking tot kunstmest;
- productie van een NH_4-rijke waterige oplossing uit afvalwater middels membraan capacitieve de-ionisatie (MCDI).

De NFUEL technologie is commercieel beschikbaar, de andere twee technologieën zijn nog in ontwikkeling.

Uit de studie blijkt dat het gebruik van duurzame ammoniak als grondstof voor de productie van kunstmest op een schaal van 1000 ton per jaar (1,5 MW NFUEL) economisch niet haalbaar is vanwege de hoge kostprijs van de productie van duurzame ammoniak ten opzichte van fossiele ammoniak. Uit de economische analyse blijkt dat voor de productie van duurzame ureum minimaal 20.000 ton per jaar duurzame ammoniak productie nodig is om economisch haalbaar te zijn. In de toekomst kan het kostprijsverschil kleiner worden door CO_2 belasting, verbeteringen in het Haber-Bosch proces en kostenverlaging van de elektrolyse installatie.

Een veelbelovend alternatief is het produceren van op nitraat gebaseerde meststoffen via luchtoxidatie op 30-50 kW schaal. Naast economische voordelen ten opzichte van kunstmest productie uit duurzame ammoniak, is de implementatie ook eenvoudiger. De faciliteit kan werken met de bestaande netaansluiting (maximaal 55 kW) op boerderijen en een gezamenlijke investering met meerdere boeren, zoals het geval is voor de duurzame kunstmest productie met behulp van de 1,5 MW NFUEL technologie, is niet nodig.
Ten slotte is de MCDI-technologie interessant wanneer er naast de productie van kunstmest ook afvalwaterzuivering nodig is.

Contents

1 Introduction

1.1 Project background

Ammonia production, as it is currently practiced, is economically and environmentally unsustainable in the long term. In 2006, ammonia produced by the Haber-Bosch process, which is the main industrial procedure, represented 1.4% of the world consumption of fossil fuel. In light of this fact, ammonia production can be achieved by replacing fossil fuels (methane) with green hydrogen from renewable electricity, which reacts with nitrogen obtained through air separation, in the Haber-Bosch process [1]. This new technology is called Power2ammonia and it also provides the option of operation on a decentralized scale.

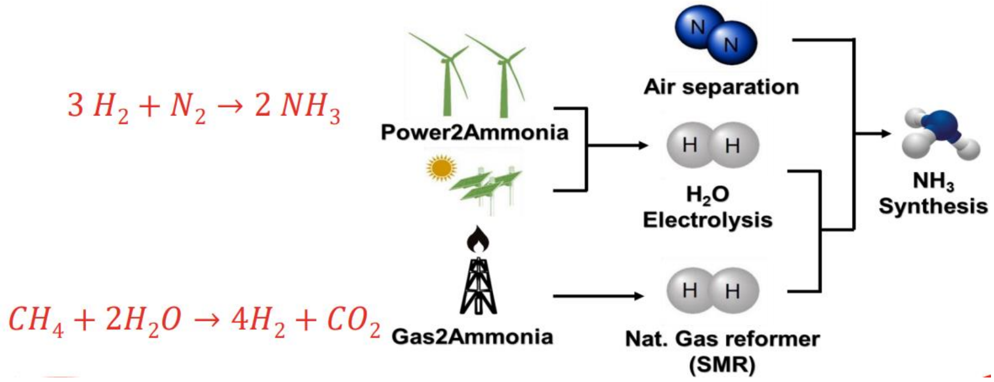

Figure 1: Schematic illustration of new sustainable path for the ammonia production by replacing methane reformer with electrolysis in hydrogen production step. [2]

Although new technologies are under investigation, none of them, except small scale Haber-Bosch ammonia synthesis coupled with water electrolysis, appear to be capable of supplying ammonia with renewable electricity in the short term [3]. Proton Ventures is one of the leading companies in the sector, constructing mini ammonia plants in three different capacities, as presented in Table 1.

Table 1: Proton Venture’s NFUEL mini ammonia plant capacities. [4]

	NFUEL 1	NFUEL 4	NFUEL 20
Capacity (t/a)	1,000	4,000	20,000
Capacity (kg/h)	125	417	2,500
Power consumption (MW)	1.5	5-6	25-30

Dutch farmers search for opportunities to install solar panels and utilize them effectively. The use of a small-scale Power2ammonia production plants in agricultural areas is the main option under investigation. The maximum capacity of renewable electricity that can be supplied using solar panels at a farmers site is assumed to be 1.5 MW.

1.2 Goal and objectives

The goal of this study is to examine the viability of using locally produced renewable electricity to produce green ammonia in decentralized agricultural areas of the Netherlands.

The objectives of the study are to:
1. Identify the economic challenges of small-scale green ammonia production.
2. Identify promising applications of green ammonia.
3. Propose business cases and evaluate their viability.
4. List recommendations that could improve the profitability of small-scale green ammonia production.
5. Propose possible alternative solutions for utilization of solar energy by farmers, apart from green ammonia production via the NFUEL facility.

1.3 Approach

It is known that the small scale production of green ammonia is economically unfavourable. For that reason, the initial step of the study is to determine the economic challenges of mini green ammonia plants in order to identify options that could improve the viability of the process. Afterwards, all the possible applications of NH_3 are listed and the ones that can benefit from decentralized production are selected. The next step is to perform a market analysis, and based on that select four business cases. The business cases are evaluated and economic recommendations are provided aiming to make the process as economical as possible.

2 Economic challenges of mini green ammonia plants

Green ammonia production is expected to be economically unviable, especially at small scale. This chapter summarises information from the literature to provide a first indication of the economic challenges.

Queensland Nitrates Pty Ltd (QNP) evaluated five potential commercialisation pathways (based on capacity) for green ammonia production to displace ammonia which is currently purchased by QNP for use at its ammonium nitrate facility at Moura [4]. These options were:

- 20kt per annum of green ammonia
- 88kt per annum of green ammonia
- 300kt per annum of green ammonia
- 500kt per annum of green ammonia
- 1mt per annum of green ammonia

The study showed that the economic viability is improved (eg. lower capital costs, lower electricity cost) with the increase of the plant scale. The only case that was viable without any subsides, grants or concessional loans was the largest scale production of 1Mt per annum. [5]

2.1 Capital costs

The installed cost for a small scale ammonia plant by Proton Ventures (20,000 mtpa) will be around 1,250 USD/tonne ammonia annual output. This value is similar to the cost for larger scale plants. For the smaller plants of 4,000 tpa the capital expenditure costs can be as high as 3,000 USD/tonne ammonia installed. There is no data for the 1,000 tpa ammonia production examined in this project, but it is expected that its capital investment will be certainly higher than 3,000 USD/tonne ammonia. [3]

The ammonia plant cost trend can be studied by examining the investment cost of the electrolyser for different capacities. An 1.5 MW N-FUEL unit could produce 1,000 tpa ammonia, at an implied energy intensity of 12 MWh per ton ammonia. With 10-11 MWh for hydrogen production from electrolysis, these data imply that approximately 90% of the power consumed by a small scale all-electric ammonia plant is used in hydrogen production. [6][7]

That means that around 1.3 MW are required for the operation of the electrolyser.
From the graph shown in Figure 2, it is clear that the investment of a small-scale 1.3 MW electrolyser is very large.

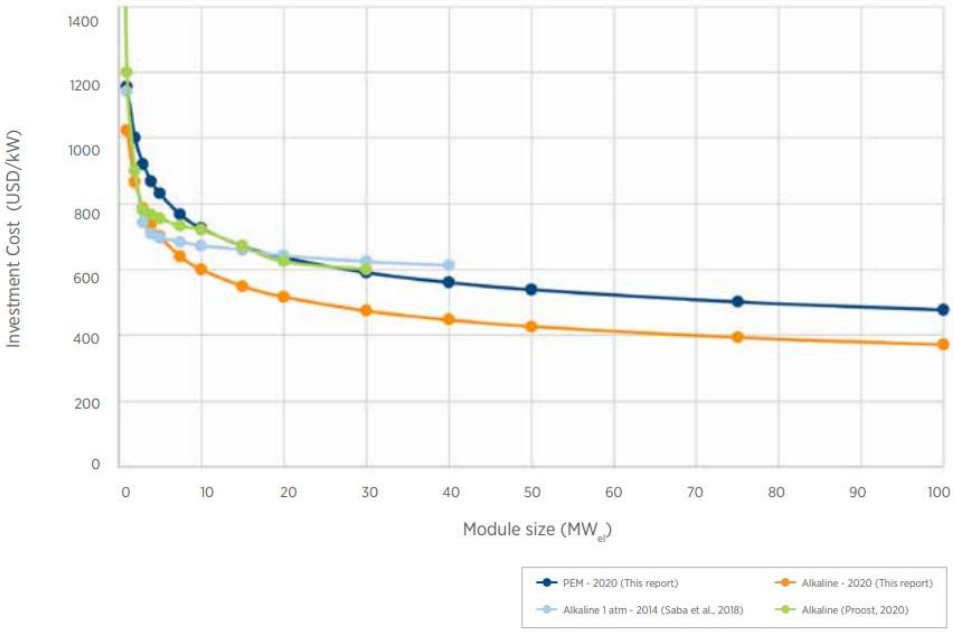

Figure 2: Electrolyser investment cost as a function of module size for various technologies. [8]

As shown in Figure 3, the electrolyser capital cost accounts for 21% percentage of the total capital costs. In order to obtain a clearer view of the dependency of capital cost on the plant capacity, a similar analysis of the ammonia synthesis unit, which accounts for 26% of the total costs, is also required.

