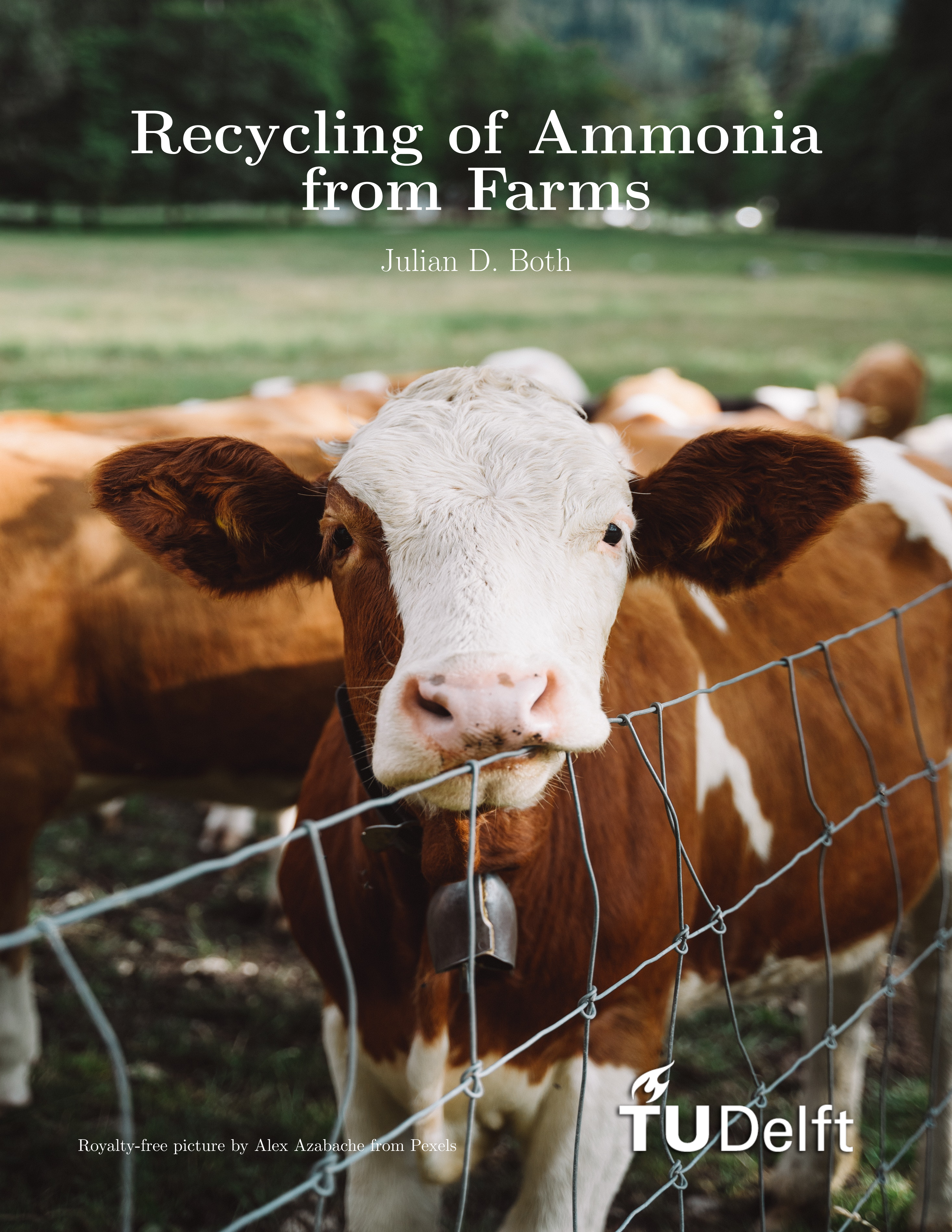
Recycling of Ammonia from Farms

Julian D. Both



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The selection and (economic) evaluation of ammonia recycling processes of manure from farms

by

Julian D. Both

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Abstract

Nitrogen emissions contribute significantly to climate change, especially in the Netherlands around Natura 2000 areas, and one of the main contributors is manure. However, not only does manure usually have high nitrogen emissions, a lot of it is in the form of ammonia, which in itself is very energy-intensive to create. Therefore MEZT developed a solution to extract ammonia from manure, reducing both nitrogen emissions and emissions from ammonia production. However, what to do with this ammonia after it is extracted was still unknown. Thus, the research question was as follows: Within the context of farms and MEZT's BPMED process, what is the best ammonia recycling process and usage, and is it financially feasible?

To answer this, first, all major potential uses for ammonia were identified, after which many uses were discarded immediately due to logical and fairly obvious reasons. Then, the remaining ammonia uses, consisting of mostly fertilizers, fuel cells, and selling it as a wholesale substance, were investigated further. For this, a scoring matrix was made based on a farmer's needs, and all technologies were scored on nine criteria (maturity/feasibility, process profitability, initial costs, reliability & maintenance, ease of use, environmental impact, safety, scalability & compactness).

From this scoring matrix, there were three clear top choices: selling as wholesale, ammonium sulphate, and enriched biochar. Since the stream to sell ammonia as a wholesale can be taken from either of the two other processes, a clear choice still had to be made between ammonium sulphate and biochar. The scoring matrix already had a fairly strong favour towards ammonium sulphate, but after also investigating the effect of manure disposal costs, upcoming RENURE regulations, grant and subsidy differences, the legality of using both substances, and the combination of using it with other streams of the MEZT process, ammonium sulphate remained as the best solution.

With this in mind, the final process was designed. Here the potassium stream was also considered and included as it was part of the ammonia stream. The final process is a flexible solution of making ammonium sulphate, potassium sulphate, their (raw) mineral concentrates and aqueous ammonia. This allows for the most flexibility depending on a farmer's needs, while having minimal additional costs and the ability to 'cut out' unwanted parts/processes.

Afterwards, an economic evaluation was made. First, precise equipment and operational costs and revenues were estimated for the ammonia processing parts, after which it was combined with the overall MEZT solution train to form the final costing and revenues. From this it was determined that the additional parts to process ammonia was relatively cheap compared to the BPMED unit of MEZT, but nonetheless the entire process was shown to be at least cost-neutral (break-even) for reducing manure emissions and in many cases even quite lucrative for a farmer to implement.

In the end, due to the new and broad nature of this topic, it was at times difficult to make very accurate estimations (especially for the costing as data is not always available), but multiple sources/methods were always checked and the final choice and financial evaluation was deemed reliable. With this, the conclusion and recommendation was given to proceed with the development of the MEZT solution train to work towards a greener and sustainable future.

Acknowledgements

I would like acknowledge the contribution and express my sincere gratitude to everyone who has helped me throughout this project. This project was no mean feat and required a considerable amount of dedication and without their help, support and supervision; this project would not be possible.

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Nomenclature

List of Abbreviations

ADP	Ammonium-Dihydrogen Phosphate
AFC	Alkaline Fuel Cell
ANFO	Ammonium Nitrate / Fuel Oil
AS	Ammonium Sulphate
BPMED	Bi-Polar Membrane Electro-Dialysis
CAPEX	Capital Expenditures
CCS	Carbon Capture and Storage
CFC	Chlorofluorocarbons
DAP	Diammonium phosphate
ED	Electro-Dialysis
EU ETS	European Union Emissions Trading System
GHG	Green-House Gasses
GSD	Greenhouse Solar Dryer
HEX	Heat EXchanger
HVAC	Heating, Ventilation, and Air-Conditioning
IBC	Intermediate Bulk Container
ICE	Internal Combustion Engine
KS	Potassium Sulphate
LHV	Lower Heating Value
LPG	Liquid Petroleum Gas
MAP	Mono-Ammonium phosphate
ODP	Ozone Depletion Potential
OPEX	Operating Expenditures
RENURE	REcovered Nitrogen from manURE
SOFC	Solid Oxide Fuel Cell
UAN	Urea and Ammonium Nitrate water solution
VMS	Vacuum Membrane Stripper

List of Symbols

A_P	Membrane permeability coefficient	-
c	solute molar concentration	mol/l
C	Cost (of component)	€
ΔH°	Enthalpy change	kJ/mol
ΔT_m	Mean temperature difference	°C
E_p	Potential energy	J
i	van ’t Hoff index	-
J	Membrane flux	L/m^2hr
M	Molar mass	g/mol
n	Number of moles or scaling exponent	mol or -
Π	Osmotic pressure	Pa
P_O	Feed osmotic pressure	kPa
P_T	Transmembrane pressure (TMP)	kPa
Q	Heat or energy transfer per second	J or W
R	Ideal gas constant (8.314)	-
S	Sizing parameter (e.g. m^2 or L/hr)	various
T	Temperature	K or °C
U	Overall heat transfer coefficient	W/m^{2}K
W	Work done	J

1 Introduction

Since the dawn of mankind people have been farming for sustenance and in the last 100 years with a rising global population agriculture has grown rapidly. As the years went by, fertilizers were used more to keep up with demand and meat is now being eaten more than ever before due to growing middle and upper class needs.

In more recent years however, the environment and climate change has also become increasingly important and the fact that agriculture accounts for 10-15% of all human-induced gas emissions (see figure 1 for example) is no small matter [1]. On top of that, the gas emissions from Agriculture such as nitrous oxides (NOx) and ammonia (NH_3) can cause health problems and can harm the local environment, contaminating rivers and disrupting the ecosystem.

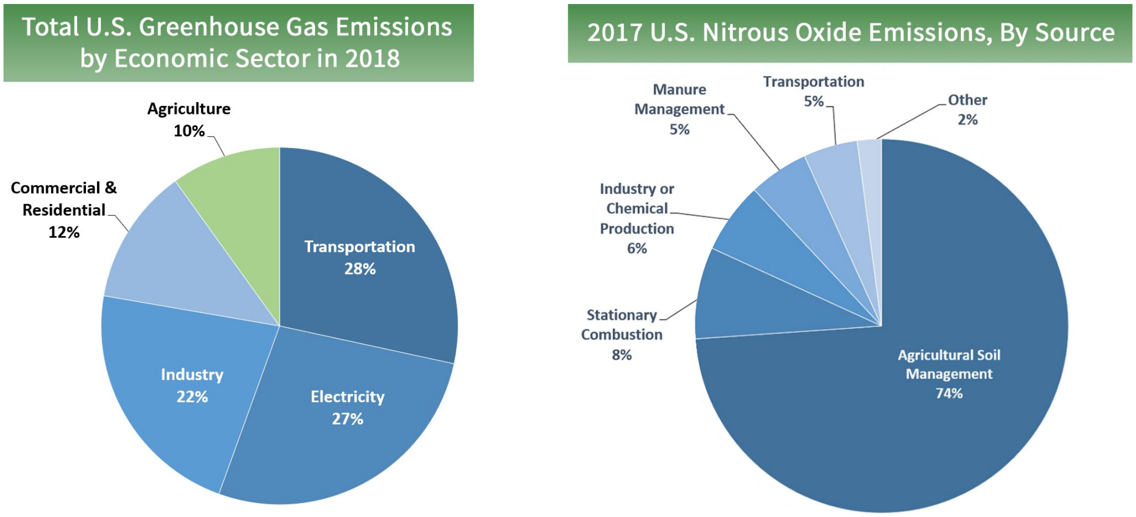


Figure 1: Overview of US agricultural gas emissions [2]

In 2019 this culminated in the Dutch ‘nitrogen crisis’ where approximately 18,000 construction and infrastructure projects near Natura 2000 areas were halted due to high nitrogen deposits [3]. Of these high nitrogen deposits, it was found that 46% originated from the agricultural sector, which is by far the largest source (67% even if you exclude nitrogen originating from foreign countries and values from the US are even higher, see figure 1) and the vast majority of this 46% comes from ammonia emissions [4].

Clearly then, this is a major problem that needs to be tackled. In essence, there are three main ways this problem can be solved.

The first way is to reduce the agricultural output. Currently, within the Netherlands there are talks about halving the number of cars on the road and closing Schiphol airport [5] (a large central European travel hub) and reducing the number of farm animals allowed in farms (even going as far as to half all animal production [6]) to lower nitrogen emissions. However, this is a very sensitive topic, especially reducing the farm capacity. Not only is this terrible for local farmers and employment, most of the Dutch produce is exported to other countries (the Dutch are globally the second largest exporters of produce after the US [7]), meaning that it will mostly harm the Dutch export. Then via simple supply and demand a new equilibrium will be set where other countries will likely increase production to compensate to some extent. This in itself is also a problem since the Netherlands is a leader in sustainable and efficient agriculture and has one of the lowest emissions output per yield [7], meaning that the other countries that pick up on lost production (even if total production is less) will likely emit relatively more harmful emissions. Overall then, this is not a great step forward to reducing global nitrogen emissions.

The second way is to persuade farmers to use fewer fertilizers and protein-rich concentrates that are made using nitrogen-rich materials. The downside of this is that it will significantly lower the yield of meat and crops, thus requiring vastly more arable land and livestock for the same output.

The third way to solve the emissions problem is to take the harmful emissions out of agriculture. The main source of emissions from Agriculture, at least for the livestock which is heavily debated, is from manure, which comes mainly in the form of methane, nitrogen-oxides and ammonia. Whether it be in the barn, a manure (slurry) storage or re-using manure as fertilizer, it releases these harmful emissions. Therefore, if it is possible to somehow prevent these emissions from being released from manure, it will significantly lower emissions and would help the crisis. Moreover, it would do so without lowering everyone's standard of living, meaning that such radical measures as halving livestock, cars or closing airports would not be necessary.

1.1 A Step Closer to the Solution

This is where MEZT's innovative new process comes in. MEZT has developed a Bi-Polar Membrane Electro-Dialysis (BPMED) process which can separate the minerals from a thin-fraction manure input [8]. By extracting the minerals (including nitrogen, potassium, phosphorus and compounds of these such as ammonia) the resulting leftover manure will be low in nitrogen and other harmful emissions-causing minerals, and the minerals can even be used for other purposes.

There are even thoughts of taking this leftover manure and bio-waste and turning it into biochar, which can then be combined with the previously extracted minerals to create Nutrient-laden Biochar. This can then be used as an efficient and low-emissions fertilizer, and since it only uses materials from the same agriculture it came from with very little leakage to the environment, it will be a form of circular agriculture, as seen in figure 2.

However, at this moment although this circular agriculture concept is excellent in theory, it is uncertain if (for example) the biochar fertilizer is the best solution for the products of the BPMED process. In fact, since both MEZT's BPMED process and TU Delft's biochar process are very novel, very little information is known about it and research is required before a definitive product usage can be chosen and the next steps can be made.

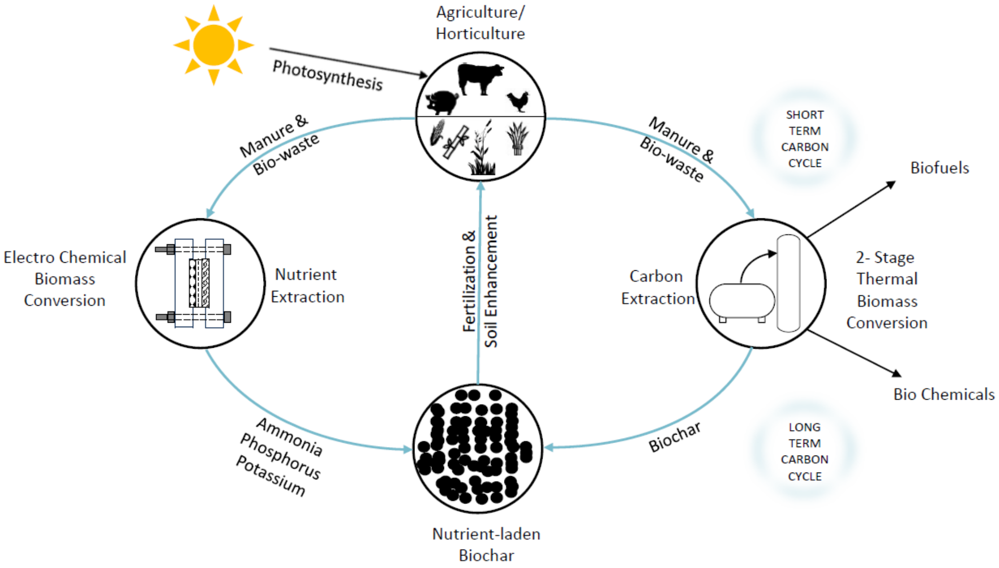


Figure 2: Low emission circular agriculture & carbon capture model [8]

1.2 Research Objective and Problem Statement

As alluded to before, the focus of this particular thesis will be to investigate the possibilities to recycle and re-use the output streams (minerals), more specifically ammonia, which is a very valuable and useful compound.

Both other main output streams, phosphorus and potassium, are somewhat cheaper to produce (albeit damaging to the environment), originating mostly from mining operations and already predominantly used for fertilizers, which is also a relatively simple and cheap process. However, mass production of ammonia originates from the Haber-Bosch process, which is a very energy-intensive process due to its high pressure (10 MPa) and moderately-elevated temperature (450 °C) requirements [9]. The chemical reaction of the Haber-Bosch process can be seen below.

$$N_2 + 3H_3 \Longrightarrow 2NH_3 \qquad \Delta H^{\circ} = -91.8kJ/mol$$

Also taking into account the energy needed to produce the hydrogen and pure nitrogen for this process, global ammonia production consumes 1 to 2% of all global energy and produces approximately 3% of global carbon emissions [10]. Mindlessly discarding or just using the valuable ammonia output for fertilizer may not be the best option. Therefore a technical and economic analysis of a range of ammonia recycling/conversion processes will be investigated on a farm scale in order to find the best process and use for ammonia. Extra care will be given to usages within the agricultural sector in order to work towards circular farming. The main problem statement can then be formed as followed:

> *Within the context of farms and MEZT's BPMED process, what is the best ammonia recycling process and usage and is it financially feasible?*

2 Understanding the Process

Before it is possible to go in-depth into finding and analysing all the different technologies and techniques for converting ammonia to valuable products, the boundary conditions of the current process needs to be known. For that, the MEZT process itself needs to be understood.

2.1 How MEZT's BPMED Process Works

In a nutshell, this is how the MEZT process works [8]. First, animal manure gets collected via grates and gutters placed underneath the livestock. For a normally sized farm and using MEZT's current setup manure will be produced at a rate of 10-30 m^3/day. This manure gets collected and placed inside a temporary holding tank. Afterwards, the manure gets separated into a phosphate-rich thick fraction and a mineral rich thin fraction using a liquid-liquid (thick-thin) separator. Afterwards the thin fraction gets filtered to remove further particles to prevent contamination and clogging before entering the BPMED.

Within BPMED, the liquid is guided along membranes over which a voltage is applied. Then due to the voltage differential, the positively charged ammonium ions (cations) are pulled through one of the membranes to form an ammonium concentrate dissolved in water [11]. Overall the extraction rate can reach 50-89% with a water purity of 99% [8]. One of the reasons why electro-dialysis (ED) is used in the BPMED is because the membranes are not as easily fouled by organic matter, thus needing replacement less frequently [12].

Afterwards, the water with concentrated minerals goes into a mineral separator in the form of a Vacuum Membrane Stripper (VMS). Here a vacuum is applied over a membrane which essentially "sucks" the ammonia gas out of the stream leaving a water stream with potassium behind. It should be noted that also quite a large amount of water gets "sucked" through the membrane in gaseous form, meaning that the ammonia stream is roughly 10% ammonia and 90% water by weight.

Afterwards, this stream can be further utilized and modified for other applications, which has not yet been determined and will be discussed in the following chapter, as the exact setup will depend on what the ammonia will be used for. An overview of the MEZT process including the inputs, outputs and flow rates that are currently in place can be seen in figure 3.

As a side note, throughout this paper a manure flow rate of 1000 L/hr is used for consistency, easy scaling of calculations to other sizes, and since the final proposed design is made for a 1000 L/hr. However, for section 6 (the final costing), a 300 L/hr manure flow rate will also be mentioned since the current prototyping costing of MEZT is for a smaller size.

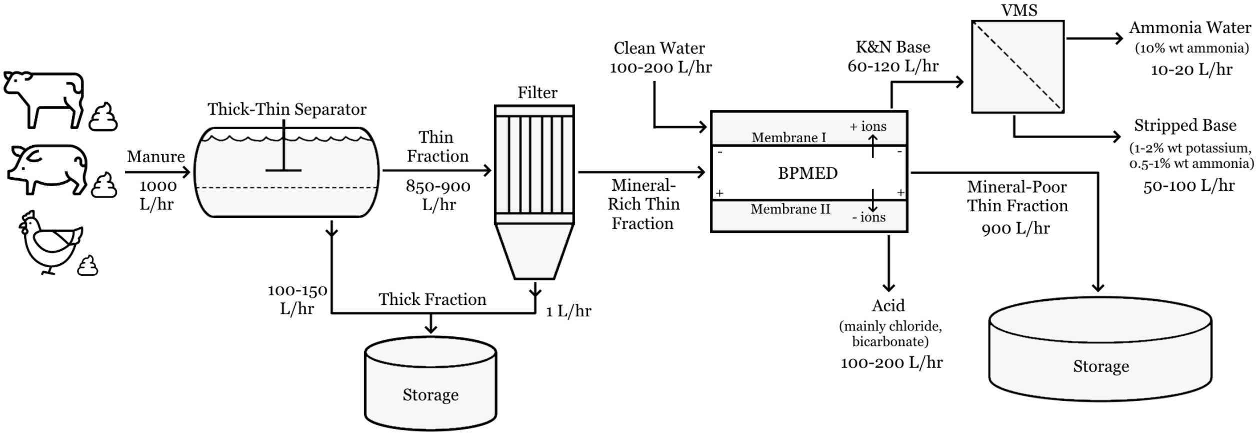


Figure 3: Simplified overview of the MEZT process [8][12]

2.2 Boundary Conditions

The following boundary conditions have been set, as determined from the process itself [8] and through discussion of the process with members of Lenntech working on the BPMED process itself [12]. For clarification, these boundary conditions are of the output of the VMS.

- 10 to 20 litres/hr liquid ammonia water flow rate. This is the expected output based on a 1000 litres/hr raw manure input, which corresponds to the 10-30m^3/day manure production of an average farm in question.
- 10% by weight ammonia in the water. This is based on experiments where the output of the BPMED produces 1% ammonia water and that the VMS can concentrate it by a factor of 10. It was noted that this is merely a rough estimate and that in the end it could be anywhere between 5% and 15% by weight, depending on how well the VMS works in practice.
- 99.9% purity of the output stream. With the filters before the BPMED, the extraction of the BPMED process itself and the VMS afterwards which only extracts gasses (and no other substances that can be in gaseous form are expected to be in the input stream), the output purity is expected to be very high.
- 20-25°C output temperature. This is a very loose estimate as currently there is no heat added or extracted and the output temperature can still change depending on the final usage.
- No specified exit pressure. The VMS will use a vacuum pump to extract the ammonia in gas form, but at what pressure it will be taken out of the process is still variable and dependant on the final use. It could for example be at atmospheric pressure.

From these boundary conditions it is evident that the final process is far from complete and in fact (as of Q2 2021) the VMS process itself is still under investigation on how to best design it and can still change depending on final use.

3 Literature Review

Instead of going in blindly to find all relevant processes that utilize ammonia, it is much more logical to first find the main uses of ammonia and then use that as a basis to search for useful processes.

3.1 Ammonia Uses

From researching several sources, the following major and minor uses of ammonia have been identified: fertilizer production, explosives production, textiles and synthetic fibres, as a chemical for synthesis, as a refrigerant, in pharmaceuticals, as an aid in the creation of pulp and paper, in mining and metallurgy, as a cleaning agent [13], for water supply purification [14], as an antimicrobial agent in food [15], for fermentation and as a fuel [16]. Further uses do exist, such as using ammonia gas to darken wood for a pleasing aesthetic appearance, but as these uses are very limited and/or insignificant, they will not be investigated.

Currently, the largest use of ammonia is for fertilizer (80%), followed by fibres/textiles (10%), explosives (5%) and the rest only account for 5% [16]. An overview of ammonia's main usage, including its specific sub-usages in the fertilizer industry can be seen in figure 4.

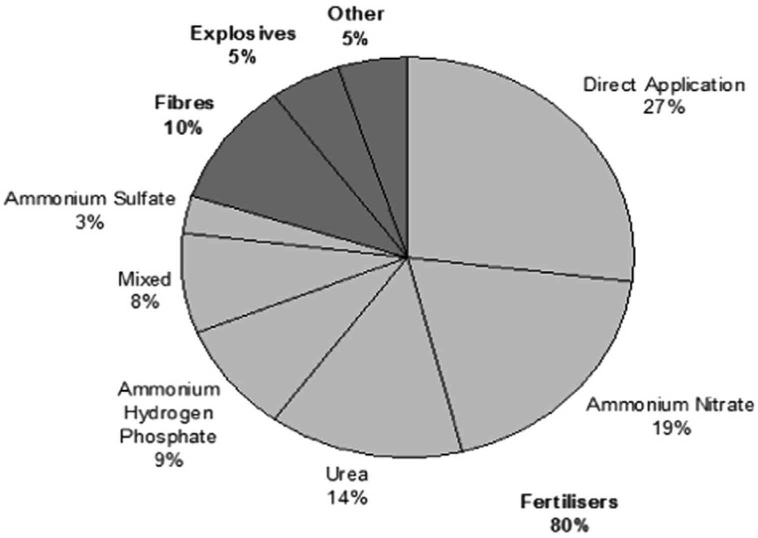


Figure 4: Overview of global ammonia's usage by percentage [16]

To narrow down the search for processes, it is possible to discard a lot of these processes early on using simple deductive reasoning. In table 1 and 2 you will find a list of the discarded uses of ammonia and the reason why, with considerations to a farmer's perspective.

Table 1: Discarded ammonia uses and the reason why

Use	**Explanation**	**Reason for discarding**
Explosives	Ammonia can be turned into Nitric acid, HNO_3, and then into ammonium nitrate, NH_4NO_3, which can then be used for explosives. In fact, 80% of explosives used in North America comes from ammonium nitrate [17]	Not only is there an inherent danger in producing explosives that farmers have no use for, the exact same ammonium nitrate is commonly used as a fertilizer, making explosives production redundant
Pharmaceuticals	Ammonia is used in manufacturing soda ash and nitric acid for use in certain drugs, such as antimalarials, Vitamin B, and sulphonamide which inhibits bacterial growth. [13]	Pharmaceuticals require only a small amount of very pure ammonia and for drugs the price of higher quality ammonia is not a deciding factor. Plus, the health concerns of using ammonia originating from manure is a hindrance
Mining and metallurgy	Ammonia is used for extracting zinc and nickel via an ammonia leaching system (or even using the aforementioned explosives in the form of ANFO), as well as bright annealing (nitriding) steel during manufacturing [13]	Theoretically possible, but only a little amount of ammonia is used in this industry where high purity is preferred for nitriding and ammonia is a small cost contributor, so a strong case is difficult to make. Additionally, farms are generally not close to mines or metallurgic facilities
Pulp and paper	Ammonia can aid in the pulping of wood by breaking apart the bonds between the cellulose fibres, making it usable for making paper. Additionally, ammonium chloride can help improve the wet-strength of paper such as tissue paper	Just like the mining industry, it's theoretically possible, but livestock and produce farms, especially in the Netherlands with few tree farms, have no major use for wood pulping. Moreover, aqueous ammonia is used, which is already the BPMED output, so selling the ammonia as wholesale would be the option for this [18]
Water supply purification	Ammonia has been added to (drinking) water treatment for over 70 years as it prolongs the effectiveness that chlorine has in water through the formation of chloramines [19]	Like pharmaceuticals, there are health concerns of adding ammonia originating from manure to 'clean' drinking water, as it may contain harmful pathogens
Antimicrobial agent in food	Due to being strongly antiseptic, anhydrous ammonia is sometimes used commercially to destroy and reduce microbial contamination of meats such as beef, most notably McDonald's "pink slime" hamburger patties	Like water purification, the health concerns of using ammonia originating from manure is a problem, in addition to the health doubts of using pure ammonia. Also, very little ammonia is used in the meat, so manufacturers would opt for purer, safer options

Table 2: Discarded ammonia uses and the reason why (continued)

Use	**Explanation**	**Reason for discarding**
Fermentation	ammonia solutions of roughly 16% to 25% are used as a nitrogen source for microorganisms, such as yeast, in the fermentation industry and to adjust the pH-levels during fermentation [20]	Similar reasons to its use as an antimicrobial agent in food and additionally, very small quantities are used as ammonia's toxic properties would quickly kill yeast in higher concentrations (above 0.1%) [21]
Fibres and textiles	Ammonia can be used as a key ingredient to make artificial fibres such as Nylon [13] and ammonia is also sometimes used to pre-treat wools and fabrics to improve tear strength, dye absorption capabilities and thermal stability [22]	Although at first considered, farmers are very unlikely to create their own nylon and nylon products and for the pre-treatment of wool and fabrics ammonia is one of the lesser popular chemicals to use. Additionally, aqueous ammonia is often used instead.

Besides these uses which are fully discarded, some other uses can be partially discarded. For example, with the synthesis of chemicals, only certain chemical products are applicable and useful. For example, one of the main chemical synthesis that can happen with ammonia is for nitric acid in the production of explosives or fertilizer (as mentioned in the previous table) and nitroglycerin for a vasodilator to dilate blood vessels (similar to pharmaceuticals) [13]. Other common chemical synthesis of ammonia include hydrogen cyanide (HCN), sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$) and hydrazine (N_2H_4) (as used in rocket fuel) [13]. Clearly then, not all chemical synthesis options will be discarded. Rather, they will only be considered if they are a required step for a possible use.

This leaves only a few ammonia uses left to investigate. These are fertilizers, as a fuel source, as a cleaning agent (or aqueous wholesale) and as a refrigerant (or compressed/liquidized gas wholesale). The reasons why these are useful to investigate will be mentioned in their respective sections.

3.2 Wholesale Pure Gas or as a Refrigerant

One possible use for ammonia is as a refrigerant. Ammonia has favourable properties for refrigeration including a low boiling point of -33.3 °C and high latent heat of vaporization, allowing for an energy-efficient vapour-compression cycle and although its corrosive properties meant that its use was limited in the past, the increased environmental concern of chlorofluorocarbons (CFCs) mean that ammonia as a refrigerant is rising in popularity [23]. Unlike CFCs, which are very potent greenhouse gasses that also damages the ozone layer, ammonia has an ozone depletion potential (ODP) of 0.00 and has a vastly lower environmental impact if released into the atmosphere [23].

This, along with emissions regulations becoming stricter means that ammonia is now more frequently used in anything from HVAC chillers and air conditioning to thermal storage systems and heat pump systems. In some cases ammonia's properties allow it to be used in very specific applications such as on the International Space Station [23].

In fact, ammonia can even be used in conjunction with secondary fluids (like water) in many similar applications, but for this subsection pure ammonia gas (or as a compressed liquid, for easier storage) will be considered. Aqueous ammonia is considered in a separate subsection later on.

3.2.1 Extracting Ammonia Gas from Water

For the pure application, a process is needed to extract the pure ammonia from the aqueous solution. However, extracting ammonia gas from water is easier said than done. This is because ammonia gas is extremely soluble in water, which is exactly the output of the MEZT process.

From research, there are 2 very broad ways to separate ammonia from water: either chemically by adding (for example) acids to either create salts or to change the pH so that it is very easy to separate from the water, and secondly, mechanically, which requires a more precise setup. Since one of the goals of MEZT is to create a form of circular farming that is more environmentally friendly, the chemical route will not be chosen, as not only will additional chemicals be added, there will be an inevitable waste stream once the ammonia gas is extracted from the (for example) salt.

Mechanically and physically speaking, with ammonia's boiling point of -33°C and water's boiling point of 100°C, it should be easy to separate, but ammonia's strong interaction with water makes it very difficult. When ammonia is dissolved in water a part of the ammonia reacts to form ammonium and hydroxide ions, as denoted by the following reversible equation.

$$NH_3 + H_2O \rightleftharpoons NH4^+ + OH^-$$

When one tries to heat up or boil this mixture, the reaction gets pushed to the left where protons move from $NH4^+$ to OH^- to form water and ammonia again. Essentially, ammonia's solubility in water is lower at higher temperatures. The problem is that at these higher temperatures water is also evaporating. In fact, simple distillation is generally seen as a non-viable way to extract ammonia from water [24]. Further research for mechanical separation of ammonia from water yields many papers of removing very small quantities from waste water via stripping where it is discharged into the atmosphere [25].

Fortunately, there is a solution and it also already utilizes the VMS step. Instead of trying to separate the liquid ammonia-water combination at standard atmospheric pressure where solubility is a problem, the gas mixture of ammonia and water that comes directly out of the VMS at a much lower pressure can be used [26]. This is because at the very low pressures there is significantly less molecular interaction between ammonia and water. Then instead of evaporating the ammonia, the water can be condensed, by using a cold trap.

If the vacuum pressure of the VMS is set at 2 kPa, water would condense at just under 20 °C (17 °C), whereas ammonia would stay in gas form. Cooling the mixture from its original roughly 25 °C down to 10 °C would ensure that all the water condenses, as seen in figure 5. Now, since the water ends up in liquid form, it is possible for the ammonia gas to re-dissolve in it. Fortunately, at such low pressures the solubility of ammonia in water is less than 5%, as seen in figure 6.

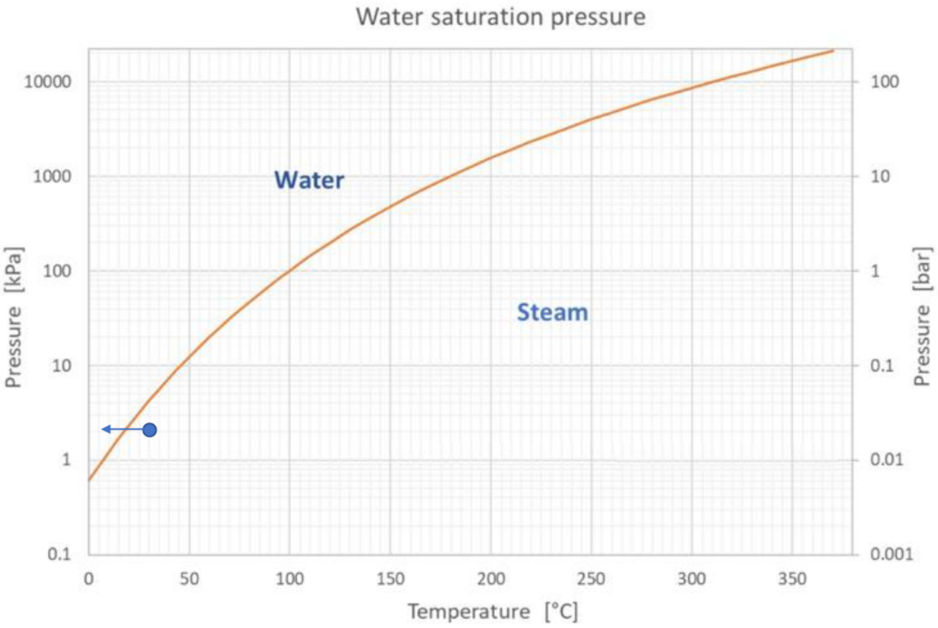


Figure 5: The saturation pressure of water at different temperatures and pressures [27]

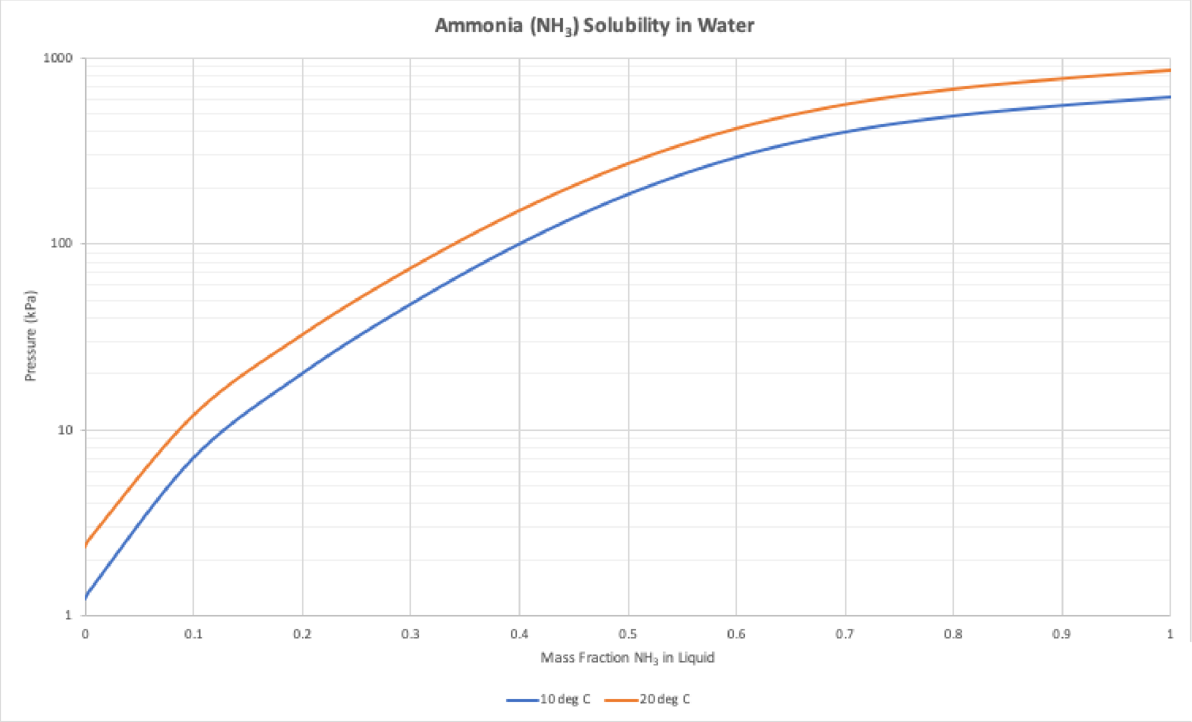


Figure 6: The solubility of ammonia in water at different temperatures and pressures [27]

This cold trap step can be placed in between the membrane and the vacuum pump of the VMS system and after the whole process there will be very close to pure ammonia leaving the vacuum pump and the remaining water with less than 5% ammonia can either be discarded or perhaps even recycled back into the input stream. An example schematic setup from a recent paper that separated ammonia from phosphorus (same method, different chemical) via this method can be seen in figure 7.

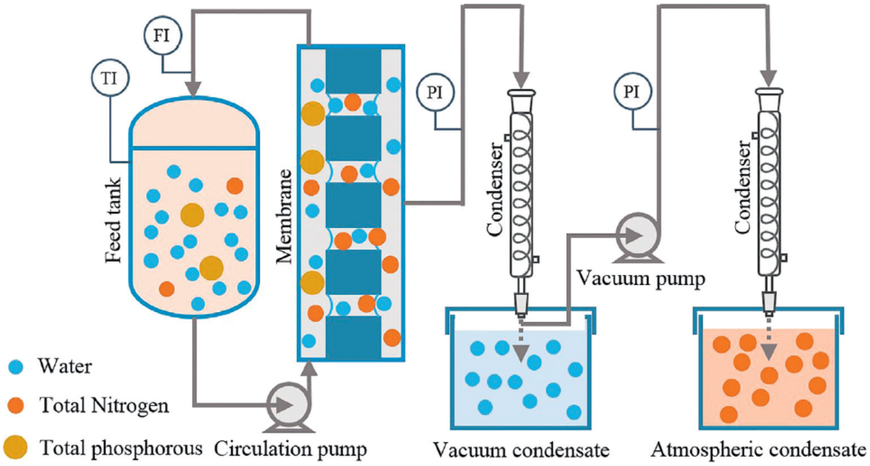


Figure 7: Example schematic setup of VMS with two cold traps (condensers) [28]

It should be noted though that with this process the gasses flow at quite a high speed due to taking up a lot of volume, meaning that the cold trap and cooling column might not cool optimally or some water droplets may enter the vacuum pump, which the paper from B. Qiu et.al. (2020) accounted for by adding an extra atmospheric condenser after the vacuum pump to catch eventual water coming through. Either way, this can be taken into account when designing the final process, perhaps via a flash drum. Finally, another compressor and storage tank would be needed to compress and store the liquid anhydrous ammonia, since storing it as a gas would take up far too much space.

3.3 Wholesale Aqueous or as a Cleaning Agent

One possible use for the ammonia is to use it as cleaning agent or to sell it wholesale. The reason these two are combined is because ammonia as a cleaning agent and ammonia sold in wholesale can both be the same output, namely aqueous ammonia with a 25% concentration.

Cleaning ammonia for household use is roughly 5-10% ammonia by weight dissolved in water, but stronger industrial cleaning solutions which might be necessary for tough farm conditions are mostly 25% ammonia by weight [14]. Although farms do not have a huge need for ammonia as a cleaning agent, aqueous ammonia does give a streak-free shine that is useful on stainless steel and glass surfaces which can typically be found in greenhouses or storage tanks on farms.

Coincidentally, one of the ways ammonia is often sold wholesale is via the same 25% concentration. Therefore, once a small amount is reserved for cleaning, the remainder can be sold wholesale.

Ammonia is typically sold in 2 ways: either in pure liquid form in a compressed tank, or as aqueous ammonia with a typical 25% ammonia concentration by weight, which is applicable here.

As of Q2 2021, global ammonia wholesale price in aqueous 24.5-25% form has a price of approximately \$150.00 - \$350.00/tonne, whereas anhydrous compressed liquid ammonia of 99.9% purity costs approximately \$600.00 - \$1500.00/tonne (logical: 4 times the ammonia, 4 times the price) according to wholesale marketplace Alibaba.

However, prices for the Dutch market are different as transportation, taxes and mark-ups increase the price. Smaller sized 25 litre jugs of 25% industrial grade ammonia sell for approximately €1 /litre with the lowest found price being €0.80 /litre [29], whereas bulk prices are mostly kept ”on request” due to competition. Fortunately, after getting in touch with Vivochem, a large Dutch B2B chemical wholesaler, the bulk price of 24.5% ammonia was given as €210 per metric tonne (ex. BTW) when ordering a truck load (23-28 metric tonnes) [30]. This, at a density of 0.91 g/mL at 20°C, translates to a low price of €0.191 /litre. If we consider the unprocessed output of the MEZT process at just 10% concentration, the price would be expected to be lower proportionally by the amount of ammonia, since the water price is negligible.

At first thought, one might think that practically speaking this might not be the best choice, as wholesale purchasers would not want to go around to all farms frequently to pick up the relatively small quantities of ammonia produced daily. However, on a farm with plenty of space it should be possible to place or construct a large storage tank to hold enough ammonia for an entire tank truck (up to 30,000 litres), thus making it much more enticing (and cheaper transportation-wise) for wholesalers to purchase ammonia from farms.

3.3.1 Concentrating Aqueous Ammonia

If an ammonia concentration of 10% is sufficient, then simply using the output of the VMS process without cold trap is sufficient and simple. However, if one wants to concentrate it to (for example) the 24.5-25% as often available in wholesale, it is a different story. Concentrating an ammonia mixture is similarly difficult to getting pure ammonia gas, just like in the previous subsection, due to ammonia’s solubility.

Fortunately, there is a relatively simple solution that essentially is an in-between step of using the full power of the cold trap and no cold trap at all. If one uses a shorter or smaller cold trap with less cooling power, it is possible to achieve partial condensation, thus only extracting some of the water. Alternatively, it is also possible to use an ammonia water bubble absorber, using some of the ammonia gas output to further concentrate some of the 10% ammonia input [31], although a carefully designed cold trap will use less energy as the same flow only needs to be partially cooled.

3.4 Ammonia Fuel Cells

Yet another plausible use for ammonia is in a fuel cell where ammonia and oxygen from the air is converted into harmless nitrogen and water to create electricity. There are many different types of fuel cells, but the principle is mostly the same for all of them. Fuel enters at the anode side, while the oxidant enters at the cathode side. Then when an electric current is applied through the circuit from anode to cathode, either positive H^+ ions move from anode to cathode or negative O_2^- ions move from cathode to anode, depending on which type of fuel cell is used [16].

Out of all fuel cells, the most significant types are the low temperatures cells, including Alkaline fuel cells (AFC), Solid polymer fuel cells (SPFC) and Phosphoric acid fuel cells (PAFC), and the high temperature cells, including Molten carbonate fuel cells (MCFC) and Solid oxide fuel cells (SOFC). It is also possible to distinguish ammonia fuel cells into direct ammonia fuel cells, which uses ammonia directly and currently offers the better efficiency, and indirect ammonia fuel cells, where ammonia first gets cracked into hydrogen, which is then used in the fuel cell. Of these, the ones that are most compatible and shown to be effective with ammonia as a fuel are the AFCs and the SOFCs, so these will be investigated [32].

3.4.1 Alkaline Fuel Cells

AFCs are characterised by their lower operating temperature and through their use of a potassium hydroxide (KOH) electrolyte. They operate by feeding oxygen from the air into the cathode where it is combined with water and electrons to form hydroxide ions which are transferred through the electrolyte, as shown in the following equation.

$$O_2 + 2H_2O + 4e^- \implies 4OH^-$$

Then ammonia, which is supplied at the anode, captures the hydroxide and releases nitrogen, water and electrons, which is captured as electricity, as seen in the following equation.

$$2NH_3 + 6OH^- \implies N_2 + 6H_2O + 6e^-$$

These 2 equations can also be combined to give the following overall AFC reaction.

$$4NH_3 + 3O_2 \implies 2N_2 + 6H_2O$$

Although it is possible to operate this type of fuel cell at room temperature, the power density is rather low and finding a good cathode and anode catalyst is difficult. There is also the problem that ammonia can cross over through the polymeric membrane electrolyte which can lower the efficiency [32]. However, an ammonia AFC produced by GenCell will be available to purchase within 2021 and has specifications and a price available, making it valuable for comparison, especially since ammonia SOFCs are not commercially available yet and still in development [26].

3.4.2 Solid Oxide Fuel Cells

SOFCs operate slightly differently and are characterised by their high operating temperatures. Ammonia SOFCs can either be based on proton conducting electrolytes (where H^+ ions move from anode to cathode) or oxygen ions (where O_2^- ions move from cathode to anode), however, a thermodynamic analysis has indicated that peak power-density of the proton conducting electrolytes-based SOFCs is 20 to 30% higher because of a higher anode hydrogen concentration, which is why it will be chosen here [32]. Moreover, as a preliminary matter to point out, the document from CramChem stated that a SOFC could be the best choice based on the available literature and as proven by him [26]. An overview of the proton conducting electrolytes-based SOFC (specifically SOFC-H) can be seen in figure 8.

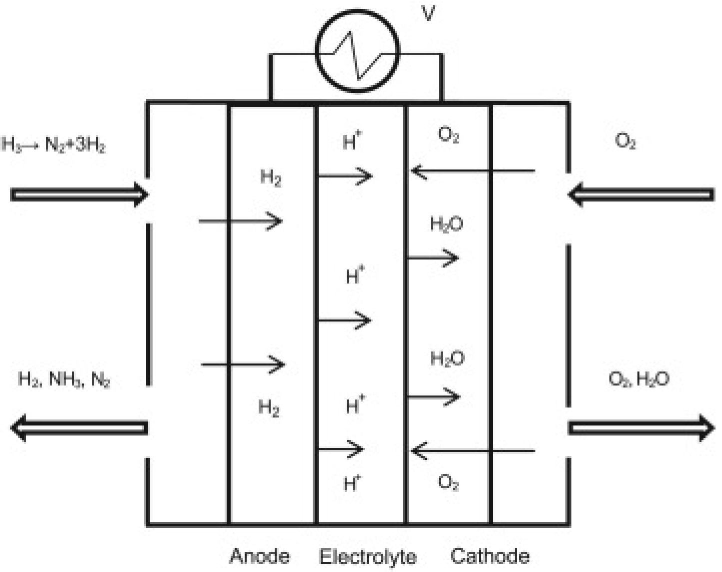


Figure 8: Schematic overview of the SOFC-H process [32]

Within the SOFC-H, at the anode the following two reactions take place.

$$2NH_3 + 5O_2^- \Longrightarrow 2NO + 2H_2O + 10e^-$$

$$2NH_3 + 3NO \Longrightarrow 5/2N_2 + 3H_2O$$

However, because of the slow diffusion of O_2^- through the electrolyte, the first of these reactions is the rate limiting one, meaning that some Nitric Oxide (NO) is being produced at the anode. Fortunately it is possible to remove the formation of NO by using a $BaCeO_3$ and $BaZrO3$ doped catalyst to facilitate ammonia decomposition and prevent the formation of NO. The reaction at the anode will then be as followed.

$$2NH_3 - 6e^- \Longrightarrow N_2 + 6H^+$$

In this case the thermal decomposition becomes more significant at higher temperatures above 500 °C. Alternatively, it is also possible to use a Ni/Y_2O_3 based catalyst for the ammonia composition. A SOFC stack with this catalyst has been proven to work and at 770 °C the SOFC stack showed no significant degradation after 1000 hours [33]. Lastly, it is also possible to add an auto-thermal cracker made of a $CoCeZr$ composite oxide before the SOFC, which oxidises part of the NH_3 to provide heat for the decomposition [33].

3.4.3 Alternative to Fuel Cells

Although many newer investigations are on the usage of ammonia in fuel cells, there is also the idea of using ammonia gas in a much simpler internal combustion engine (ICE). Ammonia's unfavourable combustion properties mean that in Diesel and compression ignition engines its use is limited to co-combustion where it is burned alongside a traditional fuel [34].

However, in spark ignition engines it is possible to run up to 100% ammonia gas fuel via the use of specific spark plug arrays or via plasma jet igniters. Disassociating part of the ammonia into H_2 as a fuel promoter using a catalyst is also possible [35]. In fact, studies on the use of ammonia in traditional (e.g. automotive) ICEs have been around since the 1960's [35]. Unfortunately, although even NO_x emissions are lower, the specific fuel consumption is 2 to 2.5 times higher than using traditional hydrocarbons and (for example) liquid petroleum gas (LPG) has a similar to cheaper price per litre too. Therefore its use in a traditional ICE generator is not a great idea, not to mention that electricity from the power grid is cheaper yet again that that produced from a generator.

3.5 Fertilizers

Finally, the most obvious use of ammonia is through the use of fertilizer. After all, it accounts for approximately 80% of global ammonia usage [16]. Here, all major ammonia-originating fertilizers have been investigated. It should be noted though that blends of different fertilizers have not been investigated, but these are essentially combinations of fertilizers that a farmer can compile themselves.

3.5.1 Direct Application

When applied directly as a fertilizer, ammonia can be applied in two general ways. Firstly, aqueous ammonia can be sprayed on crops or soil or even injected slightly below the surface. The plants then can absorb the nitrogen in the soil in form of ammonium (NH_4^+) and nitrate (NO_3^-), which happens through the plant's ammonia transporters [36].

It is also possible to directly apply the fertilizer in gas form. In this case the stored compressed liquid (anhydrous) ammonia gets injected via special tractor-drawn shanks and knifes 10-20cm under the surface, after which the ammonia directly gasifies and can be absorbed by the moisture in the soil [36].

Both of these options are very simple ways to apply ammonia to crops, however, because of the direct application a significant amount of ammonia can evaporate into the atmosphere, especially with the direct gas application. In fact, since the output of the BPMED and VMS can most easily make aqueous ammonia and since the direct application of aqueous ammonia releases less ammonia into the atmosphere, the direct gas application will not be considered.

3.5.2 Enriched Biochar

Enriched biochar is another possible use for the ammonia. Essentially the process of creating enriched biochar consists of first making the raw biochar (from the thick fraction of manure in this case) and then enriching it using the ammonia (and possibly also other minerals) from the BPMED process. Compared to the direct application, biochar has significantly lower nitrogen emissions and it also uses the thick-fraction of the manure that would otherwise be left un-utilized (although normal 'raw' biochar could also be produced alongside other processes and sold).

Creating biochar
To create biochar a farmer starts with a relatively dry (ideally about 15% moisture) bio-based input that is placed in a pyrolysis reactor, in which five subsequent steps occur [37]:

1. **Drying & Conditioning:** First most of the remaining moisture is removed as the biomass gets heated above 100 °C. Above 105 °C the biomass will start to condition, where it breaks down and softens. Now chemically bound water will also be released.
2. **Torrefaction:** Once heated to roughly 200-280 °C the chemical bonds in the biomass also start to break down and will release oxygenated volatile organic compounds such as acetic acid and methanol, along with CO and CO_2. At this stage the process is still endothermic, meaning it requires a heat input.
3. **Exothermic Pyrolysis:** At 250-300 °C the thermal decomposition becomes much more rapid, releasing tar and combustible gasses such as CO, CO_2, CH_4, and H_2. At this point the breakup of large biomass polymers causes the process to be exothermic, allowing it to be self-sustaining up to 400 °C and will leave a carbon-enriched charcoal residue.
4. **Endothermic Pyrolysis:** Further heating to about 500-600 °C drives off and decomposes more volatile compounds in an endothermic process, leaving a high carbon content. At this point about 20-35% of the oven-dry feed is turned into char (for wood at least).
5. **Activation & Gasification:** Finally, above 600 °C it is possible to inject small amounts of air or steam to raise the surface temperature to 700-800 °C, allowing one of two processes (albeit for a lower 20% yield): activation, which releases more volatiles and adds acidic functional groups, but a lower yield, or gasification, which injects a lot more air/steam to create a gas that can be used to generate power.

The exact temperatures, durations and steps can vary as it can all affect the outcome of the gas, bio-oil and biochar yield, including biochar properties (mineral content, ash content, etc.). A general diagram of when and how long torrefaction and pyrolysis (the two main stages) happen can be found in figure 9.

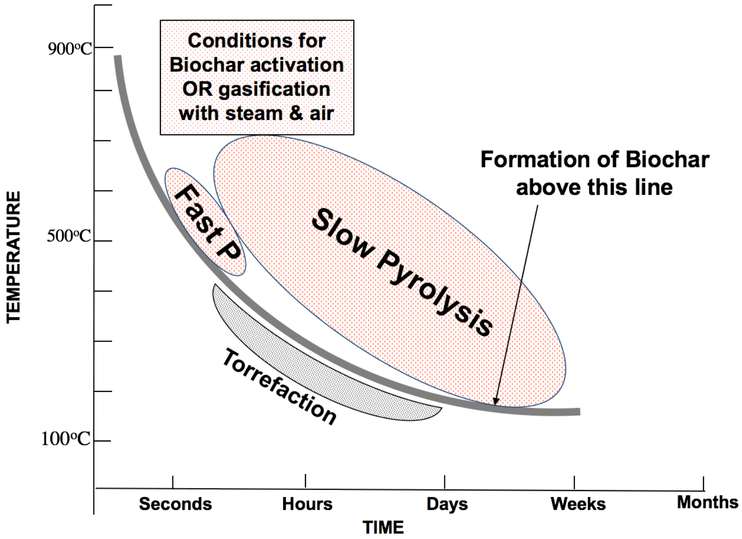


Figure 9: Overview of the temperatures and duration for pyrolysis and torrefaction to occur [37]

A more detailed pyrolysis reactor stage can be designed if it is eventually chosen, but more important at this stage is the steps around it. For example, the thick fraction of manure has substantially more water content than traditional biochar inputs such as wood, meaning some pre-treatment is necessary. In such cases water is sometimes extracted using a dewaterer and/or dryer before entering the pyrolysis stage.

From research, raw pig and cattle manure has a solid content of roughly 6-12% or less if flushing is applied, which is the case for MEZT's setup [38]. However, if manure is turned into biochar, it ideally needs to be at least 25% solid content (max 75% water) before it can be used in a dryer and subsequent pyrolysis reactor [39]. Fortunately, after the thick-thin separator, the thick fraction is typically 20-65% dry matter, meaning that it is likely to be dry enough for use in a dryer, confirming that the thick-thin separator is sufficient as a dewaterer [38].

For the dryer, many technologies exist, from energy-free greenhouse solar dryers (GSD) to a rotary, flash, disk or cascade dryer, or even a superheated steam dryer [40]. If this technology gets chosen, the best dryer type will be investigated, but in the grand scheme of things they all function in the same way: adding some form of heat to the biomass in order to extract moisture.

After drying, the biomass enters the pyrolysis reactor. Although more precise specifications are not known yet, from a research paper on the pyrolysis of swine manure, the process yielded 55.7% bio-oil (of which 52% is water content), 34.2% biochar, and 10.1% pyrolysis gas. It was also noted that the energy demands to maintain the pyrolysis process is 1.8MJ/kg of feed [39].

The Lower Heating Value (LHV) of biodiesel-oil (vegetable oil) is 42.2 MJ/kg, which at the 28.9% (55.7% * 52%) weight yield of pure oil means that per kg of biomass input, 12.2 MJ worth of bio-oil is produced, which is more than enough to maintain pyrolysis and excess can be used for drying, stored, or used elsewhere.

Enriching Biochar

Once the biochar has been made, it is time to enrich it. Biochar has generally been recognized to have good ammonia up-take capabilities due to biochar's good adsorption properties. Once biochar is enriched, the ammonia will also stay in it for a long time: 12 days under lab conditions and air flows, which is quite long, yet an increase in nitrogen uptake by plants was still registered, indicating that the ammonia was not irreversibly bound [41].

In order to enrich biochar with ammonia, the most frequently occurring option is via a gas-adsorption column. Within this process, gaseous ammonia is injected in the column containing biochar after which the surface oxygen groups react with the oxidized black carbon surface to form amines and amides at ambient conditions or potential chemical ring structures at higher temperatures. At ambient conditions, the ammonia can also act as a Lewis or Brønsted acid, forming an amide or ammonium salt after reacting with a carboxyl group on the surface, as seen in figure 10.

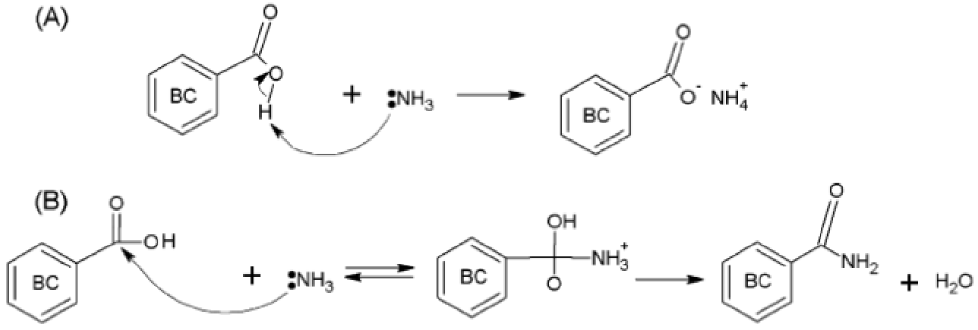


Figure 10: Ammonia reacting to form either a Brønsted (A) or Lewis (B) acid [41]

Within water treatment, it was found that biochar can also adsorb ammonium from aqueous ammonia. In low-concentration aqueous ammonia (50mg/L or about 5%), the biochar ammonia adsorption rate was between 15.8 and 17.6 mg/g for 9 different tested biochars, albeit at 10 hours. Although it also noted that the Langmuir maximum adsorption capacity of biochar is above 200 mg/g, meaning that with a higher ammonia concentration input, higher adsorption might be possible [42]. However, not much literature is found on if aqueous ammonia enriched biochar is suitable as a fertilizer and one can imagine that as the biochar dries out again that the ammonia may evaporate. For this reason, only the gas ammonia enrichment will be considered.

In the end, many factors can affect how well biochar adsorbs ammonia, ranging from the pH level of the biochar to the temperature and duration of adsorption to the quantity of surface acidic groups [41]. More precise conditions will be investigated if this option is chosen.

However, generally both non-activated and steam activated biochar can adsorb 0.6-4.7 mg-N/g, whereas acid (nitric acid HNO_3) activated biochar can adsorb 17.5-52 mg-N/g, which is significantly higher [43]. It is also possible to treat the biochar with a high temperature CO2–ammonia process, promoting ammonification and giving a 3.91 wt.% nitrogen content in biochar, although it should be noted that the starting nitrogen wt.% wasn't noted in this paper [44].

Overall Production Estimate
Taking the thick-fraction 'wet' input as 100 to 150 L/hr and assuming a density of roughly 1 kg/L, the previous estimate of the thick fraction (20-65% dry matter) can be used to estimate a dry biomass input in the pyrolyser of 20 (low) to 97 (high) kg/hr. If the 34.2% biochar yield from (assuming) fully dry input is taken, the final biochar yield is 6.8-33.2 kg/hr.

The ammonia production from the MEZT process yields 10-20L of 10% weight ammonia, which at a density of 0.957kg/L is 0.95 to 1.91 kg/hr of ammonia. In a worst case scenario of lowest ammonia production at highest biochar production, the 0.95kg per 33.2kg biochar will result in 2.86% ammonia enrichment, which is already on the higher end of the adsorption spectrum. The high end could even result in 28% enrichment if the process were to allow it, but in reality it can safely be assumed that there is sufficient ammonia to enrich the biochar as much as possible and there will very likely even be ammonia gas left over to sell as wholesale.

3.5.3 Ammonium Sulphate

Another possible fertilizer use of ammonia is by converting it to ammonium sulphate. Ammonium sulphate is typically used for soils that are alkaline, since this fertilizer releases a small quantity of acid, which lowers soil pH, along with the ammonium ions (the nitrogen source for plants). literature has shown that one of the reasons why this fertilizer is not dominant is due to its relatively low nitrogen content (compared to ammonium nitrate), which translates to higher transportation costs [45]. However, since in MEZT's case production and consumption happens at the same place, this should not be a particularly large concern.

As the acidity suggests, ammonium sulphate is made using an acid, specifically sulphuric acid, in a very simple process denoted by the following reaction. At 17.031 g/mol for NH_3, 98.08 g/mol for H_2SO_4 and 132.14 g/mol for $(NH_4)_2SO_4$, per kg NH_3 a total of 2.88 kg H_2SO_4 is required and 3.88 kg $(NH_4)_2SO_4$ is produced.

$$2NH_3 + H_2SO_4 \Longrightarrow (NH_4)_2SO_4$$

Although ammonium sulphate is also often produced as a by-product of other processes, such as caprolactam production or coke oven by-product, the synthetic production for MEZT's case can happen via two main methods [46]. Firstly, it is possible to use aqueous ammonia and mix it with liquid sulfuric acid in a batch-like process. Once both liquids are combined, stir gently to ensure all components react together to form the ammonium sulphate salt dissolved in water. The second way is to spray a very fine mist of liquid sulfuric acid in a gas-ammonia reaction chamber resulting in the salt. In this case the liquid sulfuric acid input will very likely be concentrated in water, so the moisture still needs to be extracted, but for this the reactor will be at an elevated temperature such as 60 °C where the additional reaction heat will vaporize the remaining water, leaving the pure moisture-free salt behind [45]. Either way, in MEZT's case it would be favourable to add slightly more sulfuric acid than necessary in order to ensure all ammonia is reacted, thus preventing unnecessary nitrogen emissions from occurring.

Commercially this second method is more favourable as the pure salt makes for easier and cheaper transportation, as no unnecessary water needs to be transported (in addition to the aforementioned relatively low nitrogen content), but as mentioned before, it should not be a problem on the farm where it is both consumed and produced.

The simplest process would be to take the raw 10% aqueous ammonia and via batch production mix it with pure (95%+) sulphuric acid to create ammonium sulphate of roughly 30% wt. dissolved in water. However, an alternative was suggested by CramChem [26]. Instead of using the straight 10% ammonia, a condenser (as mentioned in earlier sections) is used to increase the concentration to 40%. This in turn means that after the vacuum pump some of the ammonia stream evaporates while a majority part stays aqueous, which in itself is not very noteworthy. However, if a high concentration (96% wt.) sulfuric acid is added, the final ammonium sulphate production will be concentrated to 71% wt., which is very close to the saturated limit of 74% wt. In this way you can still benefit from simple equipment while having a higher concentration that is easier to transport. If required/wanted, it would also be possible to add a dryer afterwards to get a powdered product, although this is more energy intensive. An overview of this process along with values based on a 300 L/hr manure input can be found in figure 11.

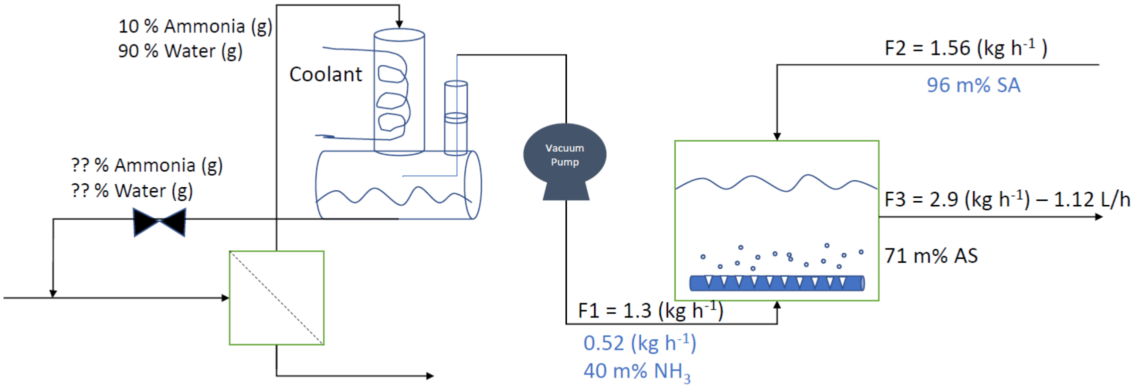


Figure 11: Overview of suggested concentrated ammonium sulphate production [26]

3.5.4 Urea

Urea, chemically known as $CO(NH_2)_2$ or sometimes CH_4N_2O is also a popular fertilizer. Currently over 90% of global urea production gets used for fertilizer [45] and one reason for Urea's popularity is that it has the highest nitrogen content of all solid nitrogenous fertilizers (46%), thus allowing for lower transportation costs [47].

Similarly to some other fertilizers, urea breaks down in the soil, giving of ammonium that can be taken up by plants. However, normal urea has relatively high nitrogen emissions compared to other fertilizers as it releases its ammonia relatively quickly. One typical solution is to turn it into a controlled-release fertilizer where the urea granules are encapsulated in an inert sealant [45].

Urea is made industrially using the Bosch–Meiser urea process, which reacts ammonia and carbon dioxide in two equilibrium reactions. The first reaction is a rapid exothermic reaction where gaseous CO_2 reacts with liquid ammonia to form ammonium carbamate ($H_2N - COONH_4$) at a high pressure and temperature (roughly 160-190 °C and 110-175 bar), as seen below [48].

$$2NH_3 + CO_2 \rightleftharpoons H_2N\text{-}COONH_4 \qquad \Delta H^\circ = -117kJ/mol$$

Afterwards a slow endothermic reaction (decomposition) of the ammonium carbamate occurs, turning it into water and urea via the following reaction.

$$H_2N\text{-}COONH_4 \rightleftharpoons H_20 + (NH_2)_2CO \qquad \Delta H^\circ = +15.5kJ/mol$$

Both reactions occur in the same reactor, forming an equilibrium. The overall reaction is still exothermic, so no additional energy needs to be added, but it should be noted that according to Le Chatelier's principle, conditions that favour the formation of carbamate unfortunately have a negative effect on the equilibrium of urea conversion, which is why the high temperature (for the first reaction) is compensated by using a high pressure in the second reaction [48]. Even so, the urea conversion will never be complete, meaning that the urea needs to be separated from the ammonium carbamate.

Separation of urea can be done in several ways [49]. Originally (and perhaps most simply), a "straight through" urea reactor would reduce the system pressure down to atmospheric, which in turn allows carbamate to decompose into CO_2 and ammonia, allowing the solid urea to be collected, while the remaining gasses could be used for other processes, such as ammonium nitrate production, since re-compressing the ammonia and CO_2 was not economically feasible. Later, carbamate was fully recycled by depressurizing in stages, where carbamate was decomposed in a steam-heated decomposer and then condensed in a carbamate condenser, or alternatively via a distillation column, after which the solution was re-inserted in the reactor stage. Figure 12 has an overview of this full-recycle process.

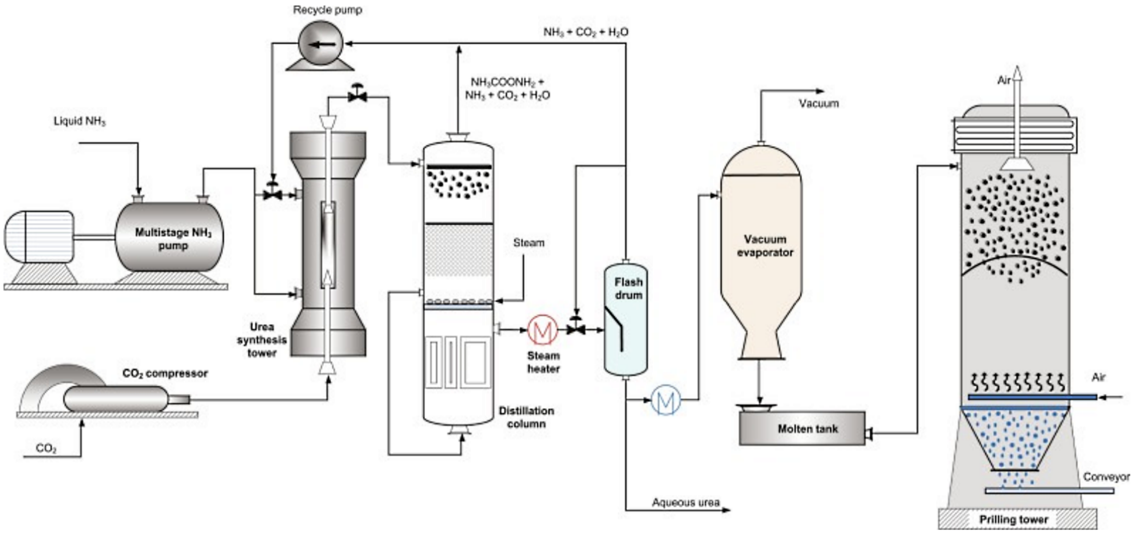


Figure 12: Overview of the full-recycling urea production process [50]

There is also an alternative process possible that has become more popular in recent years: stripping [49]. Not only does this resolve the moisture recycling of the previous full-recycle process (which has an adverse effect on the reaction), it works of the partial pressures of the reactants by suppressing the partial pressure of just one reactant. Here CO_2 is first partially fed into a stripper, flushing out the free ammonia and reducing the partial pressure of ammonia. This is in turn carried directly to a full-pressure carbamate condenser after which the resulting ammonium carbamate liquor can be passed immediately to the main reactor. This is beneficial as it eliminates much of the recycling process and the process itself can also be partially integrated and as such it is now the most popular option for urea production. An overview of this newer stripping process can be seen in figure 13.

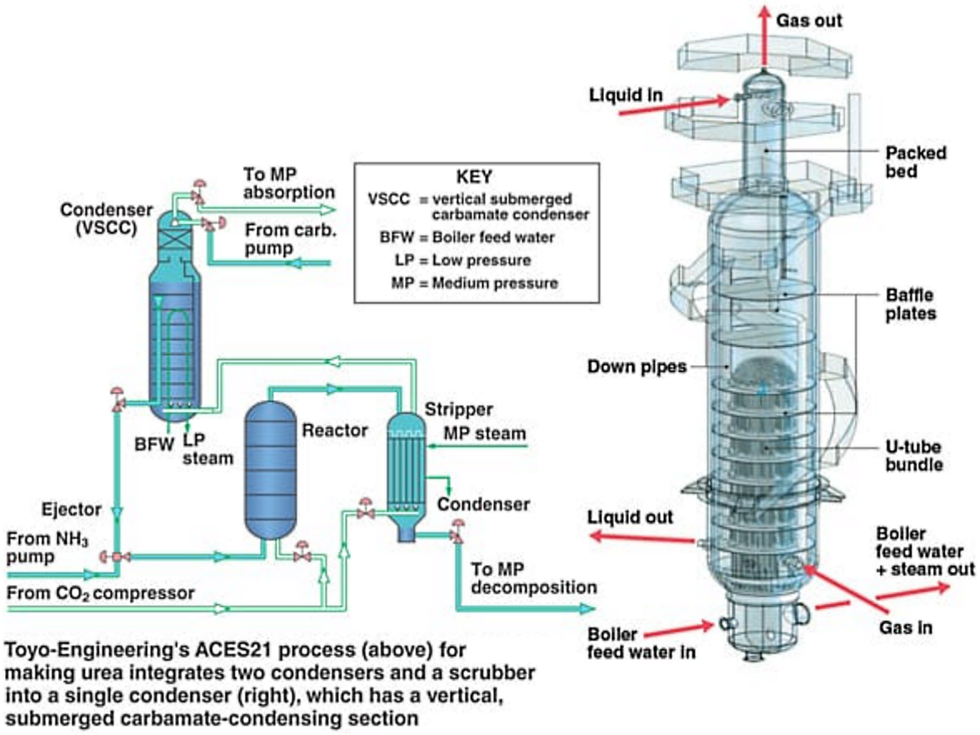


Figure 13: Overview of the urea production process via the stripping method [51]

Nevertheless, there are still some downsides (in general of urea production) that one needs to consider for urea's production in a farm.

- The equilibrium reaction to urea is rather slow (30-60 minutes to reach equilibrium at 170 °C), meaning that a particularly large pressure vessel is required [48].
- A very large quantity of CO_2 is required for this reaction. In a farm there is no suitable CO_2 supply and industrial urea production often occurs right next to raw ammonia production since the Haber-Bosch process produced a lot of CO_2 [45].

- Ammonium carbamate is very corrosive to metals, including high quality stainless steel, meaning that specialised materials along with methods to reduce corrosion (e.g. a continuous air stream injected in the reactor) are required. This requires relatively frequent checks for corrosion and more complex equipment [45].
- One of the side reactions is Biuret, which is poisonous to plants and reduces growth rate. In the reactor this is prevented by using excess ammonia, but in the stripper and afterwards this reaction can occur until the temperature is lowered [48].
- Isocyanic acid is formed when urea is heated at lower pressures, which happens during the granulation process. This acid is also harmful and poisonous when breathed in [48].

Overall, for a large, dedicated urea production plant next to raw ammonia via the Haber-Bosch process, the CO_2 requirements, extra complexity of the process, frequent observation and necessary considerations are not a deal breaker, but on a small farm scale a simpler, more robust and fool-proof option is preferred, meaning that for the next section urea production is unlikely to fare well.

3.5.5 Ammonium Nitrate

Ammonium nitrate (NH_4NO_3) is another possible fertilizer that utilizes ammonia. As mentioned earlier on, although ammonium nitrate is commonly used in explosives such as ANFO, it is actually the second largest global ammonia usage for fertilizer, just behind direct application [16]. Compared to urea, ammonium nitrate is somewhat less nitrogen-rich (33.5% vs 46%), which does increase transportation costs if sold, but in return it is more stable and emits less nitrogen [52].

Nitrogen is predominantly made via 3 methods [53]. Firstly, a Salt metathesis reaction of either Ammonium sulphate (already a fertilizer) and Barium nitrate, or Ammonium chloride and Silver nitrate. Secondly via the nitrophosphate process of Calcium nitrate with ammonia, water and CO_2. Thirdly, via the acid-base reaction of ammonia with nitric acid. This last one is the most intriguing for two main reasons. Firstly, it is most predominant in literature and most popularly used in practice (possibly an indicator that it has some advantage over the other 2 methods) and secondly, since it uses nitric acid, which can be made from ammonia, it requires no additional chemical inputs.

The acid-base reaction process is as followed. Ammonia gas is combined with concentrated liquid nitric acid (50-70% wt. concentration) in a neutralizer chamber (essentially the reactor) where the following reaction occurs, creating aqueous ammonium nitrate [54].

$$HNO_3 + NH_3 \Longrightarrow NH_4NO_3$$

Directly after the reaction the melt/solution is concentrated to approximately 83%, but since this reaction is highly exothermic at a resulting melt/solution temperature of about 150 °C, the remaining moisture can quickly evaporate in an evaporator stage, leaving a high 95-99.8% concentration melt [54]. Afterwards, the melt enters a spray tower, which sprays the molten melt finely in cooler ambient air, solidifying the ammonium nitrate into small prills (granules). Then afterwards these prills can be further processed, such as dried and treated with a coating to prevent caking, and then stored and used. An overview of this process can be seen in figure 14.

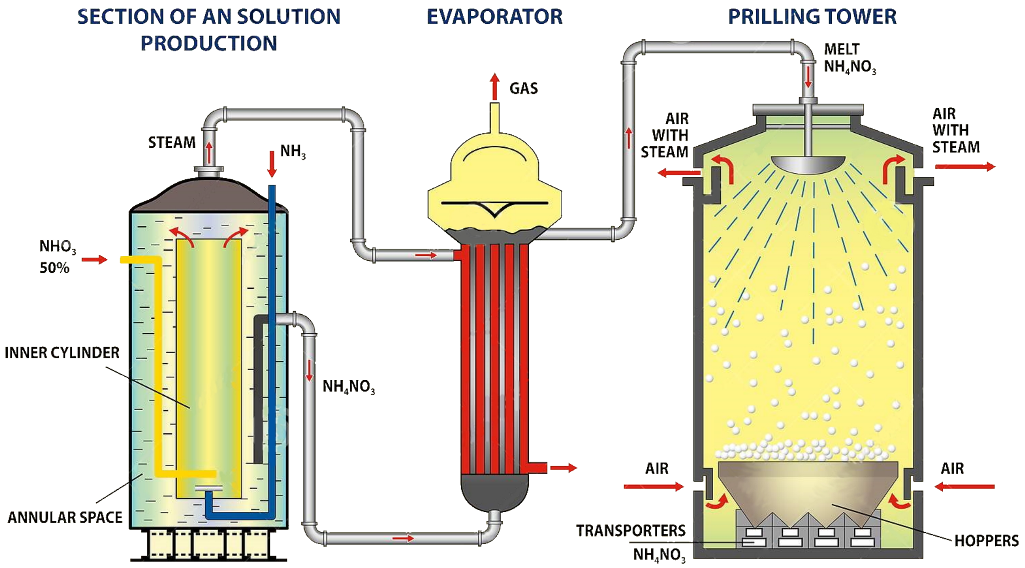


Figure 14: Overview of the ammonium nitrate production process [55]

However, before this acid-base reaction process can occur, a nitric acid input is still required. Instead of buying this in bulk, nitric acid can be produced from raw ammonia and oxygen from the air via the Ostwald process.

Within the Ostwald process, first ammonia gas along with pre-heated and pre-compressed oxygen from the atmosphere (air) is mixed together before entering a reactor with a platinum and rhodium catalyst [56]. Here the following reaction occurs, forming nitric oxide gas and water.

$$4NH_3 + 5O_2 \implies 4NO + 6H_2O$$

This reaction is highly exothermic, with an enthalpy of -905.2 kJ/mol, resulting in this stage being at a temperature of roughly 600–800 °C and a pressure of 4-10 bar. This first stage is also about 96-98% efficient, releasing some nitrogen, nitrous oxide and water via secondary reactions [56].

Afterwards, the stream needs to be cooled down before entering the second stage. This can be done (for example) via cooling water, which can be turned into steam to drive a turbine in order to extract power. As part of stage 2, in an absorption apparatus, two more reactions occur, as seen below. The nitric oxide from the first stage is oxidized to form nitrogen dioxide gas, which is then easily absorbed by water, forming nitric acid and more nitric oxide (which can again be recycled and mixed with oxygen in the same absorption apparatus) [56].

$$2NO + O_2 \implies 2NO_2$$

$$3NO_2 + 2H_2O \implies 2HNO_3 + NO$$

These second stage reactions are also exothermic and can occur simultaneously in both gas and liquid stage in the absorption apparatus, favouring lower temperatures (thus the cooling beforehand) and higher pressures. An overview of a commercial nitric acid process can be found in figure 15.

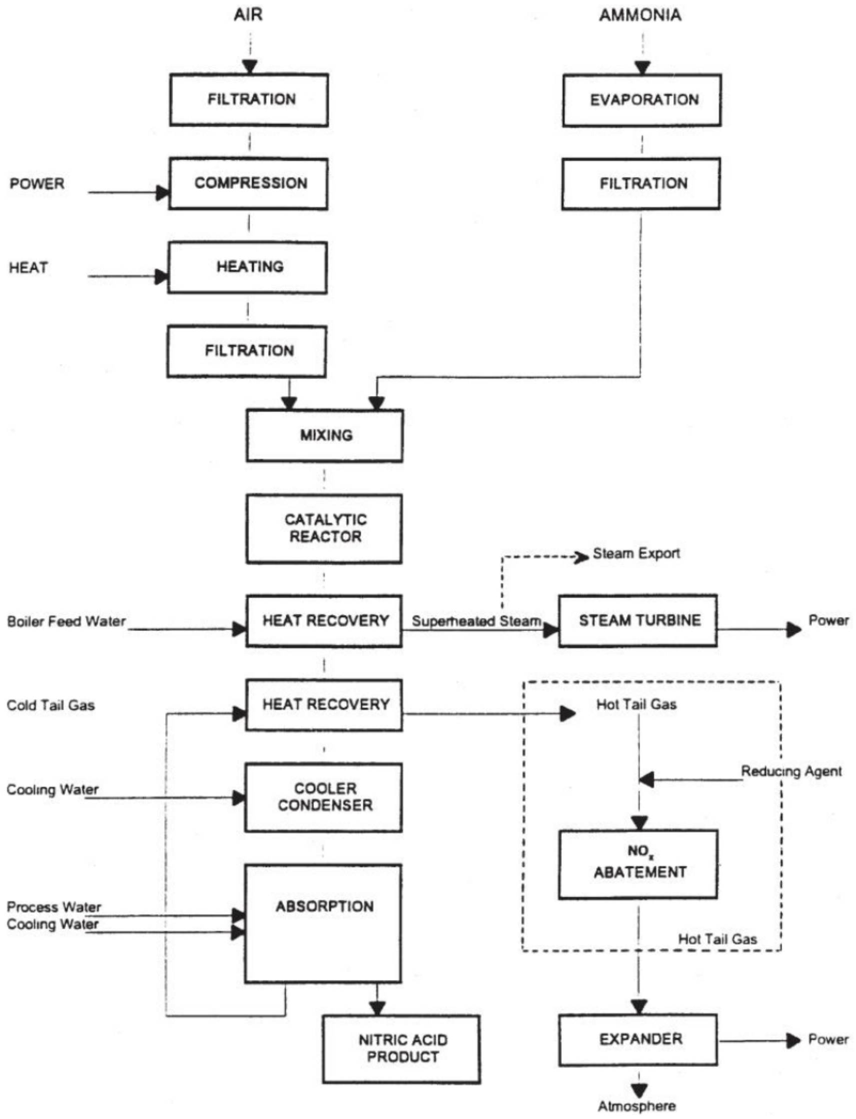


Figure 15: Overview of the nitric acid production process [56]

Altogether, producing ammonium nitrate is rather complex, requiring a whole separate nitric acid production plant before the ammonium nitrate can even be produced, not to mention the copious amount of heat that would be a shame to waste. On the one hand, compared to urea, the process is somewhat more complex (although urea is by no means a simple process either) and ammonium nitrate is explosive, but on the other hand, it only requires ammonia and air as an input and the setup appears to be less sensitive to changes (urea would form poisonous biuret and isocyanic acids, whereas for ammonium nitrate the effect of non-ideal situations is less worse) with wider allowed temperatures and pressures, meaning it could be easier to implement in a farm setting compared to urea. Of course, it is also possible to purchase the nitric acid separately, which would make the process vastly simpler, but this could potentially be more costly.