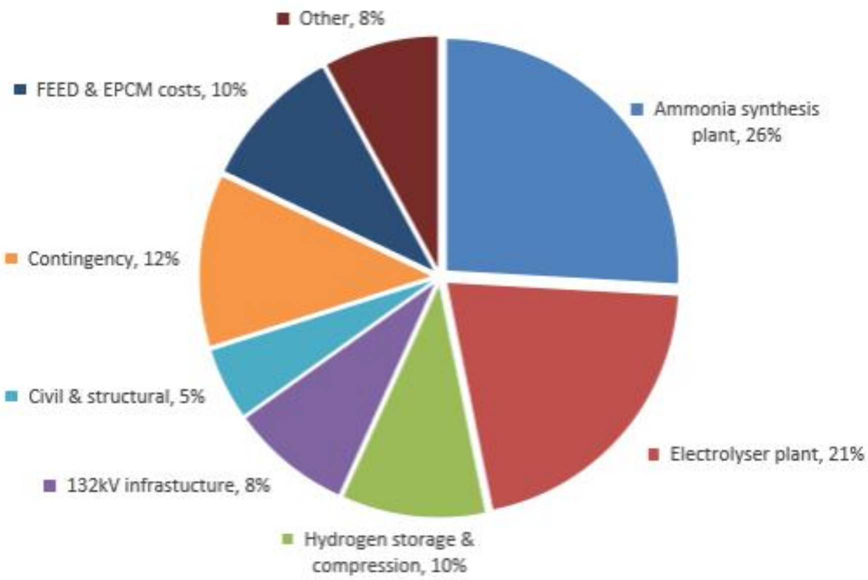

Figure 3: A breakdown of a 34 MW green ammonia project’s capital costs. [5]

2.2 Operating costs

Similarly to the CAPEX, the energy consumption of the plant also increases significantly when the capacity is very low. According to a study from 2020, the conventional Haber-Bosch process can be improved using an absorbent-enhanced process for ammonia removal, which can reduce the energy consumption up to 8 kWh/kg at small scale (see Figure 4). The 120 kg/h (1,000 mtpa) production rate, which corresponds to 1.5 MW usage, is indicated with a blue circle. The graph shows that the energy consumption is higher for 1.5 MW compared to larger scale. Additionally, the graph suggests that the performance could be slightly improved using the absorbent-enhanced Haber-Bosch process. [7]

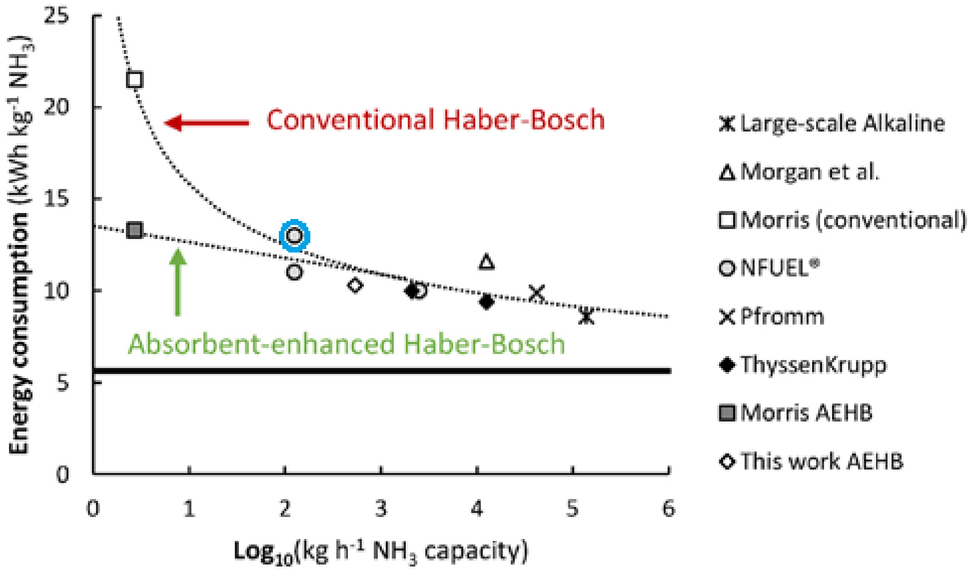

Figure 4: Energy consumption of various electrolysis based Haber-Bosch processes at various ammonia capacity levels (at ≥100 bar operating pressure for conventional processes, absorbent-enhanced processes are denoted by AEHB). [7]

Small scale ammonia units require a higher specific energy consumption than large scale units, because of the effects of economics of scale and the less integrated design. The latter leads to less co-generation and/or heat integration, which usually does not pay off for smaller units. In addition, smaller units have higher heat losses and relatively higher fugitive emissions. [3]

For large-scale electrolysis-based conventional Haber-Bosch plants, the energy consumption is nearly constant (about 9–11 kWh kg^{-1} ammonia). However, upon further scale-down, heat transfer limitations become relevant for conventional high-pressure, electrolysis-based Haber-Bosch plants (see Figure 4). This can be tackled by designing the process for less severe process conditions (i.e. lower operating pressure and temperature than conventional Haber-Bosch plants). A solution proposed by Cussler et al., is a low-pressure ammonia synthesis process (at 10–30 bar). This technology combined with an absorbent-enhanced process for ammonia removal, constitute the Absorbent-enhanced Haber-Bosch. Additionally, these conditions are preferable for small-scale intermittent operation due to increased heat losses to the environment upon scale-down. [7]

The NFUEL units are designed to withstand rapid power fluctuations. The control philosophy is based on rapid on-standby circles, with negligible power consumption during stand-by mode. Labor costs are minimal as the monitoring & control of the unit will be done remotely through a wireless secure internet connection, and minimal operational presence will be required for the unit's control. [9]

3 Applications

The possible applications of decentralised green ammonia production are the following:

1. Fuel for land or maritime (direct combustion of NH_3 or mix of diesel 70% /NH_3 30%);
2. Energy storage & fuel for electricity production (cracking prior to combustion) (more attractive/easier than H_2 storage);
3. deNOx fluid;
4. NH_3 refrigerant;
5. Fertilizers (urea, CAN, mix with phosphorus/potassium);
6. Precursor for the production of other chemicals (ammonium nitrate).

The first two options have attracted a lot of interest over the last years, because the generation of ammonia from renewable electricity enables its use as a fuel. Direct firing of NH_3 would give the highest efficiency, but this would require the development of a complete new combustor, which requires much time, resources and investments and a probability for high NOx emissions. Time to market for large scale applications is estimated to be between 5 and 10 years. [10] Cracking prior to combustion makes sense, especially when combined with storage of ammonia for use in case of intermittency of renewable electricity. This scenario will be essential at a stage of deep decarbonization, but currently it is challenging to make it economically viable. [10] Green ammonia is expected to become a technically viable and economically competitive fuel (without any subsidies) for decarbonization of the electricity sector by 2040. Towards this goal, current research focuses on improving the performance of large scale electrolysers. Hence, both options 1 and 2 are suitable for larger scale production in the very long-term, and not for a small scale 1,000 mtpa ammonia production plant in the next years. [11]

NH_3 is used to prevent the emission of NOx in power plants or road transportation (DeNOx-application) and as a refrigerant gas. In both cases, ammonia needs to be distributed to industries, so there is no benefit in decentralized production that could offset the higher production costs. Hence, these options are not going to be evaluated further. Additionally, refrigeration requires NH_3 purity up to 99.97%. Proton Ventures claim they can produce high-purity ammonia with the NFUEL facility, which meets the commercial requirements.

Approximately 90% of NH_3 production is used as feedstock for fertilizers. [10] The fertilizer sector can benefit from the advantages of decentralized production that are described in chapter 5. Hence, the main application targeted in this report is the use of green ammonia as fertilizer in the local agricultural area.

Lastly, ammonia can be upgraded to other valuable chemicals. The most popular application is the manufacturing of ammonium nitrate, which is directly produced from ammonia without the need of other reactants and is widely used in explosive manufacturing as an oxidizing agent. This option is also evaluated in the report.

4 Market analysis

4.1 Decentralized Location for fertilizer production

The agricultural and urban area of the Netherlands can be seen in Figure 5. The mini ammonia plant should operate in a rural area, distant from other fertilizer production facilities. The four largest production sites of the Netherlands (Yara Sluiskil B.V., OCI Nitrogen BV, ICL Fertilisers and Rosier Nederland) are also shown in Figure 5. [12] The area of Hoeksche Waard is used as a reference case in the current project and is shown with a black pin. Hoeksche Waard has a surface of approximately 247 km^2, of which 190 km^2 (77%) has an agricultural function.

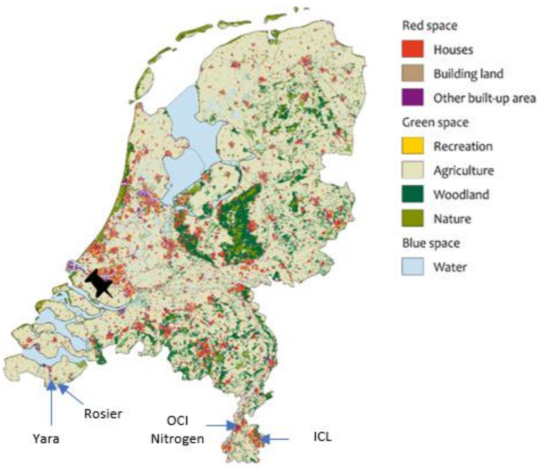

Figure 5: Land use in the Netherland in 2012. Hoeksche Waard is indicated with the black pin. [13]

As shown, in Figure 6, it is located at an "orange" zone, which means that the power generated by solar panels and the sunshine-hour per year are above average. Hence, the location is suitable for renewable electricity production.

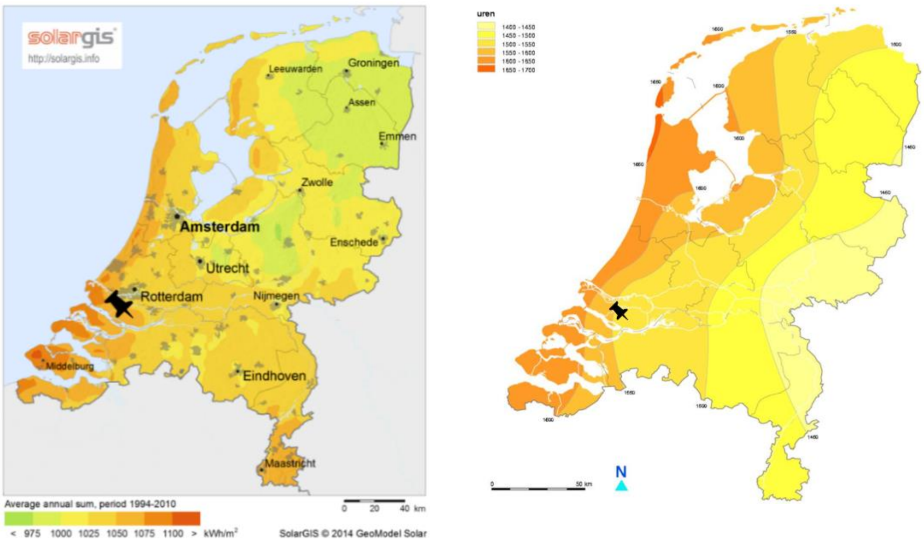

Figure 6: Average annual solar energy production in the period 1994-2010 (left). [14]
Average sunshine-hour per year (right). [15]
Hoeksche Waard is indicated with the black pin.

In Figure 7, the wind turbine distribution across the country is presented. Most of the wind turbines are located near the coastline, because of the strong wind in that part of the country. There is some overlapping of solar panels and wind turbines, especially in the north part of the Netherlands. At such locations, where both sunshine-hours and wind velocity are sufficient, a combination of small turbines and solar panels is feasible in order to increase the electricity production capacity. Wind energy becomes profitable with an average wind speed of at least 5.5 m/s, so Hoeksche Waard is not an ideal location of that purpose. [16]

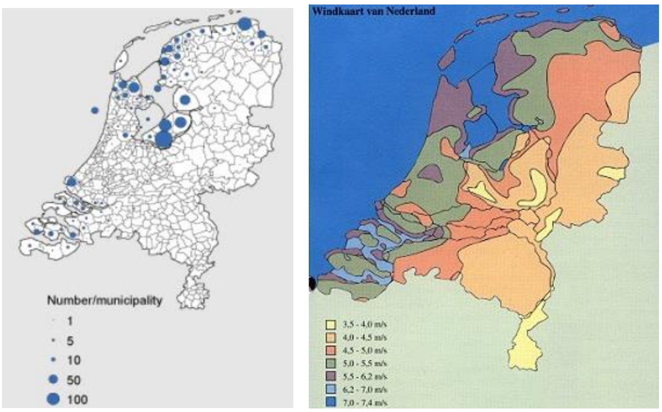

Figure 7: Map of the wind turbines in the Netherlands in 2006 (left). [15]
Average wind speed at 10 metres high in the Netherlands (right).

4.2 Demand of chemicals derived from ammonia

To determine the fertilizer demand in the Netherlands, three fertilizer databases were examined: ifastat, faostat and knoema. [17]–[19] Knoema is selected as the most reliable, especially because it includes references to the original data. According to the Knoema database, the most widely used agricultural fertilizers in the Netherlands are presented in Figure 8, which shows the tonnes of fertilizer use in 2018.

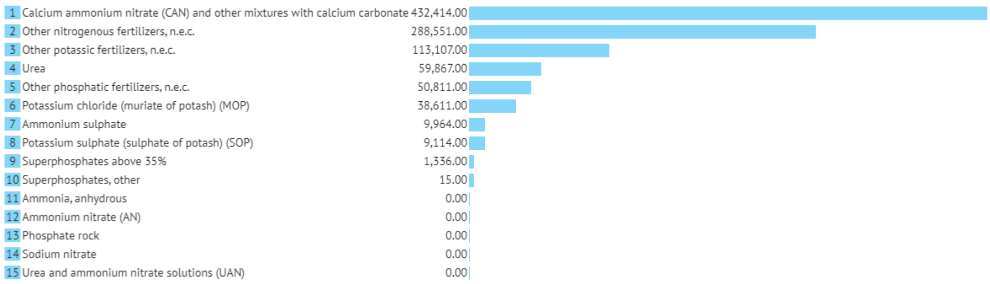

Figure 8: Agricultural use of fertilizers in Netherlands for the year 2018 (tonnes). [19]

The total agricultural land of the Netherlands was reported at 53.31% in 2016. This number corresponds to 22,146 km^2. The total amount of fertilizer used in 2018 is 1,003,790 tons, which corresponds to 45 tons/km^2.

The use of ammonium nitrate as fertilizer is banned in the Netherlands due to safety issues. The use and storage of anhydrous ammonia in Europe has almost been eliminated due to other type of regulations. [20][21]

The most commonly used fertilizer is calcium ammonium nitrate (CAN) which accounts for 432,313 tons for the whole Netherlands or 19.5 tons per/km^2. Since Hoeksche Waard's arable land is 190 km^2, this area needs 3,710 tons of CAN per year.

Yara and Proton Ventures have indicated that it is not yet economically attractive to produce urea on a relatively small scales (<20,000 mtpa ammonia) due to the high investment costs. [2]

Ammonium sulphate is not promising because it is primarily recovered as a by-product from production of caprolactam or from reaction of coke oven off-gasses with sulfuric acid.

Ammonium nitrate is has zero consumption in the Netherlands as a fertilizer, because it is banned due to its high safety risks. However, the Netherlands imports the product in large quantities for other uses, as shown in Figure 9. [19], [22] Producing ammonium nitrate in small quantities for any use will enable safer handling of the product and could replace importing.