3.5.6 Ammonium Phosphates

All ammonium phosphates are included in one section since they are very closely related to each other. These include triammonium phosphate $(NH4)_3PO_4$, diammonium phosphate $(NH4)_2HPO_4$ (DAP) and monoammonium phosphate $(NH_4)H_2PO_4$ (MAP), which is also known as ammonium dihydrogen phosphate (ADP). Because of these being so closely related, in literature ammonium phosphate could sometimes refer to any of these three substances.

In any case, the production starts off with phosphoric acid and ammonia, both commonly in aqueous form. When combined in a tube reactor, the exothermic reaction forms monoammonium phosphate as denoted by the following reaction [57].

$$H_3PO_4 + NH_3 \Longrightarrow (NH4)H_2PO_4$$

However, monoammonium phosphate can also react with more ammonia to form DAP via the following reaction.

$$(NH4)H_2PO_4 + NH_3 \Longrightarrow (NH4)_2HPO_4$$

This DAP is a favourable product as it is a very popular and reasonably stable fertilizer, giving both nitrogen and phosphorus to plants [58]. It is also possible for DAP to react further with yet another ammonia molecule to form triammonium phosphate, via the following reaction. However, triammonium phosphate is inherently unstable and quickly turns back into DAP, releasing the ammonia it has captured in the process [57].

$$(NH4)_2HPO_4 + NH_3 \Longrightarrow (NH4)_3PO_4$$

After the DAP process, if sufficient ammonia was used, most of the remaining hot slurry will be DAP and it can be granulated and dried (commonly combined in a drum-granulator drier) and then sieved [59]. In practice though, it is slightly more complex. Due to both reactions being exothermic and happening in the same area at the same time, quite some heat is made and DAP can gradually decompose to create MAP, releasing ammonia. This decomposition occurs from 70 °C onwards and if the temperature rises to above 155 °C, DAP breaks down into ammonia, nitrogen oxides and phosphorus oxides [57].

This requires post-processing to treat the ammonia gas, but the MAP by-product can stay as it is also a useful fertilizer. Because of this, a balance needs to be struck. If the input ammonia and phosphoric acid is very concentrated in little water, less moisture needs to be extracted for granulation, but more DAP is decomposed into MAP and gasses, requiring more exhaust gas processing to extract ammonia gas and prevent further emissions [60]. Similarly, if the inputs are more hydrous, the water can capture more heat during the reaction, keeping the products cooler and purer, but then more moisture needs to be extracted later for granulation. In reality, although numbers vary, the reactors and resulting slurry are generally at around 115 °C, presumably just hot enough to boil off the majority of moisture, while having little decomposition [59]. An overview of the DAP production process, without exhaust gas treatment system, can be seen in figure 16.

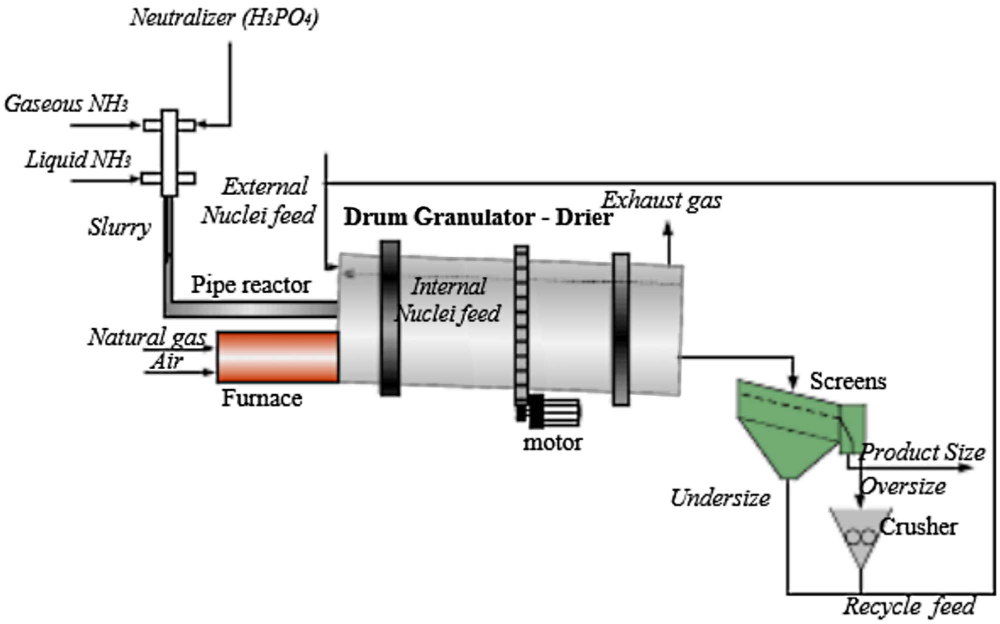


Figure 16: Overview of the DAP production process [59]

However, besides DAP, it is also possible to produce the MAP (by-)product on its own. MAP fertilizers are still popular, albeit to a lesser extent, and one key difference is the nitrogen content: MAP has 10-12% nitrogen and 21-27% phosphorus compared to the 18% nitrogen and 20% phosphorus of DAP fertilizers [61].

Producing MAP fertilizers is very similar to DAP, owing to the similar characteristics and reactions. In fact, the same pipe reactor and drum granulator-drier setup as before can be used, but with different input ratios and concentrations. Now a 1:1 molar ratio of phosphoric acid to ammonia is required and the temperatures can be slightly higher to promote the aforementioned decomposition of DAP. Alternatively, a pipe-cross reactor can also be used where the heat generated by the reaction evaporates the water and solidifies the MAP [61]. In theory, it should be possible to react all ammonia with phosphoric acid to create MAP as you can place the reactor temperature above DAP's decomposition temperature and below MAP's composition temperature (which is higher at 190-200 °C), but in practice some MAP will still decompose to ammonia gas, nitrogen oxides and phosphorus oxides like DAP, thus requiring exhaust gas post-processing like gas scrubbing [62].

In the end, since the MEZT's process will produce ammonia, having the farm produce a more nitrogen-rich fertilizer requiring a lower quantity of phosphoric acid is favourable, not to mention that due to DAP's higher popularity finding a potential buyer is less difficult. Therefore, for the following section DAP production will be predominantly considered for ammonium phosphates.

3.6 Last Considerations on Farm Size and Fertilizer Usage

One last thing to consider before the next section is regarding the final product to be made. Many of the processes that create fertilizers have the option to either have a solid/granular output or have the output be in aqueous form. Commercially, the solid/granular output is preferred since the lack of water means no unnecessary extra transportation costs, which can add up significantly. However, in a farm setting, fertilizers are produced and consumed in the same place, so the cheaper, simpler aqueous output process can be chosen, at least, if the farm consumes all the fertilizer it produces.

At first thought, 10-30 m^3/day manure output, or 1000 L/hr is a very large amount and the pure ammonia output is 0.95 to 1.91 kg/hr, which accumulates to 8,322-16,732 kg/yr. In the case of (for example) ammonium sulphate, this would produce approximately 32 to 65 tonnes of fertilizer. A usage check is therefore required.

In the Netherlands, 68% of produced manure has little to no transportation costs, since it is used as fertiliser on the same farm it is produced and these farms are predominantly dairy farms [63]. Not only that, farmers in the Netherlands typically use up to 385 kg of pure nitrogen per hectare per year, of which 170 kg may legally originate from manure (or up to 245 kg in cases of derogation) and the remainder is to be supplemented using artificial fertilizers [64]. This means that approximately half of a farm's nitrogen needs are already met with all manure in approximately 68% of cases, so processing all manure to be used as fully legal fertilizer should be possible.

Further calculating, the 0.95-1.91 kg/hr of pure ammonia at a pure nitrogen concentration of 82% results in a pure nitrogen production of 6824-13720 kg/yr. This means that the production is sufficient for roughly 40 hectares (17-80 hectares taking the lowest and highest values).

An average dairy cow in the Netherlands produces roughly 80 kg of manure a day, meaning that for the 1000 L/hr manure input of the MEZT process, the farm will have approximately 300 cows. In the Netherlands, a "megastal" (mega-stable) has 250 cows or more and account for fewer than 3% of Dutch farms [65] and the average farm as of 2020 has 105 cows [66]. It is then safe to assume that MEZT is dealing with a reasonably large farm. In the Netherlands, the average farm can quickly have 50 hectares or more of arable land (even more so in the North of the Netherlands), which is more than the roughly 40 hectares worth of fertilizer that will be produced [67].

In the end it is thus a reasonably safe assumption that the farm will consume all the fertilizer it produces, meaning that for the following section the cheaper aqueous output is considered for the fertilizer production, if applicable.

4 Technology Review

Now that all processes are known it is possible to review all available technologies and processes in order to determine the best one possible. For the reader's ease of use, the final scoring table will already be given in the following subsection with justification coming afterwards.

4.1 Selected Processes

As evident from section 3, certain processes and technologies can be discarded early on with high levels of certainty, such as the fuel cell alternatives (modified ICE) and lesser popular or more complex versions of processes that use many additional chemicals. Below is a list of the processes that are investigated.

- **Wholesale gas**: Via the method of CramChem, where a cold trap in the VMS extracts all moisture and subsequently compresses and stores it.
- **Wholesale aqueous**: As either the direct 10% aqueous output or the 25% output, for which the same method as wholesale gas is used, but only partial condensation.
- **Alkaline Fuel Cell (AFC)**: Ammonia gas is fed into a fuel cell, producing electricity. Essentially a simple process.
- **Solid Oxide Fuel Cell (SOFC)**: Very similar to AFCs. Niels from CramChem tested this with aqueous ammonia as an input and it was shown to work, but very little research is found in practice, thus for this analysis also gaseous ammonia is used.
- **Enriched biochar**: The thick fraction of manure gets dried and sent into a pyrolysis reactor, which is heated by the resultant gasses and oils from the reactor. Afterwards the biochar gets enriched in a gas adsorption column and stored.
- **Ammonium sulphate**: Aqueous ammonia reacts with concentrated sulfuric acid. The resulting concentrated solution gets stored.
- **Urea**: Compresses CO_2 and ammonia reacts in a reactor after which it is separated in separate stages. The analysis will be broad enough to apply to both the full-recycle option and the stripping option.
- **Ammonium nitrate - 100% made**: The full process of first making nitric acid from ammonia and air and then having this nitric acid react with more ammonia in the ammonium nitrate reactor.
- **Ammonium nitrate - bought**: A variation on the previous process where the whole first nitric acid production part has been left out and it is instead bought in from other suppliers.
- **Ammonium phosphate**: Phosphoric acid combined with ammonia reacts to form DAP after which it is dried in a drier-granulator. In this case, DAP was chosen and MAP will not be investigated as it uses more ammonia and is a more popular, nitrogen-rich fertilizer.

4.2 Key Assumptions and Score Overview

Although some general scoring criteria can be assumed, it would be wise to first make some key assumptions to aid in the creation of the scoring criteria. These key assumptions are based on the wants and needs of farmers and society.

Farmer:

- *Sustainable & profitable business model*: A process that allows the farmer to earn a decent living and continue with his practices for decades to come.
- *Safety & well-being*: For both the farmer and his animals to live a healthy and safe life without fear of harm.

Society:

- *Biodiversity & conservation*: Reducing emissions of CO_2 and N, including mineral leaching to the ground and waterways/oceans. Includes working towards a circular model for scarce/finite minerals.
- *Food security*: Regenerative agriculture, regarding consistent ground fertility and productivity.

Using these key assumptions and some other common ideas that still have an (indirect) effect, an overall scoring matrix can be created, which is found in the following table.

	Max Score Possible	Wholesale Gas	Wholesale Aqueous*	AFC	SOFC	Enriched Biochar	Ammonium Sulphate	Urea	Ammonium Nitrate - Full	AN - bought in nitric acid	Ammonium Phosphate
Maturity/Feasibility	3	3	3	1	0	2	3	1	1	2	2
Process Profitability	5	4	5	2	2	4+	3	1	3	0	0
Initial Costs	4	3	4	0	0	1	3	0	0	2	1
Reliability, Maintenance	3	3	3	2	2	1	3	0	0	2	1
Ease of use	3	3	3	2	2	2	3	1	2	3	2
Environmental Impact	4	1	2	3	3	3	3	1	2	2	1
Safety	3	3	3	2	2	1	2	0	1	2	1
Scalability	3	3	3	3	3	2	3	0	1	3	2
Compactness	2	2	2	1	1	1	2	0	1	1	1
Total	30	25	28	16	15	17	25	4	11	17	11

Table 3: Overview of scoring all relevant processes, including final score
* At direct 10% output. The score for 25% would be in between 10% and gaseous.

4.3 Justification Summary

In the following subsections each part of the scoring criteria will be justified. However, since the full justification ended up being over 30 pages long, a shorter summary of the outcome for each criterion is made here and the full justification, including explanation on why each criterion is worth how many points and why, can be found in appendix A. Eventually it was quite clear that one of the wholesale ammonia, enriched biochar or ammonium sulphate options would come out on top, so they are talked about in slightly more detail.

4.3.1 Maturity/Feasibility

In this criterion two main things are combined into one: how well-studied and known a process is (maturity) and how realistically the process can be implemented in farm conditions. These two elements are combined into one criterion since quite often they are closely related (e.g. an immature technology is unlikely to already be feasible on a farm).

For the scoring, both the wholesale ammonia options and the ammonium sulphate option are very mature processes that are simple and easy to implement, leading to a high score. Meanwhile, both alkaline- and solid oxide-fuel cells are still very young technologies with many unknowns leading to a low score, with SOFC's higher temperatures and longer start-up times leading to a slightly worse score than AFCs. The enriched biochar option is also a very young technology, but the process of enrichment is simple and mostly easy to implement resulting in a fairly good score. The ammonium sulphate option is perhaps the most mature and simplest, being only a very simple chemical reaction happening in a chamber, giving the highest score possible. Finally, the remaining options are all very mature with some options being over 100 years old and used globally, but some have particularly complex processes with unfavourable conditions (high pressure, temperature, etc.) which drastically lowers their feasibility.

4.3.2 Process Profitability

This criterion focuses on the profitability of the process itself, not taking the initial machinery and setup cost into consideration. Here the major power, input and output ingredients are estimated at (where available) up-to-date European prices. The final process profitability is then normalised per 1000 kg of pure ammonia for easy comparison.

For both of the wholesale ammonia options, there are no inputs, but there is a considerable cooling requirement. Fortunately, the combination of high ammonia selling price and low priced electricity from a farm's solar panels still results in a profitable option.

Both fuel cell options had only ammonia as input and electrical power as output. However, the produced electricity is not worth all that much, especially considering that selling power back to the grid earns less money.

For the enriched biochar, determining the process profitability was difficult, but even with a relatively low estimate for the enrichment process, it was profitable.

Ammonium sulphate is a very simple process with only some simple mixing of sulphuric acid with the aqueous ammonia. The sulphuric acid does cost some money, but it is overall still decently profitable.

Urea, ammonium phosphate and ammonium nitrate (where nitric acid is bought in) ended up being clear losers in the scoring matrix, so won't be discussed in much detail, but their profitability ended up being very low with sometimes the selling product being worth *less* than the ingredients needed to make it. The only exception is the full ammonium nitrate process (where nitric acid is also made from ammonia), which ended up having a decent profitability.

4.3.3 Initial Costs

This scoring criterion is on the initial (upfront) cost to purchase and install the equipment in the first place. For this, the individual costs of all major components are identified and then multiplied using their respective installation factors from Sinnott and Towler. Originally all cost estimation values/equations from Sinnott and Towler or another reputable source was going to be used, but the flow ended up being far below those minimum sizing floors to be usable (about 5 ml/s ammonia and water combined), so smaller equipment had to be sourced online.

Bulk storage was also costed using IBCs, which ended up being suitable for practically all chemicals used and a cost-effective solution, costing about €155 a piece for a proper 1000 L certified unit [68]. Where possible, a tanker-truck load of IBCs was costed for storage.

For the wholesale ammonia options, the (10 kW) cooling system and flash drum were major components, with the VMS and vacuum pump already being part of the 'standard' MEZT system/costing and equal for all processes. For the cooling system, there were three possibilities in total, as evident from figure 17. The air-con/chiller option ended up being cheaper to buy/install since it does not require a large and expensive heat exchanger, but in theory the ground water cooling could be cheaper to run.

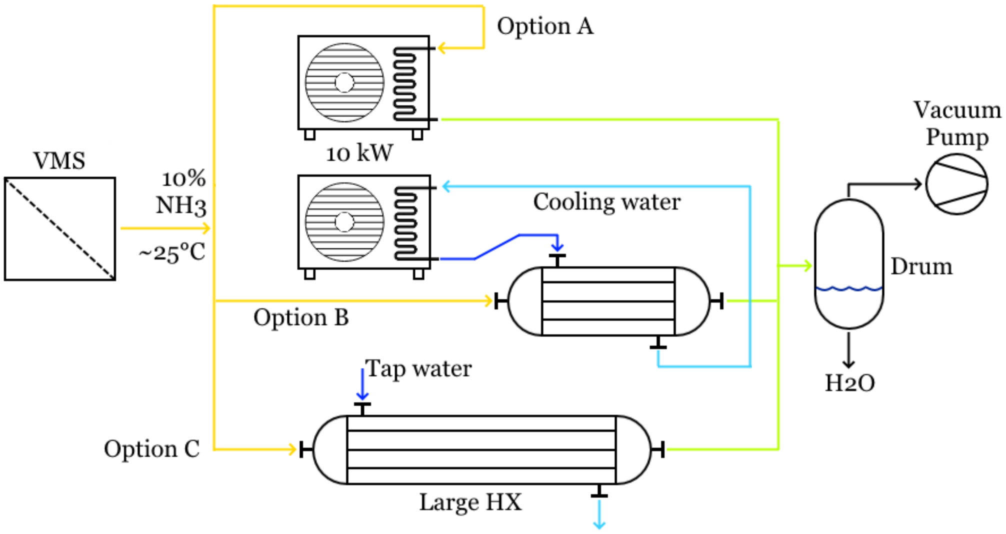


Figure 17: 3 options for water condensation, applicable for 25% and 100% NH_3 concentrations

For the fuel cells, the only commercial AFC source has very high costs, not to mention the gaseous ammonia input requires the process from the gaseous wholesale option. SOFCs have no current cost, but both AFCs and SOFCs are estimated to be cheaper in the future.

For enriched biochar, only the enrichment process will be considered for an "apples to apples" comparison. Since it requires a gaseous input, the initial cost from the gaseous ammonia will be taken and a gas adsorption column needs to be costed, which ended up costing a not inconsiderable amount of money.

After some research, it was determined that for the ammonium sulphate option it may be possible to use the IBC storage tank as the reaction chamber and the long residence times means mixing may not be necessary. Thus, it ended up having one of the cheapest initial costs.

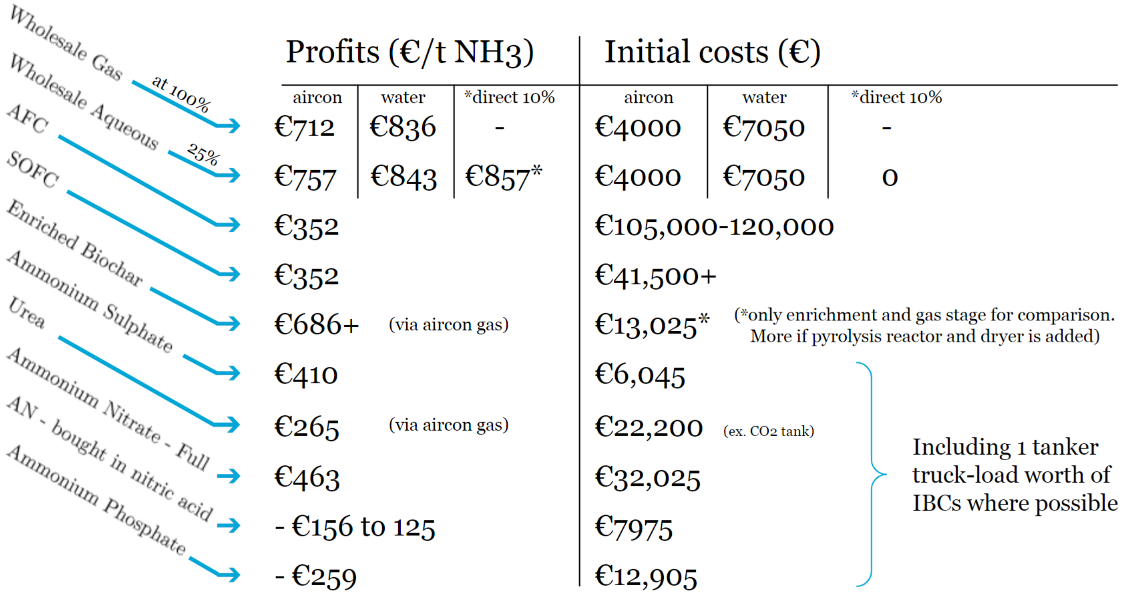
Urea on the other hand ended up being a complex process with many steps, unfavourable conditions and requiring a large CO_2 storage tank for input, making it one of the most expensive options.

The full ammonium nitrate option also ended up being similarly expensive with even more components, but at least no expensive CO_2 storage tank. If the nitric acid is bought in though, the price is considerable lower due to greater simplicity.

Finally, ammonium phosphate was somewhere in the middle of the pack in terms of initial costing, having a relatively simple reaction stage, but requiring a whole gas post-processing stage for harmful by-products (gasses).

A final overview of the initial costs and process profitability for all processes can be found in figure 4. Please note that the rest of the MEZT solution train is not included here.

Table 4: Profitability and initial costs of all investigated processes



	Profits (€/t NH3)				Initial costs (€)			
	aircon	water	*direct 10%		aircon	water	*direct 10%	
Wholesale Gas at 100%	€712	€836	-		€4000	€7050	-	
Wholesale Aqueous 25%	€757	€843	€857*		€4000	€7050	0	
AFC	€352				€105,000-120,000			
SOFC	€352				€41,500+			
Enriched Biochar	€686+			(via aircon gas)	€13,025*			(*only enrichment and gas stage for comparison. More if pyrolysis reactor and dryer is added)
Ammonium Sulphate	€410				€6,045			Including 1 tanker truck-load worth of IBCs where possible
Urea	€265			(via aircon gas)	€22,200			(ex. CO2 tank)
Ammonium Nitrate - Full	€463				€32,025			
AN - bought in nitric acid	- €156 to 125				€7975			
Ammonium Phosphate	- €259				€12,905			

4.3.4 Reliability, Maintenance

This criterion is on how dependable the process is and how frequently it requires check-ups or replacement of perishables (e.g. filters). Since in many cases no real values can be found, the score will be based of the complexity of the process itself as well as logical deduction.

For the wholesale ammonia options, the process is quite simple. Since there is only an additional cooler and flash drum and possibly a heat exchanger (which both aren't even moving parts), the reliability can be considered good and the only required maintenance would be an occasional check-up of the air-conditioning unit of the cooler.

The fuel cells are also a fairly simple one stage process, which also suggests good reliability and low maintenance, but due to the novelty and high temperatures, (long term) reliability may not be established yet, leading to a slightly low score.

The enriched biochar option has only an adsorption column with a movable hopper, which at first alludes to good reliability. However, the biochar can have contaminants or large hard pieces. This means that especially for the small scale (since 'chunks' are relatively large), there might be frequent jamming and regular cleaning may also be required, which harms its score. Also, if the other steps before enrichment are included too (pyrolysis reactor, dryer, etc. which have a less than stellar reliability), the overall reliability lowers too.

Ammonium sulphate on the other hand is extremely simple and essentially could have no moving parts and minimal maintenance, leading to the highest score possible

Both the urea and full ammonium nitrate option have high temperatures, high pressures and many steps to the process, which is bad for both reliability and maintenance, resulting in the lowest score. Meanwhile, the ammonium nitrate process where the nitric acid is bought in is drastically simpler, improving score, and ammonium phosphate also has a fairly simple process, but with an additional post-processing part for the exhaust gasses which requires frequent maintenance, resulting in a mediocre score.

4.3.5 Ease of Use

This criterion is on how easy the process is to use for the farmer. This includes if it requires frequent operation/input by the farmer, if it can be automated, and if the system is easy to setup and use initially (i.e. "plug and play").

For wholesale ammonia, the score is high, since as long as the cooler is turned on, ammonia of a higher concentration is made without necessary input and it can also be automated.

The fuel cells are in a way similarly simple in operation and setup, but the score is slightly lower since the electricity would ideally be produced at the time of the day where the electricity price is highest. Also, more planning is required from the farmer due to the long start-up times.

The enriched biochar option is not very complex, but it does require input from a farmer. If it is set up as a batch production, the raw biochar needs to be replenished manually, and the cleaning and unjamming would have to happen manually too. Nonetheless, if the process is automatically set up and the jamming is infrequent, it can still be decent.

The ammonium sulphate option is also very simple and can easily be automated without needing a farmer's input. The tanks could even be filled with sulphuric acid beforehand, which would make the setup almost fool proof, resulting in a high score.

For the remaining processes, they could all be automated to an extent, but the complex systems, unfavourable conditions and potentially hazardous side products require it to be setup properly (i.e. not plug and play). Also, they may potentially require frequent check-ups by the farmer to ensure everything is still working properly. Only the ammonium nitrate with bought acid achieves a good score out of these remaining processes due to essentially being simple to set up and does not require much attention from a farmer.

4.3.6 Environmental Impact

This criterion is fairly self-explanatory, looking at the environmental impact of both the process itself and the final product/fertilizer that is made by the process.

Both wholesale ammonia options get a neutral/middling score since the produced ammonia is sold, so it does not necessarily reduce emissions (normal fertilizer would still be required by farmers), but on the other hand, emissions are also not really being produced. However, it does essentially displace "bad" ammonia produced by the intensive Haber Bosch process, which does help a bit. The gaseous ammonia process also scores slightly lower due to requiring extra electricity for the further ammonia concentrating.

Fuel cells are slightly better, since it produces completely clean electricity. However, it still does not reach the maximum score since farmers would still be using normal fertilizers, often originating from environmentally unfriendly sources.

The enriched biochar option is quite good, since it replaces some conventional fertilizer while producing few emissions and it even stores some carbon in the ground for a longer term. However, the process of creating biochar essentially combusts some of the manure, producing emissions and lowering the score.

For the remaining options, the emissions produced by the fertilizer had some conflicting information (see appendix A for the tables on the emissions of each), but generally ammonium sulphate had the lowest emissions (both from the fertilizer and process) and urea had some of the highest emissions. Meanwhile, ammonium nitrate had emissions that were roughly in the middle resulting in a middling score and ammonium phosphate had middling product emissions, but quite some harmful side-products as emissions that lowered its score.

4.3.7 Safety

This criterion is on how safe the process is to use and about the consequences in case something goes wrong. For this, the concept of *inherently safer design*, consisting of the 4 main pillars (minimization, substitution, moderation and simplification), is used. The safety of ammonia itself is excluded, since it is consistent for all processes.

For the wholesale ammonia options, the process is essentially just cooling and extracting water with no unusual or extreme substances, meaning no significant safety hazards are involved.

The fuel cells are also similarly simple, but the high operating temperatures do introduce a safety hazard, slightly lowering the score.

The enriched biochar does have some safety concerns. The biochar itself is very dry and almost pure carbon, thus being very flammable. Also, in case the ammonia in the adsorption column is not fully adsorbed, there will be ammonia gas expelled into the surrounding environment, creating a larger toxic hazard for people and animals than just aqueous ammonia like the other processes. The steps before enrichment (especially pyrolysis) aren't particular very safe either, resulting in an overall low score.

For the ammonium sulphate option, the process can be so simple that there is essentially nothing to go wrong. However, the sulphuric acid itself is harmful/toxic if the container breaks or leaks, but since this is very unlikely to happen, the safety is still scored highly.

Urea has high temperatures, high pressures, toxic and corrosive substances and high complexity, resulting in an overall terrible safety score. The full ammonium nitrate process is not much better, having slightly lower temperatures and less corrosive substances, improving the score slightly. When the ammonium nitrate is bought in, the process is simplified further at less extreme conditions, improving the score yet again, but it is still not perfect.

Finally, ammonium phosphate has essentially an averagely safe process, with some heat being created and requiring storage for the phosphoric acid, but the side-products (exhaust gasses) really lowers the score, which are corrosive, irritating and damaging to humans in low concentrations. Failure of the exhaust treatment part of the process could cause some serious harm to those close-by.

4.3.8 Scalability

This criterion is on how easy the process can be sized up to a central-processing scale or sized down to a smaller micro-farm scale. This criterion may not be extremely important right now, but in the future for MEZT to scale up and expand their company it could be very useful.

The wholesale ammonia options, fuel cells, and ammonium sulphate options are all inherently scalable, being simple processes that can be adjusted for practically any size. Needless to say, they achieve a fairly high score. The same holds true for the ammonium nitrate which has the acid bought in bulk.

Meanwhile, the urea and full ammonium nitrate processes are really meant for only a large scale and as evident from the rest of the scoring matrix, the current farm scale is already too small for them. Thus, they achieve a low score.

Finally, the enriched biochar and ammonium phosphate processes are both processes which can work at the current farm scale or larger, but really cannot be practically scaled down. For biochar, the size of the biochar chunks/pieces themselves are the limitation, and for ammonium phosphate, the exhaust gas processing step requires a certain number of steps/controls that are limiting.

4.3.9 Compactness

This criterion is on the physical size and footprint of the system. Although a farm has a lot of space available, a smaller, more compact system is still preferred, since the same space could otherwise be used for other (farming-related) activities instead.

The wholesale ammonia and ammonium sulphate processes are both very compact, with only a small cooling unit and some sulphuric acid storage being needed respectively. Meanwhile, the urea process is large and complex, with a lot of space being required, especially since it has long residence times requiring a large volume.

The rest all have middling scores. Fuel cells can essentially be compact, but the unit from GenCell showed a surprisingly large footprint (8 m^2). Similarly, the enriched biochar process may also require a fairly large adsorption column and if one also considers the prior steps such as pyrolysis reactor and dryer (which both need to lay flat), the space is also particularly large. Meanwhile, the ammonium nitrate process has many steps which could take up some space, but each step is fairly compact, and vertical space integration may be possible. The ammonium nitrate process where the nitric acid is bought in reduces some of this space, but requires an additional nitric acid tank, equalizing the score. Finally, ammonium phosphate has a middling size too, with the exhaust gas processing taking up a potentially large amount of space.

4.4 Last Considerations

From the scoring matrix, the final choice can be narrowed down to one of the wholesale options (direct 10%, 25% or 100% using air-con or water-cooling), ammonium sulphate, or (due to the profitability) enriched biochar. However, before the definitive final choice can be made of these options, a few final points need to be taken into consideration that were not (or could not) be taken into account in the scoring matrix for these options.

4.4.1 Manure Disposal Cost

The manure disposal cost was lightly touched upon before, but since this cost is significant, it will be clarified more. According to the supervisors, the disposal cost of the thick fraction of manure is €15-25 /tonne. Assuming the higher end of thick fraction production (150 kg / 1000 L manure) and the ammonia flow rate (0.95-1.91 kg/hr), a total of 78-158 tonnes of thick fraction is made per tonne of ammonia, which amounts to €1170-3950 of disposal costs per tonne ammonia. This far exceeds the profit margins of any of the processes and is very significant.

At first thought, enriched biochar would seem like the superior options as it uses the manure turned into biochar and thus there are no disposal costs. However, this does not matter. For all other processes it is also possible to process the manure into (non-enriched) raw biochar, which can then be sold for approximately €200 /tonne. This is also the reason why the scoring looked at the enrichment of biochar instead of the entire process. Moreover, the supervisors mentioned that due to the aforementioned dangers and scoring results, the manure likely will be turned into (regular) biochar at a 3^{rd} party central plant after which it will be enriched on-site. This would mean that no matter the process, the left over thick fraction can be turned into (normal) biochar.

4.4.2 Price Fluctuations & RENURE

This paper assumes prices as of Q2 2021, however, traditionally prices for both ingredients and the final products have fluctuated quite a bit. Fortunately, in most cases this is not a problem as the price of the final product depends on the inputs which are often in proportion to the final product price. For example, if wholesale ammonia prices increase, it would also increase other options that use ammonia, such as ammonium sulphate. Thus, one option would not gain an advantage over another. Similarly, if global natural gas prices (the main determinant of ammonia prices) increase, all options would become more lucrative in the same proportions and vice versa (since the MEZT solution is independent of gas prices). Regarding other natural resources (such as the sulphur for sulphuric acid), since those are difficult to predict, those fluctuations will not be considered.

However, one price fluctuation that does matter is biochar. Unlike pure ammonia or ammonium sulphate, enriched biochar is still in its infancy. The processes used to make it are still not widely adopted and even regular un-enriched biochar has not been used in agricultural applications until recently. Combining that with the fact that farmers know very little about it and thus are willing to pay the (currently likely too high) asking price [69], the price itself is not "set in stone" as to say. One source even says that in the long run the current €200 /tonne price may drop to below €100 /tonne [70]. Although no data is found, a similar trend can be assumed for the enrichment stage as the wide (and currently high) profit margin of biochar enrichment may stabilise into a smaller range of lower profit margins where the per-nitrogen quantity price will be similar to alternatives.

Another price fluctuation is that of ammonium sulphate, since the upcoming RENURE (REcovered Nitrogen from manURE) implementation could affect prices. RENURE is an upcoming legislation that works towards circular economy where processed nitrogen fertilizers that are (partially) derived from manure can be used in areas where there is currently a manure fertilization limit (the 170 kg N/ha/yr) [71]. Figure 18 more clearly shows the concept.

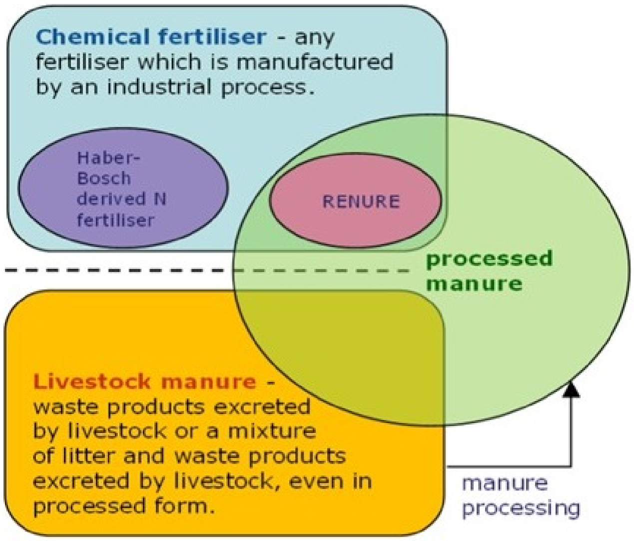


Figure 18: Overview of the classification of processed manure turned into fertilizer

Ammonium sulphate (and mineral concentrates) count towards RENURE and at first it was thought that perhaps due to the approval, demand would go up for this fertilizer, increasing price. However, it is quite the opposite. If it is approved, farms will likely start producing ammonium sulphate from their manure as it can now be used on their land and they would have lower manure disposal costs. However, regular ammonium sulphate production and usage is unaffected by this, meaning there will be more suppliers in the future. Getting in touch with Herre Bartlema from "De Boer aan het Roer" via personal correspondence, he mentioned that RENURE will turn ammonium sulphate into a displacement market ('verdringingsmarkt'), where it is estimated that the price would drop by as much as 60%.

Overall, combining the roughly 50% future price reduction of biochar with up to 60% price reduction for ammonium sulphate means that there is no clear winner or preference of either substance.

4.4.3 Payback Period

As evident from table 4, the initial costs are not very close together. Thus, the payback period is a significant consideration, as it would determine how important the initial costs truly are. For example, if the payback period is very short, it would be better to choose for the option with the higher profits, but if the payback period is very long, it would perhaps be wiser to go for the less profitable option where the break-even point is sooner (as the entire system likely has a finite life).

However, at the time of writing (Q2 2021) it is still not certain if the MEZT process should replace a farmer's entire manure usage, or if it will only be used once the manure usage on the land has reached it maximum quota. Therefore 2 considerations will be made: a full-time and a part-time usage. As mentioned at the end of section 3, Dutch farmers typically use up to 385 kg of pure nitrogen per hectare per year, of which 170 kg may legally originate from manure (or up to 245 kg in cases of derogation) [63]. For the part-time usage, the worst derogation case will be taken, which with the assumption that the farmer has enough manure for the remaining capacity, means that only 36.4% (140/385) of the manure will be transformed by the MEZT process. In reality a farmer likely does not have enough manure for the remainder of his/her fertilizing needs, but then again, not all farms have the extended derogation allowance. Thus, this 36.4% is a reasonable in-between estimate. The payback period can then simply be multiplied by a factor of 2.75 (1/0.364).

Taking an average pure ammonia production of 1.43 kg/hr (in the middle of the 0.95-1.91 kg/hr range), 1 tonne is made every 699.3 hours or 29.1 days. Per year, 12.53 tonnes of pure ammonia would be produced. With this and the values from table 4, the final payback period for each of the relevant final processes can be calculated, which can be found in table 5.

Table 5: Overview of all relevant payback periods

	Payback Period in years (or months)	
Equipment Type	**Fully utilized**	**Part-time (36.4%)**
Direct 10% NH_3 wholesale	0	0
25% NH_3 air-con	0.42 (5)	1.161 (14)
25% NH_3 water-cooled	0.67 (8)	1.834 (22)
100% NH_3 air-con	0.45 (5)	1.232 (15)
100% NH_3 water-cooled	0.67 (8)	1.851 (22)
Ammonium Sulphate	1.18 (14)	3.237 (39)
Enriched Biochar	1.52 (18)	4.167 (50)

As evident, even in the worst case scenario with the longest payback period, the break-even point is at 4 years, which can be considered acceptable. However, one should not forget that the rest of the entire MEZT solution train is not included in this. That will undoubtedly lower the profits and increase the payback period (due to additional initial costs). Thus, since that 4 years could increase to well over 10 years when adding the rest of the MEZT solution train, it might be necessary to discard such a process due to a too long payback period (e.g. payback period longer than reasonable service life). In any case, both the ammonium sulphate and enriched biochar have a similar payback period, with ammonium sulphate having an overall lower profitability, but also shorter payback period. Thus, no clear winner arises between these 2 options.

4.4.4 Potential for Grants/Subsidies

One of the possibilities for additional revenue is through CO_2/carbon certificates or emission rights. The principle is as followed: every firm has the right to emit a certain amount of CO_2 and if they are under their limit they can sell their emission rights to a firm that is over their limit via the European Union Emissions Trading System (EU ETS). Similarly, if one can permanently capture CO_2 it can be exchanged for a CO_2 certificate in the same manner [72]. As of Q2 2021, the price for a CO_2 certificate is at an all-time high above €50 /tonne [73].

Although none of the processes actually permanently capture CO_2, there is a real reduction in global CO_2 since the ammonia is not made from traditional fossil fuels, but from the green MEZT process. In fact, per tonne pure NH_3, 2.6 tonnes of life-cycle greenhouse gasses (GHG) are produced [74], resulting in a current carbon certificate equivalent price of €130 per tonne ammonia, which *should* be applicable to all processes.

However, this additional revenue cannot be cashed in. The current carbon credits system accounts for fuel usage, transportation and travel, power (electricity) usage and heating/gas, not bought products such as fertilizer. Thus, that the eventual fertilizer (or wholesale ammonia) comes from greener sources does not matter for carbon credits. Instead, the original 'dirty' ammonia producers (using natural gas) need to purchase carbon certificates to offset their carbon emissions, which directly affects the wholesale ammonia prices. In simpler terms, the emissions cost is already included in the ammonia market price (of €867 /tonne) and thus MEZT can sell ammonia at the higher market price without the need to pay for carbon compensating certificates.

Moreover, one could think that the (enriched) biochar option may be eligible for additional carbon credits as biochar is one of the given examples of Carbon Capture and Storage (CCS). Normally, when permanently stored, it is eligible for carbon credits. However, on a farm this is explicitly not the case, as by adding biochar to a farmer's soil, the carbon is not permanently captured (since it will be absorbed by plant-life) and is thus not eligible for carbon credits [75].

Another issue is that even though carbon emissions are included in carbon certificates, nitrogen emissions (the main reduction potential of MEZT) are not included at all. Systems to include nitrogen rights have been proposed and shown to lead to lower emissions [76], but until recently the only real nation-wide limits to nitrogen emissions is the mandated nitrogen limit per hectare (including the previously mentioned derogation rules) [77]. Fortunately, recently it has been possible to temporarily rent out nitrogen-space ('stikstofruimte'), but this varies per province and not only does the farm the leases the nitrogen-space have to demonstrably decommission their nitrogen use, the leaser can only use 70% of this capacity [78]. One source even claims that prices of up to €100 per kg (not tonne) of nitrogen are possible, which is very significant [79].

At the end of the day, finding actual nitrogen-space ('stikstofruimte') values for farms has proven to be very difficult and it varies per farm and per permit. On top of that, there have been many changes recently and likely there are many still to come, especially with international pressure by organizations such as Greenpeace and the World Wide Fund to reduce nitrogen emissions in the Netherlands and plans to take the Netherlands to court if emissions aren't reduced quickly enough [80]. Combined with that there is a program for subsidies for "innovative farm systems", which is determined on a per-case basis [81] means that there is definitely a potential for either reduced costs or increased revenues. However, to accurately determine a value for this at this moment is going to be very difficult. However, it is almost certain that no matter the chosen process, some form of subsidy will be coming in the near future.

4.4.5 Combination with Other Outputs

The focus of this paper is mainly on the ammonia output as it is the most significant output that also saves the most emissions. However, if it is relatively easy for one of the processes to also utilize the unused streams in some way, it would be valuable to consider and could affect the final choice. Thus, this is investigated.

Besides the 10-20 L/hr 10% ammonia stream, as evident from figure 3, there is also a 50 - 100 L/hr stripped base stream with a 1-2% wt. concentration of potassium and a 0.5-1% wt. concentration of ammonia. Even though the concentration is much lower, the flow rate is higher, so the overall mass flow rate of ammonia and potassium is still significant.