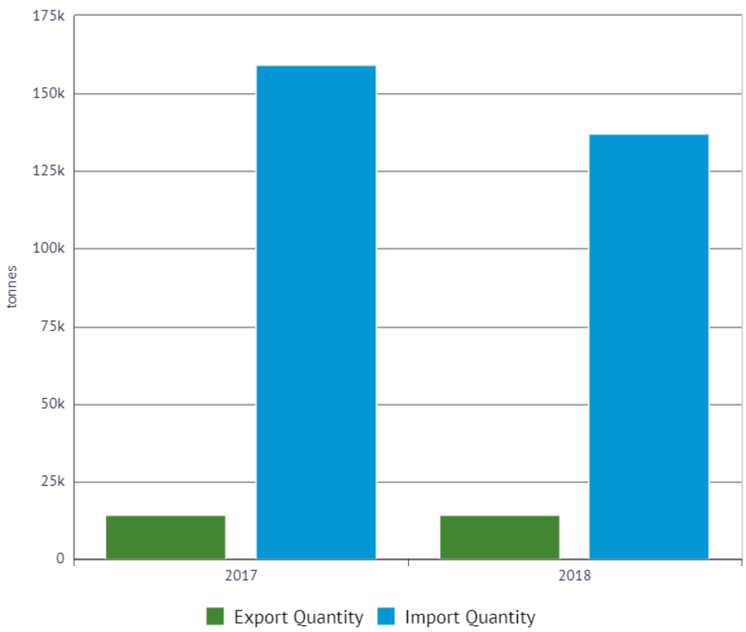

Figure 9: Ammonium nitrate import and export in Netherlands for the year 2017 and 2018 (tonnes). [19]

In Figure 10 and Figure 11, import and export quantities of more fertilizers is presented. As it can be seen, ammonium sulphate, ammonia anhydrous, calcium ammonium nitrate and NPK fertilizers are mainly exported because they are produced in large quantities. On the other hand, monoammonium and diammonium phosphate are mainly imported similar to ammonium nitrate, but in much smaller quantities. Their consumption as a fertilizer is minimal (1,100 tonnes according to IFASTAT), so they probably find other applications.

Similarly to ammonium nitrate, there is an opportunity to replace the import of ammonium phosphates. However, it is less promising due to the lower demand of the product and the fact that there is no unique advantage of local small scale production (like safer transportation and handling).

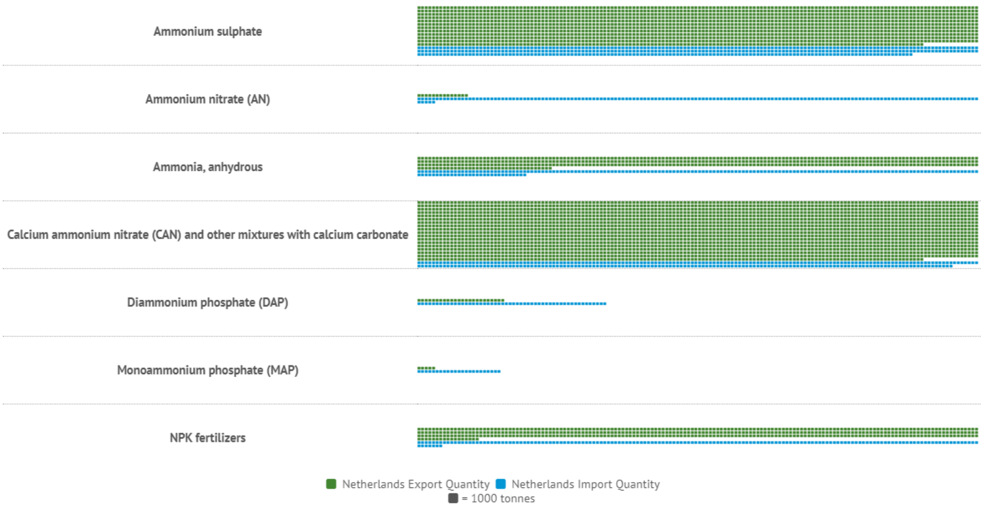

Figure 10: Overview of import and export quantities of fertilizers in the Netherlands in 2017.

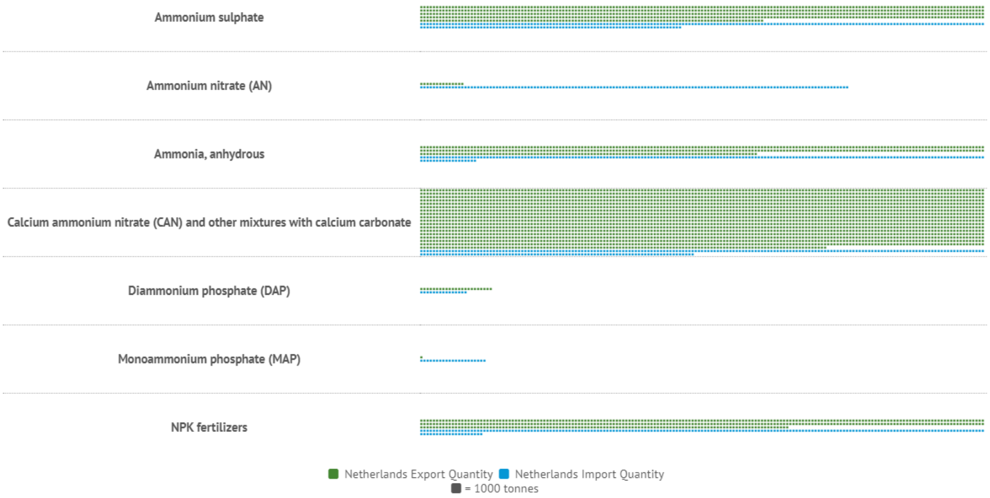

Figure 11: Overview of import and export quantities of fertilizers in the Netherlands in 2017.

5 Business cases

The production capacity in this project is 1,000 mtpa of green NH_3. This production rate requires 1.5 MW of renewable electricity which is provided using solar panels in a decentralized area of the Netherlands. If additional power is required, wind turbines could be consider as well. A summary of the drawbacks and advantages of small scale ammonia production is given below.

Drawbacks of 1kt green NH_3 production:
- Uneconomical compared to conventional ammonia production.
- Very high investment cost compared to larger scales (see chapter 2).
- Higher energy consumption compared to larger scales (see chapter 2).

Advantages of 1kt green NH_3 production:
The NFUEL facility can withstand power intermittency. This means that the grid connection costs can be avoided. In general, connection to the grid is only beneficial for large scale production.
- Inexpensive and not permanent installation. Mini ammonia units are modular, fully transportable, containerised and can be installed in various locations with minimum installation costs. [6]
- Less transportation costs. The small quantities produced can be utilised at local scale.
- Low operating costs. The mini ammonia plants are designed so that the individual components can operate unmanned. Monitoring & control of the unit will be done remotely through a wireless secure internet connection. [9]
- Safety: Transportation and storage of large quantities of ammonium nitrate can be dangerous because of its high explosiveness. Hence, small decentralized production of the chemical could be beneficial.

Three business cases based on NH_3 derived products are developed with the aim to make the small scale green NH_3 production (1,000 mtpa) commercially viable:
1. Production of AN for any use in the Netherlands.
2. Production of CAN fertilizer for local applications.
3. Production of MAP/DAP fertilizer for use in the Netherlands.

Next, a fourth (4) business case based on a different technology for micro scale green fertilizer production will be presented. In that case, nitrogen of air is used to produce nitric acid via solar power, which can later produce calcium nitrate or potassium nitrate fertilizer. The scale of this facilities are smaller than NFUEL1, targeting approximately 1 hectare of agricultural land.

Furthermore, business case 5 is presented, which is larger scale of Urea or UAN production for fertilizer use. This case dives into the economic unviability of small scale Urea production to determine the capacity at which the process could be competitive.

Finally, in business case 6, the MCDI module that is developed in TNO could be used to concentrate NH_4^+ ions from industrial wastewater in clean water solution. The scale that is analysed produces 1340 tons of which has a similar Nitrogen content as the NFUEL1 production.

5.1 Business case 1: Production of AN from NH_3

Ammonium nitrate transportation and large quantity storage is restricted by government regulations because of serious safety issues. This case aims to replace part of the ammonium nitrate that is imported to the Netherlands saving on transportation costs and enabling safer handling and storage of smaller quantities.

5.1.1 *Production method*

Production of HNO_3:

In order to produce HNO_3, the Ostwald process can be followed, during which Ammonia is converted to nitric acid in 2 stages: [23]

1st stage:

Ammonia oxidation by heating with oxygen in the presence of catalyst to form NO and water.

$$4NH_3\ (g) + 5O_2\ (g) \rightarrow 4NO\ (g) + 6H_2O\ (g)$$

2nd Stage:

Two reactions are carried out. Initially NO is oxidized again to yield NO_2 in an absorption apparatus containing water. Then NO_2 is absorbed by the water, yielding HNO_3 and NO.

$$2NO\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$$

$$3NO_2\ (g) + H_2O\ (l) \rightarrow 2HNO_3\ (aq) + NO\ (g)$$

The NO is recycled, and the acid is concentrated to the required strength by distillation, if needed. The last step can also be carried out in air (absorption tower):

$$4NO_2\ (g) + O_2\ (g) + 2H_2O\ (l) \rightarrow 4HNO_3\ (aq)$$

Overall reaction:

$$2NH_3\ (g) + 4O_2\ (g) + H_2O\ (l) \rightarrow 3H_2O\ (g) + 2HNO_3\ (aq)$$

Production of NH_4NO_3:

The neutralisation reaction is highly exothermic and proceeds with high speed. [24]

$$NH_3\ (g) + HNO_3\ (l) \rightarrow NH_4NO_3\ (s) \quad \Delta H = -146\ kJ/mol$$

The final product derived from 1,000 tons green NH_3 is 2,353 tons AN.

5.1.2 *Economic viability*

A study in Sweden examined the options of producing ammonium nitrate at small scale using green ammonia. [25] It considers production of 1 t/d NH_3, which is 3 times less than NFUEL1 production capacity. The whole process (shown in Figure 12) uses 2 MW of electricity, of which only 0.4 MW are needed for the electrolysis part. It is known that the electrolyser accounts for approximately 90% of the total electricity usage in NH_3 production, so the nitric acid and ammonium nitrate production steps account for 1.5 MW of electricity. [25]

Scaling this up to 3 t/d, which is NFUEL1 capacity, a total of 6MW is required:

- 1.3 MW for the electrolysis;
- 0.2 MW for compressor, ammonia production and air separation;
- 4.5 MW for nitric acid and ammonium nitrate production.

That means that the installation requires 4 times more electricity power than the solar panels can provide.

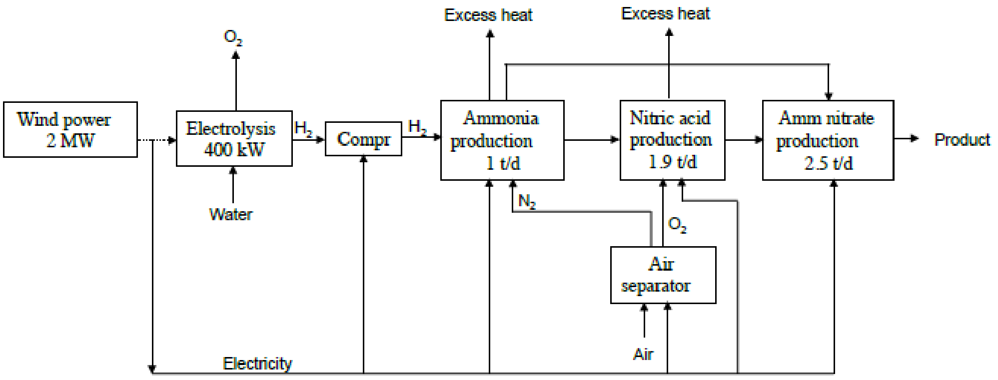

Figure 12: Small-scale ammonium nitrate production process using renewable electricity. [25]

An estimation of the total production costs is presented in Table 2. The table shows that further processing of NH_3 into AN increases the total cost by 56%. The cost increase for AN production (56%) might be even larger for the selected NFUEL1 capacity, because the electrolyser costs are expected to decrease more than the AN process costs, while scaling up (3 times larger production). [25]

Table 2: Production costs per year for small-scale production of ammonium nitrate fertilizer using electricity from wind power. [25]

	Total annual cost (M€)	**Costs per kg AN (€)**
Electricity generation, wind power	0.13	0.14
Hydrogen production	0.23	0.25
Hydrogen storage for 5 days production	0.05	0.06
Ammonia production	0.40	0.45
Nitric acid production	0.24	0.26
Mineral fertilizer production	0.22	0.25
Total, production costs at factory gate	**1.26**	**1.41**

The total cost of the fertilizer is estimated at 4.23 €/kg N. According to the study the current fossil alternative costs 1.08 €/kg N, hence, the proposed process is not economically favourable. If only the NH_3 production is considered, the resulted total cost is 2,420 €/ton NH_3.

In the case of NFUEL facility, the ammonia production cost will be reduced. In order to make the process competitive the nitric acid and mineral fertilizer production steps need to become more economical. According to a study from Sydney university, there is a new process called “Johanna” specifically designed for small scale ammonium nitrate production. [26] Still, the process requires at least 17,000 tpa AN production, which is 7 times larger than the NFUEL1 capacity, used in the current study.

Overall, the process is uneconomical and uses 6 MW of electric power supply, which definitely requires coupling of solar panels (max. 1.5 MW available) with wind turbines.

5.2 Business case 2: Production of CAN from NH_3

Calcium ammonium nitrate is the fertilizer with the highest consumption in the Netherlands. This means that the demand is high in the local area. This case aims to take advantage of the local production that saves costs by eliminating transportation of the product to the consumer.

5.2.1 Production method

CAN Is produced by mixing ammonium nitrate (AN) solution with ground limestone (mostly $CaCO_3$) and/or calcium carbonate ($CaCO_3$) and/or dolomite ($CaMg(CO_3)_2$). [24] Alternatively, it can be obtained by mixing NH_3 with the by-product calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) of the nitrophosphate (ODDA) process, which also produces $CaCO_3$. However, this option will not be analysed in this report as it adds extra steps and by-products, which increases complexity and reduces economic viability at small scale. An overview of a typical ammonia based fertilizer production site is presented in x 1: Block diagram of N-based fertilizer production.

The AN is obtained as described in described in chapter 5.1.1.

According to Achema, Yara and Agrolinz Melamine, the CAN fertilizers typically contain 27% Nitrogen. [27][28][24] This means that the NH_4NO_3 accounts for 77.14% of the total CAN produced. Hence, in order to meet the CAN requirements for the area of Hoeksche Waard, 2,862 tons of NH_4NO_3 should be produced.

From the stoichiometry, 1 mol of NH_3 produces 1 mol of NH_4NO_3, and also 1 mol of NH_3 produces 1 mol of HNO_3. Hence, overall 2 mol of NH_3 produces 1 mol of NH_4NO_3. This translates into 1220 tpa of NH_3 to cover the need of CAN in the area of Hoeksche Waard. This number is slightly higher than the 1,000 tpa that the NFUEL1 facility can produce.

Hence, a total of 3,050 tpa CAN fertilizer is produced, 77.14 wt% of which is produced in-house and 22.86 wt% is purchased. Limestone is one of the cheapest compounds in the world, so this will not be a significant issue.

5.3 Business case 3: Production of MAP/DAP from NH_3

Ammonium phosphate is among the fertilizers with the lowest consumption in the Netherlands. However, there is an amount of monoammonium phosphate (MAP) and diammonium phosphate (DAP) that is imported in the Netherlands as shown in Figure 10 and Figure 11. This business case aims to replace part of the imported MAP/DAP for any use in the Netherlands. The advantage compared to business cases 1 and 2 is the simplest manufacturing process, which significantly reduces the cost in small-scale production. The only step required after NH_3 formation, is its mixing with phosphoric acid.

The process for manufacturing MAP is relatively simple. In a common method, a 1:1 ratio of ammonia (NH_3) and phosphoric acid (H_3PO_4) is reacted and the resulting slurry of MAP is solidified in a granulator. Similarly, a 2:1 ratio of NH_3 and H_3PO_4 produces DAP.

Using the capacity of NFUEL1, the quantities of the produced fertilizers are the following:

MAP:	6,765 tpa	14.8% of the product consists of NH_3
DAP:	3,882 tpa	25.7% of the product consists of NH_3

The important drawback of this case is the fact that only 14.8% or 25.7% w/w of the product is produced in-house. The major part of the product needs to be purchased. Hence, the manufacturing of ammonium phosphate is unattractive, unless there is a source of pre-existing phosphate rock or phosphoric acid that could be utilized.