Alternatively, the input stream of the VMS can also be taken, which would mean that a VMS may not be necessary at all. At first thought the input stream would be a combination of both output streams, which would also ensure that the mass flow is balanced, but after further consultation with Tobias from Lenntech, it was discovered that the input stream and resulting stripped base stream have partial recycling to them (meaning the 50-100 L/hr stripped base output is a net value). This means that mass balance in the simplified model is not conserved and thus the input stream cannot simply be calculated as a combination of output streams. Fortunately, not only does this not affect the entire previous ammonia analysis (which does not have a recycle stream), the input stream specifications are known: a net flow rate of 60-120 L/hr with an NH_3 concentration of 1-1.5% and a K concentration of 1.2-2.4%. The real flow rate is higher due to the added recycle stream, but this can be ignored for this analysis as only the net output would be used/tapped from the stream. Also, this stream is still under investigation by Lenntech, so values may not be final.

As a side note, the potassium is dissolved in the water as potassium hydroxide (KOH), which affects calculations. Unlike aqueous ammonia which dissolves and still reacts as ammonia, the potassium permanently reacts to form KOH, meaning the reactions happen from potassium hydroxide as a starting point. Thus, this 1.2-2.4% K concentration needs to be converted to a KOH concentration. This is easy, as with the molar weights, the reaction of 39.1 g/mol potassium with already present water forms 56.1 g/mol potassium hydroxide resulting in this concentration being 1.43 times higher, or 1.72-3.43% KOH.

Although an extensive review just like for ammonia could be made, the combination of processes comes down to two logical options which use the same/similar method of ammonium sulphate. The biochar option unfortunately cannot be easily combined with the potassium stream. Biochar tends to already be rich in potassium [82] and thus further enrichment is difficult to achieve and ineffective. If for whatever reason this further enrichment process is chosen, the order is also important, because if the biochar is already enriched with ammonia, then adding the aqueous solution to enrich the biochar will wash away the ammonia.

Option 1: Separate and Sell
For the first of these options, the VMS stripped base output can be further processed to remove ammonia and then the pure potassium hydroxide can be sold. The price of pure potassium hydroxide is around 600-850 USD/tonne pure on Alibaba and one Dutch supplier (Bredox BV) was found selling 90%+ purity KOH flakes for €750 /tonne, which is €833 /tonne pure [83]. Peculiarly, 90%+ concentrated flakes are sometimes also offered for as low as €250 /tonne in Asia. Nonetheless, refining the potassium hydroxide appears to bring in good revenue close to that of ammonia.

However, refining to separate the remaining ammonia from potassium hydroxide is easier said than done. Both chemicals are very hygroscopic (attracting water) and as evident from the MEZT solution train, separating ammonia from potassium hydroxide is best done by a VMS, but adding another VMS onto the current VMS will yield diminishing returns and there will still be ammonia in the stream. Evidently, properly separating these 2 substances is very difficult, but there is a very crude solution: to boil or evaporate the substance. ammonia vaporises very easily (along with water), but potassium hydroxide has high thermal stability and a melting and boiling temperature of 360 °C and 1,327 °C respectively, meaning that by adding heat one can easily separate the ammonia and the vast majority of water to form solid flakes.

Unfortunately there are two problems. Firstly, the energy requirements per mass of potassium would be immense. Taking the ideal (highest concentration) scenario, 2 kg of potassium is dissolved in an additional 98 kg of water (or 2.86 kg KOH in about 97 kg water), which needs to be evaporated. Using similar calculations as for the air-conditioning costs (75°C ΔT, 2256.4 kJ/kg heat of vaporisation at 100°C, etc.), a total of 224.9 MJ or 62.3 kWh of energy is required per 2.86 kg KOH. Turning this into a per-tonne value, 21,781 kWh or 78,631 MJ is needed, which even at the lowest solar panel price of €0.065 /kWh leads to €1,416. For the non-ideal scenarios this would be even higher and coincidentally, for gas heating prices (converted from per cubic meter to per kWh) the price is nearly identical or even slightly higher.

Another problem is that one cannot just evaporate the fluid in open air as a tremendous amount of ammonia gas would be released in the atmosphere. It would eventually be possible to capture this evaporated moisture and ammonia and condense it, but then this would have the exact same effect as the VMS, albeit at a purer concentration and a vastly higher energy cost.

Option 2: Combine and Make Fertilizer
The second main option is to take the full flow before the VMS and to combine it with sulphuric acid to create a mixture of ammonium sulphate and potassium sulphate. Potassium hydroxide reacts with sulphuric acid in the same way as ammonia does and potassium hydroxide is also a common fertilizer. The resulting combined fertilizer would then have both the Nitrogen and Potassium of the common NPK rating of fertilizers.

To calculate the costs and profits of this, first the reactions need to be known. In relatively low KOH concentrations (which is the case in the diluted stream), the following reaction occurs.

$$2KOH(aq) + H_2SO_4(aq) \Longrightarrow K_2SO_4(aq) + 2H_2O$$

Taking the relevant molar masses of each substance (KOH = 56.1 g/mol, H_2SO_4 = 98.1 g/mol, K_2SO_4 = 174.3 g/mol, H_20 = 18.0 g/mol) and scaling up, per tonne of pure KOH input, 874 kg of sulphuric acid is needed and 1553 kg of potassium sulphate is produced (along with 321 kg of water). Coincidentally, at the same place the bulk ammonium sulphate prices for the Netherlands were found (HLP Roden), a bulk pure potassium sulphate price was also given at €481 /tonne [84]. Combining this with the Dutch Brenntag sulphuric acid price of €194.30 /tonne from earlier on means that one tonne of KOH requires (0.874 * €194.30 =) €170.0 of investment for a revenue of (1.553 * €481 =) €747.0, resulting in a per tonne pure KOH profits of €577 /tonne.

This results in a very similar conclusion as was drawn earlier with ammonia. Selling the pure potassium (or potassium hydroxide) substance would lead to the highest overall profits, if the process is possible and a buyer can be found, but the fertilizer option is also still profitable if sold (actually even more so than ammonium sulphate) and can actually feasibly be used on the farm directly.

The only thing one should watch out for in this case is that the final fertilizer is very diluted, meaning a larger storage is needed. In fact, using only the 10% ammonia stream and sulphuric acid results in a roughly 30% concentrated fertilizer dissolved in water, but from the calculations below, with this larger much more diluted output stream, the overall fertilizer concentration is only one third of that. Moreover, if it is used to spray on the field, the lower concentration means that a farmer with his/her tractor may need to make multiple trips instead of just one (for example). One possible solution is if the farmer has a sprinkler or other irrigation system, it would be possible to use this low-concentration fertilizer for it instead of water; however, since the Netherlands gets plenty of rain, few farmers have such a system. The legality of just spraying aqueous fertilizer on land is also questionable and will be investigated next.

4.4.6 Legality of Possible Outputs

One of the concerns raised by the supervisors on the consideration of the final choice was if farms are allowed to use aqueous forms of fertilizers or not since liquid fertilizers have higher ammonia emissions and (slightly) lower nitrogen utilization compared to solid fertilizers according to the Wageningen University [85]. Logically speaking, the current solid fertilizers are widely used, and even the potential alternatives such as biochar have proven to have lower (or at least no worse) emissions than conventional fertilizers, meaning it comes as no surprise that these are legal.

However, although there are laws on reducing emissions for livestock and excess manure production, there appears to be no negative laws or regulations hindering the use of fertilizers dissolved in water. In fact, the current regulations do not even explicitly disallow the use of pure aqueous ammonia on farms, despite high emissions, and the web links on the Dutch government website lead straight to the rules that have been largely unchanged since 1992 [86].

This was investigated further just to be sure, and eventually companies were found that supplied and delivered the service of ammonium sulphate [87] and potassium sulphate [88] as a liquid fertilizer. Also useful to note, both these companies and the 'Nederlandse Centrum voor Ontwikkeling van Kringlooprpecisebemsting' (NCOK) [89] recommend either injecting it underground or to use the more flexible liquid form to precisely spray/drop the liquid fertilizer at the plant root zone. It was also found that the upcoming EU RENURE regulations state that during RENURE application, emissions should be minimized by "injection, immediate incorporation of surface-applied materials or equivalent measures" [71], which also support this.

The NCOK source also mentions a possible use for the left over stripped base output in case wholesale ammonia is made. The stripped base output is essentially a mineral concentrate, which can be used as a fertilizer additive. When one unit of mineral concentrate (containing ammonia and potassium of both about 0.4-1% concentration [90]) is combined with 3 units of regular manure ('drijfmest'), it can make a suitable fertilizing additive [89]. On top of being legal, the mineral concentrate does not count as an organic fertilizer, meaning it does not contribute to the maximum allowed manure usage on land. Furthermore, the slow working NPK component of manure mixed with the fast working ammonia-based nitrogen of the mineral concentrate mean that emissions and nitrogen release is at an overall acceptable level.

4.4.7 Miscellaneous Considerations

Very briefly, there are 2 more points to mention before the final choice is made. Firstly, the final choice does not have to necessarily have to be only one process; it can be a combination of multiple processes. Also, the farmer may have different needs depending on the time of year or even personal preference, so a combination option would provide flexibility and be well-suited.

Secondly, both ammonium sulphate and potassium sulphate will make the ground they are fertilizing slightly more acidic (ammonium sulphate more so than potassium sulphate). This is not necessarily bad as most farmland favours a slightly acidic ground, but it should be kept in mind as a too acidic farmland can stunt growth [85]. Fortunately, even in the worst case where farmland becomes too acidic, it is possible to add lime to recover (increase) the pH to normal values.

5 Process Design and Modelling

After the technology review, a final choice can finally be made. This is then further worked out and any hurdles left over are resolved before a final process overview is made. Afterwards, calculations can be made to specify the streams

5.1 Final Choice

As mentioned at the start of the *Miscellaneous Considerations* subsection, the final choice was narrowed down already to one of the wholesale options, ammonium sulphate or enriched biochar. This has been narrowed down further, because the price fluctuations allude to the profitability of enriched biochar not being particularly better than ammonium sulphate and because biochar does not offer any particular advantages regarding manure disposal costs (all processes can make normal biochar), payback period and grants and subsidies, while also having some real disadvantages as seen from the scoring table (e.g. safety and reliability). On top of that, the ammonium sulphate option can integrate the other potassium-rich stream(s) whereas biochar cannot. Although that second stream is a much lower concentration, the flow rate is higher, so there is a substantial amount of valuable substances. Therefore, the enriched biochar option can be discarded with a reasonable level of certainty, at least at a farm scale.

The final chosen solution is a **flexible combination** of creating **the raw mineral concentrates, the ammonium sulphate, potassium sulphate** and **25% wholesale ammonia** where the farmer can switch between the processes they desire. Originally a simple setup was chosen where either the VMS input would be used to make a combined fertilizer or (with the switch turned the other way) the wholesale ammonia would be created with the stripped base side-product being used as a mineral concentrate for on the farm (see *Legality* section).

However, after further investigation the final chosen setup is slightly different. Since the produced fertilizer from the VMS input may not have the right NPK ratings for the farm land, some form of flexibility to change the ratio of concentrations is desired. Therefore, an extra switch/valve will be added to the stripped base to turn that into a combined fertilizer as well (of a slightly different NPK ratio), and a switch is also added after the VMS vacuum pump so that if the cooling is turned off that 10% aqueous ammonia can be turned into only ammonium sulphate. These outputs can then be combined to varying degrees to give the farmer an optimal NPK ratio and the only additional costs are from extra IBC tanks, valves/switches and a few hoses, which are all quite cheap.

Overall this option aims to provide maximum flexibility for the farmer depending on their needs and wants and it also is beneficial for MEZT. In case at a later point MEZT would like to focus on one of these options, it would be possible to 'cut out' the other unwanted part and proceed without needing to make changes (besides updating the initial cost analysis for removing components).

5.2 Further Calculations/Considerations

At this point almost all information is ready to create the final process diagram. However, a few more considerations need to be made to fully define the final process. They are listed below in no particular order.

5.2.1 Ammonia Output Concentration

Out of all wholesale ammonia concentrations, the 25% concentration was chosen because the 100% gaseous concentration does not give any appreciable additional revenues while requiring more energy and more difficult storage circumstances. Similarly, the 10% output is the simplest to realize, but a buyer may not be possible to find and as evident from the cost analysis, using excess electricity from solar panels brings the cost of concentrating it to 25% down significantly.

5.2.2 VMS Alternative

During this whole paper a VMS was assumed, as suggested by MEZT themselves and CramChem with their initial setup, and alternatives requiring additional chemicals were rejected. However, as a final check, a liquid-liquid stripper such as the one produced by BLUE-tec was also suggested by one of the supervisors as an alternative [91]. It works on the basis of a pH swing where a raised pH (and temperature) results in an increased proportion of ammonia in the gaseous phase. The ammonia gas then passes through a gas permeable membrane where it reacts with sulphuric acid to make ammonium sulphate: the same fertilizer as made in the suggested process. An overview of this process can be seen in figure 19.

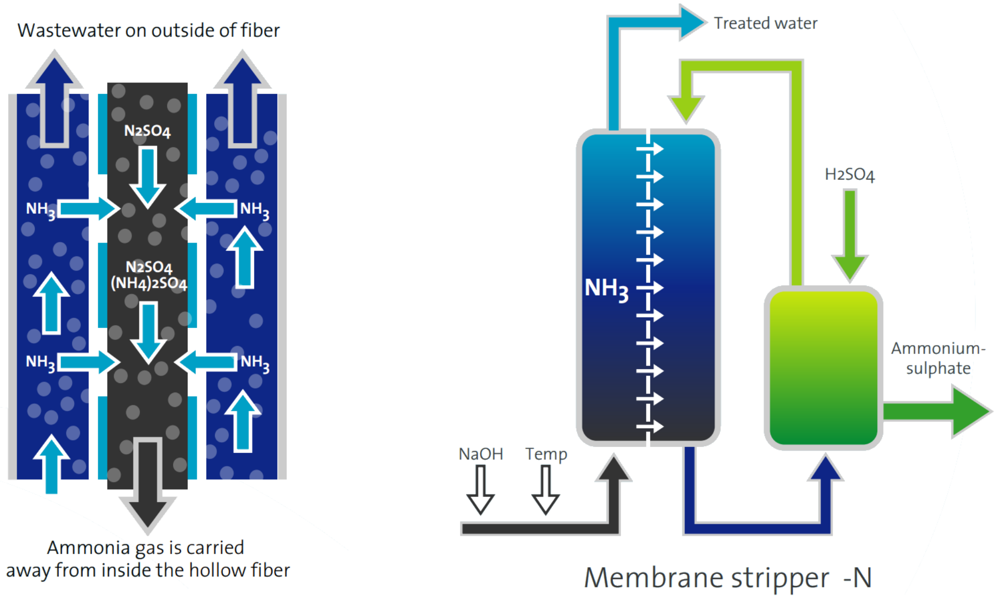


Figure 19: Overview of the liquid-liquid stripper to create fertilizer [91]

Traditionally, during this process $NaOH$ is added as base to increase the pH enough to force ammonia into its gaseous form, however, this would likely require a large amount of $NaOH$, increasing cost and introducing additional waste to deal with. One of the supervisors suggested that the KOH present in the input stream may act as the base to increase the pH enough for the pH swing to be in effect. Thus, this was investigated.

To begin with, the equilibrium points of aqueous NH_4 and gaseous NH_3 needs to be known. Although various calculations could be done, this data is readily available, as seen in figure 20.

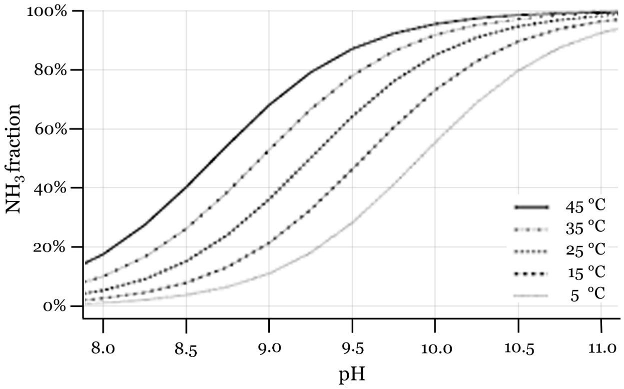


Figure 20: The effect of pH on the NH_3 and NH_4 ion equilibrium at various temperatures [92]

Evidently, a pH of above 11 is ideal for most ammonia gas to be extracted. Now the pOH and resulting pH is calculated of the current stream, which consists of mainly the hydroxide (OH^-) anions originating from the NH_3 and K molecules in the stream.

$$K + H_2O \Longrightarrow KOH + H_2$$

$$KOH \rightleftharpoons K^+ + OH^-$$

From these equations, one mole of K creates one mole of OH^-, leading to the same molar concentration. Now, at a molar mass of K = 17.031 g/mol and a 1% K weight concentration, this 10 g of K per litre divided by 39.0983 g/mol results in a molar concentration of 0.25577 M. Therefore the 1.2-2.4% input flow has a 0.3069-0.6138 M OH^- concentration. Luckily, the K^+ ion essentially has no acidity, so the pH can directly be calculated from the OH^- molar concentration as followed:

$$\text{pOH}= -log[0.3069\text{-}0.6138] = 0.513\text{-}0.212$$

$$\text{pH}= 13.487\text{-}13.788$$

Similar calculations can be done for ammonia alone, resulting in a pH of around 11. Ammonia does disassociate into basic OH^- and acidic NH_4^+ ions, but the basic OH^- ions are stronger. For this reason ammonia tends to be called a weak base, whereas KOH is a strong base. What is more important to note is that the weak base ammonia contributes slightly more to the pH until it has been extracted (after which the pH 'drops' back down to the KOH only levels).

From this high pH it can be said confidently that 100% of the ammonia is available in (dissolved/non-ionic) gas form for the liquid-liquid stripper (and coincidentally, that also means it is available more easily for the VMS to extract in gaseous form). However, this does not necessarily mean that all of the gas is transported through the membrane. This is investigated next.

To bring it down to the bare essence, the flux J (L/m^2hr) can be calculated as followed, where A_P is the membrane permeability coefficient, otherwise known as the mass transfer coefficient (i.e. how easily the molecules can pass through the membrane), P_T is the transmembrane pressure (TMP, in kPa. i.e. the pressure across the membrane) and P_O is the osmotic pressure (in kPa) that causes diffusion to occur and caused by the concentration difference between the two sides [93].

$$J = A_P * (P_T - P_O)$$

However, from investigating the function of the BLUEtec liquid-liquid stripper, it appears to not rely on a direct pressure difference and mentions only diffusion. At first thought, this does not appear to be a huge driving force, so this was investigated. Assuming an ideal solution (for simplicity's sake), Jacobus van 't Hoff created an equation for this osmotic pressure as followed [94].

$$\Pi = icRT = 2182 \text{ Pa} = 2.2 \text{ kPa}$$

i = van 't Hoff index = 1 for most non-electrolytes (in this case too)
c = solute molar concentration (i.e. the ammonia = 0.5872-0.8807 M)
R = ideal gas constant = 8.314 J/K/mol
T = Temperature in Kelvin (25C = 298 K)

This osmotic pressure assumes the highest concentration possible (1.5% in the feed), no concentration in the permeate and ideal conditions. This 2.2 kPa is almost a factor 50 lower than the vacuum pump would create and in fact, this 2.2 kPa decreases as more ammonia is extracted from the feed, which would not be the case for the current VMS setup. Thus, the flux would be a factor 50 lower (assuming a similar membrane permeability coefficient), requiring a membrane that is 50 times larger for the same ammonia mass transfer and recovery. A smaller membrane would of course not recover as much.

If one now takes into consideration that these membranes are a particularly expensive component that currently according to MEZT need to be replaced/serviced (bi)annually, having this cost be 50-fold larger is a deal breaker.

Now, if a pump is added to 'push' the ammonia through or 'suck' it from the permeate side, essentially an identical operation to the VMS is achieved. The only difference is that with the BLUEtec method the ammonia reacts quickly so that the concentration on the permeate side is still zero, whereas for the VMS the vacuum takes away the ammonia (and water, since they have a similar molecule size. H_2O = 0.275 nm, NH_3 = 0.326 nm) quickly, so that the concentration on the permeate side of the membrane stays close to zero. Additionally, with a liquid-liquid stripper, it would not be possible to extract pure ammonia as it always reacts, limiting the usefulness. Therefore, for all these reasons (especially membrane cost), the current vacuum-powered VMS choice will be kept.

5.2.3 Final Cooling Option

Earlier on 3 options were given for cooling and condensing the gaseous ammonia and water stream (see figure 17), but of these options a choice still needs to be made. Cooling using ground water ended up being the cheapest option, requiring only a relatively low powered pump. However, as elaborated on in appendix A, using that option would have a very small temperature difference and practically no margin of error. If the ground water ends up being slightly warmer than expected or if the heat exchanger is slightly out of tune for whatever reason, then it would be nearly impossible to compensate, putting the entire MEZT setup at jeopardy. Thus, that option will be discarded.

The other two options (both using cooler/air-conditioning units) are much more lenient, as any deficit or surplus can be 'caught' by increasing or decreasing the power of the cooling unit. Because of this feasibility (along with not being that much more costly to run), one of the air-conditioning options is chosen. Now the big question is if the gaseous ammonia-water combination can be used directly in an air-conditioning unit (for greater simplicity and integration).

Upon further investigation, it is not feasible to directly connect the mostly water vapour-containing mixture to the air-conditioning unit as a refrigerant, since not only is water not a particularly great refrigerant, it would require a compressor within the current vacuum loop (which should also act as a vacuum pump for the membrane), which compresses the vacuum water and ammonia mixture, cools it, and then 'reliefs' the pressure back to vacuum pressure. This is rather complex and unnecessarily power intensive. Fortunately, an alternative has been found, which is an industrial water chiller. These units are available at the 10 kW unit size requirement and it essentially consists of an air-conditioning unit with heat exchanger built directly into it. An overview of a chiller can be found in figure 21.

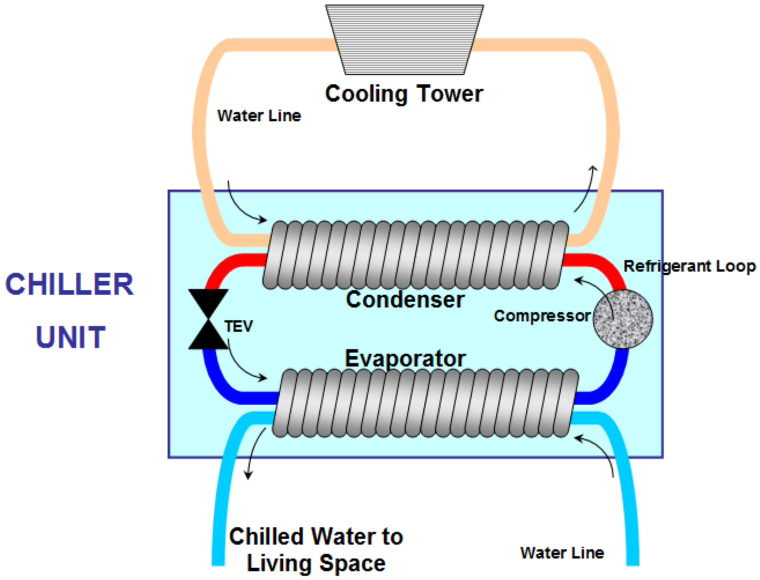


Figure 21: Overview of how a water chiller functions [95]

However, these chillers are designed for water and not vapour. This was investigated, starting with the flow rate. In total about 19.1 kg/hr of combined water and ammonia passes through the VMS. At 2 kPa and saturation temperature (17 °C), water vapour density is about 0.0145 kg/m^3 [96]. However, for ammonia a density could not be found at these conditions. Fortunately, the majority of the flow is water vapour, so the same density will be assumed.

Thus, an up to 19.1 kg/hr mass flow would be an up to 1317 m^3/hr (or 366 L/s) near vacuum flow rate. Although this number may not be entirely realistic as the membrane and vacuum pump would mean these are non-ideal conditions, this is still a very large number and could be a reason for concern. In a regular heat exchanger, air-conditioning unit or chiller with a reasonably small heat exchanger, this large flow rate would result in a very short residence time. However, as there are very few actual molecules to cool in a specific volume, the vapour is cooled/condensed much more quickly. This agrees with the heat exchanger calculations from the detailed initial costing, as the heat transferred relies on the temperature difference, area and heat transfer coefficient and all these are practically constant for the new gaseous input besides heat transfer coefficient.

Consulting figure 28 from the appendix, a 'normal' chiller setup has a refrigerant service fluid and water process fluid resulting in an overall heat transfer coefficient of about 800 W/m^2K. Taking the new setup where the process fluid is condensing water, the heat transfer coefficient is theoretically around 1000 W/m^2K, which is higher than before, so theoretically a 'normal' chiller designed for water would work just as well (or perhaps better) on the condensing water. However, at the completely other side of "condensing aqueous vapours" is "low pressure air and gas" which would result in an overall heat transfer coefficient around 50 W/m^2K. This makes drawing conclusions difficult as in the designed situation there is a low pressure condensing aqueous vapour, which is a combination of the two. *Technically*, the condensing vapour still applies, but just to be sure, literature was checked.

The 1000 W/m^2K overall heat transfer coefficient consists of a process fluid (the condensing water) heat transfer coefficient of roughly 2800 (2600-3000) W/m^2K. In literature, a source was found on vacuum membrane distillation, which is actually a very similar setup to the vacuum membrane stripper. There a process fluid heat transfer coefficient of 4000 W/m^2K was given during condensation at a slightly higher pressure of 3 kPa [97]. The similarity of their setup can be seen in figure 22, where the yellow highlighted area is equal to the current VMS.

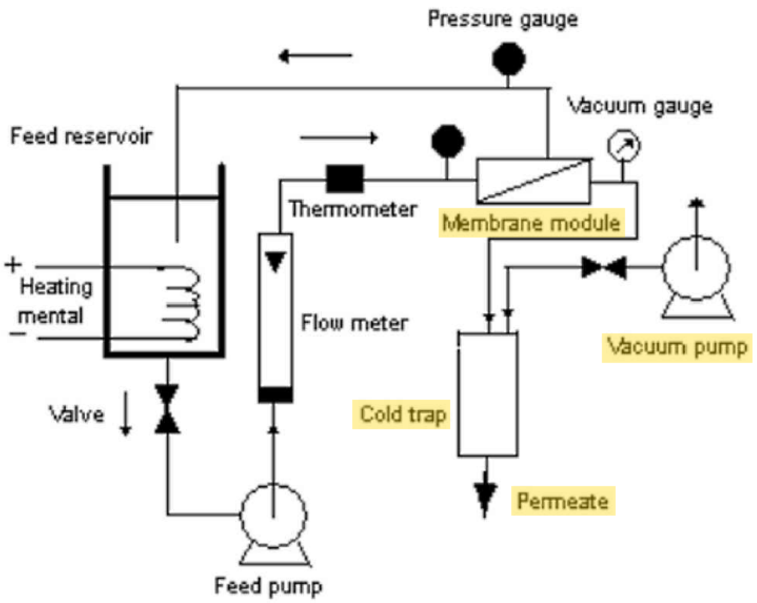


Figure 22: Overview of the very similar Vacuum Membrane Distillation setup [97]

Another literature source was also found on the steam condensation in a tube under vacuum conditions. From that source, a process side heat transfer coefficient of 5000 W/m^2K and up was given, although the vacuum pressure was unknown [98]. From these sources, it can be concluded that the higher overall heat transfer coefficient at vacuum conditions does not negatively impact the final result, and thus an equivalent or greater heat transfer coefficient (e.g. 1000 W/m^2K) can be assumed. Therefore, at least from a heat transfer point of view, the direct water chiller is sufficient to have a gaseous input. Some industrial water chillers even use stainless steel piping and plate heat exchangers for the chilling, which would make it particularly useful for the corrosive properties of ammonia.

Admittedly, the flow characteristics and turbulence itself is not investigated and for the high flow through a small pipe, there surely would be some restriction, but investigating this on its own would be rather difficult. Thus, for now the chiller will be assumed under the assumption that it would require some practical/prototype testing. Otherwise, simply a heat exchanger will be added with larger piping suitable to the very low density/high flow rate.

5.2.4 Valves/Switches

On the topic of valves, in the current setup there are several of them. A farmer would like to have control over which output he/she chooses and the combination thereof, so there are 2 possibilities. Firstly, a manual setup with simple valves that have to be turned by hand is possible. This is the cheapest and simplest option, but it can be difficult for the farmer to setup as they may not be knowledgeable on the system and also, if a combination of outputs is desired to create a certain NPK rating or concentration, the valves have to be opened partly, which can be difficult to fine-tune. The second option is to use electronically controlled valves, such as solenoid valves. Although these cannot open part-way, a computer system would allow the farmer to just push a button (or type in an NPK ratio) and the system would intermittently open and close the solenoids to create the desired ratio automatically. For a farmer this is also more fool proof.

Surprisingly, a 0.5 inch (or 12.7mm, one of the smallest commercial sizes available) diameter stainless steel solenoid valve can be had for as little as €20 [99], which is not drastically different from an equivalent manual valve (€4), especially when considering the entire cost of the system. Moreover, with normal circumstances (water at "Gravity to Low Pressure") a 0.5 inch pipe can sustain up to 1500 L/hr of water with minimal pressure loss [100], which is vastly more than any of the flows in the system, so this smallest commercial size is more than sufficient. Now, the manual option does require a controller to be added, but these are generally not too expensive and for eventual mass production, it would be possible to create their own controller (using a Raspberry Pi Zero for example, below €30).

Filling up the tanks with sulphuric acid could essentially also be done automatically using solenoid valves and flow-meters. However, at the very low flow rates, a very precise (and specialised) flow meter is required and these are quite very expensive (several hundred euros). Also, with a known concentration of IBC tank inputs, one can simply calculate the amount of sulphuric acid needed for a full tank beforehand, mark this level on the IBC tank and simply fill each tank manually with sulphuric acid. Besides simplicity, this also has the benefit of being consistent (which a low quality flow-meter and solenoid might not be).

5.2.5 Extracting Water from the Drum Tank

One more point to address is the drum flash tank. A vacuum pump is at the gas-side, but a system still should be made for the condensed water side (bottom output). Traditionally via the original cold trap concept this would be batch-based, but this is not useful for the continuous MEZT process. Initially one could think of placing another vacuum pump, however, this has two downsides. Firstly, this will add quite some cost as vacuum pumps are not cheap and also consumes electricity, and secondly, the vacuum quantity needs to be set just right to 'pump' the water out. Too low and water builds up in the tank, but too high and the water gets all pumped away, allowing the ammonia gas to also be pumped. Thus, a simpler solution is suggested using intermittent solenoid valves. If a small reservoir is placed under the drum with a valve just above and below it, it would be possible to fill up that reservoir with water, then close the top valve and open the bottom valve, releasing the water while not releasing the vacuum pressure. Then after the water has dropped out (a few seconds at most), the bottom valve can close and the top valve can open, allowing it to fill with water again. By using electric solenoid valves, a program can be written to frequently open and close the valves, thus requiring only a small reservoir which minimally disturbs the vacuum in the main system.

5.3 Final Process Overview & Calculations

For the design of the final process, the fundamentals of process intensification were used [101]. Thus, intensification in all four domains (thermodynamic, functional, spatial and temporal) has been considered. Although this will not be discussed explicitly, to put it simply it looks at simplifying the process, eliminating unnecessary steps or energy usages and seeing if more complex systems can be replaced with more robust, simpler systems. In fact, the concept of *inherently safer design* used for the safety justification is also a part of process intensification and many of the ideas are transferable.

The final process can be found in figure 23 on the following page.

As evident, the output of the BPMED can be used either directly as a mineral concentrate/fertilizer or it can enter the VMS. When entering the VMS, part of the flow is deflected (the stripped base) which can either be used directly or turned into a fertilizer, whereas another smaller part of the flow is extracted through the VMS membrane. The vacuum on the membrane extracts ammonia along with water, which subsequently gets cooled (if 25% aqueous ammonia is desired), which condenses part of the water at near vacuum pressure while ammonia stays gaseous. In the flash drum the condensed water 'drops' out the bottom to be recovered and reused as an input of clean water, while the gaseous ammonia and water vapour enters the vacuum pump. Upon exiting the vacuum pump, the pressure is suddenly ambient again, (almost) instantly condensing the water and subsequently having the remaining ammonia gas dissolve in it (as it dissolves very easily). Then (if 25% aqueous ammonia is desired), the aqueous ammonia can be stored or sold, or if only 10% aqueous ammonia is made (when the cooler is turned off), the ammonia can be stored and turned into ammonium sulphate fertilizer to be used on the farm. Overall, the final process is actually quite very simple and robust, allowing for any of options A through G to be used by switching valves on or off or to have the process modified by removing certain parts depending on the farmer's liking.

Also, if one looks closely, a mass imbalance can be seen. Although great care was taken to ensure mass is conserved as much as possible, at the VMS the input and output (especially the stripped base) do not coincide. For example, at the input the stream has 1.2-2.4% K concentration, but after the VMS (which extracts no potassium at all), the stripped base suddenly has only 1.0-2.0% K, despite some water being extracted which would *increase* the concentration slightly. This disparity is due to these values being physically measured from the prototype setup and all further calculations are based off of this. Unfortunately, the only way to solve this disparity is through further prototype or full scale testing with more accurate equipment.

Furthermore, figure 23 already has some key values associated with it. These mass rate and concentration calculations can be found in appendix B. From those calculations a few more useful key values have been derived, which can be found in table 6 afterwards.

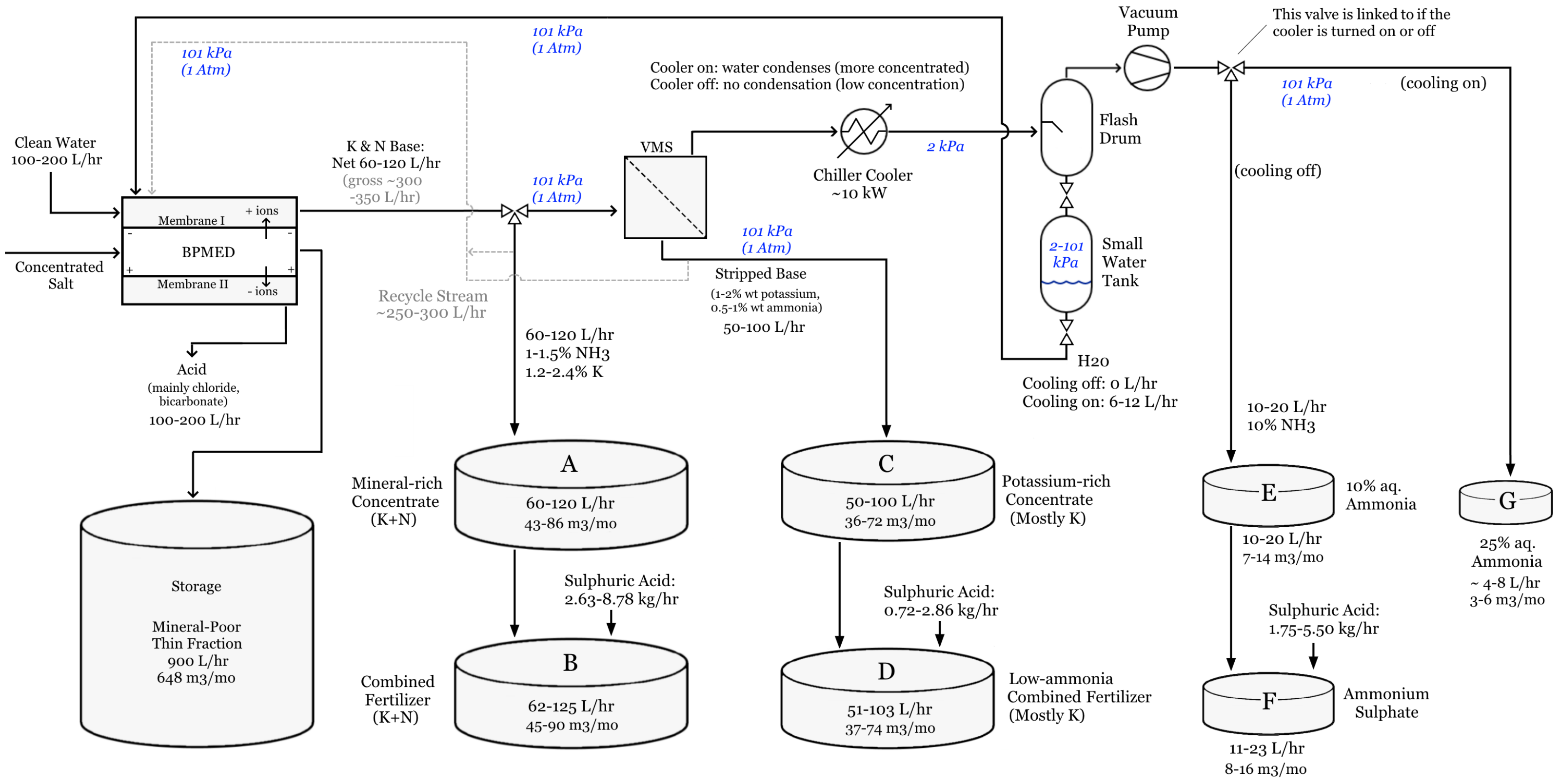


Figure 23: Overview of the final process, including some key values

Please note that the rest of the MEZT process up to the BPMED (as seen in figure 3) is not included for simplicity's sake.

Table 6: Overview of key (hourly) outputs of the final process

	Process Tank Output						
	A	**B**	**C**	**D**	**E**	**F**	**G**
Input H2S04 (kg/hr)	0	2.63-8.78	0	0.72-2.86	0	1.75-5.50	0
H2SO4 cost (€/hr)	0	0.526-1.756	0	0.269-1.076	0	0.550-1.100	0
Output substance (kg/hr)	0.60-1.80 NH3 1.03-4.12 KOH	2.33-6.98 AS 1.59-6.21 KS	0.25-1.00 NH3 0.72-2.86 KOH	0.97-3.88 AS 1.11-4.44 KS	0.96-1.91 NH3	3.71-7.41 AS	0.96-1.91 NH3
Output nutrients (kg/hr)	0.49-1.47 N 0.72-2.88 K	0.49-1.47 N 0.72-2.88 K	0.21-0.82 N 0.50-2.00 K	0.20-0.82 N 0.50-2.0 K	0.78-1.56 N	0.78-1.56 N	0.78-1.57N
Nutrient concentration	0.82-1.23% N 1.20-2.40% K	0.78-1.14% N 1.15-2.24% K	1.00-2.00% K 0.41-0.82% N	0.40-0.79% N 0.98-1.94% K	8.20% N	6.33% N	20.50% N
Output Sell Value (€/hr)	1.372-4.974	1.352-4.823	0.810-3.239	0.776-3.105	0.818-1.637	0.926-1.853	0.818-1.637
Net ingredient Value (€/hr)	1.372-4.974	0.826-3.067	0.810-3.239	0.507-2.030	0.818-1.637*	0.376-0.753	0.818-1.637*

NOTE: This net value only includes ingredient purchase and sell prices, nothing more. See section 6 for the full analysis.
NOTE 2: The net ingredient value per hour is coincidentally also equal to the per m^3 *manure value.*

What is perhaps more interesting than the individual streams are the possible combinations of streams. Essentially, with variable switches/valves (that let a part of the flow go through), there can even be an infinite number of combinations of all tanks possible. The total value of these streams would then be in between the value of streams when the valves are 100% open or closed. A quick overview of the combinations if valves are only fully open or fully shut, including net ingredient values can be seen below. Please note that the farmer's metric (price per tonne or m^3 manure) is the same, since per hour 1000 L of manure is used as input here.

- Only A → €1.372-4.974 /hr
- Only B → €0.826-3.067 /hr
- C and E → €1.628-4.876 /hr (same value as C and G in theory)
- C and F → €1.186-3.992 /hr
- C and G → €1.628-4.876 /hr
- D and E → €1.325-3.667 /hr (same value as D and G in theory)
- D and F → €0.883-2.783 /hr
- D and G → €1.325-3.667 /hr

Very important to note; the mineral concentrates have a higher theoretical value due to containing more pure chemicals and not needing sulphuric acid, but at the very low concentrations it will be unlikely to find a suitable buyer, especially due to excessive transportation costs.

In addition, option A appears to be a better option compared to option B. Option A is the mineral-rich concentrate which has a higher concentration than C (especially for ammonia) and thus it might not be as suitable to use on a farmland due to emissions. Thus option A is combined with sulphuric acid to form option B which is definitely allowed, but has a lower market value.

Also, at first sight option E seems to be a better option compared to option G (same monetary value, but no cooling). However, although both options produce aqueous ammonia, option E is more diluted, making it more difficult to find a suitable buyer (which in turn may lower the price a farmer can receive for it).

Eventually, the final choice is up to the farmer to determine what fits best with his/her farm and most likely only the ammonia will be sold and the rest will be used on the farm. Also, the chosen option would depend on the new emissions (and RENURE) regulations that are coming in the coming years, especially for the mineral concentrates.

Another peculiar thing to note is that when one considers the total output of the system, the combined options C through G give a different total nutrient output than option A or B (0.99-2.38 kg/hr N and 0.50-2.00 kg/hr K versus 0.49-1.47 kg/hr N and 0.72-2.88 kg/hr K). This is because of the recycle stream on the stripped base output. The values are also logical because the recycle stream is quite concentrated in potassium, but not in ammonia as the VMS extracts most of the ammonia of the full stream going by it (roughly 300 L/hr). Thus, because of the higher ammonia mass flow past the VMS, it can extract more NH_3 mass than would otherwise be (net) taken away for stream A. This in turn explains the mass imbalance.