5.4 Business case 4: Air to nitrates

New routes towards the production of “green” fertilizers have been opened by the application of plasma technology and the utilization of atmospheric air. This technology is used to extract nitrogen directly out of air, break it down with plasma and dissolve it into water in the form of nitrate. For the purpose of this study, two start-up companies were contacted to obtain information about the technology readiness and the performance of the process: Nitricity (USA) and VitalFluid (Netherlands).

This option differs from the NFUEL1 facility which would be needed in business cases 1, 2 and 3 in two important ways:

1. Nitric acid is traditionally produced from ammonia. Producing directly nitrates (or nitric acid) from air reduces the manufacturing steps, which is very important in making small scale applications economically viable.
2. The production capacity is much smaller (30-50 kW) compared to NFUEL1 (1.5 MW), which means that each farmer can have their own production unit (or many of them) and a collaborative investment is not required. Additionally, Dutch farmers have an already-existing connection to the grid with a maximum capacity of 55 kW. Hence production at a scale of a few kW can be advantageous, because it enables a slow transition to green locally produced fertilizers without essentially requiring installation of solar panels.

5.4.1 Nitricity

Nitricity is a company based in San Francisco and specializes in producing ready-to-use nitrogen fertilizers with only air, water, and renewable electricity.[29] Their technology is based on the synthesis of nitric oxide by oxidation of nitrogen in the air, which is later upgraded easily to $Ca(NO_3)_2$ or KOH by mixing it with $CaCO_3$ or KOH respectively.

$2\ HNO_3 + CaCO_3 \rightarrow H_2O + CO_2 + Ca(NO_3)_2$
$HNO_3 + KOH \rightarrow KNO_3 + H_2O$

Nitricity describes $Ca(NO_3)_2$ as a “premium” fertilizer whose role is to replace CAN. Hence, this option is great for the Netherlands, as CAN is the fertilizer with the highest consumption.

Currently, there is one plant that has been operating by Nitricity for 1 year. Its capacity is 0.45 tpa. They plan on scaling-up the production in the coming months by constructing a facility that produces 1.36 tpa $Ca(NO_3)_2$,which corresponds to a 1.05 tpa HNO_3. That means that every farmer can have their own facility to produce the fertilizer they use in the farm in a micro-scale.

The facility will operate at 50kW with 25% capacity (6h per day). The total costs of $Ca(NO_3)_2$ are 1.85 €/kg. The price of CAN is 1.59 €/kg, according to Nitricity, it can be found at 170 €/100kg in Sigma-Aldrich, and it can reach low prices of 300-600 /ton when purchased in large quantities (>20 tons). Assuming that each farmer will not purchase and store several tons at once, this makes the Nitricity product market competitive. The efficiency is 77kWh/kg N, which according to Nitricity should be improved in the coming years. The fertilizer is produced in aqueous solution, it enters the irrigation line and is then applied in the field. It can also be produced in solid form, but that would increase the production cost. The whole process diagram can be seen in Figure 13. [29]

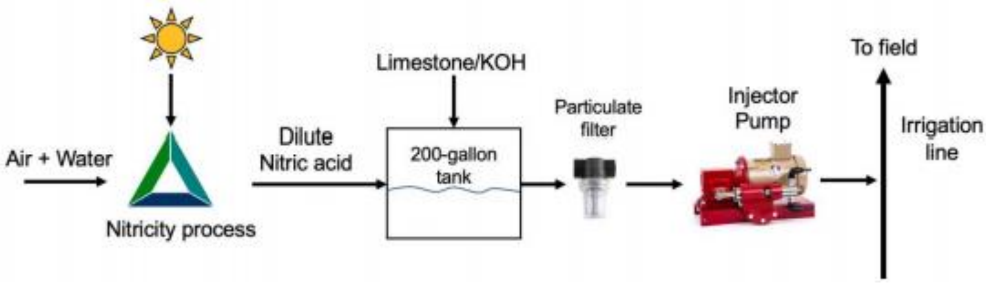

Figure 13: Block diagram showing the integration of the nitric acid generator and irrigation system. [29]

The biggest capital investment is the solar panels, which could also be avoided by connecting to the grid instead, if electricity is cheap. This can be an option for the first years of a new operation in order to test the facility.

5.4.2 *VitalFluid*

VitalFluid is located in TU Eindhoven campus. Similarly to Nitricity, it uses plasma technology to react and dissolve nitrates in water. Ambient air is brought into the plasma phase with electrical energy, the activated air is then brought into contact with water. Reactive oxygen and nitrogen dissolve into the water creating plasma activated water (PAW). The product can be mixed with limestone or other compounds to form fertilizer, but the company focuses on selling the enriched water as the final product. The idea is that the plasma-activated water can be valuable for the corps both as a fertilizer and a disinfectant.

The equipment varies in capacity from 5-30 kW, with the largest capacity to produce 1700 g/h of NO_3^- (27 mol/h). The facility can operate approximately 8-10 hours per day and it is capable of supplying 1 hectare with the required amount of nitrogen. Hence, in order to supply nitrogen to the whole agricultural area of Hoekse Waard 19,000T VitalFluid facilities would be needed (if all of them require Nitrogen as fertilizer). The produced water typically contains 0,03 -0,1% NO_3^-. This amount can be increased with recirculation of the plasma-activated water, reaching up to 30% of NO_3^- (maybe even more, but the efficiency of the process will decrease).

The lifetime of the facility is guaranteed to be at least 5 years. It is expected to be more, but it is hard to estimate because the company just reached the commercialization phase. The CAPEX of the 30 kW facility is 180,000 € and OPEX is 0.31 € per mol NO_3^- produced (one sold at this price in the United States). The cost includes free maintenance and online monitoring to ensure proper operation. Finally, the size of the 30 kW facility is 3 x 1.2 x 2.5 meters and it can be seen in Figure 14 along with some specification of the process.

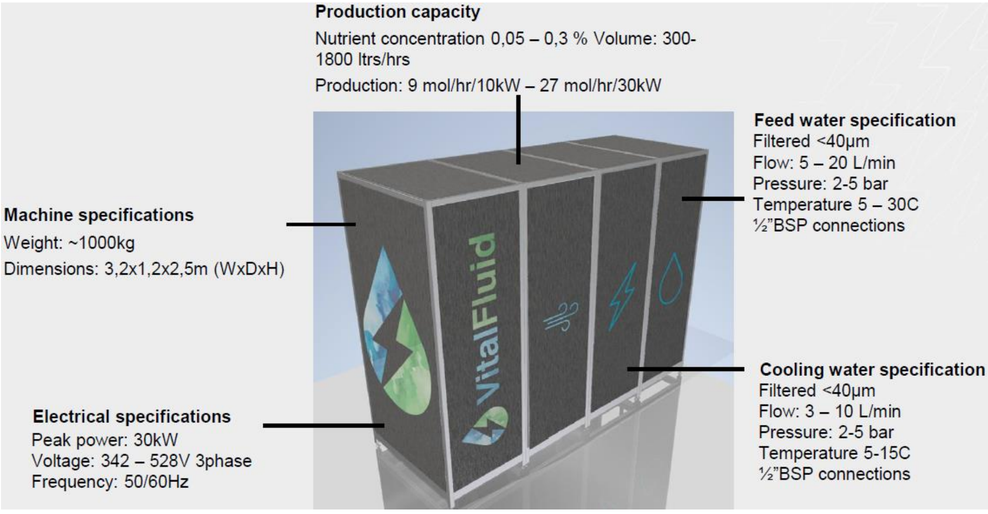

Figure 14: 30kW "Lightning in a box" unit from VitalFluid.

5.5 Business case 5: Urea/UAN production

Urea is the most important nitrogenous fertilizer in the market, with the highest Nitrogen content (46%), and according to Figure 8 it is widely used in the Netherlands. Additionally, green Urea production from NH_3 has extra environmental benefits as it also requires CO_2 that is obtained via carbon capture. In the recent years, liquid fertilizers are in the spotlight in arable farming, being claimed to offer several advantages. The liquid alternative of urea is Urea Ammonium Nitrate solution (UAN), which is produced by combining urea, nitric acid, and ammonia. It can be applied more uniformly than non-liquid forms of fertilize, and it can be mixed with other nutrients, enabling farmers to reduce costs by applying several materials simultaneously rather than making several separate applications.

However, as mentioned in previous chapter 4.2, according to Yara and Proton Ventures, the production of green Urea is not economically attractive on scales <20,000 mtpa NH_3 due to high investment costs. [2] In a recent study of 2021, small-scale green urea price was determined using 4 schemes and compared to small-scale grey urea and large-scale industrial grey urea production. Small scale production was considered as 13,000 mtpa of urea which corresponds to 7,400 mtpa NH_3 (7 times larger than the NFUEL1 facility). [30]

The results are presented in Figure 15, where the 4 scheme represent the following:
- Scheme 1: urea price without Clean Development Mechanisms (CDM)
- Scheme 2: urea price with CDM
- Scheme 3: urea price without CDM and projected investment cost for battery, PV, and electrolyzer in 2030 (3a) and 2050 (3b)
- Scheme 4: is a combination of Scheme 2 and 3 in 2030 (4a) and in 2050 (4b).

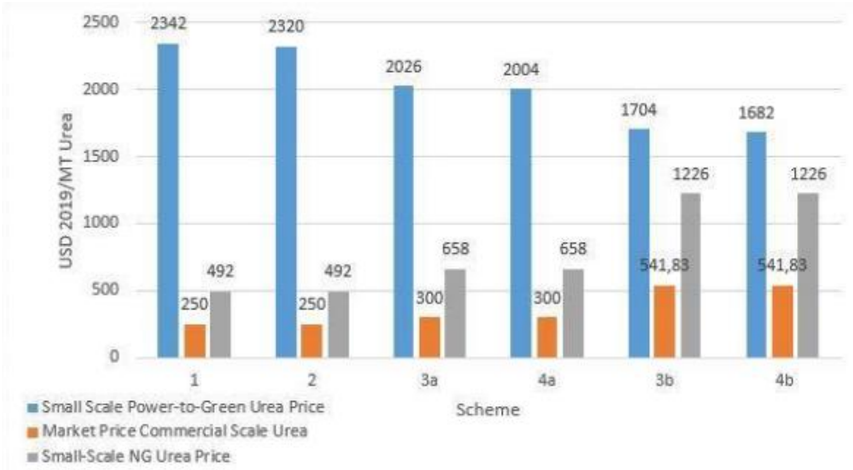

Figure 15: Urea price comparison with 4 proposed schemes. [30]

From an energy perspective, the power-to-green urea is less efficient than its conventional counterpart, leading to a 500% increase in total energy consumption. As shown in Figure 15, a significant reduction of green urea price from the base year is not present earlier in 2030; however, in 2050 a 27% reduction in price is noticed. The addition of revenue through CDM initiative is not able to reduce green urea price, only enabling a reduction of 1.2%. [30]

Although green urea price does not decrease significantly throughout the study, its hypothetical counterpart rise in price is a subject of interest. In 2019, a hypothetical small-scaled plant with an equal output as the design basis experience a 200% increase in price by 2050. Hence, conventional urea is volatile due to increase in incoming rise of gas price, but green urea does not follow the same trend due to its feedstock being water and electricity. [30]

Overall, power-to-green urea could not compete even with the upcoming cost reduction of PV-electrolysis and battery in 2030 and 2050. There is no scheme and year where the cost of a small-scaled power-to-green urea is comparable with a large-scaled commercial urea, or a hypothetical small-scaled natural gas-based urea. It is then to be noted that power-to-green urea is not economically feasible for a production of 7,400 mtpa NH_3, and it would be even less economical for NFUEL1 scale. The same applies for power-to green UAN production, where additional steps are required after urea synthesis increasing the costs even more. The concept could only be relevant for remote areas without gas reserves. [30]

5.6 Business case 6: NH_4^+ from wastewater

NH_4^+ ions can be isolated from municipal wastewater streams using membrane capacitive deionization (MCDI) coupled with Ion Exchange (IE) process. According to a TNO study, aqueous solution of 1,341 tons of ammonium ions can be produced per year from a wastewater feed of 505 tons/day. The initial NH_4^+ concentration is assumed to be 2500 mg/l (livestock effluents).

Based on the energy data for carbonate/bicarbonate removal and Na^+ removal (hydrolysate), the energy requirement for NH_4^+ removal from livestock effluents was estimated at **300 kJ/mol**.

The CAPEX is estimated at 11.67 M€/y and the OPEX at 2.41 M€/y. The 76% of the CAPEX is the cell cost, which has a lifetime of 5 years. Hence the overall product NH4 cost is estimated at 3,300 €/ton. This the most expensive Nitrogen fertilizer presented in this report, and its application would be limited because the municipal wastewater needs to be available close to the agricultural land. The technology would only be interesting in case, apart from fertilizer, the wastewater treatment is also of primary importance, as the MDCI process is cost competitive with biological treatment and POU reverse osmosis (see Figure 16).

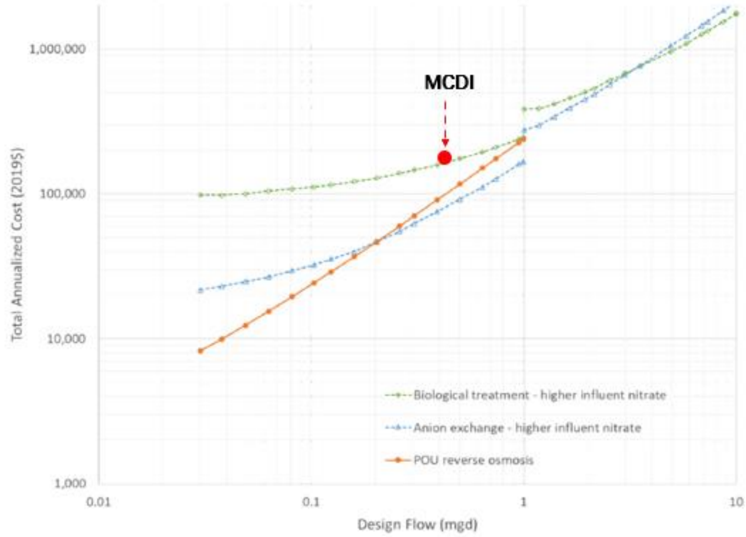

Figure 16: Comparison of nitrate treatment costs.

6 When is green ammonia to fertilizer production economically viable?

All business cases 1, 2 and 3 seem to be economically not feasible. However, green ammonia plants for local fertilizer production do exist, while having a capital intensity of approximately 1,600-1,900 €/ton NH_3.

Three plants, that are all located in the USA are listed below: [31]

1. Plant located in Wyoming and commissioned in 2017. It was invested by Simplot and constructed by Linde, and it produces 600 stpd or 200,000 mtpa of MAP. Excess of phosphate rock was already present, so green NH_3 aimed at utilizing the already existing compound.
2. Almost completed plant located in Nebraska. It was invested by Fortigen and constructed by Gorham, and it produces 100 stpd of NH_3, which, in contrary with Europe, is not restricted for fertilizer application in the United States.
3. Plant located in California, but not constructed yet. It is invested by Grannus and it will produce 80,000 mtpa of NH_3. Part of it will also be converted in urea and also used for power polygeneration.

The aforementioned processes differ from local production in the Netherlands in two important ways. Firstly, they operate at much larger production scale (at least 30 times larger). Additionally, the resulting NH_3 undergoes minimal further processing to produce the final fertilizer product, while in some cases other reactants (phosphate rock) are already available. These characteristics are the key factors for their economic viability.

7 Economic Recommendations

Current grey ammonia cost amounts for 300 €/ton (without transportation), while green ammonia cost for NFUEL20 is estimated at 742 €/ton (it will be higher for NFUEL1). A detailed green NH_3 economic evaluation presented in chapter 5.1.2 estimated the costs of 1 t/d NH_3 production (1/3 of NFUEL1 capacity) at 2,420 €/ton. In this chapter, suggestions in order to create a positive business case are presented.