6 Economic Evaluation

In this section an overall economic evaluation will be made of the entire MEZT system. Since only part of the whole MEZT system was evaluated in this paper, a document was given by MEZT with rough cost and revenue estimations of the rest of the setup. This also includes the BPMED, VMS and vacuum pump. With all this included, there are actually not that many additional costs to investigate, which are listed below.

However, what is very important to note is that the document provided by MEZT is for their first smaller prototype at a 300 L/hr manure input rate, not the full 1000 L/hr as they are planning for in the future. Since all their estimates have already been made for that scale and since for certain components such as the BPMED no alternative costs can be found (due to its novelty), **in this section the final costing/revenues table will first be made for 300 L/hr manure**, after which it will be scaled up to a 1000 L/hr manure input for the sake of completeness.

Required Additional Components:

- Cooler/chiller unit (and potentially an extra heat exchanger)
- Flash drum
- Small water tank
- Storage tanks (Only a certain quantity of volume will be costed, as total volume produced is roughly independent of which choice is made)
- Valves, electronics & piping (if applicable)

Additionally, besides the current operating expenditures (energy, consumables, etc.) the following costs and revenues are needed.

- Cooler/chiller electricity cost
- Valve electricity costs (likely to be negligible)
- Vacuum pump electricity cost (since it is not included in the MEZT costing)
- Sale (or net savings from purchasing) the final products
- Minor savings of water costs (6-12 L/hr)

Besides just simple costs and revenues as stated above, a distinction will be made for small scale/single production and large scale mass production of the unit. This will only have an effect on the initial capital expenditure as water, electricity and ingredient prices are consistent for both small and large scale production.

6.1 Capital Expenditures

In this section the capital expenditures for each component will be discussed.

6.1.1 Cooler/Chiller Unit

As mentioned previously a 10 kW cooler/chiller will be required for a 1000 L/hr manure input. This may sound like a very large quantity, but condensing the water takes significantly more energy than just cooling it down. Double checking the calculations, about 8.18 kW of cooling is required for the maximum possible flow at 25% concentration (or 2.45 kW at 300 L/hr manure). Thus, a 10 kW (or 3 kW) cooling unit will give a little bit of extra leniency.

Similarly, a water chiller was chosen as *in theory* their built-in heat exchangers have sufficient capacity to also cool/condense water. However, not any water chiller can be sourced. Ammonia is corrosive, so one with stainless steel components is required, which is possible as many chillers are rated for drinking water. Secondly, a lot of water chillers have a cooling coil in a bath to cool water, but this is not ideal for gas condensation. Fortunately, plate heat exchanger chillers are available too, which are much more suited for gaseous applications.

For the 1000 L/hr manure stream, although 'regular' 10 kW units with copper-coil exchangers can be had for under €1000, a unit with a stainless steel plate heat exchanger was sourced for €1327 meeting the desired requirements [102]. Including shipping and import taxes, this is closer to €2000 and if one includes piping and installation (including potential minor modifications to be better suited to gaseous applications), a cost of €3000 can be assumed. This would be the same for both small and large scale production as this is already a mass produced unit. For the smaller 3 kW unit, finding a similarly suitable unit is more difficult, as the cheaper copper-coil exchangers are used much more frequently. However, a unit was nevertheless found for €834 [103], which with similar shipping, import taxes and installation factors comes to about €2000.

A quick note on this: although the chiller works in theory, testing is needed to make sure that the chiller also works well *in practice* (e.g. due to a too constrictive flow or other unforeseen characteristic). If the built-in heat exchanger of the chiller is not suited, the chiller can be connected to an external heat exchanger (cooled by the chilled water) that is specifically designed for condensing gasses. From the detailed cost analysis, a stainless steel plate heat exchanger for a very small 5 °C temperature difference was costed at €6108 all-inclusive. For the larger temperature difference possible by the chiller (at least 10 °C), this cost can be brought down (as the surface area is halved), but according to the cost estimation formula that was used, the cost cannot be reduced significantly since it reaches a cost estimation floor, at around €5400 (for 1000 L/hr manure). For the 300 L/hr manure flow rate, it is outside the range of the cost estimation formula (about 0.375 m^2 area, whereas the minimum size for the estimation is 1 m^2 area), but for a small scale, custom made heat exchanger, it is unlikely to be much less than €5000. For larger scale production, contact should be made with manufacturers such as Alfa Laval to find a suitable heat exchanger, but sadly prices are not provided.

The total chiller cost for both small and large scale (at 1000 L/hr) is then approximately €3000, or about €8400 if the chiller heat exchanger ends up not having the right characteristics. For 300 L/hr manure, this cost will only be slightly smaller at €2000 and €7000.

6.1.2 Flash Drum and Water Tank

From the detailed cost estimation section, a cost estimation was made which can directly be copied here. Flash drums meant to be used for air/oil separation can be had for as little as 50 USD, which with a "pressure vessel" installation factor of 4 would cost €166. This would be the large scale production and a suitable unit would need to be sourced capable of vacuum rating. For small scale/single production, an industrial grade 5 L vacuum-rated reservoir with the ports in the right locations to serve as a flash drum has been sourced for €155 including shipping in the Netherlands [104]. With a similar installation factor of 4, this would be €620. For both 300 and 1000 L/hr manure inputs, these costs are approximately the same, as the components are already very likely larger than necessary and smaller sizes will have only marginal cost savings, if available at all.

For the water tank right below the flash drum, as it is very similar in size, purpose and requirements, the same 5 L stainless vacuum will be sourced. With a small maximum hourly water flow of up to 12 L/hr (or 3.6 L/hr at 300 L/hr manure), this water tank will only need to be emptied once every 25 minutes (or 83 minutes at 300 L/hr) using automatic valves. For mass production, a smaller custom made tank that empties more frequently would likely be most suited and although no exact price can be given, in Asia companies make small production runs (50 units or more) of custom to-order stainless steel containers "from €20 onwards" (e.g. Jiangmeng Yoco Co. Ltd.). This would eventually be in-line with the mass produced air/oil separator as flash drum above.

The total cost would then be about €330 mass produced, or €1240 for small-scale production.

6.1.3 Storage Tanks

For the storage tanks, not every single tank will be costed individually, as most likely it will vary per farm and their requirements/wants. Thus, instead a total volume will be costed, as the total volume of output produced is roughly independent of which choice is made (up to 90 m^3/month at 1000 L/hr or 27 m^3/month at 300 L/hr manure).

The costing document provided by the supervisors already noted that 3 large containers of 20-50 m^3 each would cost €20,000 in total, resulting in a total size of 60-150 m^3. This should be sufficient for about 1.5 months at 1000 L/hr or 5 months at 300 L/hr manure, which should be enough time to use everything on land or to sell it. After all, to sell it wholesale, it would be sold by the truckload, which is typically 25-30 m^3, so the 60-150 m^3 storage allows for a truckload's worth of storage of a few different outputs. To check with this paper's initial estimate, from the detailed cost analysis, new UN-certified 1000 L IBCs are €155 each, which means the €20,000 can buy 129 IBCs (=129 m^3), which is about the same size. Thus, the €20,000 estimate is good for both small and large scale, since the storage containers are already mass produced.

6.1.4 Valves, Piping and Electronics

All the costing mentioned previously already include installation factors, so additional piping costs are not necessary. However, the valves may not be included. Essentially every IBC has its own valve built in already, but the 3-way and 2-way solenoid valves should still be costed. In total there are 2 3-way solenoid valves and 2 2-way solenoid valves. After further investigation, no small

3-way stainless steel solenoid valves could be found that were equally or more cost-effective than the 2-way solenoid valves, but one can simply make one themselves by using 2 2-way solenoid valves and a T-junction piping. Thus, in total 6 2-way solenoid valves are used. Taking the previously mentioned €20 per solenoid valve cost (which is the same for both 1000 and 300 L/hr as this smallest common unit is already larger than required), this would amount to €120. Adding a miscellaneous installation factor of 2.5 (for additional wiring/connectors), this comes to €300.

Furthermore, a control unit needs to be included. Fortunately, the BPMED is electronically controlled too, so a computer is already available to run the control unit and activate the solenoids. A program should also be made so that the farmer can simply put in their desired NPK value and the computer calculates which valves should open when. This should be a relatively simple program to create, with the cost ranging from almost €0 if it is made by a student and spread out over mass production, to perhaps a few thousand euros if made by a professional that runs into some problems (e.g. 50 hours at €50 /hr = €2500). After consulting with the supervisors, this programming cost is already included in the capital cost of the BPMED unit, so this will not need to be costed separately.

6.2 Operating Expenditures and Revenues

In this part, the operating expenditures and revenues will be mentioned. First, the hourly rates of all components will be mentioned (for consistency throughout the report) and then at the end it will be converted to an annual basis, in line with the document provided by the supervisors. All of these operating expenditures scale linearly with size, so both 1000 L/hr manure values and 300 L/hr manure values will be given.

6.2.1 Cooler/Chiller Electricity Cost

The sourced unit has a 10.46 kW cooling capacity and only consumes about 3 kW of power. However, only 8.18 kW is required in the 'worst case' scenario where the most ammonia water is produced. Scaling this 3 kW down results in 2.35 kW. Then, assuming solar power is used on the farm which would otherwise be sold at a price of €0.065 /kWh (mentioned in the detailed technology evaluation), the net effective cost is up to €0.153 /hr at maximum production (or half that at the lower ammonia production). For the 300 L/hr manure stream this would then be €0.0458 /hr.

6.2.2 Valve Electricity Cost

Although the value is likely to be negligible, it is still useful to quickly consider. For the very small units, no power consumption data could be found, however, slightly larger units were found with a constant power consumption of around 4 W. For the 6 2-way valves this amounts to 24 W, or about €0.0016 /hr or €14 /yr, which is indeed negligible.

6.2.3 Vacuum Pump Electricity Cost

Although a vacuum pump is included in the costing provided by MEZT, the pumping power requirement itself is not included. Since there is a realistic chance that this power requirement could be significant, this is investigated.

At a constant state, essentially the vacuum pump is pumping 2 kPa vacuum conditions to 100 kPa ambient conditions. For this the combined gas law formulae can be used to approximate the energy requirements, assuming ideal gas conditions.

First, taking the values calculated earlier (19.1 kg/hr at 0.0145 kg/m^3 = 1317 m^3/hr = 366 L/s), and the simple $PV = nRT$ formula, one can say that when the pressure increases by a factor of 50 (2 to 100 kPa), the volume would decrease by a factor of 50, leading to 7.318 L/s. The molar mass flow is also needed. The molar mass of water and ammonia is very similar (17.03 vs 18.01 g/mol), so since water is the largest component, water molar mass will be assumed. At 19.1 kg/hr or 5.3055 g/s, this equates to 0.2946 mol/s. Now, assuming the process is roughly isothermal, the following equation can be used [105].

$$W = n * R * T * ln(V_2/V_1)$$

Filling this equation in with n = 0.2946 mol, R = 8.314, T = 288 K, Volumes of 7.318 and 366 L gives a work done of 2,760 J, which since this is per second, is equal to 2.76 kW. In reality, the process is likely closer to adiabatic than isothermal, as the vacuum pump works fairly fast, thus not allowing much heat transfer to the environment (see figure 24). In that case the power requirement would be different. Although this could be calculated manually, this is not as simple, but fortunately an online calculator exists for this, specifically for water vapour and allowing the exact conditions to be entered [105]. For isobaric conditions, this results in a power requirement of 3.66 kW. This calculator can also calculate the isothermal energy requirement, which comes to 2.85 kW, which is very close to the 2.76 kW calculated manually. Thus, it can be considered as fairly reliable.

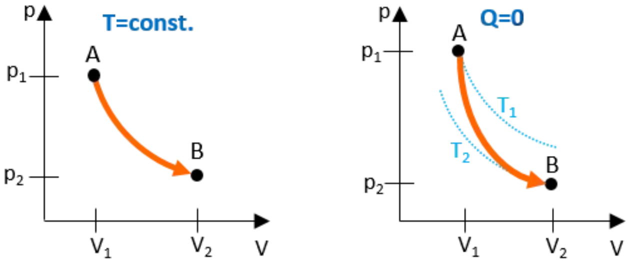


Figure 24: Isothermal versus Adiabatic pressure and volume changes [105]

Overall, between the 2.76 kW and 3.66 kW, the 3.66 kW will be assumed, as the vacuum pump is not 100% efficient. Multiplying this value with the €0.065 /kWh electricity price results in €0.238 /hr, which is roughly similar to the cost of cooling. All these calculations are for 1000 L/hr, but for 300 L/hr manure it simply scales down to 1.1 kW and €0.0793 /hr, or about €636 /yr.

6.2.4 Sale of (or Net Savings from Purchasing) the Final Products

The ingredient costs and savings were already mentioned in the *Process Design and Modelling* section, so they will not be repeated here. However, to very briefly summarize, the net ingredient revenue stream can range from roughly €1-5 /hr (at 1000 L/hr) or €0.3-1.5 /hr (at 300 L/hr) depending on which streams are desired and the eventual concentration (output) of the BPMED. Unfortunately, the range is rather wide as the output of the BPMED has both a varying flow rate (varying by a factor of 2) and a varying concentration (also varying by a factor of 2), so that the eventual ingredient revenue spread varies by a factor of 5 is not unusual.

There is also a minor additional savings from the 6-12 L/hr of water that is returned to the BPMED as it reduces the 100-200 L/hr fresh water requirement. This may not be a lot on an hourly basis (about €0.01 /hr), but on a yearly basis it can be significant enough to recycle (€44-87 /yr at a water price of €0.83/m^3 [106]). For 300 L/hr, this is of course slightly less: €13-26 /yr.

6.3 Overall Evaluation

Overall, all these costs included, the total additional initial cost (excluding €20,000 for storage) could vary quite significantly. For large scale production, the cost can be as low as €2,630 per unit for 300 L/hr and €3,630 for 1000 L/hr. For small scale production, the initial cost can potentially be as high as €8,540 for 300 L/hr or €9,940 for 1000 L/hr if an additional heat exchanger is required in both cases. As evident from the cost distribution in figure 25, the big difference is in if the additional heat exchanger is required or not and besides that the cost is actually quite consistent. For the sake of rather overestimating than underestimating the cost, a higher-end cost of €9,000 will be assumed and the rest of the table will be largely independent of small- and large-scale production.

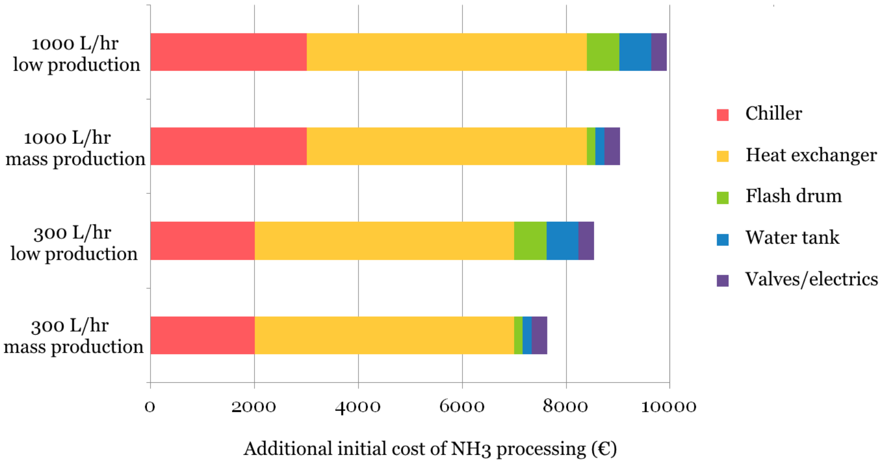


Figure 25: Overview of the additional initial cost of ammonia processing for each circumstance

Similarly, the total operating costs and revenues are (almost, with the exception of valves and electronics which is practically negligible) independent of scale as product sale and energy/water prices are consistent on the market. Adding all operating costs and revenues from before (at 1000 L/hr) comes to about €0.6-4.6 /hr (-€0.3826 /hr energy & water costs and +€1-5 /hr net ingredient sale), depending on the eventual final conditions and choices. Similarly, for 300 L/hr this would be €0.2-1.4 /hr. Taking the document given by MEZT, all capital and operating expenditures and revenues for the 300 L/hr manure, and any modifications to the data into consideration, it all culminates to form the newest up to date economic evaluation in table 7.

Table 7: Complete overview of MEZT system costing and revenues at 300 L/hr manure

COMPONENT	**CAPEX**	**OPEX /yr**	**NOTES**
Prefab urine/manure catchment	€ 22,500	€ 650	
Thick-thin separator & piping	€ 42,500	€ 3,500	for 2 m3/hr
Drum filter	€ 10,000	€ 500	for 5+ m3/hr, with filters
Buffer basement for thin fraction	€ 6,000	€ 0	
MEZT ED, BPMED unit & original VMS	€ 200,000	€ 25,000	for membranes (1x per 2 yrs)
		€ 500	water usage (500 m3/yr)
		€ 650	vacuum pump cost (1.1 kW)
MEZT container, isolated, air-conditioned	€ 16,000	€ 250	
Extra solution to process NH3 (this paper)	€ 9,000	€ 400	OPEX for cooler and valves
Buffer for raw mineral concentrates	€ 20,000	€ 0	20-50 m3 silo 3x or IBCs
Fertilizer mixer, piping and H2SO4 storage	€ 3,000	€ 250	OPEX: mixing power cost
		€ 2,000	OPEX: H2SO4, 5.5m3/yr
Buffer/storage for processed outputs	€ 20,000	€ 0	also 20-50 m3 x3
Total	€ 349,000	€ 33,700	
Including unforeseen costs	€ 383,900	€ 35,385	10% (CAPEX), 5% (OPEX)
Including project management	**€ 422,290**	**€ 37,154**	10% (CAPEX), 5% (OPEX)

Original manure disposal volume (m3/yr)	2,409	300 L/hr, 22 hrs/day
Manure disposal cost per m3	€ 16.60	€10-25 /m3
Original disposal cost without MEZT	€ 40,000	€ 10,000 remains afterwards

LIFETIME COSTS PER YEAR	**No SBV**	**With SBV**	**Notes**
Depreciation over 7 years	€ 60,327	€ 30,164	50% subsidised by SBV
Interest payments (at 5%)	€ 21,115	€ 10,557	50% subsidised by SBV
Feedstock electricity and misc. water	€ 1,500	€ 1,500	independent of subsidy
Maintenance, calibration, all above costs	€ 37,154	€ 26,008	30% subsidy: Phase 3 SVB
Total CAPEX & OPEX	€ 120,096	€ 68,229	
Total CAPEX, OPEX & disposal costs	€ 160,096	€ 108,229	
Costs / m3	**€ 49.85**	**€ 28.32**	
Costs including disposal / m3	**€ 66.46**	**€ 44.93**	

REVENUES PER YEAR	**Assumption**	**Amount**	**Notes**
Reduction in manure disposal costs	75%	€ 30,000	24-60K range
Reduction fertilizer purchase & output sale	-	€ 7,800	3.6-12.0K, varies per process
Reduction in cattle feed	5%	€ 15,000	
Reduction in saw dust	50%	€ 7,500	5-20K
Reduction in cow illness & medical costs	20%	€ 10,000	50K at 100%
Total revenues per year		€ 70,300	
Total revenues /m3		**€ 29.18**	

New Disposal cost after MEZT /m3	**€ 37.28**	**€ 15.75**	Positive means costs
Savings on disposal costs /m3	**- € 20.67**	**€ 0.85**	Positive means savings
Savings per year after investment	**- € 49,796**	**€ 2,071**	Positive means savings

Within this table, many values were not previously mentioned in this paper as they were outside the scope until now. Those values have been double-checked (see appendix C in case there is any doubt on these numbers) and minor changes were made where necessary to ensure they are still accurate and logical. Also, please note that the table assumes 22 hour per day operation, 365 day operation. The 2 hours a day is for eventual downtime to clean and maintain the system.

As evident, the additional initial investment and operating costs required for ammonia processing described in this paper is relatively small, especially compared to some of the equipment that needs to be custom made, such as the ED and BPMED unit at €200,000. This bodes well for the chosen ammonia processing system in this paper, but the very high custom equipment cost is not good for the overall costing.

In fact, assuming a disposal cost of €16.60 $/m^3$ from before the entire MEZT system is implemented, the new disposal cost is above €37 without any subsidies, but just €15.75 $/m^3$ with subsidies, which represents a €0.85 $/m^3$ savings. This is barely positive, but on an annual basis it still represents a net savings of €2,048. What one should also consider is that certain revenues are not included because they are unavailable at this moment, such as the sale of emission rights (which will be affected by the newer Dutch regulations coming next year) and the effect/value of having a good image (e.g. a 'green' label on milk can give a farmer a revenue of €0.01 /L), which on an annual base can be very significant in a positive way.

Nonetheless, purely looking at it from an economic standpoint from this table, one might say that although the MEZT system is still profitable, a farmer may also want to consider other more profitable alternatives. However, another way of looking at it is that a farmer can now vastly reduce their emissions at no additional cost to them, which could push them towards adopting the MEZT system anyway.

Also, in the future, if the Dutch government does actually consider reducing livestock due to nitrogen emissions, then implementing the MEZT system would also reduce emissions, thus allowing a farmer to retain more of their livestock. This in turn would also bring in/save a considerable amount of money.

Yet another perspective is that with depreciation set at 7 years, the savings are very close to zero, meaning that 7 years is approximately the break-even point. This 7 years is about in line with other 'green' solutions such as solar panels, which are now widely adopted by many farmers. Similarly to solar panels then, after the 7 years there is no more depreciation or interest payments, which would result in a new manure disposal cost of - €1.16 $/m^3$, representing a savings of €17.763 $/m^3$, or about €42,800 for the 2,408 m^3 of manure processed per year. At that point the solution is very lucrative. Now, this does not take into account the additional maintenance and repair that comes with an older machine, but assuming there are no significant breakdowns, this is a good solution. Thus, an overall recommendation can be made to proceed with the MEZT system.

6.4 Quick Sensitivity Analysis

To check if the recommendation to proceed is true for most cases, a quick cost sensitivity analysis is made by varying the inputs of the updated excel file and looking at their effects on savings.

- **Disposal Cost**: Currently set at €16.60 $/m^3$, but can range from €10-25 $/m^3$ in practice. At €10 $/m^3$, the savings are -€4.09 $/m^3$, whereas at €25 $/m^3$, the savings are €7.16 $/m^3$. This is a large variance in profitability and the disposal cost really affects if this solution should be used or not. The break-even point is at a disposal cost of about €15.50 $/m^3$, so it can be said that as long as a farmer pays more than that currently, their savings will be positive during the depreciation period (with the default 'average' values in the excel file).
- **Depreciation Period**: Currently set at 7 years. If this time is decreased to 5 years, savings will be - €4.15 $/m^3$ (costs more money), but at 10 years the savings are €4.62 $/m^3$ and at 15 years €7.54 $/m^3$. Thus, a farmer would want a depreciation period of more than the current 7 years, but not too long as at one point the savings will plateau due to interest payments.
- **CAPEX and OPEX**: Both have a direct effect on the annual costs and revenues per m^3, so they can be investigated as one. Currently there's already a 10% 'unforeseen' cost included in CAPEX and 5% in OPEX. If the total CAPEX is increased by 10%, the new savings is - €0.83 $/m^3$, whereas decreasing it by 10% results in savings of €2.55 $/m^3$. Similarly, increasing or decreasing the OPEX by 10% results in savings of - €0.22 and €1.94 $/m^3$ respectively, which both are a smaller difference. Thus, a 10% change in CAPEX has a larger effect than OPEX and the focus in the future should be on reducing this initial investment cost.
- **Revenues**: Besides CAPEX and OPEX, these should not be forgotten. A 10% increase results in savings changing to €3.78 $/m^3$, whereas a 10% decrease results in savings of -€2.06 $/m^3$. This is in fact a larger effect than CAPEX, meaning that an accurate estimation of the revenues is very important. Overall then, the focus to improve on ranked from highest to lowest is Revenues, then CAPEX, and then OPEX.

A graphical overview which summarises the above points can be found in figure 26. The plateauing effect of the depreciation period and the linear nature of the other factors can clearly be seen.

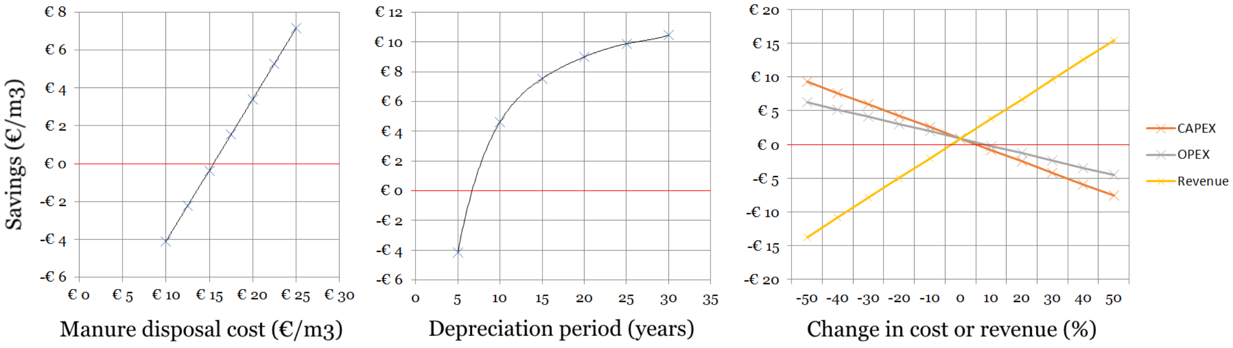


Figure 26: Graphical overview of the sensitivity analysis

6.5 Scaling Up to 1000 L/hr

For the previous section the 300 L/hr was assumed as all equipment has been costed fairly accurately by MEZT for that amount, but is also possible to roughly estimate the cost and revenue overview for 1000 L/hr through scaling. For this, scaling laws can be used, which can be applied to each individual component. The scaling law is as followed [107].

$$C_2 = C_1 * (S_2/S_1)^n$$

Here, C_2 is the new cost at 1000 L/hr, C_1 is the old cost at 300 L/hr, (S_2/S_1) is the ratio of new over old manure flow rate (1000/300) and n is the scaling exponent. A value for n below 1 indicates economies of scale (for larger components) is present and according to Sinnott and Towler, it can be as low as 0.4-0.5 for specialty chemical manufacture, 0.7 for typical petrochemical processes, or as high as 0.8-0.9 for processes using a lot of mechanical work, such as mixers or gas compression [107]. Thus, $n = 0.9$ will be used for mechanical parts, $n = 0.7$ will be used for more 'normal' processes and structure-related costs ($n = 0.7$ was also mentioned for storage tanks for example) and $n = 0.5$ will be used for the more specialised, complex parts, such as the BPMED.

These chosen values are on the high (pessimistic) side and compared to other examples online, all these exponents could potentially be lowered by around 0.1-0.2 [108], but for the sake of rather overestimating than underestimating the costs for the first production series, they will be kept as-is for now. After all, it will be easy for MEZT to adjust these values in the future when more is known and as one will see, the conclusion of this paper will not change because of it.

Furthermore, for the BPMED there is certainly still a learning curve and the price per unit will most likely decrease over time as more is known about the process and as improvements are made (i.e. the technology matures). However, practically all other parts (construction, filter, thick-thin separator, etc.) are already at or close to the end of the learning curve. Because of this, no learning curve will be implemented for the sake of simplicity and because it would be very difficult to put a specific number/exponent on it. Nevertheless, it is something for MEZT to keep in mind.

Combining all this, in table 8 a newer overview of the overall MEZT system costing and revenues can be found for 1000 L/hr manure, including the scaling exponent applied to each costing component. Please note that the OPEX costs scale linearly, so they have no exponent (or essentially an exponent of 1).

As evident, scaling up the capital expenditures is non-linear, getting cheaper per L/hr manure capacity as size increases. However, the revenues and operating expenditures do scale linearly with size (including costs such as membrane replacement, as doubling the size requires double the membrane area, thus double the number of membranes to be replaced), thus showing no decrease in revenues per m^3.

In the end, as evident from both the quick cost analysis and from table 8, the larger size results in greater savings, both per m^3 (€6.99 vs €0.86, subsidised) and per year (€56,150 vs €2,070). Thus, the MEZT solution is (significantly) more lucrative for farms with larger manure disposal quantities.

Table 8: Complete overview of MEZT system costing and revenues at 1000 L/hr manure

COMPONENT	**CAPEX**	**OPEX /yr**	**CAPEX SCALING EXPONENT (n)**
Prefab urine/manure catchment	€ 58,950	€ 2,167	0.8
Thick-thin separator & piping	€ 125,597	€ 11,667	0.9
Drum filter	€ 23,228	€ 1,667	0.7
Buffer basement for thin fraction	€ 13,937	€ 0	0.7
MEZT ED, BPMED unit & original VMS	€ 365,148	€ 87,166	0.5
MEZT container, isolated, air-conditioned	€ 37,165	€ 833	0.7
Extra solution to process NH3 (this paper)	€ 16,432	€ 1,333	0.5
Buffer for raw mineral concentrates	€ 46,456	€ 0	0.7
Fertilizer mixer, piping and H2SO4 storage	€ 7,860	€ 7,500	0.8
Buffer/storage for processed outputs	€ 46,456	€ 0	0.7
Total	€ 741,230	€ 112,333	
Including unforeseen costs	€ 815,353	€ 117,950	
Including project management	**€ 896,889**	**€ 123,848**	

Original manure disposal volume (m3/yr)	8,030	1000 L/hr, 22 hrs/day
Manure disposal cost per m3	€ 16.60	€10-25 /m3
Original disposal cost without MEZT	€ 133,333	€ 33,333 remains

COSTS OVER LIFETIME	**No SBV**	**With SBV**	**Notes**
Depreciation over 7 years	€ 128,127	€ 64,063	50% subsidised by SBV
Interest payments (at 5%)	€ 44,844	€ 22,422	50% subsidised by SBV
Feedstock electricity and misc. water	€ 5,000	€ 5,000	independent of subsidy
Maintenance, calibration, all above costs	€ 123,848	€ 86,693	30% subsidy: Phase 3 SVB
Total CAPEX & OPEX	€ 301,819	€ 178,179	
Total CAPEX, OPEX & disposal costs	€ 435,152	€ 311,512	
Costs / m3	**€ 37.59**	**€ 22.19**	
Costs including disposal / m3	**€ 54.19**	**€ 38.79**	

REVENUES PER YEAR	**Assumption**	**Amount**	**Notes**
Reduction in manure disposal costs	75%	€ 100,000	80-200K range
Reduction fertilizer purchase & output sale	-	€ 26,000	12-40K, varies per process
Reduction in cattle feed	5%	€ 50,000	
Reduction in saw dust	50%	€ 25,000	16.6-66K
Reduction in cow illness & medical costs	20%	€ 33,333	166K at 100%
Total revenues per year		€ 234,333	
Total revenues /m3		**€ 29.18**	

New Disposal cost after MEZT /m3	**€ 25.01**	**€ 9.611**	Positive means costs
Savings on disposal costs /m3	**- € 8.40**	**€ 6.993**	Positive means savings
Savings per year after investment	**- € 67,486**	**€ 56,154**	Positive means savings

NOTE: In the 2 cases with $n = 0.8$, the component consisted of approximately half mechanical ($n = 0.9$) and half 'normal'/structural ($n = 0.7$) costs.
NOTE 2: Due to scaling, this cost/revenue overview is likely less accurate than at 300 L/hr.

7 Conclusion and Recommendations

7.1 Conclusion

To reiterate, the original problem statement is as followed, which can essentially be split up into two separate parts: identifying and evaluating all relevant ammonia processes and (financially) working out the final chosen process.

> *Within the context of farms and MEZT's BPMED process, what is the best ammonia recycling process and usage and is it financially feasible?*

To conclude for the first part, it can be said with confidence that the best solution was chosen for a farmer's context. By first identifying all major uses for ammonia, even some lesser known uses were considered and no major usages were left out. From here, the usages that were impractical or not useful for a farmer were discarded and remainder were thoroughly investigated on 9 scoring criteria (Maturity/Feasibility, Process Profitability, Initial Costs, Reliability & Maintenance, Ease of use, Environmental Impact, Safety, Scalability and Compactness).

There were two clear winners from the scoring matrix, being wholesale ammonia and ammonium sulphate, but due to the relatively high estimated profitability of enriched biochar, it was investigated further despite having a lower score in the matrix. Wholesale ammonia could be tapped from one of either the enriched biochar or ammonium sulphate stream, so a distinction had to be made between enriched biochar and ammonium sulphate. Therefore, the key differences were investigated for manure disposal costs, upcoming RENURE regulations, grant and subsidy differences, legality of using both substances, and the combination of using it with other streams of the MEZT process (most notably potassium). From this, ammonium sulphate remained as the best solution.

Combining this, the final process was designed. Here, perhaps somewhat out of the scope of the initial assignment, the potassium stream was also investigated and included as it was also part of the input stream. From that, turning potassium into potassium sulphate was shown to be a good solution, but a detailed usage analysis like that of ammonia was not made. The final process ended up being a flexible solution of making ammonium sulphate, potassium sulphate, their (raw) mineral concentrates and aqueous ammonia. This solution of providing multiple options allows for the most flexibility depending on a farmer's needs (the outputs can be combined to give varying NPK-ratings for example), while having minimal additional costs and the ability to 'cut out' unwanted parts/processes in case a farmer only wants certain streams. Additionally, although not explicitly stated, the final solution also has many of the high scoring benefits of the scoring matrix, such as good safety, scalability, etc.

Thus, it can be concluded with a fairly high level of confidence that this is the best ammonia recycling process for a farmer, given the MEZT solution train.

To answer the second main part of the research objective (the financial feasibility), a short process profitability and initial cost evaluation of all investigated processes was already made during the scoring of the matrix to ensure that whatever final process was chosen would be a good financial decision. Then, once the final choice was chosen, a more detailed economic evaluation was made. All required equipment for the ammonia processing was identified and costed using online sources, taking installation factors into consideration, and the more detailed operational costs and revenue streams were identified. The initial costs were also estimated for small scale and large scale production in case MEZT is going to produce many of their units. However, as was quickly discovered, not only does the cost of the additional process to process the ammonia scale little with size, it is much cheaper than the rest of the MEZT solution train, so focus should be on reducing the cost of the rest of the solution train.

After the ammonia processing part was evaluated, an initial costing and revenues document from MEZT was provided which contained values for the rest of the MEZT system at a manure flow rate of 300 L/hr for their pilot setup. However, in the future full size systems at a flow rate of 1000 L/hr are planned, but the costing was unknown. Thus, a final overall costing and revenues table was created first for the 300 L/hr manure flow rate and then, using scaling factors, the future 1000 L/hr manure flow rate costs and revenues were estimated. The excel file MEZT provided was also updated to automatically adjust to different manure flow rates, manure disposal costs, depreciation periods, loan interest rates and scaling factors.

The conclusion of the financial evaluation part is that at the 300 L/hr manure flow rate and at average/middling values, the MEZT solution train was just barely profitable over the lifetime of the system. This still leads to a positive recommendation as it means a farmer with the MEZT system transforms from being a 'dirty' farmer to a 'clean' farmer at no additional cost. Moreover, the sale of emission rights and having a 'good image' was not even included as those values are extremely difficult to predict with the upcoming regulation changes in the Netherlands, but they certainly add further positive value. Also, after the equipment has been depreciated/written off, without the depreciation and interest costs, the MEZT system would more than completely eliminate manure disposal costs, given that the system does not experience unusually high repair/maintenance costs at the end of its life.

Naturally then, at the 1000 L/hr manure flow rate, the initial costs scaled non-linearly, but revenues did and thus the profitability was higher, making the MEZT solution even more lucrative. Thus, although there may be a few cases for some farmers where the MEZT solution is not financially profitable (e.g. a farmer with a very low manure flow rate and low disposal costs), for most situations of large-scale farms the MEZT solution can be both profitable and good for the environment, and thus the recommendation can be made for MEZT to proceed with developing their system.

7.2 Difficulties/Limitations

Nonetheless, despite the overall positive outcome, this project was not without its difficulties and limitations. The major ones are listed below in no particular order, but fortunately most issues were resolved and do not negatively affect the outcome of this paper.

- In the end, due to the new and broad nature of this topic, it was at times difficult to make very accurate estimations (especially for the costing data) as data is not always readily available, so for each individual analysis point, it may not be 100% accurate. However, for the purpose of this paper it was still accurate enough and since multiple sources/methods were always checked, the final choice and financial evaluation can be considered to be reliable.
- Similarly, time is also a limitation. In many cases only a rough estimation was made or predicted for a certain value, since the full accurate calculation would be long enough to be its own small paper. For example, for estimating the required heat exchanger, it *should* be an iterative process of designing the heat exchanger down to the individual pipes/layers and materials and estimating the heat transfer based on that, but in this paper only a simple 'one step' calculation is made. This is because in this paper it is just one point to analyse out of many points. Nonetheless, even with just one step, the rough estimations are roughly right, so although accuracy may be mediocre at times, reliability can be considered to be high.
- Many biases such as measurement error, omitted variables bias, amongst others, are highly unlikely to be present and can even be considered irrelevant due to the nature of this assignment. However, the one bias that could potentially be present is self-selection bias during the selection of the final process. Fortunately, this is still unlikely to be present due to the analytical nature of selection and usage of numerical values where possible to make the evaluation of technologies.
- Another limitation of this paper is caused by the large variance of the streams. As mentioned previously there is a fluctuation in flow rate and concentrations of the streams (both by a factor of 2), meaning that the output can vary significantly. In this paper, equipment was costed for the worst case scenarios, meaning that some cost savings are potentially left on the table. Similarly, for profitability the average values were taken, but if the output flow rates and concentrations are at the low end or high end it could have a significant impact on the profitability. Unfortunately, the only way to resolve this is to experiment further and/or measure the actual values on a prototype/pilot system.

7.3 Recommendations & Further Research

Finally, a few recommendations can be made for MEZT to look further into, where many are also a point of future research on this topic.

As mentioned before, one recommendation would be to investigate if the chiller actually works with the vacuum ammonia-water stream in practice. As mentioned previously, the heat transfer capabilities and material requirements should be sufficient, but a chiller is technically not made for vacuum pressures and perhaps more importantly, it's not made for gaseous conditions. Although advanced modelling and simulation would be possible, trying this out in practice on the pilot scale would be the quickest way to test this. In this paper the worst case scenario (including a heat exchanger) was used in the costing, but the additional heat exchanger accounts for more than half of the cost of the additional ammonia processing system. Thus, significant potential cost savings are at play.

Another recommendation, which is also a point of future research, is on the (enriched) biochar. On a farm scale, enriched biochar was shown to not be an optimal solution, but on a larger (central processing) scale it may have great potential. Thus, if MEZT wishes to diversify or expand their business, it would be interesting to further investigate/research the biochar process for a larger scale. Perhaps a deal could even be struck to buy manure from current MEZT system-holders at a marginally reduced price, since the MEZT process already extracts a lot of moisture making the torrefaction and pyrolysis process easier and more efficient (since less heat is used to evaporate water), thus creating a win-win situation.

Furthermore, in this paper strictly the mechanical and financial aspects were investigated and it has shown to be a good venture. However, the effect of implementing the MEZT system on many farms was not investigated. More specifically, a detailed stakeholder analysis could help MEZT estimate how well the system will be adopted by society, by identifying potential social or regulatory hurdles, and perhaps even identifying competitors. Similarly, some form of policy analysis could also prove to be helpful, since currently the profitability of the MEZT system relies heavily on subsidies and any changes to the national (or European) policy could significantly affect the adoptability and profitability.

Also, the safety was briefly touched upon in the overall scoring of the individual processes, but it was not done for the final process. Although the process is very similar to the only ammonium sulphate process from the scoring matrix and no major safety issues are expected, a more in-depth safety analysis could be useful just in case.

Finally, perhaps somewhat obvious and easier said than done, one big recommendation is to try and somehow reduce the capital cost of the current BPMED setup. Currently it is by far the largest cost component and has a huge effect on profitability. Reducing the cost (via economies of scale or even just advancements in technology over time) would make the MEZT system more lucrative to farmers.

Overall, even with some limitations and points for future investigation, the conclusion and recommendation is given to proceed with the development of the MEZT solution train and to work towards a greener and more sustainable future.

References

[1] Tamme van der Wal, “Precision farming could help reduce climate gas emissions,” March 2018. [Online]. Available: https://www.futurefarming.com/Smart-farmers/Articles/2018/3/Precision-agriculture-helps-reduce-climate-gas-emissions-266218E/

[2] US Environmental Protection Agency, “Agriculture sector emissions,” 2019. [Online]. Available: https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions

[3] NOS News, “Stikstofcrisis raakt veel meer bedrijven: ’onze frustratie is enorm,” October 2019. [Online]. Available: https://nos.nl/collectie/13799/artikel/2306987-stikstofcrisis-raakt-veel-meer-bedrijven-onze-frustratie-is-enorm

[4] Rijksoverheid RIVM, “Herkomst stikstofdepositie, 2018,” November 2019. [Online]. Available: https://www.clo.nl/indicatoren/nl0507-herkomst-stikstofdepositie

[5] Piet Hermus, “Halveer de autostapel en sluit schiphol,” March 2021. [Online]. Available: https://www.nieuweoogst.nl/nieuws/2021/03/30/halveer-de-autostapel-en-sluit-schiphol

[6] Peter Winterman, “D66 wil veestapel halveren: drastische afname stikstofuitstoot,” September 2019. [Online]. Available: https://www.ad.nl/politiek/d66-wil-veestapel-halveren-drastische-afname-stikstofuitstoot~a7872ea4/?referrer=https%3A%2F%2Fwww.google.com%2F

[7] Kate Whiting, “These dutch tomatoes can teach the world about sustainable agriculture,” November 2019. [Online]. Available: https://www.weforum.org/agenda/2019/11/netherlands-dutch-farming-agriculture-sustainable/

[8] Adriaan Lieftinck, & Edward Sibeijn, “Mezt, on farm circular operating model,” March 2021.

[9] P.W. Atkins et. al., *Shriver and Atkins Inorganic Chemistry*, 5th ed. New York: W. H. Freeman and Company, 2010.