There are significant costs that can be avoided with local green ammonia facilities, and some of them are necessary in fossil alternatives. These are the following:

- Grid connection costs: According to Proton Ventures, avoiding grid connection can save approximately 108 €/ton (for NFUEL20 capacity) This value will be larger for NFUEL1 capacity. [2] However, a study from ISPT concluded that it is not feasible to invest in a Power2ammonia facility directly connected to a wind turbines or solar panels, because the capacity for H_2 storage needed to overcome the time periods when there is no electricity production is substantial. [10]
  With grid connection, the buffer capacity needed is approximately 2 tons (4hours). According to TNO HyDelta study, if 12 hours of buffer H2 capacity are available (>2 times larger capacity than with grid connection), the NH_3 Haber-Bosch process could operate at a minimum turndown rate of 30% at hours without RES input. The back-up power requirements are estimated at an additional 25% for 60% full-load hours of RES plant. This extra cost needed for buffer capacity and back-up power, in case of no grid connection, is considered negligible for the purpose of this study.
- Transportation costs: In remote areas the cost to the customer of ammonia produced locally can be as much as 85-125 €/ton lower than that of ammonia supplied from large scale plants. [3]
- CO_2 tax: If tax equal to 20 € per ton of CO_2 emissions is assumed, then 33 € per ton can be saved compared to grey ammonia. [2]
- Fertilizer storage costs: There is not a specific estimation of the storage costs, since the needs and circumstances of all industrial users and fertilisers users vary considerably. However, the storage costs will be definitely lower in case of decentralized local production of fertilizer. Especially in business case 4 of very small scale production, Nitricity claims that the storage cost is not significant.

The aforementioned costs that were described in bullets can be included in the grey and green ammonia overall cost of production. This results in potential cost of:
Grey ammonia: 300+125+33 = 458 €/ton
Green ammonia NFUEL20: 742-108 = 634 €/ton

Further recommendations to improve the feasibility of business cases 1, 2 and 3 are the following:

- All farmers should be contracted to buy the fertiliser beforehand. It is important to immediately use locally the produced fertilizer.
- The NFUEL1 hardware could be treated as a long term lease, taking advantage of the cheap installation costs and the ease of transport. The plant could operate at different locations, without being a fixed asset. In that way, the capital intensity will be reduced. [6]
- Obtain investment subsidies (e.g. Dutch, European).

8 Conclusions and next steps

In this project, the decentralized small-scale production of green ammonia and Nitrogen-based fertilisers was investigated. Two technologies were evaluated for this purpose:

- Proton Ventures' NFUEL green ammonia production via green hydrogen and Haber-Bosch process and further processing to fertilizer.
- Nitrate production via oxidation of nitrogen from air and further processing to fertilizer.

The technologies were evaluated in 6 different business cases:

1. Production of ammonium nitrate for use in the Netherlands using NFUEL technology.
2. Production of calcium ammonium nitrate fertilizer for local application using NFUEL technology.
3. Production of ammonium phosphate fertilizer for local application using NFUEL technology.
4. Production of nitrate fertilizer for local microscale application using nitrogen oxidation technology.
5. Production of urea or urea ammonium nitrate fertilizer using NFUEL technology.
6. Production of NH_4 rich aqueous solution from waste water treatment for local application.

According to literature, producing green ammonia via a small scale Haber Bosch process (NFUEL) is proven to be economically challenging, resulting in a cost at least 2.5 times higher than the fossil alternative, for a capacity of 20,000 tpa. In the current project a smaller capacity of 1,000 tpa is selected, which is expected to increase the capital intensity and the energy consumption of the plant even more. Taking into account additional costs for transport, CO_2 tax and grid connection will reduce the cost gap between the two technologies, and new technologies like absorbent enhanced Haber Bosch process can mitigate the cost intensity of small plants. However, these are not enough to prove NFUEL1 green ammonia production economically competitive.

The market analysis showed that the fertilizer with the largest consumption in the Netherlands is CAN. The manufacturing process of CAN from ammonia consists of several process steps and in traditional production facilities it is highly integrated with the production of other fertilizers. The economic evaluation showed that further manufacturing of ammonia to AN or CAN will result in approximately 56% additional increase of the total costs, which makes clear that these business cases are economically not feasible.

Manufacturing of MAP/DAP would be more economical because of the simplicity of its manufacturing process, but requires purchasing/having available phosphoric acid which amounts for at least 75% of the final product. Such a facility does exist in the United States, where phosphate rock is excessively available and the plant capacity is at least 40 times larger than the NFUEL1 capacity considered in the current report.

It is concluded that the use of ammonia for fertilizer production at the scale of 1.5 MW (NFUEL1) is not economically feasible. The alternative solution of producing nitrate-based fertilizers via air oxidation at 30-50 kW is selected as the most promising option. The emerging technology is presented in business case 4 and apart from the economic advantages compared to ammonia conversion, it is preferable because of its easier introduction to the farms. The facility can operate utilizing the existing grid connection (maximum 55 kW) that farmers possess and it enables a simpler transition to green fertilizers without requiring collaborative investment by numerous farmers in an agricultural area.

The production of green urea would be very promising, as it requires CO_2 and NH_3. However, the economic analysis proved that at least 20,000 mtpa NH_3 production is necessary, as it was also claimed by Yara and Proton Ventures. Lastly, the MCDI technology that was studied in another TNO project, is too expensive for the production of Nitrogen based fertilizer, but it would be competent in case wastewater treatment is needed aside from the fertilizer.

9 Signature

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Appendix 1: Block diagram of N-based fertilizer production

The ammonia-based fertilizer production process is well integrated, as can be seen in Figure 17. Small scale production of a specific fertilizer should have fewer manufacturing steps or more efficient unit operations like eg the sorption enhanced Haber Bosch process. Otherwise the large scale integrated plant will always be economically favourable.

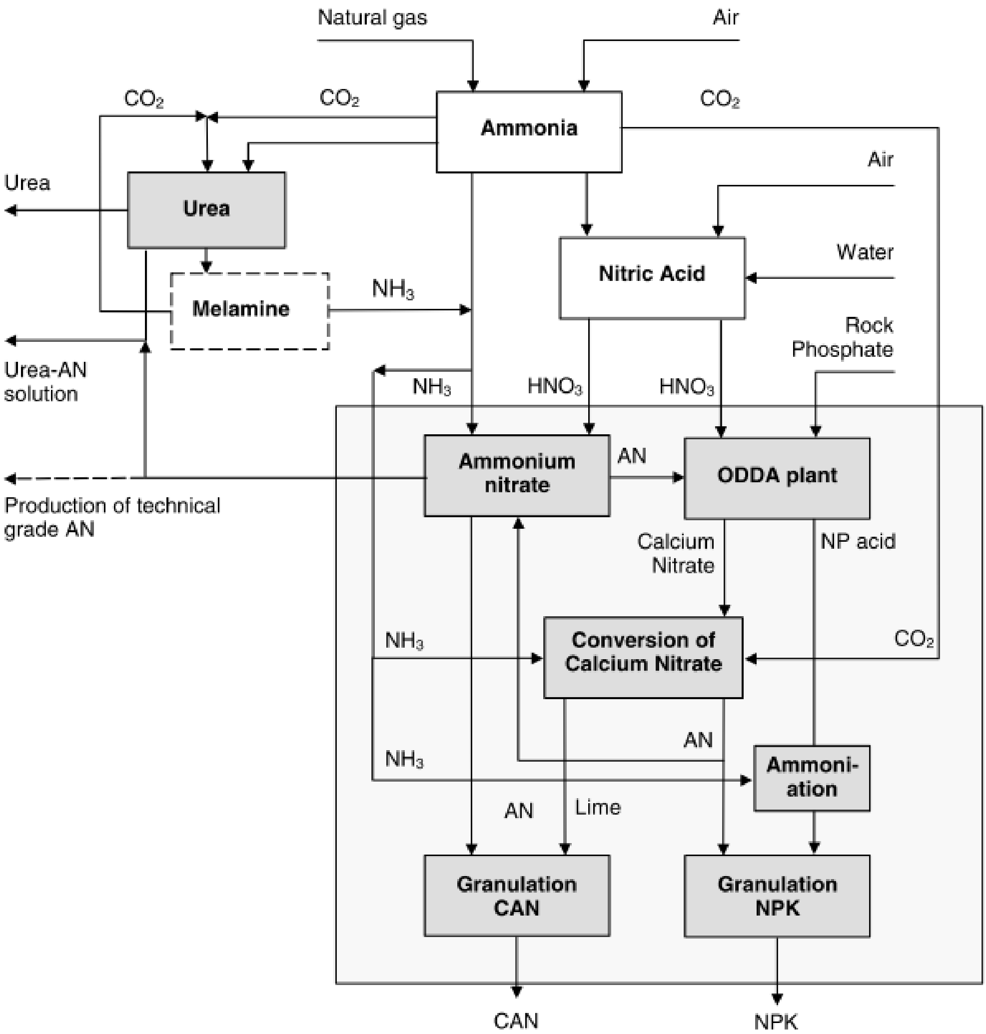

Figure 17: Block diagram of the production of fertilisers (shaded) and of substances used for the production of fertilisers at Agrolinz Melamin GmbH. [24]