[10] Lehigh University, “Electrochemically-produced ammonia could revolutionize food production,” July 2018. [Online]. Available: https://phys.org/news/2018-07-electrochemically-produced-ammonia-revolutionize-food-production.html

[11] Nico Verdoes et. al., “Overzicht en beoordeling van technologie voor verwaarden van mest,” in *rapportage WP 2 NL Next Level Mestverwaarden.* Wageningen University & Research, 2021, pp. 53–55.

[12] Tobias Opschoor, “Private meeting on how the process works and boundary conditions,” April 2021.

[13] Vasileios Rizos et. al., “Composition and drivers of energy prices and costs in energy intensive industries,” *CEPS Special Report*, vol. 85, no. Chp.2, pp. 19–20, 2014.

[14] New York State Department of Health, “The facts about ammonia,” May 2005. [Online]. Available: https://www.health.ny.gov/environmental/emergency/chemical_terrorism/ammonia_tech.htm#:~:text=About%2080%25%20of%20the%20ammonia,pesticides%2C%20dyes%20and%20other%20chemicals.

[15] Dawna Winkler, & Kerri B. Harris, *Antimicrobial Interventions for Beef.* College Station, Texas: Department of Animal Science, Texas A&M University, 2009.

[16] Ahmed Afif et.al., “Ammonia-fed fuel cells: a comprehensive review,” *Renewable and Sustainable Energy Reviews*, vol. 60, no. 1, pp. 822–835, 2016.

[17] Barbara Demeneix, “Ammonium nitrate and iodine: a look back at the explosive history of two essential substances,” October 2020. [Online]. Available: https://theconversation.com/ammonium-nitrate-and-iodine-a-look-back-at-the-explosive-history-of-two-essential-\substances-146448#:~:text=A%20mixture%20of%2094%25%20porous,terrorist%20attacks%2C%20but%20also%20legally.

[18] J. S. Kim, Y. Y. Lee, & S. C. Park, “Pretreatment of wastepaper and pulp mill sludge by aqueous ammonia and hydrogen peroxide,” *Applied Biochemistry and Biotechnology*, vol. 84, no. 1, pp. 129–139, 2000.

[19] Water Quality Association, “Ammonia in drinking water,” 2021. [Online]. Available: https://www.wqa.org/learn-about-water/common-contaminants/ammonia#:~:text=Ammonia%20in%20Drinking%20Water&text=Ammonia%20has%20been%20used%20in,chlorine%20added%20to%20drinking%20water.&text=Partial%20adsorption%20of%20chloramines%20(from,by%20GAC%20may%20liberate%20ammonia.

[20] Murli Dharmadhikari, “Nitrogen metabolism during fermentation,” 2021. [Online]. Available: https://www.extension.iastate.edu/wine/nitrogen-metabolism-during-fermentation

[21] Yukio Watanabe et.al., “Construction of engineered yeast producing ammonia from glutamine and soybean residues (okara),” *AMB Express*, vol. 10, no. 70, 2020.

[22] A. Włochowicz, & E. Stelmasiak, “Change in thermal properties of wool after treatment with liquid ammonia,” *Journal of thermal analysis*, vol. 26, pp. 17–22, 1983.

[23] Dave Rule et.al., *ASHRAE Position Document on Ammonia as a Refrigerant*, 1st ed. Atlanta, Georgia: ASHRAE, 2017.

[24] Janice Del Mar, “Why is distillation not a viable way to separate ammonia from water?” May 2012. [Online]. Available: https://chemistry.stackexchange.com/questions/174/why-is-distillation-not-a-viable-way-to-separate-ammonia-from-water

[25] Environmental Protection Agency, *Wastewater Technology Fact Sheet: Ammonia Stripping.* Washington DC: Office of Water, 2000.

[26] ChramChem, “Mezt research project: Contract research (confidential),” April 2021.

[27] Engineering ToolBox, “Ammonia thermophysical properties,” 2008. [Online]. Available: https://www.engineeringtoolbox.com/ammonia-d_1413.html

[28] B. Qiu et.al., “Simultaneous recovery of phosphorus and nitrogen from liquid digestate by vacuum membrane distillation with permeate fractional condensation,” *chinese journal of chemical engineering*, vol. 28, no. 6, pp. 1558–1565, 2020.

[29] Schippers Bladel BV, “Ammoniak 25%, 18 kg,” 2021. [Online]. Available: https://www.schippers.nl/--2509675.html?channable=00847f696400323530393637355c&gclid=CjwKCAjwvMqDBhB8EiwA2iSmPEsbmmND3C4na8GPnWomNRDps-xabSZynlcPj8Dps1\XXolpXN4e0GxoCjBEQAvD_BwE

[30] Odin van Dael, “Wholesale 24,5% price inquiry via personal correspondence,” April 2021.

[31] Jesús Cerezo et. al., “Experimental study of an ammonia-water bubble absorber using a plate heat exchanger for absorption refrigeration machines.” *Applied Thermal Engineering*, vol. 29, no. 5-6, pp. 1005–1011, 2010.

[32] Ahmed Afif et.al., “Ammonia-fed fuel cells: a comprehensive review,” *Renewable and Sustainable Energy Reviews*, vol. 60, pp. 822–835, 2016.

[33] Takeou Okanishi et.al., “Comparative study of ammonia-fueled solid oxide fuel cell systems,” March 2017.

[34] Stephen H. Crolius, “Ammonia-powered internal combustion engines,” November 2016. [Online]. Available: https://www.ammoniaenergy.org/articles/ammonia-powered-internal-combustion-engines/

[35] C. Mounaïm-Rousselle & P. Brequigny, “Ammonia as fuel for low-carbon spark-ignition engines of tomorrow’s passenger cars,” *Frontiers in Mechanical Engineering*, vol. 6, no. 70, 2020.

[36] “Nutrient Source Specifics: Ammonia,” *International Plant Nutrition Institute*, no. 10. [Online]. Available: https://www.ipni.net/publication/nss.nsf/0/B3789D0EA4F386A5852579AF007630EA/$FILE/NSS-10%20Ammonia.pdf

[37] Stephen Joseph, Paul Taylor, & Annette Cowie, “Basic principles and practice of biochar production and kiln design,” July 2020. [Online]. Available: https://biochar.international/guides/basic-principles-of-biochar-production/#introduction

[38] R.W. Melse, & F.E. de Buisonjé, “Manure treatment and utilisation options.” Wageningen University Research, 2020.

[39] R. González et.al., “Biochar and energy production: Valorizing swine manure through coupling co-digestion and pyrolysis,” *Journal of Carbon Research*, vol. 6, no. 2, pp. 43–63, 2020.

[40] Wade A. Amos, *Report on Biomass Drying Technology*, 1st ed. Golden, Colorado: National Renewable Energy Laboratory, 1998.

[41] Kurt Spokas, Jeff Novak, & Rodney Venterea, "Biochar's role as an alternative n-fertilizer: Ammonia capture," *Plant and Soil*, vol. 350, no. 1, pp. 35–42, 2012.

[42] Fei Gao et.al., "Removal of aqueous ammonium by biochars derived from agricultural residuals at different pyrolysis temperatures," *Chemical Speciation & Bioavailability*, vol. 27, no. 2, pp. 92–97, 2015.

[43] Kyoung S. Ro et.al., "Removing gaseous nh3 using biochar as an adsorbent," *Agriculture: Effects of Biochar on Soil Fertility and Crop Production*, vol. 5, no. 4, pp. 991–1002, 2015.

[44] Xiong Zhang et.al., "Nitrogen enriched biochar modified by high temperature co2–ammonia treatment: Characterization and adsorption of co2," *Chemical Engineering Journal*, vol. 257, no. 1, pp. 20–27, 2014.

[45] Karl-Heinz Zapp et.al., *Ullmann's Encyclopedia of Industrial Chemistry.* Weinheim: Wiley-VCH, 2010.

[46] U.S. Environmental Protection Agency, *Ammonium Sulfate Manufacture: Background Information For Proposed Emission Standards.* North Carolina: Research Triangle Park, 1979.

[47] Encyclopedia Britannica. Urea. [Online]. Available: https://www.britannica.com/science/urea

[48] Mark Brouwer, "Thermodynamics of the urea process," in *Process Paper.* UreaKnowHow.com, 2009, pp. 1–15.

[49] Jozef Meessen, "Urea synthesis," *Chemie Ingenieur Technik*, vol. 86, no. 12, pp. 2180–2189, 2014.

[50] Ahmad Rafiee, Kaveh Rajab Khalilpour, & Dia Milani, *Polygeneration with Polystorage for Chemical and Energy Hubs.* Academic Press, 2019.

[51] Gerald Ondrey, "Newsfront: Spotlight on ammonia and urea," October 2008. [Online]. Available: https://www.chemengonline.com/newsfront-spotlight-on-ammonia-and-urea/?printmode=1

[52] Prathibha S. Rao, "Ammonium nitrate," in *Encyclopedia of Toxicology (Third Edition).* Elsevier, 2014, pp. 209–211.

[53] European Fertilizer Manufacturers' Association, *Production of Ammonium Nitrate and Calcium Ammonium Nitrate, Booklet No. 6 of 8.* Brussels: EFMA, 2000.

[54] U.S. Environmental Protection Agency, *Background Report AP-42 Section 6.8 Ammonium Nitrate Fertilizer.* North Carolina: Research Triangle Park, 1993.

[55] Rayeneh Group, "Ammonium nitrate," November 2019. [Online]. Available: https://rayeneh.com/ammonium-nitrate/

[56] European Fertilizer Manufacturers' Association, *Production of Nitric Acid, Booklet No. 2 of 8.* Brussels: EFMA, 2000.

[57] James G. Speight, *Environmental Inorganic Chemistry for Engineers.* Butterworth-Heinemann, 2017.

[58] "Nutrient Source Specifics: Diammonium Phosphate," *International Plant Nutrition Institute*, no. 17. [Online]. Available: http://www.ipni.net/publication/nss.nsf/0/66D92CC07C016FA7852579AF00766CBD/$FILE/NSS-17%20Diammonium%20Phosphate.pdf

[59] Gediminas Valiulis, & Rimvydas Simutis, "Modeling of continuous fertilizer granulation-drying circuit for computer simulation and control purposes," in *ICINCO 2009, Proceedings of the 6th International Conference on Informatics in Control, Automation and Robotics - Signal Processing, Systems Modeling and Control, Milan, Italy, July 2-5, 2009.* INSTICC Press, 2009, pp. 98–103.

[60] Sampatrao Manjare, & Rajendra Mohite, "Application life cycle assessment to diammonium phosphate production," *Advanced Materials Research*, vol. 354-355, pp. 256–265, 2011.

[61] "Nutrient Source Specifics: Monoammonium Phosphate (MAP)," *International Plant Nutrition Institute*, no. 9. [Online]. Available: http://www.ipni.net/publication/nss.nsf/0/2F200FA9C8C946F0852579AF00762904/$FILE/NSS-09%20Monoammonium%20Phosphate.pdf

[62] U.S. Environmental Protection Agency, *Background Report AP-42 Section 8.5 Ammonium Phosphate.* North Carolina: Research Triangle Park, 1993.

[63] WUR, "Mest: Een waardevolle grondstof," 2019.

[64] Oene Oenema, "Cdm-advies: 'milieueffecten bij geen derogatie van de nitraatrichtlijn'," 2020.

[65] Dieter Verhue et. al., "Opvattingen over megastallen: Een onderzoek naar het maatschappelijk draagvlak voor megastallen en de opvattingen hierover," 2011.

[66] Harold van der Meulen, "Gemiddeld 105 melkkoeien per bedrijf," December 2020. [Online]. Available: https://www.agrimatie.nl/ThemaResultaat.aspx?subpubID=2232&themaID=2272&indicatorID=2100&sectorID=2245

[67] Ton van Leeuwen, "Areaal cultuurgrond op melkveebedrijven fors hoger in 2019," February 2021. [Online]. Available: https://www.agrimatie.nl/PublicatiePage.aspx?subpubID=2523&themaID=2753&indicatorID=2761&sectorID=2245#:~:text=De%20melkveebedrijven%20in%20de%20Kleiregio,de%20vier%20regio's%20in%202019.

[68] Cubicenter, "Nieuwe ibc 1000l zwart - kunststof pallet mauser," 2021. [Online]. Available: https://cubicenter.eu/Nieuwe-IBC-1000L-Zwart-kunststof-pallet-Mauser

[69] Refertil, *Advance Compost and Biochar Processing: Solution for Economical Phosphorus Recovery Conference.* Toledo, Spain: Refertil International Conference, 2015.

[70] Anna Austin, "Biochar: Beyond the hype," 2011. [Online]. Available: http://biomassmagazine.com/articles/4080/beyond--the--hype

[71] D. Huygens et.al., *Technical proposals for the safe use of processed manure above the threshold established for Nitrate Vulnerable Zones by the Nitrates Directive (91/676/EEC).* Luxembourg: Publications Office of the European Union, 2020.

[72] Peter Smit, "Markt loopt warm voor koolstofboeren," May 2021. [Online]. Available: https://www.nieuweoogst.nl/nieuws/2021/05/14/markt-loopt-warm-voor-koolstofboeren

[73] EMBER, "Daily eu ets carbon market price (euros)," 2021. [Online]. Available: https://ember-climate.org/data/carbon-price-viewer/

[74] Xinyu Liu, Amgad Elgowainya, & Michael Wanga, "Life cycle energy use and greenhouse gas emissions of ammonia production from renewable resources and industrial by-products," *Journal of Green Chemistry*, vol. 22, no. 17, 2020.

[75] Paula Nijman, "Carbon credits for biochar production," July 2020. [Online]. Available: https://northsearegion.eu/carbon-farming/news/carbon-credits-for-biochar-production/

[76] Leo Joosten, Gerard Migchels, & Marieke van Leeuwen, *Mogelijkheden tot vermarkten van reducties in ammoniakemissie in het westelijk veenweidegebied.* Wageningen: Wageningen Livestock Research, 2019.

[77] Rijksdienst voor Ondernemend Nederland, "Hoeveel stikstof landbouwgrond," January 2021. [Online]. Available: https://www.rvo.nl/onderwerpen/agrarisch-ondernemen/mest/gebruiken-en-uitrijden/hoeveel-stikstof-landbouwgrond

[78] bij12, "Extern salderen," 2021. [Online]. Available: https://www.bij12.nl/onderwerpen/stikstof-en-natura2000/vergunningen-en-toestemmingsbesluiten/extern-salderen/

[79] Linda Janssen, "Milieurechten niet langer weggeven maar verkopen," August 2019. [Online]. Available: https://www.nieuweoogst.nl/nieuws/2019/08/06/milieurechten-niet-langer-weggeven-maar-verkopen

[80] NOS, "Greenpeace dreigt overheid met rechtsgang om stikstofbeleid," May 2021. [Online]. Available: https://nos.nl/artikel/2381529-greenpeace-dreigt-overheid-met-rechtsgang-om-stikstofbeleid

[81] Ellen Koekkoek, "Stikstofuitstoot nederland: hoe zit het?" March 2021. [Online]. Available: https://www.kvk.nl/advies-en-informatie/innovatie/duurzaam-ondernemen/stikstofuitstoot-nederland-hoe-zit-het/#beleid

[82] Jeffrey M. Novak, Mark G. Johnson, & Kurt A. Spokas, "Concentration and release of phosphorus and potassium from lignocellulosic- and manure-based biochars for fertilizer reuse," *Frontiers in Sustainable Food Systems*, vol. 2, p. 54, 2018.

[83] Bredox BV, "Caustic potash flakes fcc/food," 2021. [Online]. Available: https://www.alibaba.com/product-detail/Caustic-Potash-Flakes-FCC-Food_124490544.html?spm=a2700.galleryofferlist.normal_offer.d_title.102251e3Rr9TLU

[84] HLP Agri, "Meststoffen," 2021. [Online]. Available: http://www.hlpagri.nl/

[85] Commissie Bemesting Grasland en Voedergewassen, *Bemestingsadvies.* Wageningen: Wageningen Livestock Research, 2021.

[86] European Union, "Richtlijn 91/676/eeg van de raad van 12 december 1991 inzake de bescherming van water tegen verontreiniging door nitraten uit agrarische bronnen," December 1992. [Online]. Available: https://eur-lex.europa.eu/legal-content/NL/TXT/HTML/?uri=CELEX%3A31991L0676&from=EN

[87] Kastelijn BV, "Vloeibare kunstmest injecteren," 2021. [Online]. Available: https://kastelijnbv.nl/klepelmaaien/

[88] EcoService Europe B.V., "Vloeibare kunstmest," 2021. [Online]. Available: https://www.ecoservice-europe.com/nl/kunstmest/vloeibare-kunstmest/

[89] Nederlandse Centrum voor Ontwikkeling van Kringlooprpecisebemsting, "Af- en uitspoeling van nitraat in de ruggenteelt. hoe voorkom je dit ? instructievideo," April 2021. [Online]. Available: https://www.youtube.com/watch?v=dgEMt0y6mww

[90] BERGS Advies, "Mineralenconcentraat, wat is dat nou eigenlijk?" April 2019. [Online]. Available: https://www.bergsadvies.nl/mineralenconcentraat-wat-is-dat-nou-eigenlijk/

[91] BLUE-tec BV, "bluetec ammonia membrane stripping," 2021. [Online]. Available: https://static1.squarespace.com/static/58f87f33f7e0ab4a98ac7a58/t/59357e5117bffce2d15a6256/1496677969991/ammonia+stripping.pdf

[92] T. Kohn, L. Decrey, & B. Vinneras, *Chemical Disinfectants*, 4th ed. East Lansing: Michigan State University, UNESCO, 2017.

[93] Khalil Atasi et.al., *Membrane Systems for Wastewater Treatment.* Virginia: The Water Environment Federation, 2006.

[94] Lewis G. Newton, "The osmotic pressure of concentrated solutions and the laws of the perfect solution," *Journal of the American Chemical Society*, vol. 30, no. 5, pp. 668–683, 1908.

[95] Kevin J. North, "Diagram showing the components of a liquid-cooled chiller," January 2016. [Online]. Available: https://en.wikipedia.org/wiki/Chiller#/media/File:Water_Cooled_Chiller_Diagram.png

[96] Engineering Toolbox, "Saturation pressure and density of water vapor for common temperatures," 2004. [Online]. Available: https://www.engineeringtoolbox.com/water-vapor-saturation-pressure-air-d_689.html

[97] Bhausaheb Pangarkar et.al., "The heat and mass transfer phenomena in vacuum membrane distillation for desalination," *World Academy of Science, Engineering and Technology*, vol. 37, 01 2010.

[98] Mohammed Kamil & Louay Mahdi, "Predicting of steam condensation heat transfer coefficient in horizontal flattened tube," *Journal of Engineering and Sustainable Development*, vol. 24, 11 2020.

[99] Honqi Valve Store, "Dn15 normally closed solenoid valve stainless steel ip65 waterproof solenoid valve," 2021. [Online]. Available: https://nl.aliexpress.com/item/1005002748857091.html?spm=a2g0o.search0302.0.0.10355d00KukMeI&algo_pvid=null&algo_expid=null&btsid=2100bdd016228031937494524ec2c5&ws_ab_test=searchweb0_0,searchweb201602_,searchweb201603_

[100] Hy-Tech Roof Drains, "How much water can flow through a pipe (gpm/gph)?" November 2020. [Online]. Available: https://hy-techroofdrains.com/water-flow-through-a-pipe/

[101] Juan Gabriel Segovia-Hernández, & Adrián Bonilla-Petriciolet, *Process Intensification in Chemical Engineering*, 1st ed. Switzerland: Springer, 2016.

[102] Zhangjiagang Rihong Machinery, "Sml-3f series air-cooled industrial chiller," June 2021. [Online]. Available: https://www.alibaba.com/product-detail/Superb-technology-chiller-brand-chiller-blast_1600145561509.html?spm=a2700.details.0.0.17584340Mgx5iN

[103] Dongguan Naser Machinery, "1hp glycol mini chiller 3kw air cooled water scroll chiller," June 2021. [Online]. Available: https://www.alibaba.com/product-detail/1hp-glycol-mini-chiller-3kw-air_1600233030332.html?spm=a2700.7724857.normal_offer.d_title.5ed66539F1ScWj

[104] Zhuolong, "Zhuolong air reservoir tank hoge druk verticale 4-port rvs gas opslag 5l 1/2 1/4npt," June 2021. [Online]. Available: https://www.amazon.nl/zhuolong-Reservoir-Verticale-4-Port-Opslag/dp/B08X9V81R3/ref=asc_df_B08X9V81R3/?tag=nlshogostdde-21&linkCode=df0&hvadid=494675556931&hvpos=&hvnetw=g&hvrand=2731612738117315986&hvpone=&hvptwo=&hvqmt=&hvdev=c&hvdvcmdl=&hvlocint=&hvlocphy=9065100&hvtargid=pla-1247316797228&psc=1

[105] Wojciech Sas, "Combined gas law calculator," April 2021. [Online]. Available: https://www.omnicalculator.com/physics/thermodynamic-processes

[106] WaterNet, "Wat kost een kuub water?" 2021. [Online]. Available: https://www.waternet.nl/veelgestelde-vragen/drinkwater/wat-kost-kuub-water/

[107] Ray Sinnott, & Gavin Towler, *Chemical Engineering Design*, 5th ed. Oxford: Butterworth-Heinemann, 2009.

[108] Eddy Herbas, "Estimating cost models: Power-sizing model," September 2012. [Online]. Available: http://engineeringandeconomicanalysis.blogspot.com/2012/09/power-sizing-model.html

[109] Kenneth Emerson et.al., “Aqueous ammonia equilibrium calculations: Effect of ph and temperature,” *Journal of the Fisheries Board of Canada*, vol. 32, no. 12, pp. 2379–2383, 1975.

[110] X. A. Le et.al., “Research and produce fertilizer from npk fertilizer and biochar for agricultural production,” *ARPN Journal of Engineering and Applied Sciences*, vol. 15, no. 1, 2006.

[111] N.H. Mohd Razif et.al., “Thermophysical properties analysis for ammonia-water mixture of an organic rankine cycle,” *Jurnal Teknologi*, vol. 75, no. 8, pp. 13–17, 2015.

[112] PriceWise, “kwh-prijs,” 2021. [Online]. Available: https://www.pricewise.nl/energieprijzen/kwh-prijs/

[113] Engineering ToolBox, “Water - heat of vaporization,” 2010. [Online]. Available: https://www.engineeringtoolbox.com/water-properties-d_1573.html

[114] Peter van der Wilt, “Salderen en terugleververgoeding zonnepanelen,” April 2018. [Online]. Available: https://www.consumentenbond.nl/zonnepanelen/salderen-en-terugleververgoeding-zonnepanelen

[115] Well Control BV, “Aardwarmtesystemen,” 2010. [Online]. Available: http://www.wellcontrol.nl/aardwarmtesystemen.html#:~:text=Het%20grondwater%20wordt%20vanaf%20ca,celsius%20afhankelijk%20van%20de%20locatie.

[116] Feili Pump Co., Ltd., “3fld2.7-22-24-180 dc solar submersible pump deep pump solar system mini solar pump,” 2021. [Online]. Available: https://www.alibaba.com/product-detail/3FLD2-7-22-24-180-dc_60728726529.html

[117] Grzegorz Kulczycki et.al., “The effect of various types of biochar mixed with mineral fertilization on the development and ionome ofwinter wheat (triticum aestivum l.) seedlings and soil properties in a pot experiment,” *Agronomy*, vol. 10, 2020.

[118] Carbon Gold Ltd, “Organic biochar fertiliser,” 2021. [Online]. Available: https://www.carbongold.com/biochar/fertiliser/

[119] Wakefield BioChar, “Wakefield kickstart biochar from biosolids – 1 cu/yd,” 2021. [Online]. Available: https://www.wakefieldbiochar.com/shop/wakefield-kickstart-charged-biochar/

[120] Argus Media Group, *Argus Sulphuric Acid, issue 18-39*, London, 2018. [Online]. Available: https://www.argusmedia.com/-/media/Files/sample-reports/argus-sulphuric-acid.ashx?la=en&hash=28D8CDEF485998FED5806750D90A916D3F3DED19

[121] Zouping Boyi Chemical Industry CO., LTD., “fertilizer (nh4)2so4 ammonium sulphate price,” 2021. [Online]. Available: https://www.alibaba.com/product-detail/fertilizer-NH4-2SO4-Ammonium-sulphate-price_1600111983647.html?spm=a2700.details.0.0.52e65535WvKl

[122] Frans Agro, “Ammoniumsulfaat 21% n (25 kg),” 2021. [Online]. Available: https://webshop.fransagro.be/nl/product/12262-ammoniumsulfaat-21-n-25-kg/

[123] BoerEnBusiness, “Scherpe daling co2-prijs door coronamaatregelen,” 2020. [Online]. Available: https://www.boerenbusiness.nl/energie/artikel/10887124/scherpe-daling-co2-prijs-door-coronamaatregelen

[124] Index Mundi, “Urea monthly price - euro per metric ton,” February 2021. [Online]. Available: https://www.indexmundi.com/commodities/?commodity=urea&months=120&currency=eur

[125] Chamber of Commerce Modena, “Italy: Prices of mineral fertilizers,” February 2021. [Online]. Available: https://www.clal.it/en/index.php?section=concimi#nitrato

[126] S. Jackson, & E. Brodal, “A comparison of the energy consumption for co2 compression process alternatives,” *8th International Conference on Environment Science and Engineering*, vol. 167, 2018.

[127] J. C. G. Walker, *Evolution of the Atmosphere.* New York: Macmillan Publishing Company, 1977.

[128] Grand View Research, *Nitric Acid Market Size, Share and Trends Analysis Report By Application.* San Francisco: GVR, 2020.

[129] ECHEMI, “Phosphoric acid china domestic price,” April 2021. [Online]. Available: https://www.echemi.com/productsInformation/pd20150901061-phosphoric-acid.html

[130] S. Donatello, D.Tong, & C.R. Cheeseman, *Production of Technical Grade Phosphoric Acid from Incinerator Sewage Slush Ash (ISSA).* London: Imperial College London, 2010.

[131] Shijiazhuang Xinlongwei Chemical Co., Ltd., “H3po4 phosphoric acid 85,” 2021. [Online]. Available: https://www.alibaba.com/product-detail/H3po4-Phosphoric-Acid-85_1764432156.html?spm=a2700.7724857.normal_offer.d_title.61205ff9BusRGB

[132] Index Mundi, “Dap fertilizer monthly price - euro per metric ton,” February 2021. [Online]. Available: https://www.indexmundi.com/commodities/?commodity=dap-fertilizer&currency=eur

[133] Russ Quinn, “Dtn retail fertilizer trends,” February 2020. [Online]. Available: https://www.dtnpf.com/agriculture/web/ag/crops/article/2020/09/02/fertilizer-prices-decline-dap-map#:~:text=DAP%20was%20up%20significantly%2C%20or,average%20price%20of%20%24430%2Fton.&text=MAP%20was%20up%20%246%2Fton,price%20was%20at%20%240.39%2Flb.

[134] D.E. Garrett, *Chemical Engineering Economics*, 1st ed. New York: Van Nostrand Reinhold, 1989.

[135] Airco prijzen.nl, “Kosten airco plaatsen,” 2021. [Online]. Available: https://aircoprijzen.nl/plaatsen/

[136] Alfa Laval, “Alfacond,” 2021. [Online]. Available: https://www.alfalaval.com/products/heat-transfer/plate-heat-exchangers/gasketed-plate-and-frame-heat-exchangers/alfacond/

[137] GenCell Ltd., "Gencell a5 off-grid power solution," 2021. [Online]. Available: https://www.gencellenergy.com/our-products/gencell-a5/

[138] Battelle Memorial Institute, *Manufacturing Cost Analysis of 1 and 5 kW Solid Oxide Fuel Cell (SOFC) for Auxiliary Power Applications*, 1st ed. Columbus, OH: U.S. Department of Energy, 2014.

[139] P.H. McMurry, H. Takano, & G.R. Anderson, "Study of the ammonia (gas)-sulfuric acid (aerosol) reaction rate," *nviron. Sci. Technol.*, vol. 17, no. 6, pp. 335–342, 1983.

[140] CO2Meter.com, "Co2 tank safety precautions," 2019. [Online]. Available: https://www.co2meter.com/blogs/news/co2-tank-safety-precautions#:~:text=CO2%20cylinder%20pressure%20is%20about,a%20rate%20of%20535%3A1.

[141] ASCO Carbon Dioxide LTD, "Asco co2 storage tanks polyurethane insulated," 2021. [Online]. Available: https://www.ascoco2.com/fileadmin/PDF_Download/PDF_Produkte/PDF_CO2_und_Trockeneis_Zubehoer/CO2_Lagerung/en/ASCO_Polyurethane_Insulated_CO2_Storage_Tanks.pdf

[142] H. Connor, "The manufacture of nitric acid: The role of platinum alloy gauzes in the ammonia oxidation process," *Platinum Metals Rev*, vol. 11, no. 1, 1967.

[143] Franz Sperner, "Rhodium-platinum gauzes for ammonia oxidationa study by scanning electron microscopy," *Platinum Metals Rev*, vol. 20, no. 12, 1976.

[144] Pien van Engen, "Nederland heeft minste duurzame energie van hele eu, 'dit jaar wel versnelling'," January 2020. [Online]. Available: https://nos.nl/artikel/2320040-nederland-heeft-minste-duurzame-energie-van-hele-eu-dit-jaar-wel-versnelling

[145] Si Gao, Thomas H. DeLuca, & Cory C. Cleveland, "Biochar additions alter phosphorus and nitrogen availability in agricultural ecosystems: A meta-analysis," *Science of the Total Environment*, vol. 654, pp. 463–472, 2019.

[146] E. Rizhiya et.al., "Nitrogen enriched biochar-compost mixture as a soil amendment to the haplic luvisol: effect on greenhouse gas emission," *Biologia*, vol. 75, 08 2019.

[147] Food and Agriculture Organization of the United Nations, *Global estimates of gaseous emissions of NH3, NO and N2O from agricultural land*, 6th ed. Rome: FAO, 2001.

[148] Frank Brentrup and Christian Pallière, *Energy efficiency and greenhouse gas emissions in European mineral fertilizer production and use*, 9th ed. Brussels: Fertilizers Europe, 2011.

[149] Yara International ASA, "Reducing ammonia emissions from agriculture," November 2017. [Online]. Available: https://www.yara.com/globalassets/pure-nutrient--ammonia/reducing-ammonia-emissions-from-agriculture.pdf/

[150] Ludwig Hermann, Fabian Kraus, & Ralf Hermann, "Phosphorus processing—potentials for higher efficiency," *Journal of Sustainability*, vol. 10, no. 1482, 2018.

[151] Anna-Mari Heikkilä, *Inherent safety in process plant design An index-based approach.* Espoo: Valtion teknillinen tutkimuskeskus (VTT), 1999.

[152] Canadian Centre for Occupational Health and Safety, "Sulfuric acid osh fact sheet," 2021. [Online]. Available: https://www.ccohs.ca/oshanswers/chemicals/chem_profiles/sulfuric_acid.html

[153] Mallinckrodt Baker, Inc., "Phosphorus pentoxide msds number: P4116," 1996. [Online]. Available: https://hazard.com//msds/mf/baker/baker/files/p4116.htm

[154] US Department of Energy, "Fuel cell technologies office," 2015. [Online]. Available: https://www.energy.gov/sites/prod/files/2015/11/f27/fcto_fuel_cells_fact_sheet.pdf

[155] Riooleringsmarkt, "Kelder prefab beton 15 m2," 2021. [Online]. Available: https://www.rioleringsmarkt.nl/producten/kelder-prefab-beton/kelder-prefab-beton/kelder-prefab-beton-15-m2

[156] Wilbert Beerling, "Mestscheider huren? kopen vaak goedkoper," in *Veehouderij Techniek*. Wageningen University and Research, 2014.

[157] drijfmesttechniek, "De kosten van een mestscheider," 2021. [Online]. Available: https://www.drijfmesttechniek.nl/nieuws/mestscheider-prijs/

[158] A. Evers et.al., *Economic perspectives of manure separation on dairy farms*, 421st ed. Wageningen: Wageningen UR Livestock Research, 2010.

[159] MA KOI BV, "Pond filtration verkoopprijzen 2021," 2021. [Online]. Available: https://cdn.webshopapp.com/shops/270115/files/371614326/prijzen-2021-part-en-dealer-nl-14-06-2021.pdf?_ga=2.137861616.1996062266.1623879631-648462483.1623879631&_gac=1.61467998.1623879864.CjwKCAjwwqaGBhBKEiwAMk-FtHLIwcQw4k8WMfomlGPNrFPrT_lMa7Tbm-ISWYq6OvukPPCWD-Lc7BoCercQAvD_BwE

[160] BrinkBox, "Assortiment nieuw en gebruikt containers," 2021. [Online]. Available: https://www.brinkbox.nl/assortiment

[161] Brabant Water, "Tarievenregeling: tarieven per 1 januari 2021," 2020. [Online]. Available: https://www.brabantwater.nl/sites/default/files/documents/Tarieven/Tarievenregeling_Brabant-Water-2021-online.pdf

[162] Oklahoma State University, "Nueweb: Ammonium chloride," August 2004. [Online]. Available: http://www.nue.okstate.edu/N_Fertilizers/Ammonium_chloride.htm

[163] Naoyuki Ishikawa et.al., "Effects of ammonium chloride fertilizer and its application stage on cadmium concentrations in wheat (triticum aestivum l.) grain," *Plant Production Science*, vol. 18, no. 2, pp. 137–145, 2015.

[164] EChemi, "Ammonium chloride china domestic price," June 2021. [Online]. Available: https://www.echemi.com/productsInformation/pd20160226180734047-ammonium-chloride.html

[165] CEIC Data, “China: Market price: Monthly avg: Fertilizer: Ammonium chloride, 23.5%,” April 2021. [Online]. Available: https://www.ceicdata.com/en/china/china-petroleum--chemical-industry-association-petrochemical-price-fertilizer/cn-market-price-monthly-avg-fertilizer-ammonium-chloride-235

[166] A. Holleman, E. Wiberg, & N. Wiberg, *Inorganic Chemistry (illustrated ed.).*, 1st ed. San Diego: Academic Press., 2001.

A Appendix 1: Score Justification

In this appendix the more detailed scoring justification can be found. In many cases placing a score on a value was easier said than done, especially if it is to be backed up by solid sources. Thus, a shorter summary is found in the main text and the extended version with more 'proof' and calculations can be found here.

A.1 Maturity/Feasibility

Essentially this is two separate scoring criteria mixed into one. Maturity is for how long and how well-studied the process is, whereas feasibility is defined as how realistically the process can be implemented in farm conditions. They are combined here, since in most cases the more mature and well-studied solutions have relatively simple practical applications and solutions available. However, in cases where the process is particularly complex, it would be more difficult to implement a simple rugged version, so this is also taken into account. This criterion was given a maximum scoring of 3 (average) since it is a key indicator if the process can actually be implemented in a farm, which is very important, but as it also uses some aspects that have overlap with other criteria (e.g. more complexity will also have an effect on cost and reliability), it was kept down to 3 points.

Wholesale gas and aqueous ammonia: Here the process is the same for both, which is part of the VMS. Upon further research, VMS is sometimes also referred to as Vacuum Membrane Distillation and its use for ammonia has been mentioned as far back as 1975 [109]. Seeing as the process is quite simple and the development of membranes more popular in practice in the last decades, it is safe to assume that this process is quite mature and certainly feasible. Thus it receives a score of 3.

Alkaline fuel cells: Like many other fuel cells, these are still very new and in development for commercial availability. Overall there are still many unknowns, but they are proven to work in practice for an extended duration of time. For this, AFCs will receive a score of 1.

Solid oxide fuel cells: These are very similar to AFCs, but their development, despite on paper being more promising, is further away from practice. Moreover, a commercial AFC is offered for sale in 2021 (from GenCell), whereas no commercial SOFCs are for sale yet. Additionally, the higher temperatures and longer start-up times for SOFCs make it even less feasible for a farm. Overall this results in a score of 0.

Enriched biochar: This is a concept that is also fairly recent, with the earliest publishing mentioning it dating from 2006 [110]. However, as it promises a greener alternative to fertilizers in an age where environmental concerns are paramount, it has gained a lot of attention and research in very little time, meaning it is more mature than one would initially think. Nevertheless, there are still many specific unknowns, but for a practical application it is sufficient and since the process is reasonably simple, it will receive a score of 2.

Ammonium sulphate: This process is incredibly simple. Seeing as it is simply a continuous neutralizing reaction of aqueous ammonia and sulphuric acid in what in layman terms essentially amounts to dumping everything in a big container in the right proportions, it should come as no surprise that documents dating back well into the 19^{th} century can be found. A maximum score of 3 points is therefore not out of place.

Urea: This process, despite not being particularly simple, is already a fairly mature process, originating from the Bosch–Meiser urea process of 1922. Being a fertilizer and process that is used around the world, it is well-researched and a lot is known about it, but the process itself has non-ideal conditions with several recycle streams, poisonous by-products that stunt plant growth, and high corrosion, meaning that it requires constant monitoring that it is unlikely to receive on a farm. Thus, despite its maturity, it will only score a 1 due to its low feasibility.

Full ammonium nitrate that is produced from **only ammonia and air**: This a rather complex process. Like Urea, the Ostwald process is roughly a century old and a lot of research has been done, but the medium pressures and high temperatures, combined with that additional heat recovery is desired for the large temperature drop within the process, means that one is dealing with a complex process requiring control. Compared to urea, the overall conditions can be a bit more relaxed, but the process is more complex, meaning it still only scores 1 point.

Ammonium nitrate where the **nitric acid is bought in bulk**: Here the process is not any more mature, but it is vastly simpler and much more feasible to use in a farm application, resulting in only a simple acid-base reaction that requires a slight temperature control and possibly an evaporator and prilling tower, thus receiving a score of 2.

Ammonium phosphate; or more specifically DAP, is in essence a simple acid-base process with average maturity. However, what complicates this process is that the temperature needs to be regulated closely to assure solid granulation while having minimal emissions. Even so, additional scrubbing or cyclones is required to prevent excessive emissions, which lowers the feasibility of this process, giving an overall score of 1.

A.2 Process Profitability

This section is about how profitable the process itself is. It takes into account the basic costs of the inputs and the sale price of the outputs, as well as rough estimates of energy requirements (if applicable and significant), all from after the BPMED part onwards. This part is the most important aspect as for large scale adoption the process itself may not cost more money than it makes, thus being worth a total of 5 points. For the sake of consistency and ease of comparison, the process profitability will be expressed in euros per metric tonne of pure ammonia produced ($€/tonNH_3$). In other words, for every 1000 kg of pure ammonia made by the MEZT process (which is constant), how much profit (or losses) are made? Also useful to point out: farmers tend to convert their costs to per tonne of manure, which can easily be done as 1 tonne of ammonia is created by 524 - 1052 tonnes manure, so simply divide the profits by roughly 750 to get per tonne manure profits.

Wholesale gas and aqueous ammonia: In this simple process only the VMS needs to be taken into account and there is no raw material input cost in both cases. For the sake of consistency, the vacuum pump itself will not be taken into account as all processes use it anyway. However, the cold trap is specific to this process.

In both cases, at a 10% input concentration, a total of 9000 kg additional water needs to be cooled per tonne ammonia. The cold trap cools the mixture down from 25 °C to 10 °C, and for this an isobaric specific heat capacity of 4.134 kJ/kg*K for a 25% ammonia concentration was used [111] as a rough estimate (only slightly lower than pure water at 4.20 kJ/kg*K). This results in the following energy requirement (at 1 MJ = 0.277 kWh).

$$Q = 10,000kg * 15°C * 4.134kJ/kg * K = 620,100kJ = 172.2kWh$$

If one assumes cooling is done via electricity at an ideal (albeit unrealistic) 100% efficiency, combined with an average Dutch electricity price of €0.22 /kWh [112], it results in a cost of €37.88 cooling cost per metric tonne ammonia. However, this does not yet include the condensation of water itself. Unfortunately, the condensation requires significantly more cooling, as water has a high latent heat of vaporization of 2465 kJ/kg at the VMS's 2kPa and roughly 10 °C [113], which is even slightly higher than at ambient conditions. For a final 25% ammonia concentration, 6000 kg of water needs to be condensed. The resulting energy requirement is then as followed.

$$Q = 6,000kg * 2465kJ/kg = 4,790MJ = 4108kWh$$

This results in a cost of €903. Similarly, for a pure gaseous ammonia output, all 9000 kg needs to be condensed, which would be 1.5x the mass and thus 1.5x the price, resulting in a cost of €1356 per ton ammonia. At a later point during the initial costing, it was discovered that the 100% efficiency was very inaccurate. It turns out that per kW of actual cooling; only $1/3^{rd}$ of a kW or even slightly less is needed to achieve the cooling, since a lot of the cooling occurs via cooling the warm refrigerant with (free) cool air. Thus, these values actually need to be adjusted. The new process cost for air-conditioning is about €301 (25%) or €452 (100%) per ton ammonia.

Regarding sale price, as mentioned in section 3, the wholesale sell price of 24.5% aqueous ammonia was given as €210/ton [30]. Adjusting this to a pure ammonia price results in €857/ton ammonia, where the water sale price is negligible (€0.83 $/m^3$ water [106]). For pure gaseous ammonia, although no value was given from Vivochem, prices appear to follow the same trend as aqueous ammonia. This is because originally most ammonia originates from the Haber-Bosch process, which gives gaseous ammonia, so gaseous ammonia is not more expensive than aqueous ammonia per tonne of pure ammonia. The overall profits per tonne 25% aqueous ammonia and 100% gaseous ammonia are as followed.

$$Profits = €857 - €38 - €301(25\%)/€452(100\%) = €518(25\%)/€367(100\%)$$

As evident, the cooling costs for condensation make this option substantially less profitable. After discussing this with the supervisors, it was discovered that many farmers have solar panels on their roofs that create (substantially) more electricity than consumed. Thus, for a true cost to the farmer, it would be better to calculate the costs using the electricity feed-in compensation price ("terugleververgoeding") rather than the raw price from the grid, as that would be the price they receive for selling their excess electricity. In the Netherlands, the Consumentenbond conducted a research in 2018 analysing all these prices where they ranged from €0.04 tot €0.12 /kWh, with the majority being between €0.06 and €0.07 /kWh, so a €0.065 /kWh price will be assumed [114]. Thus, a new cost of €89 (25%) or €134 (100%) per ton ammonia and €11 for the non-condensing cooling will be assumed. This results in new profits of €757 (25%) or €712 (100%) per tonne ammonia input.

However, the roughly €100 to €140 per tonne ammonia costs are still significant enough that it would be useful to look for alternatives. Firstly, and most simply, finding a buyer for the pure 10% ammonia output stream. This is the simplest option and will net you the highest €857/ton profits, but finding a buyer may be more difficult. The second solution would be to cool the cold trap using non-electric, cheaper alternatives, such as ground water or tap water. In the Netherlands, groundwater hovers around 10 to 12 °C at a depth of 10 m whereas tap water averages around 13 °C [115]. This results in a very small temperature difference (requiring relatively large heat exchangers) and even the inability to fully cool the stream to the required temperature in some cases. However, for completeness, this has also been investigated.

Wholesale via ground/tap water cooling: If the cooling is to be done via normal tap water or ground water, the temperature difference may not be great enough for effective cooling. Upon closer inspection, the actual condensation temperature is around 17 °C, meaning that a much tighter 15 °C lower boundary could essentially also be used, which is higher than the original 10 °C and more importantly, higher than the ground/tap water temperature of 10-12 °C. With this, an average temperature difference of 5 °C might be possible.

In the "initial costing" subsection after this subsection further heat exchanger calculations are done, but with this 5 °C, a new temperature drop for the cooling water can be calculated, as it will drop from about 25 °C to 15 °C (a drop of 10 °C). The water requirement can then be calculated. The non-condensing cooling per tonne ammonia is decreased from 172.2 kWh for 15 °C to 114.8 kWh for 10 °C. Adding this to the 4108 kWh or 6162 kWh for 25 % and 100 % desired output respectively results in a total energy requirement of 4223 kWh (25%) or 6277 kWh (100%), which (at 1 MJ = 0.277 kWh) is equal to 15245 MJ and 22660 MJ. Then, with a *Cp* value of 4.20 kJ/kg*K for water, a 10 °C increase in cooling water temperature and these powers, the following mass of water is needed.

$$25\% : m_{water} = 15,245,000kJ/(4.20KJ/kg * K * 10°C) = 362,976kg = 363m^3$$

$$100\% : m_{water} = 22,660,000kJ/(4.20KJ/kg * K * 10°C) = 539,523kg = 539.5m^3$$

This at an average tap water price of €0.83/m^3 [106] would cost €301 for 25% or €447.8 for 100%, which is rather expensive and more so than air-conditioning. Clearly, at the massive water requirements, tap water is not feasible; especially considering it is not certain if these temperature differences are even attainable. Thus, ground water will also be considered.

For groundwater, the water is free, but a large amount of water needs to be pumped. Via very simple potential energy calculations, to lift (assuming 25% concentration for now) 362,976 kg of water per tonne of ammonia, the following calculation is made:

$$E_p = m * g * h = 362,976kg * 9.81m/s^2 * 10m = 35,607,946J = 35.6MJ = 9.86kWh$$

Although this does assume 100% efficiency, the resulting €2.20 (or €3.25 for 100%) is extremely small. For a more realistic cost, the specifications of a commercially available unit will be used. With MEZT's maximum output of 1.91 kg ammonia per hour, it would take 523.5 hours to get a whole tonne of pure ammonia, or in other words, per hour 694 L of water pumping is required. At

100 % this would instead be 1040 L/hr. A unit was found specifically for wells with a rated flow of 800 L/hr and a rated head of 15 m, which can be adjusted for either a higher flow or head [116]. This consumes 180 W, which for the 523.5 hours is 94 kWh, or about a factor 10 larger. This would then cost €20.73 per tonne ammonia, bringing the profits up to a much more respectable €836 per tonne ammonia at 100%. If the pump can be fine-tuned for the 25% concentration, it would be $1/3^{rd}$ less, bringing profits up to €843.

Alkaline fuel cells: Similar to wholesale, for fuel cells there are no other input requirements besides the pure ammonia. For this cost analysis, the specification of the first commercially available AFC by GenCell can be used [26]. The AFC from GenCell consumes 2.5 kg/hr anhydrous ammonia (approximately double the production of the MEZT process) and produces 4 kW of power. For 1000 kg of pure ammonia, it would then produce 1600 kWh of electricity, which at the electricity price of €0.22 /kWh would be worth €352. However, two important things should be noted. Firstly, when one sells excess electricity back to the grid, the value received is significantly less than what it is purchased for. Secondly, and perhaps more importantly, the value of the electricity made from ammonia is worth less than the ammonia itself, not to mention the additional cost of the fuel cell itself.

Solid oxide fuel cells: Very similar to AFCs with near-identical inputs and outputs. The slightly higher efficiency (60% versus 50-60%) of SOFCs would net slightly more power, but the longer start-up time may negate this to some extent. Overall, the result will be about the same. However, as mentioned in the wholesale part, the cost can increase drastically if the gaseous ammonia is required. Fortunately, it may be possible to use the low 10% concentration aqueous ammonia stream directly. As already mentioned before, this was tested and shown to work in practice by CramChem, but no literature could be found on it.

Enriched biochar: Regarding prices, since biochar is fairly new and there is a lot of variation in different biochars and enriched biochar prices, creating a very accurate profitability estimate is difficult. In fact, a paper from 2015 mentioned that prices for biochar ranged wildly from €100-1000/ton [69], whereas a newer 2020 study mentioned a raw biochar price in Europe as low as €200 /tonne and it mentioned average prices for biochar aiming at "agricultural applications" (possibly implying some form of enrichment) hovered around €250-420/tonne without mentioning the specific composition [117]. Another commercially available biochar did mention the composition, being 5-5-5 NPK rated (albeit in small expensive packaging at €2298/tonne) [118] and another biochar was found with "a nitrogen concentration up to 6 times higher and phosphorus up to 10 times higher than pure biochar" for roughly 500 €/tonne [119].

It is clear then that placing an exact price on enriched biochar is going to be very difficult and perhaps the price variation could be due to enriched biochar being seen as a premium household fertilizer or because farmers know very little about it, and thus are willing to pay the asking price [69]. This could allude to enriched biochar prices decreasing as more is known about it. Moreover, what is important to note is that this enriched biochar option is the only option that uses the thick fraction of manure. However, in all other cases that (unused) thick fraction could also be turned into raw (unenriched) biochar or simply spread on the field as a low-emissions carbon-rich source. Therefore, for an apples to apples comparison one should really look at the added value of enriching the biochar, which should be slightly easier to estimate.

Taking the 5-5-5 NPK as an example, 5% N enrichment requires (at 82% N content) 6.1% ammonia enrichment, which means one tonne of ammonia gas can enrich 16.4 tonnes of biochar. Taking the values from the process (0.95-1.91 kg/hr NH_3 and 6.8-33.2 kg/hr biochar), the final biochar production per tonne ammonia is between 3.5 and 35 tonnes. The 16.4 tonnes is right in in the middle of this, meaning that most likely all ammonia produced can enrich all biochar produced at around 5% enrichment.

Taking the previously mentioned €200 per tonne raw biochar price and €250-420/tonne enriched biochar price, a minimum mark-up of €50 per tonne can safely be assumed. At that price, the profits per tonne ammonia would be (16.4 t * €50) €820. In reality the mark-up will likely lay higher, which at €100 would result in €1640 in profits. However, one important thing to note is that biochar is still relatively new and the sale prices (and thus future mark-ups) will be lower, so only the €820 price will be assumed. Furthermore, the enrichment requires a gas ammonia input that cannot (easily) be substituted, so the gas VMS costs are also added. For this, the air-conditioned costs will be used as it is certain to work, whereas the ground water costs may not be certain yet. This gaseous cost of €134 per tonne brings the final profits down to €686 per tonne ammonia.

Ammonium sulphate: This is a very simple process with the only requirements besides ammonia being the 2800 kg sulfuric acid per tonne ammonia and perhaps a slow stirrer for aiding the reaction by mixing it together. The stirrer can be fairly small and low-powered and thus will be assumed as a negligible power cost, leaving only the materials to calculate.

The current global wholesale price for sulfuric acid (H_2SO_4) on Alibaba is around 200 USD/tonne (180-250 mostly) at a 98% concentration, or €165 /tonne. One document showed a European spot price for sulfuric acid as low as €60-63 /tonne in 2018 [120], whereas an invoice from Brenntag supplied by MEZT mentioned a price of €194.30 /tonne.

Meanwhile, perhaps contradicting to initial logic, ammonium sulphate sells for a substantially lower price on the global market. Global prices hover around 90-150 USD/tonne on Alibaba or about €95 per tonne. Searching further, in one case a price as low as €50 /tonne was found [121]. However, in Europe the situation is different. Although prices are more difficult to find, a supplier in Belgium was found selling 25 kg bags at 8.06 (ex.btw) if purchasing 40 bags or more, resulting in €322 /tonne [122] and a Dutch supplier HLP is selling ammonium sulphate at a bulk price of €250 /tonne [84], which both is substantially more than in Asia.

Taking these European prices (buy 2.88 tonnes at €194.30 /tonne, sell 3.88 tonnes at €250 /tonne), an overall profit of €410 per tonne ammonia is reached.

Urea: Besides ammonia, urea requires a carbon dioxide input. From the chemical equations, it can be deduced that 2 mol ammonia and 1 mol carbon dioxide eventually react to form 1 mol urea and 1 mol water. Using the molar weights (NH_3 = 17.03 g/mol, CO_2 = 44.01 g/mol, $urea$ = 60.06 g/mol, H_2O = 18.01 g/mol), it can be calculated that per 1000 kg ammonia, 1292 kg of CO_2 is needed and it produces 1763 kg urea.

The price for carbon dioxide is generally low, hovering around €20/tonne in the Netherlands and sometimes even lower [123]. Meanwhile, urea prices are higher at €275 / tonne in Eastern Europe [124], €364 /tonne in the Netherlands if after-treated with a coating to reduce emissions (Novurea brand) [84], or even €393 /tonne in Italy according to the Modena chamber of commerce [125]. Since basic urea will be created without any protective coating around a prill, the lower end price will be chosen.

Besides the material prices, the process requires no additional heating or cooling, although at the start both ammonia and carbon dioxide gasses are compressed to a high pressure of 110-175 bar. For carbon dioxide, coincidentally a paper was found on compressing it to 150 bar (right in the middle of the required range) in stages [126], as seen in figure 27.

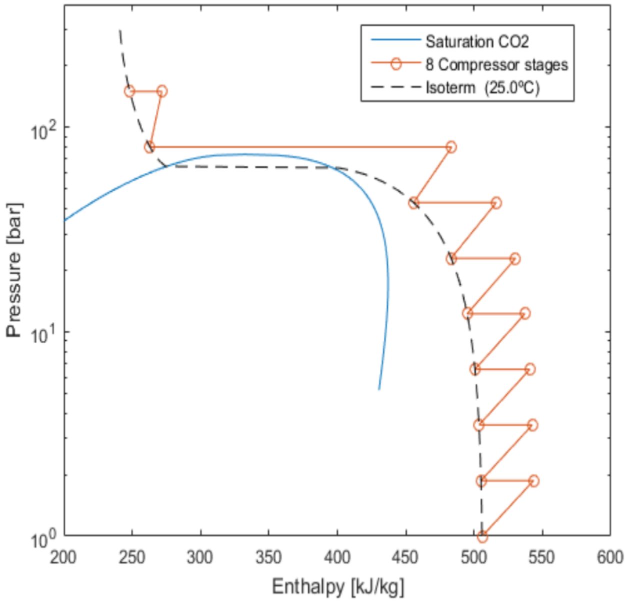


Figure 27: Compression of CO_2 from atmospheric to 150 bar [126]

This was shown to require 90-120 kWh per tonne CO_2. Taking an in-between value (105) for the required 1.292 tonnes, this would require 135.6 kWh, costing approximately €30.0. It should be noted that CO_2 usually comes delivered pre-compressed to an extent, lowering the overall compression costs, however, for this brief process cost analysis this is not included. For the ammonia compression, although no calculations are done, it will likely be in the same order of magnitude, so another €30 euros is added. Finally, since urea requires a gaseous ammonia input, the cost of turning ammonia into gas also needs to be subtracted, which is €134. This results in the following process profits per tonne ammonia input.

$$Profits = (1.763t{*}€275/t) - (1.292t{*}€20/t){-}€30{-}€30€134 = €265$$

Ammonium nitrate - 100%: By producing the ammonium nitrate entirely on the farm, it is possible to have no additional external inputs besides free air. Combining all chemical reactions, 1.5 mol ammonia creates 1 mol nitric acid and then afterwards this one mol nitric acid can react with another 1 mol ammonia to create ammonium nitrate. With the corresponding molar weights (NH_3 = 17.03 g/mol, NH_4O_3 = 80.04 g/mol), per tonne ammonia, 1880 kg ammonium nitrate is made via the full process.

The global wholesale price of ammonium nitrate hovers around €165-415 /tonne as denoted by Alibaba. However, as mentioned before, European prices can vary and generally can be higher. The Modena chamber of commerce stated the price as €255 /tonne [125], which is right in the middle of the global prices and thus will be a good estimate.

For this process there is one last potential major process cost: the compression of the air before entering the reactor. Again taking the molar quantities of the reaction and molar mass of oxygen into consideration (O_2 = 31.99 g/mol), per mol NH_3 input, 7/4 mol O_2 is required, meaning that per tonne ammonia, 3287 kg of oxygen is required from the air. Now, although by volume oxygen accounts for 21% of air, by mass oxygen actually accounts for slightly more: 23% [127]. Thus, to receive 3287 kg of oxygen, a total of 14.29 tonnes of air needs to be compressed. This air is compressed, but to a relatively low 4-10 atm, which (assuming compression costs in the same order of magnitude as the CO_2 from urea), would be roughly $1/20^{th}$ the cost per tonne for $1/20^{th}$ the compression, or about 5.25 kWh/t. In total, compression costs would then be (5.25 kWh/t * 14.29t =) 75.02 kWh or €16.51 per tonne NH_3 input.

Finally, the air does need to be heated beforehand, but the reaction is very exothermic with a lot of excess heat, which can be used to heat up the inlet air as well as be used or captured elsewhere, such as for power generation. However, for simplicity this will not be included here. Overall then, the profits per tonne ammonia are as followed.

$$Profits = (1.88t*€255/t) - €16.51 = €462.8$$

Ammonium nitrate - bought acid: Since in this process ammonia is now not used to make the ammonium nitrate, the overall production quantity would be greater. This means that even if per tonne output of AN less profit is made, the overall profits per tonne input might be similar or even greater. Via very similar calculations as before, using molar mass and equation weighing, per tonne ammonia, 3700 kg of nitric acid would be bought to produce a total of 4700 kg of ammonium nitrate.

The price for nitric acid, despite being a key ingredient in ammonium nitrate production, is higher than ammonium nitrate itself. Global prices according to Alibaba hover around 300-350 USD/tonne for a 68% aqueous concentration, or €366-427 /tonne when converted back to 100% purity. This value is backed up by a market analysis report from 2019 stating that the global average sale price for nitric acid was around 350 USD/tonne [128]. One of the supervisors noted that this price difference could be due to large stockpiles of ammonium nitrate created as a by-product of other processes which could be dragging the price down. This results in the following profits per tonne ammonia.

$$Profits = (4.70t*€255/t) - (3.70t*€366/t) = -€156$$

Ammonium phosphate: As mentioned previously, the focus is on DAP, which uses more of the ammonia and is a more commonly used fertilizer. As perhaps familiar by now, the molar weights (H_3PO_4 = 97.99 g/mol, DAP = 132.06 g/mol) and chemical equations are used to determine that per tonne ammonia, 2877 kg of phosphoric acid is needed to produce 3877 kg of DAP.

The global prices for phosphoric acid hover around 700-800 USD/tonne at an 85% aqueous concentration on Alibaba, or €683 per tonne on the low end. An updated China index price [129] and an outdated document from 2010 also noted that historically this is a reasonable and average price and sometimes even higher [130]. Curiously, one supplier was found offering a price for 85% concentration at just 100-300 USD/tonne [131], however, due to the large price difference, historical pricing, and the fact that no other supplier could be found that came close, this price will be disregarded.

However, the DAP price is significantly lower, at around €440 per tonne [132] and prices are even lower on Alibaba at just €275-375 /tonne on average. Even considering there are no other major heating or compression costs, this results in a rather disappointing profit per tonne ammonia as followed.

$$Profits = (3.877t * €440/t) - (2.877t * €683/t) = -€259$$

As a side note, MAP could have also been produced, however, this would use more of the expensive phosphoric acid per tonne output, yet have a very similar wholesale price (only 5% higher in 2020 [133]), resulting in just more losses.

Final process profits remark:
For this process profitability section, the scoring on the 0-5 scale is done afterwards with 0 denoting processes that make no or negative profits, 5 denotes the most profitable process and the rest of the values are spread somewhat linearly in between.

A.3 Initial Costs

This section is on the upfront costs to purchase and install the equipment in the first place. This will be worth a slightly lower 4 points, because profitability is still more important, but initial costs can be high enough that earning it back takes years or even decades. Essentially a profitable process with a high initial cost can still break even and be profitable overall in the long run, but a process that costs more money than it makes will never be profitable, even with non-existent initial costs.

Originally for this section the estimates were going to be made using Sinnott and Towler's industrial equipment cost estimation values, which is well documented and reliable [107]. However, one key issue arises: the lower bound of those industrial estimates tend to be in the tonnes per hour or litres per second range. However, in the case of MEZT, only 0.95-1.91 kg/hr of ammonia is made, which even at 10% enrichment accounts for an input flow of just 5 ml/s. Clearly then, small-scale equipment estimates are needed, which may be acquired via various sources.

Nonetheless, a few things can still be taken. For example, the raw cost multiplier for stainless steel versus regular carbon steel is 1.3, which is necessary in practically all cases as ammonia is corrosive [107]. Moreover, the installation factors can be taken, which is multiplied by the raw equipment cost to achieve a final cost including further equipment, construction, piping and control, labour and installation. An overview of these installation factors can be found in table 9, which has directly been taken from the book.

Table 9: Proposed industrial installation factors [107]

Equipment Type	**Installation Factor**
Compressors	2.5
Distillation Columns	4
Fired Heaters	2
Heat Exchangers	3.5
Instruments	4
Miscellaneous Equipment	2.5
Pressure Vessels	4
Pumps	4

Lastly, for bulk purchase of ingredients and storage of final products, a storage tank cost can be estimated via Sinnott and Towler, as the ingredients may be purchased once a year (for example). The smallest storage tank possible via this estimation of 10 m^3 would then cost $(5,800 + 1,600 * (10)^{0.7} =)$ 13,800 USD or €11,500. After consulting with the supervisors, the costing via Sinnott and Towler was deemed excessively expensive for the farm application, as typically either large 25-50 m^3 plastic containers are placed on a farm at a price of roughly €7000 per unit, or IBCs are used, which are 1 m^3 each and significantly cheaper. Checking the specifications of IBCs, a rigid PVC IBC appears to be most resistant to the largest range of materials which are used in this paper (offering "good resistance" or better to 95% sulphuric acid, 85% phosphoric acid, 50% nitric acid, any ammonium phosphates, ammonium sulphides and urea), although the more common HDPE IBC is just as suitable to all these chemicals except sulphuric acid. Since it is more common, a new UN-certified (thus allowing dangerous chemicals to be stored) 1000 L IBC is costed at €155 a piece [68]. This price will be used for the majority of storage tanks in this section, although since all processes require a final product storage tank, that final tank will not be included here.

Wholesale gas and aqueous ammonia: From the previous profitability section, the cooling and condensing requirements amount to 4280 or 6334 kWh/tonne NH_3 depending on if the aqueous ammonia is merely concentrated to 25% or fully gasified. This translates to a cooling requirement of 4.1-8.2 kW for 25% or 6.0-12.1 kW for 100% (the variation is due to the varying 10-20 L/hr output).

Taking 10 kW as an input, a cooling system cost can be estimated. According to an equipment pricing estimation book [134], an entire 10 kW (34,120 BTU/h) air conditioning system including all surrounding equipment and installation would cost 31,390 USD in 1989. Adjusting for inflation and exchange rates, this comes to €55,625. However, there has likely been quite some development and cost reduction in air conditioning units in the last 32 years and coincidentally, a 10.5 kW (36,000 BTU/hr) residential AC system is a common size, which including head unit and installation averages around €3500 in the Netherlands [135]. Admittedly, this may not be as heavy duty as an industrial application, but perhaps it would be possible to modify an air-conditioning unit to cool the 10% NH_3 mixture instead of the normal coolant, which would require no additional equipment, except for maybe some additional piping/controls, but likely below €4000. Alternatively, if this is not possible (e.g. material incompatibility or does not work with gaseous flow instead of liquid), it would certainly be possible to cool water and have it enter a heat exchanger with the 10% NH_3

mixture instead of the original head unit, which should be easy to implement. During this section it was also realised that the power an air-conditioning unit consumes is about $1/3^{rd}$ of the rated cooling capacity, so the 10 kW unit only consumes about 3-3.3 kW of electricity. This has been accounted for in the "process profitability" section earlier on.

Wholesale via ground/tap water cooling: If the cooling is to be done via normal tap water or ground water, as mentioned before, the temperature difference is very small (if at all feasible). For this, heat exchanger calculations are done.

Taking the Sinnott and Towler book as reference, an overall heat transfer coefficient of 800 W/m^2K can be determined, as seen in figure 28. Reassuringly, the condensing water has a vastly higher heat transfer coefficient than simply gas, which is a good sign.

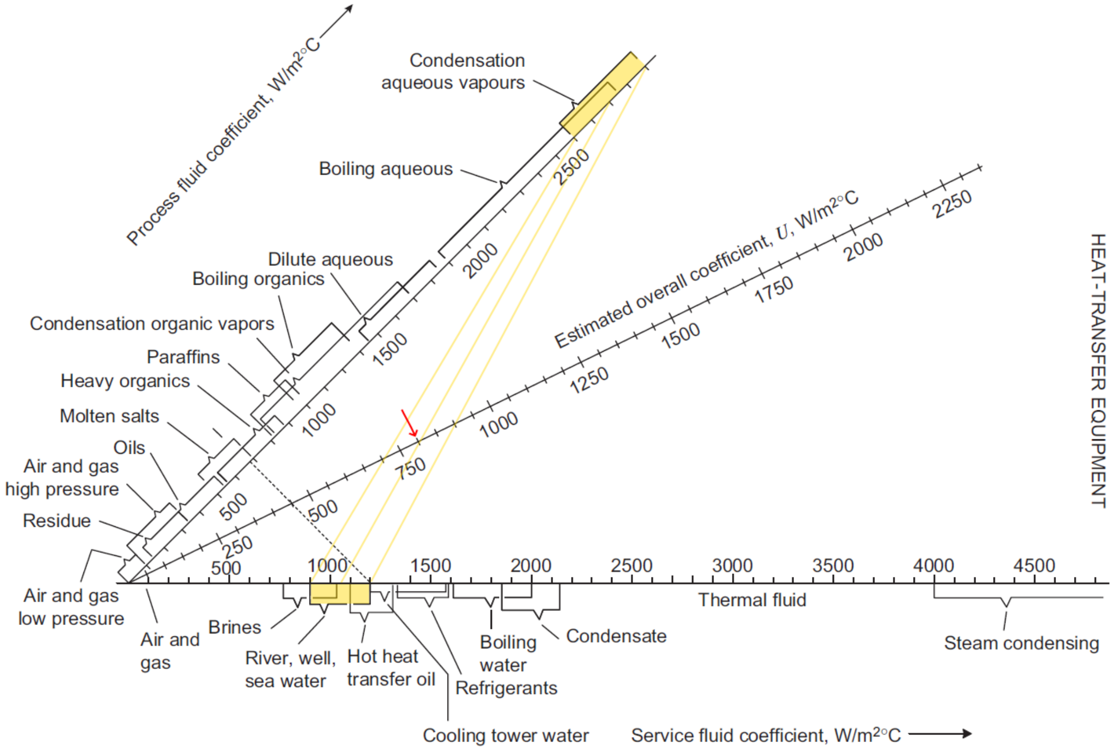


Figure 28: Overall heat transfer coefficient estimates based on fluid types [107]

Taking the 10% mixture inlet and outlet temperature as 25 and 15 °C and the cooling water inlet and outlet as 10 and 20 °C in a counter-current setup, an average ΔT_m of 5 °C can be taken. This should be a good balance between having a large enough temperature difference while still extracting the most coolness from the cooling water. Since the exact cooling requirements still vary and depend on output, a 10 kW requirement will be assumed for now that can easily be scaled. With that the following heat exchanger area can be calculated.

$$A = Q/(U * \Delta T_m) = 10,000/(800 * 5) = 2.50m^2$$

Considering the small flow, this is a fairly large heat exchanger. However, this does allow a cost estimate by Sinnott and Towler as both double pipe and plate and frame heat exchangers can be estimated from $1.0m^2$ onwards. The cooling in a cold trap coincidentally occurs often via a simple double pipe heat exchanger. This would result in the following raw cost.

$$P = 1900 + 2500 * (2.5)^{1.0} = USD8150(carbonsteel) = 10595(stainless)$$

Funnily enough, the plate heat exchanger option ends up being considerably cheaper at just 2101 USD. Checking this raw cost with similarly sized stainless plate heat exchangers on Alibaba confirms this result is realistic. Taking the 3.5 installation factor and exchange rate into consideration, a price of €6108 is acquired.

$$P = 1600 + 210 * (2.5)^{0.95} = USD2101(alreadystainlesssteel)),$$

Upon further investigation, plate heat exchangers tend to have a higher pressure drop, making them less favourable in many cases, but since a vacuum condition is wanted, this pressure drop may not necessarily be that much of a problem. In fact, plate heat exchangers exist that are specifically designed for condensing under vacuum conditions are available, such as AlfaCond by Alfa Laval [136].

In case the (more profitable) groundwater option is chosen instead of tap water, a water pump is also required to pump water from about 10 m underground. However, first the flow rate is needed. With a Cp value of 4.20 kJ/kg*K for water, a 10 °C increase in cooling water temperature and an average 10 kW requirement, the water flow is calculated as (10 kW / (4.20 KJ/kg*K * 10 °C) =) 0.238 kg/s of water, which is a factor of 50 times higher than the aqueous ammonia flow (5ml/s). Normalising this water requirement leads to 857 L/hr, which can be used to source a water pump. This 857 L/hr is right in between the low 694 L/hr and high 1040 L/hr calculated earlier on and a pump specifically for a well application has been found matching the flow rate and head, which even includes an integrated filter [116]. This costs €194, which with an installation factor of 4 for pumps would result in €776.

Lastly, a gas-liquid separator drum is required for the ammonia stream. Since this stream is very small (condensed part below 5 ml/s), the separator drum can be very small. On Alibaba the smallest drum found for 300 USD had a volume of 150 L and an hourly capacity far greater than needed. Looking further, air-oil separators follow the same principle but have much lower capacities (around 1 litre) and smaller sizes and can be bought for 50 USD. With a ”pressure vessel” installation factor of 4, this would cost €166, resulting in a total cost for this stage of €6274 for tap water applications or €7050 for ground water applications. Please note that this drum is also necessary for the air-conditioned variant.

An overview of the possibilities discussed for the wholesale can be found in figure 29. Here, option A is condensing via a household or commercial air conditioning unit with an initial cost of roughly €4000, or more if the ammonia mixture has to be passed through a separate cooler (option B). Option C is via the tap or ground-water water-cooling with a larger heat exchanger (due to a small temperature difference), with an initial cost of up to €7050.

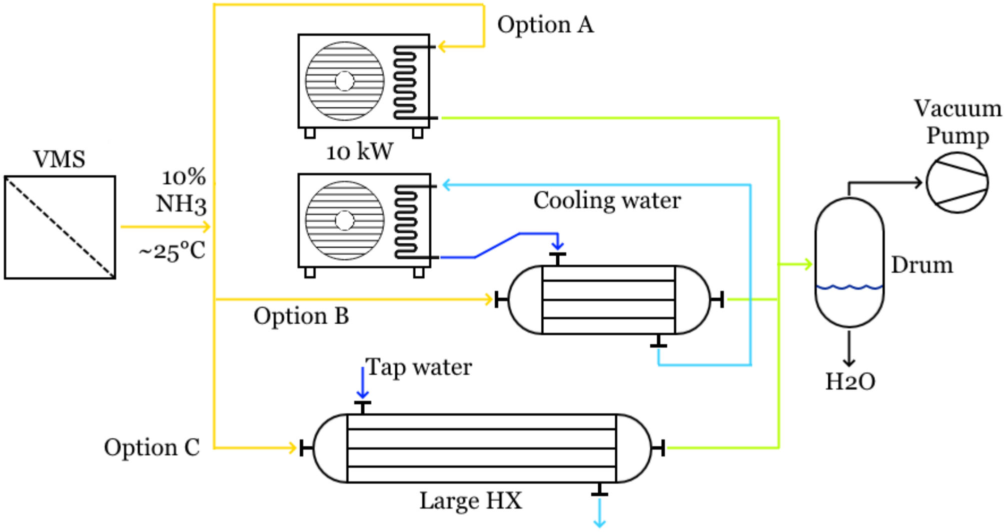


Figure 29: (Repeated from main section) 3 options for water condensation

Alkaline fuel cells: Estimating the cost for AFCs is much simpler. Gencell is currently the only known firm providing costs and specifications on an AFC that will be commercially available within the coming year. Their 4 kW unit, which consumes approximately twice the amount of ammonia as the MEZT process consumes (2.5 kg/hr vs 0.95-1.91 kg/hr) has a unit cost of €70,000-80,000 [26]. This includes all required equipment and optionally it can also come pre-installed in a 10ft container [137]. Since this includes everything except hooking it up to the ammonia supply and transport/installation, a 2.5 install factor seems excessive. Instead, a 1.5 install factor will be taken, as it is more typical for cases where only transport, installation, and final controls/checks are required [134]. This results in a final initial cost of €105,000-120,000. It should be noted though that since this technology is still in its infancy that prices will likely drop significantly in the future.

Solid oxide fuel cells: As no commercial SOFCs for ammonia fuel exist, estimating the cost is going to be very difficult, but it will likely be in the same range as AFCs. However, with the research on SOFCs, it is possible to make an estimate of capital costs in the future. A study from 2014 (which considering the rapid development may be considered outdated) investigated all-in unit costs at production quantities ranging from 100 to 50,000 units [138]. It was mentioned that a 1 kW unit, including supply connections, control units and even a manufacturer mark-up, would cost between 12,520 USD (50,000 units) and 23,129 USD (100 units). For a larger 5 kW unit, the price was only marginally higher at 15,783 to 27,056 USD. Taking an in-between value for both production quantity and power (the 0.95-1.91 kg/hr NH_3 can produce approximately 1.5-3.1 kW) would result in a price of about 20,000 USD. If one assumes a 2.5 installation factor for ”Miscellaneous Equipment”, also since for a fuel cell running on ammonia instead of the typical hydrogen there may be unforeseen additional costs, the final price is estimated at €41,500.

Enriched biochar: As mentioned before, only the enrichment will be considered for an apples to apples comparison. For this, only a gas adsorption column is required. For sizing, since 16.4 tonnes of biochar can be enriched per tonne ammonia, at the hourly ammonia flow rate, 15.58 kg to 31.32 kg/hr of biochar can be enriched. Similarly, at an ammonia gas density of 0.73 kg/m$^\mathbf{3}$, roughly 2 m^3/hr of ammonia gas is used.

The gas adsorption column is a batch process and momentarily no solutions exist for continuous adsorption columns. Thus, an adsorption column large enough for convenient biochar replacement is needed. If we assume that the biochar is to be replaced once a day, then the adsorption column needs to hold 374 to 752 kg of biochar. An activated carbon adsorber of this size according to one of the equipment estimation costing, including inflation, exchange rate and installation would cost €92,111 [134]. However, this probably is also meant for a much higher flow rate (which was not mentioned), which could explain the somewhat excessive cost considering it is simply a large enclosed cylinder with some support grids and packing.

Looking further, an activated carbon absorber able to hold 125kg of carbon and allowing a flow of 1500 m^3/hr (417 l/s) of air can be bought for €600 on Alibaba. For the maximum 752 kg/day biochar, this would then scale to €3610. Then adding a 2.5 installation factor for "Miscellaneous Equipment" results in €9025. This is a factor 10 lower than the previous estimate, but at the same time, it does exactly what it needs to do and nothing more: adsorb ammonia. It should be noted, this unit has a wide activated carbon surface area, but short residence time of air in the carbon, thus optimized for low resistance and high flow rates (and a relatively low extraction efficiency of 80%). For biochar enrichment a longer residence time is preferred, typically in the range of 50-100 minutes to fully adsorb ammonia [43]. A longer/taller and narrower column would be preferred as it gives more time (distance) for the ammonia to adsorb onto the biochar and the extra flow resistance is not a problem for the much lower ammonia flow rate. An overview of the proposed design can be seen in figure 30. Eventually it could perhaps be possible to automate it via having gated hoppers on top and at the bottom which open and close periodically.

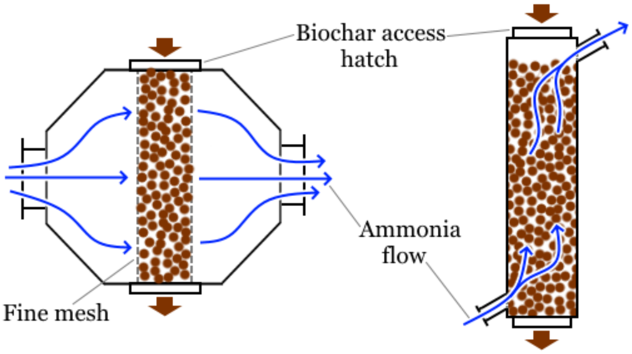


Figure 30: Biochar adsorption equipment available (left) and proposed (right)

However, since this process *requires* a gaseous ammonia input, the entire costing of the gaseous ammonia stage also needs to be added. As mentioned before, the air-con stage is chosen, so an additional €4,000 is added for a total of €13,025.

Ammonium sulphate: For this costing, only a mixer or agitator tank is necessary. Depending on the concentration of ammonia entering the tank, a bubbler may be added to the bottom in case some of the ammonia is gaseous.

To determine the size, a reaction speed or residence time is needed. Acid-base reactions generally happen very quickly, essentially immediately as soon as it is properly mixed. Searching online, a reaction time of up to 5 seconds was found, often being quicker [139]. With an aqueous ammonia flow rate of around 5 ml/s and a sulfuric acid flow rate of 0.83 ml/s, a reaction chamber of at least 30 ml is required, or about the size of a shot glass.

However, instead of a very small mixing chamber or agitator tank, which would require active mixing and a (perhaps expensive) control unit, a simple alternative will be suggested: If a much larger (but still small) tank is used, no active mixing or control is required. The dripping of the sulfuric acid from above creates a very slight mixing effect and diffusion and a (very) long residence time will ensure the rest is mixed. Moreover, a larger container will help "catch" and reduce the effect of fluctuations in ammonia concentration (if they even exist), meaning the sulfuric acid input can be set as constant. Then the reacted mixture can either be piped directly to a separate storage tank, or it could even be happening inside the final storage tank for greater compactness.

All things considered, this process can be as simple as a few hoses, a (digital) flow rate controller and a storage tank for the sulphuric acid and final product. The storage tank for a year's worth of sulfuric acid (about 26 m^3, or coincidentally about one truck-load) would consist of 26 IBCs of €155 each for a total of €4030. If we add a reasonably small installation factor for all piping and control of 1.5, the total price would come to €6045.

Urea In this case a tank for CO_2 is needed, compressors are needed to compress to 150 bar, both for CO_2 and ammonia, a synthesis reactor, a large distillation column, a small simple flash drum, and (if applicable if a solid output is wanted), a dryer and prilling tower is needed.

To calculate the reactor size, the higher boundary of residence time (60 minutes), higher boundary of flow rates (2.47 kg/hr for CO_2) and densities at operating temperature and pressure (150 bar, 170 °C, NH_3 = 134.6 kg/m3, CO_2 = 213.0 kg/m3) will be taken to acquire a reactor volume of (1.91/134.6 + 2.47/213 = 0.02578 m^3 =) 25.8 litres. Finding a proper synthesis reactor of this size for sale is going to be near impossible, especially for the extremely high pressure requirement (150 bar). Unrealistically extending a graph line in one of the costing documents down to the required size resulted in a rough price of 10,000 USD [134], whereas on Alibaba the cheapest reactors that meet both the size and pressure limitations start from about €3,000, albeit at a larger 100 L size. Since this reactor is a pressure vessel, the highest 4.0 installation factor will be assigned, resulting in a price of €12,000.

For the distillation column, without doing extensive calculations on size, different pressures, temperatures and stages within the column, finding a proper cost would be practically impossible. Even more so with the small size (assuming a size no larger than the reactor due to its long residence time; 25 L), an industrial distillation column may not even exist. The only distillation columns of this size available commercially are for small scale commercial alcohol brewing. Although likely completely unsuitable for Urea production, the roughly €700-1000 cost (with 4.0 factor, €2800-4000) of these on Alibaba should give a very rough insight of what to expect.

For the compressors, taking the 105 kWh/tonne energy requirement and 2.47 kg/hr CO2 input, a compressor system of 0.259 kW is needed. In large scale due to the huge pressure increase several stages tend to be used, but due to the low power, a single compressor will be costed. The smallest (electric) compressor that meets the requirements start around €250 from Amazon.nl and have a 1kw+ and 300 bar capability. Purchasing two (the second for the ammonia stream) and implementing the 4.0 pump/pressure vessel installation factor results in €2000.

For the flash drum, the same one as from wholesale will be assumed, being roughly €166. Finally, for the CO_2 storage tank needs, up to 21,637 kg of CO_2 needs to be stored. Small-scale CO_2 is typically stored at around 60 bar and expands at a 535:1 rate, meaning that for an approximately 1.8 kg/m^3 ambient temperature and pressure, the density in the tank will be 963 kg/m^3 [140], which align with the rough values given by the Engineering Toolbox. This would require a 22.5 m^3 pressure tank. However, commercially stored CO_2 is at lower pressures, typically only 20 bar. A typical unit has been found that can supposedly store 22,500 kg of CO_2 at 24 bar in a roughly 10 m long by 1.9 m diameter container, weighing 7000 kg [141]. Unfortunately, no price was given, but with this vessel weight, it can be estimated using Sinnott and Towler as $(10,200 + 31 * (7000)^{0.85} =)$ 67703 USD or €56,134. With a 4.0 pressure vessel installation factor this comes to over €220,000! However, this pressure vessel installation factor seems excessive since this is merely a non-cryogenic CO_2 storage tank, so instead a more relaxed installation factor of 2.0 is chosen for a tank cost of €112,268. A much smaller vessel is also possible that is then refilled (for example) monthly, but at that point it will only be filled with less than 2 tonnes or 40 euros of CO_2. Transportation and delivery costs would increase this process cost significantly, but it may be worth it over a lifetime.

Lastly, since urea requires a gaseous ammonia input, the air-con stage cost is added, meaning that with an additional €4,000, the overall cost is about €22,200 without CO_2 storage tank or up to €134,500 with a large tank. This also does not even take into consideration (for example) the steam re-heaters and recycle pumps that exist in the large scale version which likely increase the price somewhat too. A dryer and prilling tower could eventually also be implemented, but for consistency and since prills/dry fertilizer isn't needed, the aqueous output will be considered sufficient.

Ammonium nitrate - 100%: This is yet another complex process, requiring a compressor for both air and ammonia, a heat exchanger to preheat the air, a static mixer, a catalytic reactor, a heat recovery/cooling system, a condenser (which is a further cooling stage) and an absorption column. Then, to turn the nitric acid into ammonium nitrate, a second reactor is needed and (optionally) an evaporator and prilling tower.

For air compression, as mentioned previously, 75.02 kWh per tonne NH_3 is needed, which translates to a compressor power of just 71-143 watts. Alternatively, a flow rate of (1.91 kg NH_3/hr * 14.219 kg air/kg NH_3/ 1.225 kg/m3 / 60 min =) 371 L/min is required. Air compressors for car tires or model airbrush painting have the right pressure rating and can be bought for as little as €15-20, but tend to have a too low flow rate (1/5^{th} of what's needed) and a duty cycle of only half an hour. Attempting to find industrial grade air compressors, one quickly returns to the same prices as the higher pressure, higher capacity models. A final price of €1000 will thus be assumed (only for the air compressor. The ammonia gas input is assumed to already be under sufficient pressure).

For the air pre-heater/heat exchanger setup, without knowing to what temperature the air is preheated and specific chemical reaction kinetics, only a very rough estimate can be made. What is known is that after the reactor the temperature difference is very large. If one assumes a case where the air is heated from ambient to about 400 °C and the reactor output is 800 °C, an average temperature difference of 400 °C can be assumed (very roughly speaking). Via the same method as for wholesale (see figure 28 and subsequent text) the area can be determined. The 371 L/min = 6.183 L/s = 7.57 g/s air has a c_p value of between 1 and 1.1 J/gK over the whole 300-1100 Kelvin range. Taking the higher value, a heat requirement of (7.57 * 1.1 * 400 =) 3331 W is determined. If air is taken as a service fluid, a coefficient of about 50 W/m^2K is chosen, which results in an area of (3331 / (50 * 400) =) 0.166 m^2. For this, a plate heat exchanger cannot be used as their operating temperatures are far too low due to the rubber sealant between layers. A more traditional tube heat exchanger is more appropriate. As seen before, these are a factor of about 5 times more expensive, however, since the area is more than a factor 15 smaller, taking the aforementioned €6108 cost as an estimate for two 0.166 m2 heat exchangers is likely to be in the same order of magnitude.

For the static mixer, the volumetric flow rate and size is needed. However, with the wide pressure range (about 4-10 bar) and temperature range, the density of air can vary a lot. For example, if the inlet of the static mixer is at 10 bar and only 120 °C, density is about 10 kg/m^3, but at 4 bar and 800 °C, it is only 1.3 kg/m^3. Taking this worst case scenario for the largest reactor and mixer, and a 7.57 g/s air flow would be 5.82 l/s. The maximum ammonia flow rate alone is just 0.53 g/s, much smaller, and no density could be found in this supercritical phase (it likely would have reacted already), but it will be assumed similar. A total maximum flow rate of roughly 6.5 L/s can be assumed. Sinnott and Towler does allow a static mixer cost to be estimated, which is $(570 + 1170 * (6.5)^{0.4} =)$ 3043 USD. Accounting for a stainless steel construction (*1.3), exchange rates, and a 2.5 miscellaneous equipment installation factor results in a cost of €8167.

This same volumetric flow rate can be used to estimate the reactor size. The residence time for nitric acid production is very short, often with a residence time in the range of 10^{-3} to 10^{-4} s on the catalytic bed [142] and a slower 0.16 to 1.46 s for the NO oxidation. Combining the longest times together, the reactor size would be about 9.5 L. For this, no commercial reactors could be found that came close to the requirements (either way too large or too low operating temperature) and no platinum and rhodium gauze catalyst price could be found either (all prices are "on request"). Thus, for now due to its similar size to the Urea reactor, a very rough total cost of €10,000 will be estimated.

The subsequent cooling system can be done via one of two ways: either extracting all usable energy (which would require a separate (for example) micro steam turbine and exchanger setup) or via direct cooling using ambient air. Assuming the reactor output flow has similar characteristics to the input flow (i.e. a total of about 8.1 g/s and 1.1 J/gK), and a large temperature drop of 750 °C, a cooling requirement of 6.7 kW is reached. Although an industrial grade heat exchanger could be costed, a more realistic estimate would be using automotive radiators. Even smaller automotive radiators have a cooling capacity an order of magnitude greater or more, meaning that even with the lower heat transfer coefficient of flowing air through the radiator instead of water, a stainless steel car radiator should theoretically work. Radiator prices start from about €50, but stainless steel radiators do not commonly exist as aluminium radiators tend to cool better and are lighter. However, custom made radiators can be ordered for around €500 and the process of creating an aluminium or stainless steel radiator is practically identical, so that price will be assumed. With a 3.5 heat exchanger installation factor the final price is €1,750.

Finally, for the nitric acid production part an absorption column is needed. Since at this point the flow is (partially) condensed, and nitric acid has a density of 1.51 g/cm^3, the flow is much smaller. Significantly larger absorption columns/scrubbers can be had for as little as €1000, so a final price similar to the distillation column estimate of urea should be more than sufficient: €2800-4000

Afterwards, the ammonium nitrate reactor takes place. Considering in the full process 1.88 kg AN is made per kg NH_3, and hourly production rate of up to 3.8 kg/hr is established in the reactor. Taking a 1.51 kg/l density and a 22.1% concentration (see next "bought acid" part for details of these calculations), a flow rate of 11.4 L/hr is determined. Since this is an acid-base reaction, a short residence time just like for ammonium sulphate will be assumed (5 seconds) resulting in a reactor volume of just 16 ml. Just like for ammonium sulphate, a larger reactor will be assumed for simplicity and since neither extremely high temperatures or pressures are expected, a stainless steel chamber with some baffles is possible, or perhaps even directly entering the storage chamber. High pressure hydrothermal Synthesis batch reactors of 50-100 ml can be had for as little as €50 on Alibaba, so the cost of a similarly sized continuous setup will likely will not exceed €250, or €1000 with a 4.0 installation factor.

Lastly, an evaporator and prilling tower can be installed, but this is only necessary if a dry product is wanted, which for the sake of consistency and simplicity will not be considered. The overall total cost of this production is then €32,025.

Ammonium nitrate - bought acid: This section is nearly identical to the full-production method, except that only the ammonium nitrate reactor is needed and a storage tank for bought nitric acid. The production quantity is greater though, meaning some calculations on size have to be made.

To determine the concentration and thus size, first the hourly rate is determined. Here, per kg NH_3, 3.7 kg nitric acid is bought and 4.7 kg ammonium nitrate is produced, resulting in an hourly production rate of 8.98 kg/hr. At ambient conditions, this has a density of 1.72 g/cm_3 and thus a pure flow rate of 5.22 L/hr. However, the ammonia input is concentrated at 10% (20 L/hr) and the nitric acid is concentrated at 68%, which with an overall density of (0.68 * 1.51 + 0.32 * 1.00 =) 1.347 kg/l and mass rate of (3.7*1.91 =) 7.07 kg/hr, results in a flow rate of 4.68 L/hr. The total flow rate is then 24.68 L/hr with a concentration of 21.1%. The reactor size is then larger than before, but still similarly small at 34.3 ml. This still fits within the same small reactor, so the same €1000 will be costed.

For the nitric acid tank, the 7.07 kg/hr nitric acid need is taken and converted. At the respective density this results in a pure flow rate of 4.68 L/hr or 6.88 L/hr at 68% concentration. Per year this amounts to 60,269 L or about 60 m^3. This is approximately 2 full truck-loads, so only half the amount will be costed for storage to be emptied twice a year. The 30 m^3 tank consists of 30 IBCs, which with the 1.5 installation factor amounts to €6975. The overall total price for the whole system is then about €7975.

Ammonium phosphate: This process consists of a simple pipe reactor, a storage tank for the phosphoric acid, a gas post processing part and (if solid DAP is wanted) a drum-granulator drier and furnace.

For the reactor first a size needs to be determined. At a maximum 20 L/hr aqueous NH_3 input (1.91 kg/hr pure), a total of 5.50 kg/hr phosphoric acid is needed (at a 1:2.877 ratio). Taking a typical phosphoric acid concentration of 85%, 6.47 kg/hr of fluid is needed, or at a density of 1.685 kg/L (at 85% concentration, ambient conditions), 3.84 L/hr is needed. The total input is then 23.84 L/hr or 6.62 ml/s. The reaction is again a simple acid-base reaction, so a fast reaction time of 5 seconds will be assumed for a reactor size of 33 ml. The pipe reactor is essentially very simple, being a pipe where both substances enter and react together. The same €1000 reactor price will be assumed, since at this small size an accurate prediction is practically impossible. However, on Alibaba if one takes a small static mixer (still 25 L capacity, far above what is necessary) with two inputs and a 4.0 installation factor, the result is a similar €1000 price.

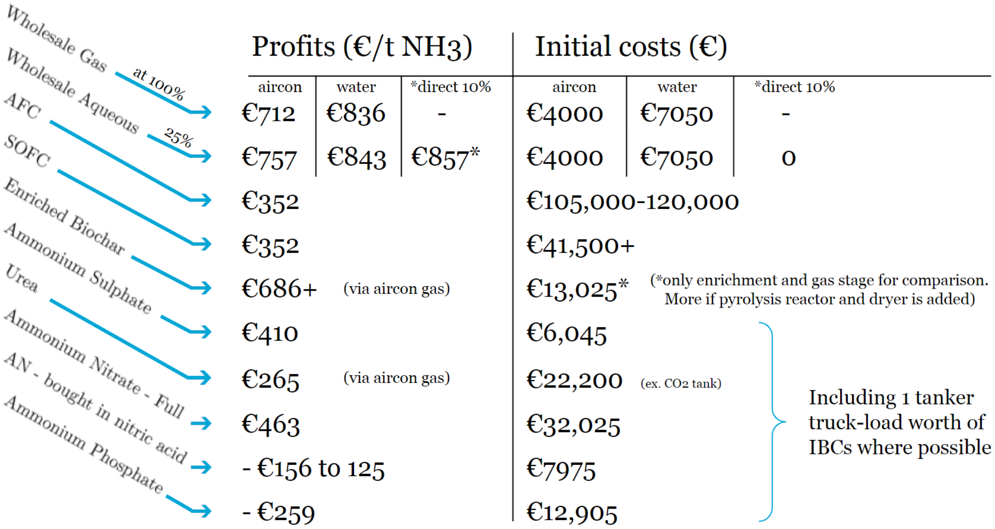
For the storage tank, taking the 3.84 L/hr input, a 33,636 L ($34m^3$) storage tank is needed for one year's worth of phosphoric acid, which is about one full truck-load. Like before, 34 IBCs will be costed at €155 each with a 1.5 installation factor for a total price of €7905.

For the gas post-processing to prevent the majority of harmful emissions, ideally a gas cyclone and multiple scrubbers would be needed. However, for simplicity the same gas absorption/scrubber estimate as before will be taken since it is far more capable than required. This would then cost €2800-4000.

Further post-processing to granulate and dry the product (essentially the dryer-granulator and small heater) has been excluded for an equal 'apples to apples' liquid output comparison and since for use on the farm it is not necessary. The final total initial cost then comes to €12,905.

Final remarks and summary:
As evident, the majority of the equipment is at a very small scale and as such the pricing should not be used for anything more than comparing the processes in this report. For a more accurate final price, producers and custom builders will need to be contacted and a specific design would have to be made too. However, for most equipment, a large scale production will bring the equipment cost down drastically. Furthermore, a truck-load worth of IBCs has been used for the input material storage tanks, but eventually it may be possible to order smaller quantities without a substantial penalty in input costs, which would decrease the storage tank costs by a fair amount. A summary of the process profitability and initial costs of all major investigated options in this paper can be found in table 10. Please do not forget that this excludes the impact of the rest of the MEZT solution train, so for the complete process the costs will be higher and profitability will be lower.

Table 10: (Repeated) Profitability and initial costs of all investigated processes



	Profits (€/t NH3)			Initial costs (€)			
	aircon	water	*direct 10%	aircon	water	*direct 10%	
Wholesale Gas at 100%	€712	€836	-	€4000	€7050	-	
Wholesale Aqueous 25%	€757	€843	€857*	€4000	€7050	0	
AFC	€352			€105,000-120,000			
SOFC	€352			€41,500+			
Enriched Biochar	€686+ (via aircon gas)			€13,025*			(*only enrichment and gas stage for comparison. More if pyrolysis reactor and dryer is added)
Ammonium Sulphate	€410			€6,045			Including 1 tanker truck-load worth of IBCs where possible
Urea	€265 (via aircon gas)			€22,200 (ex. CO2 tank)			
Ammonium Nitrate - Full	€463			€32,025			
AN - bought in nitric acid	- €156 to 125			€7975			
Ammonium Phosphate	- €259			€12,905			

A.4 Reliability, Maintenance

This section is on the reliability and maintenance. Since for most cases no real values or data can be found, logical deduction and reasoning will be used. It will predominantly look at the complexity of processes (more complexity and moving parts = less reliable), if there are perishables that need to be replaced frequently (e.g. filters) and if the system needs to be checked up on frequently due to (for example) corrosion or clogging of the system.

Wholesale gas and aqueous ammonia: If the straight 10% process is taken, there is literally no process at all, which of course has the best reliability and maintenance requirements.

When one considers the cold trap for a higher concentration output, it is slightly less simple. Using the (for example) air-conditioning unit to cool the stream would typically require annual services and check-ups to ensure the cooling keeps functioning reliably. If one uses tap water to cool and condense the stream, the pressure from the tap line is sufficient and thus reliable. However, if ground water is used, a little pump does introduce a moving component. Also, in either case, the heat exchanger might need to be occasionally checked upon as scaling or deposits (e.g. minerals) may occur that require cleaning or an occasional flush, but this is probably not going to significantly impact the process for at least a few years. Still, the overall reliability and maintenance are good for this process, thus receiving a maximum score of 3.

Fuel cells: Both fuel cell types are combined here as they are perceived to have an identical score. For maintenance, GenCell states that the unit requires semi-annual maintenance, including an air filter and electrolyte replacement. In terms of reliability, it is hard to tell. There are not many moving parts and electrical components tend to be fairly robust, which is good for reliability, but the generally high operating temperatures (600+ °C) and novelty of fuel cells means that not all kinks may be worked out. The overall score is then reasonably good, but not exceptional, for a score of 2.

Enriched biochar: At first thought one would think that only the enrichment itself will be taken into consideration for a fair comparison as other processes may produce raw biochar on the side as well. However, for the total reliability the entire process may need to be taken into consideration, since if the raw biochar production fails, the enrichment of said biochar cannot take place. Similarly, for other processes, if the raw biochar production fails, the rest can still continue as normally. For maintenance though, only the enrichment process will be taken into account.

In terms of maintenance, since biochar can crumble, come in irregular sizes and perhaps have certain contaminants or hard lumps (e.g. a cow unintentionally ate a rock), somewhat frequent cleaning may be required to prevent build-up of soot or clogging of passageways. This holds true for the entire process, including the creation of biochar before enrichment.

In terms of reliability, the process can be fairly simple. The adsorption column is nothing more than a trap for biochar with ammonia gas flowing through, thus few moving parts and reliable. The dryer can be fed by the produced fuel from the pyrolysis reactor and the pyrolysis reactor is again self-sufficient in terms of heating. It should be noted though that some form of mechanical or electrical control is needed to move the manure along the drying process and in and out of the pyrolysis reactor, such as a worm-screw for example, which introduces moving parts. On top of that, high temperatures (around 400 °C) may reduce the reliability of the system. Taking the overall only average reliability and somewhat frequent maintenance, the final score is 1.

Ammonium sulphate: This process is incredibly simple with only passive mixing of two substances at (almost) ambient temperatures and pressures. If any moving component is even needed, it would be a small pump to pump the sulphuric acid from the tank to the reactor (or reaction area). Furthermore, taking the high purity of input components, no clogging or fouling is expected. Overall, no significant maintenance or reliability issues are predicted, resulting in a maximum score of 3.

Urea: Urea is a fairly complex process with a reactor and distillation column, recycling streams with pressure reducing valves and multiple pumps pumping to very high pressures, placing the entire system under a substantial amount of stress. On top of that, the high corrosion capabilities of the substances made in the reactor, even for specially made materials, means that (in combination with high pressures) frequent check-ups are needed to prevent leaks, ruptures, and component failures. The corrosion also means parts will likely need to be replaced often, which with the complexity is no mean feat. It should come to no surprise then that the overall score is the lowest available, at 0.

Ammonium nitrate - 100%: This process is yet more complex than that of urea; however, the high pressure has been replaced with high temperatures (800+ °C). There are now also multiple heat exchangers, pumps, a condenser, an absorption column and perhaps even also an entire heat recovery system to consider, in addition to the ammonium nitrate reactor afterwards. This does not bode well for reliability, with many points of failure, moving parts (compressors), filters and heat exchangers that can leak, especially under the stress of large temperature differences.

Maintenance is not exceptionally good either, since the fresh air that is used will need a filter replaced somewhat frequently and compressors need servicing. Cleaning requirements within the system is unknown, but if a heat recovery system is used, there is perhaps a micro steam turbine that also needs servicing. It was also found that for the nitric acid reactor, the catalyst gauze has an 8-12 month lifespan before the platinum has decomposed to the point where it seizes to function [143]. All this combines to an overall score of 0.

Ammonium nitrate - bought acid: Without the nitric acid production, the process is actually fairly simple, reducing down to a simple reactor that is not too different from ammonium sulphate. Much of the same logic applies, but temperatures are a bit higher (steam generation at higher input concentrations, increasing pressure) and if the prills need to be made, there are additional steps to consider. Overall, it receives a respectable score of 2.

Ammonium phosphate: Essentially this process is a tube acid-base reactor similar to ammonium nitrate and with similar characteristics. However, the exhaust gas post processing step reduces reliability and maintenance somewhat. Precise control is needed for optimal conditions producing the least emissions which need to work reliably at all times and the (for example) absorption column or scrubber needs its scrubbing water replenished or treated often, as it cannot simply be dumped into the environment. On an industrial scale, DAP production tends to have several steps of exhaust gas treatment, which is quite complex. On top of that, if a dryer-granulator is used, you have a moving part and the bed will break up the DAP into granules, wearing itself down and requiring some maintenance. The overall score is thus a 1.

A.5 Ease of Use

This section is about how easy the process is to use for the farmer, which is largely determined by if it requires frequent operation by the farmer or if it can be automated. What will also be considered is how easily the system can be ”plug and play” and if ingredients need to be bought frequently or not. This is worth 3 points, as a system that is not easy to use may not be adopted easily by farmers or could lead to faults or problems in the eventual production of the process, which are fairly major issues. Then again, the chances of such issues occurring are not particularly large, which is why this criterion is not worth more than 3 points.

Wholesale gas and aqueous ammonia: The ease of use here is very simple. Essentially as long as the ammonia input is flowing and either the electric coolers or tap water is turned on, the process will work and a higher concentration output will be made. This is even simpler if just the direct 10% output is taken. Because of this, this receives the maximum score of 3.

Fuel cells: Since both work very similarly, the ease of use is combined here. In principle the fuel cell is also a continuous automatic process that does not require much effort by the user. Simply hook up the fuel cell system to the farm's power grid and it will provide power. However, what deducts a point from the final scoring is the long start up times of up to several hours, as it requires planning on when to turn it on and off, thus making it less user friendly. One should also consider that excess electricity produced is sold back to the grid at varying prices throughout the day that tend to be much lower than what it is bought in for, so it may be more lucrative to run the fuel cell at certain times of the day. This may be automatable, but it is not quite plug and play. Thus, the final score is 2.

Enriched biochar: Overall, this system is not too complex, but neither is it extremely simple. Traditionally the enrichment step is a batch process, which requires daily replenishment by the farmer; however, it would eventually be possible to automate this process, which would be much better for the ease of use. As mentioned in the reliability part, the possible jamming may also require frequent interference by the farmer, which would be a big ease of use penalty, but the matter of fact is that this cannot easily be predicted beforehand. By looking at online sources, at the very least it does not appear to be a major documented problem, so it will be assumed as an infrequent occurrence. Some analysis of the farm's specific manure would need to be made beforehand to ensure the system is set up ideally to maximize the biochar output, but then again, both the pyrolysis stage and enrichment stage is not very delicate with at worst, a different biochar production quantity and different enrichment quantity. Overall then, this process has some ups and downs and the score can be interpreted as either a 1 or a 2. However, assuming that an automated version is chosen and that the jamming is not a major problem (and perhaps to compensate somewhat for the reliability score of 1 given before), a score of 2 is chosen.

Ammonium sulphate: Very similarly to wholesale ammonia, this process is very simple, requiring only proper mixing between the input ammonia stream and sulphuric acid stream, which can be automated. It would essentially also be possible to fill a tank beforehand with the right amount of sulphuric acid so that if it is further filled to the top with aqueous ammonia that the full tank has the correct ratios for reaction, thus requiring even less control. The only downside compared to other processes would be that once in a while a large quantity of sulphuric acid needs to be bought, but this is not a huge effort for a farmer. All in all, this also receives a maximum score of 3.

Urea: This process is automatable and continuous and in theory can be left to run just like the much simpler processes without much needed attention. However, due to the highly corrosive nature of the process, continuous checks are needed to make sure the process is still safe to use and especially since the entire system is under tremendous pressure (150 bar), the checks have to be thorough, which may be time consuming and not easy for such a complex process. On top of that, the control system required in this process needs to prevent harmful by-products such as biuret that is poisonous for plants and stunts growth, which means a fair amount of fine tuning is necessary. Nevertheless, the process is still completely automatic most of the time, so the score is barely above the minimum zero: 1.

Ammonium nitrate - 100%: The ammonium nitrate process is similarly complex to urea and thus checks are also needed occasionally. However, due to the much lower pressures and the fact that if the system is not set up entirely correctly, the output and efficiency is simply reduced instead of making harmful side products. This makes it somewhat more resistant to being badly set up, or having negligent checks, meaning an easier case is to be made for an average farmer. It also does not require any ingredients to be bought beforehand, simplifying the process for the farmer, and the process can be fully automated. This then results in a final score of 2, despite the complexity.

Ammonium nitrate - bought acid: Very similarly to ammonium sulphate, this requires an occasional purchase of nitric acid instead of producing it on-site. Also, afterwards it needs to be mixed in the right proportions in a reactor and the output can directly be stored. This makes it fairly easy to install and set up and doesn't require much attention, leading to a good score of 3.

Ammonium phosphate: Essentially the same case can be made here as for ammonium nitrate and ammonium phosphate. The largest difference being the exhaust gas post processing that is required. Since the post-processing has (for example) a gas absorption column to absorb the bad gasses, the resulting contaminated water would need to be disposed of at a somewhat frequent rate, as well as that the system needs to be set up fairly accurately in the first place to minimize these harmful by-products. This results in an overall still fairly respectable score of 2.

A.6 Environmental Impact

This section looks at the environmental impact of both a) the process and b) the fertilizer/product itself. One of the key goals of MEZT (and society) is to reduce emissions in Natura 2000 areas and not only is this good for the environment and society, it is also good for MEZT as a better environmental impact leads to the possibility of getting more grants, subsidies and overall approval from the government. Because of this central impact on all fronts, environmental impact will be scored for 4 points; almost as high as process profitability. The one reason why it does not score 5 points is because even if the process is not particularly any better for the environment than the current situation (or perhaps even slightly worse), it may still be chosen if it is overall more profitable than traditional manure, whereas a very environmentally friendly option will not be chosen if it costs more money than it makes.

Wholesale gas and aqueous ammonia: Regarding the final product, the ammonia is sold wholesale to whomever wishes to buy it and as such it can be considered neither good nor bad for the environment. One can say that since ammonia is traditionally coming from a very energy intensive process, by selling MEZT's "clean" ammonia, it essentially displaces a small amount of "bad" ammonia from the Haber Bosch process, thus indirectly still reducing global emissions. However, this same argument can be made for all other processes in this paper, as if "green" fertilizer is made, it also reduces the need for artificial "bad" fertilizer originating from mines. Thus, regarding the final product, it will be considered neutral.

Regarding the process, it is less than stellar. For the version using tap water, a very large amount of clean water is used which is then discarded. For the versions using electric cooling, a particularly large amount of electricity is used, which considering only 7.4% of electricity came from renewable sources in 2020 [144], means a significant carbon footprint. Overall then, the neutral product, and below average process results in a score of 1, although with good argumentation, it might be brought up to a 2, which is given for the wholesale 10% solution.

Fuel cells: Like wholesale, for both AFCs and SOFCs, it would still result in farmers using additional fertilizer that likely originates from environment-destroying mines. However, the fuel cells score somewhat better, since the process output is clean electricity with the only side product being water and nitrogen, which both are perfectly harmless. Overall then, this scores well, but since it does not solve the intended farm nitrogen emissions like some other solutions in this paper, it will score 3 points.

Enriched biochar: Regarding the product, as mentioned in section 3.5.2, biochar has significantly lower nitrogen emissions than direct ammonia application. It was also mentioned that ammonia enriched biochar can stay enriched without significant leakage for a fairly long time, while still allowing plants to uptake the nitrogen [41], but not much was mentioned comparing it to other fertilizer types. This was harder to find than anticipated. Plenty of sources were found on biochar reducing nitrogen emissions when composting manure (since biochar readily absorbs ammonia) and several sources were also found comparing emissions of different types of (enriched) biochar compared to a control (no fertilizer at all), and even a meta-analysis of 124 studies was found showing that biochar did enhance the phosphorus and nitrogen soil availability compared to a control (no biochar) [145], but not much was found on comparing enriched biochar to other fertilizers. However, one source mentioned biochar enriched with ammonium sulphate produced fewer nitrogen emissions (roughly 20%) than straight ammonium sulphate [146]. Quickly scanning through similar articles reveals that no matter the case, at worst, biochar has no effect on emissions and at best, a reduction of roughly 30% backing up the previous sources. Everything combined; it can be considered that the product has relatively low emissions, even if an exact comparison is not available.

Regarding the process, the pyrolysis stage does release combustible gasses which are burnt and used to heat the pyrolysis stage and perhaps also help the dryer beforehand. However, despite CO_2 emissions, it all originates from manure and not fossil fuels, which means it has a certain element of carbon neutrality (no new carbon is added to the carbon cycle). Also, the adsorption apparatus ideally would have all the ammonia be adsorbed by the biochar, but more likely than not a small amount of ammonia still passes through straight into the atmosphere, which is not ideal.

Overall then, the good product emission properties combined with about average process emissions results in a final score of 3.

Ammonium sulphate: One of the reason why MEZT originally chose ammonium sulphate as the fertilizer (before the investigation of this paper) is because when ammonia is bound to the sulphur, it does not release any significant amount of ammonia gasses, and is thus good for the environment and contributes positively to the circular carbon cycle. It should then not be surprising that the Food and Agriculture Organization of the United Nations stated that ammonium sulphate has one of the lowest emissions of all artificial fertilizers and the lowest of all fertilizers in this paper (except biochar, which wasn't tested), as seen in table 11 [147].

Table 11: N_2O induced emissions caused by fertilizers (in % of applied N) [147]

Fertilizer	**Mean**	**Median**
Ammonium Sulphate	0.8	0.2
Urea	1.1	0.3
Ammonium Phosphate	1.4	0.8
Ammonium Nitrate	1.7	1.0
Anhydrous Ammonia*	2.0	1.4

*It should be noted though that in this table all measurements were from Costa Rica, which has tropical, moist conditions leading to very high nitrogen emissions, except for the anhydrous ammonia (via injecting gas under the ground), which was done in a temperate climate. This means that under equal conditions, the anhydrous ammonia would come out as even worse.

Regarding the process, due to its inherent simplicity, there is not any use of power or heat, nor are any emissions released during the process. However, it does require sulfuric acid for the process and although creating sulphuric acid does not release any significant amount of emissions (both via the contact process and via the wet sulphuric acid process), it does require sulphur that is mined, which is not great for the environment. Because of this, the combined overall score will be slightly less than maximum, at 3 points.

Urea: Interestingly, despite having the highest nitrogen concentration of all fertilizers (46%), in table 11 it comes out as the second lowest nitrogen emission producing fertilizer of the ones in this paper. This is in contrast to initial logic, especially considering that several prior papers looked specifically at reducing emissions from Urea. Investigating this further, a document investigating the CO_2 equivalent emissions for several fertilizers was found, which looked at direct N_2O from use, indirect N_2O via NH_3, indirect N_2O via NO_3 and also from production, which has been excluded as the production methods in this paper are not always the same as on a large scale [148]. What can be concluded from table 12 is that although urea does emit a lot more per kilogram product, it only emits a little more per kilogram of nutrients provided.

Table 12: CO_2 equivalent emissions from usage of several fertilizers [148]

Fertilizer	**kg CO_2 /kg product**	**kg CO_2 /kg nutrients**
Urea	4.22	9.21
Ammonium Phosphate	1.30	7.21
Ammonium Sulphate	1.72	8.19
Ammonium Nitrate	1.89	5,65

Yet another source was found which places urea as one of the worst emitters of ammonia, which is more in line with initial thoughts, as seen in table 13 [149].

Table 13: Comparison of NH_3 emissions from different fertilizers [149]

Fertilizer	**N lost as NH_3 (%)**
Urea	13.1
Ammonium Sulphate	7.6
Ammonium Phosphate (DAP)	4.2
Urea + Inhibitor	3.9
Ammonium Nitrate	1.3

Overall then, studies are not always in agreement with each other, likely due to the many different conditions, setups and variations in measurements (duration, concentration of fertilizer applied, etc.), which mean that a solid prediction of overall product emissions cannot be made with great certainty. For now though, it will be assumed that on average, urea's *per nitrogen* emissions (which is more important than per product) is higher than alternative options.

Regarding the production process itself, it does require some electricity/power for the compression, but then again the process heat is self-sustaining. Also, it uses CO_2 as an input rather than output, which contributes to carbon capture. Furthermore, despite the process being quite complex with recycle streams and harmful intermediate steps, a well set up plant would ideally not produce too many further emissions, but overall the process is still not excellent for emissions. All this means that regarding emissions, urea scores a final score of 1.

Ammonium nitrate - 100%: Regarding the product, the previously mentioned tables show similarly contradicting results for ammonium nitrate. Table 11 noted it as the worst nitrogen emitter of all options investigated in this paper, whereas as table 13 and its corresponding source mentioned it was the lowest emitter and claimed it was a possible solution to the nitrogen crisis, stating that if all Urea and UAN (urea and ammonium nitrate water solution) in Europe was replaced with pure ammonium nitrate, it would reduce 63% of all ammonia emissions from fertilizers in Europe [149]. Similarly, yet another source from the Wageningen University of Research mentioned that N_2O emissions from ammonium nitrate was not that much less than from cow slurry applied directly to the field (2.2% versus 3.1% of applied N) although still significantly better than sow (pig) slurry (up to 14%). The product emissions are thus also still somewhat inconclusive for ammonium nitrate, but it will be assumed that emissions are better than that of urea, which has also been mentioned in section 3.5.5 [52].

Regarding the process itself, it does require a small amount of compression (less than urea), but afterwards the whole process only has exothermic reactions and no inputs besides air. Moreover, just like urea, if set up well, there are no other final products besides ammonium nitrate. Thus, the process itself can be considered fairly low emissions. The overall score that is given to ammonium nitrate is then 2.

Ammonium nitrate - bought acid: In terms of product, the score is identical to the 100% process, with a roughly neutral to good (low) amount of emissions. In terms of the process, it is now much simpler than before and no compression or energy needs are required, as it is a simple acid-base reaction, which is all good. However, now the nitric acid needs to be bought in via this method, which means the nitric acid is almost certainly made from ammonia from the Haber-Bosch process, which produces a lot of carbon emissions. Combining the simpler better process with worse ingredients (environmentally-wise), the overall score is still a 2.

Ammonium phosphate: Like ammonium sulphate, ammonium phosphate tends to be on the lower end of emissions or at the very least, not above average in all situations, even when taking the somewhat contradicting tables from before into consideration. Thus, it will be assumed to be above average for the environment (i.e. lower emissions).

Regarding the process, although the basic process is very similar to ammonium sulphate, there are a lot more emissions for ammonium phosphate that require after treatment. Traditionally the after treatment requires multiple steps and is controlled closely, but if (for example) a farmer forgets to replenish the water that is used in the exhaust gas absorption column, the gasses may not be absorbed at all (even momentarily) which would result in a lot of emissions and these nitrogen oxides and phosphoric oxides are fairly bad emissions to have. On top of that, the process requires purchasing of phosphoric acid, which in itself is also very bad for the environment to produce. Not only does it require mined materials, there are 5 tonnes of phosphogypsum produced for every tonne of phosphoric acid and at the moment this is just filling landfills with no use, sometimes even being discharged into the sea which has long term acidification and pollution concerns [150]. Because of this, it scores just a 1 despite the fertilizer itself being fairly good.

A.7 Safety

For this section, the concept of *inherently safer design* will be used. It states that to be inherently safe, hazardous materials and operations have to be avoided and reduced in the first place instead of being controlled or having fail-safe options [151]. The 4 main methods, or pillars, to achieve inherent safety are listed below.

- **Minimization**: To reduce how much hazardous material is present at a single time. For example, by using smaller batches or a continuous process.
- **Substitution**: To replace a material or substance with another less hazardous one. For example, replacing a flammable or explosive coolant with a non-flammable one.
- **Moderation**: To reduce the strength of bad effects, such as through using lower temperatures and pressures or by using more dilute solutions rather than concentrated ones.
- **Simplification**: To eliminate possible problems via design rather than constructing additional steps to deal with said problems.

This section is worth 3 parts as safety is fairly important. Farmers will likely "set it and forget it" so it needs to be designed sufficiently well enough that a disaster of some sort cannot occur, especially if the consideration of MEZT is to try and implement the process in as many farms as possible. Also useful to note: parts that are constant for all processes will not be discussed, such as the large storage tank for products or the safety of the ammonia substance for example.

Wholesale gas and aqueous ammonia: When one considers the straight 10% output, it does not get any simpler than that. There is literally nothing to go wrong and as such it gets the highest score possible: 3. For the more concentrated versions using the cold trap, no matter the method of cooling (electric or via water), there are no batches to consider as it is continuous, the materials used are already safe (water as coolant), the process is fairly moderate with neither high pressures nor extreme temperatures (even with the air conditioned cooler hot output, touching it barehanded is unlikely to be dangerous) and the process is already quite very simple. The only possible dangers here are a leaking heat exchanger or a malfunctioning air conditioning unit, neither of which is dramatically dangerous. Thus, the final score will still be a 3.

Alkaline fuel cells: The alkaline fuel cell, taking the unit from GenCell as an example, is reasonably safe. The process itself is contained in an all-in-one system with the largest hazards being getting burnt by the hot temperatures or shocked by the electrical output, but this second point is easily contained by covering all electrical components. None of the output substances are hazardous (water and nitrogen) and one of the benefits of an ammonia fuel cell over a traditional hydrogen fuel cell is that ammonia combusts less easily, meaning that an explosion hazard is much less likely. Finally, the fuel cell does have a potassium hydroxide (KOH) electrolyte that is irritant to the skin, but not only is this contained, if it does leak, there is only a fairly small quantity to leak. Overall then, fuel cells are still reasonably safe and a score of 2 is given.

Solid oxide fuel cells: Practically all of the same things can be said for SOFCs with the one main difference being the higher operating temperatures (roughly around 700-800 °C instead of 400-500 °C), which bodes slightly worse for ”moderation”. However, this is not enough to bring the score down to a 1, so a score of 2 is still given.

Enriched biochar: The produced biochar is very dry and very flammable, which means great care needs to be taken to prevent fires from occurring. The final enrichment stage, however, is fairly simple with not much to go wrong and the batch size is only as large as necessary, although this may still be a considerable amount. Finally, the resulting biochar is not particularly hazardous for humans, since the concentration of ammonia is lower than for other fertilizers and biochar itself is not harmful. However, if one also considers the steps before enrichment, in the pyrolysis reactor manure is broken down with a lack of oxygen, creating combustible gasses. If for whatever reason any air leaks occur that allow oxygen into the pyrolysis reactor, it could potentially result in fire or even an explosion. For the overall score, since there are definitely some safety concerns that can be problematic on a farm scale, a score of 1 is given.

Ammonium sulphate: Since ammonium sulphate does not produce much heat when the acid base reaction occurs and since it only decomposes above 250 °C, the production is very safe. No temperatures nor pressures above ambient are required and even in a reaction with ammonia gas and concentrated sulphuric acid, the temperature typically does not rise above 60 °C, meaning that in the case of MEZT, an even lower temperature is expected. The simplest form of the process simply has the sulphuric acid and aqueous ammonia flow into the storage tank at similar times, thus it can be considered inherently simple. The only downside of this method is that a large storage of concentrated sulphuric acid is needed beforehand. Sulphuric acid is not only corrosive, it can cause severe burns and is very toxic [152] and in MEZT’s case, there is a lot of it at high concentration, which does not bode well for either ”minimization” or ”moderation”. Thus, an overall score of 2 is taken as despite the acid, the very simple system means that it is unlikely to leak.

Urea: The process of urea does not need too much explanation. As mentioned in previous sections, the process is complex with several recycle streams (thus not boding well for simplicity) as well as very high pressures (150 bar) and medium temperatures (which does not bode well for moderation). On top of that, the reactor is fairly large due to the long residence time (bad for minimization) and corrosive and toxic substances are made such as ammonium carbamate and biuret. Finally, the final product urea is also a slight irritant. Although also found in small concentrations in urine, higher concentrations can be damaging for the skin and respiratory tract. It should come as no surprise that the final score is then 0.

Ammonium nitrate - 100%: Just like urea, the process for ammonium nitrate is also complex, but there are some differences. This process has more heat exchangers, which result in more points of failure (bad for simplicity), and although the pressure is significantly lower, the temperature is significantly higher (up to 800 °C, not great for ”moderation”). Within the nitric acid production process nitric oxide is also produced, which can be dangerous to life in higher concentrations (as produced in the reactor), not to mention the nitric acid itself is a corrosive acid and can cause chemical burns that decomposes living tissue.

The final substance, ammonium nitrate, is normally speaking also highly explosive and it is in fact the same substance that caused the 2020 Beirut explosion. However, since it will be made under aqueous conditions, it will always be sufficiently balanced with water that an explosion is highly unlikely to happen, as any heat of the reaction is quickly absorbed by the water. When in water, ammonium nitrate is not particularly toxic either, being only slightly more dangerous than common table salt. The final score is then not great, but not as bad as urea, at 1 point.

Ammonium nitrate - bought acid: This process only keeps the final reactor turning nitric acid and ammonia into ammonium nitrate, which is a lot safer than the nitric acid production before. Essentially the same argumentations as for ammonium sulphate can be made, as in this case there still is a large storage of a concentrated and unfavourable acid and it still is a simple acid base reaction, albeit more exothermic and thus slightly less safe. Still, the overall score is the same at 2 points.

Ammonium phosphate: Again, a similar argumentation can be made here as for ammonium sulphate. The large storage of phosphoric acid, which can cause severe skin burns and tissue damage, does not bode well for ”minimization” and ”moderation” and like ammonium nitrate, the reaction is quite exothermic releasing a fair amount of heat. Where ammonium phosphate (or DAP) does worse is in the need for post-processing of exhaust gasses. These exhaust gasses are in some cases, such as the phosphorus oxides, very bad, causing corrosion, irritation and damage to mucous tracts and the respiratory system in concentrations as low as 1 mg/m^3 [153]. If for whatever reason the exhaust gas post-processing fails, it can cause some severe harm to those close by. Because of this, it scores lower, just 1 point.

A.8 Scalability

This part is about how easily the process can size up or down from its current farm scale to either micro- or macro-scale. This involves if the physics and chemistry of the process can scale without changing too much and if it can be fine-tuned for higher efficiency at a larger scale or for greater simplicity at a smaller scale. Although for a single farm the scalability is not that important, one of the goals of MEZT (in order to reach globally lower emissions) is to perhaps propose alternative scales of the MEZT solution train. For example, as farmers currently need to pay to remove excess manure, it could perhaps be possible to have a central manure processing plant on a much larger scale, which would eliminate the need to pay to have manure removed and it will also help (environmentally-wise) for farmers who do not wish to invest and place the current MEZT solution. Alternatively a smaller scale solution for much smaller, rural and/or underdeveloped farms could also aid in greater adoption. Because of this, the scalability still deserves 3 points as although it is not of key importance in this paper, it can be very intriguing to investigate in the future.

Wholesale gas and aqueous ammonia: Regarding the direct 10% output, due to its inherent simplicity it is easily scalable and as efficient on a small scale as it is on a large scale and needs no further explanation. For the higher concentrations, it is also quite scalable. No matter if tap/ground water is used or electric cooling, the process can easily be adjusted for small and large sizes. For smaller sizes, the heat exchanger will merely be smaller and compact cooling systems exist, while for large scales, the heat exchange can be made more efficient using more sophisticated exchangers and perhaps power or cooling costs can be reduced. Overall then, both score 3 points.

Fuel cells: Although still in its infancy, one of the key advantages of fuel cells (both AFCs and SOFCs) is its incredible scalability. Since a fuel cells are made out of cell stacks with many layers, it is easy to scale the process up or down and fuel cells have been proposed for anything as small as a laptop (20 W) or as large as a power plant (200+ MW) [154]. As such it gets the maximum score of 3.

Enriched biochar: For enriched biochar, the biochar creation process can perhaps not be scaled down as easily, which isn't great for scalability. The manure may have small lumps or hard bits that weren't completely digested and the smaller the system is, the greater of an effect these imperfections have, leading to clogging or jamming. Also, via the law of scaling, at a smaller size cooling the surface area (determined by area, to the power 2) of the pyrolysis machine has a greater effect than the heat generated from the process (which is determined by volume, to the power 3), which means more insulation is required to sustain the process. At small scales, it is also more difficult to control the temperature and thus the resulting biochar output and other by-products. Nonetheless, this isn't an instant barrier to smaller scales, as via batch production it is still possible to benefit from the larger (intended) scale, although a full-sized machine should be costed. For very large scales, the opposite is true: any imperfections in the manure will be even smaller and will not affect the process as much and at a large scale it is much easier to control the inputs, temperatures and thus a very predictable and consistent output is possible. Regarding the enrichment and drying process, both can easily be scaled, which is not a problem. Overall, a respectable score of 2 is given.

Ammonium sulphate: With the simplicity of this process of just mixing 2 substances together, it is inherently scalable. For very small cases, it can be as simple as measuring out and mixing the substances by hand for any amount as small as required, whereas for a large scale central station it can be turned into a regulated and continuous process, which also means no large ingredient storages are needed. Thus, a score of 3 is given.

Urea: Originally this process is designed for a (very) large scale and as evident, even at the current farm scale the process is already too complex and sophisticated for a farmer to be in complete control over, let alone at a micro-scale. At a large scale, yes, it can be made efficiently, but the smaller the scale, the less controlled and consistent the process may be, which in turn creates more unfavourable by-products. Thus, for scalability, it scores a 0.

Ammonium nitrate - 100%: Similarly to urea, the complete ammonium nitrate process is designed for a large scale and is actually not very well suited for smaller cases, even at the size of a farm. However, since the process is a bit more forgiving (the efficiency is merely lowered instead of producing harmful side products at sub-optimal conditions) and since it is possible to discard the power recovery step for simplicity (as was done in this paper) it is somewhat more scalable than urea, even if it is not realistic at small scales, resulting in a score of 1.

Ammonium nitrate - bought acid: When the process is bought in bulk, the case is similar to ammonium sulphate, as the mixing reactor can be scaled down or up easily. It should be noted though that at larger scales, not only can a larger reactor not be cooled as easily than at a small scale (due to the law of scaling), the relatively slower mixing at larger scales can result in hot spots. Fortunately, at a larger scale it is easier (or relatively cost effective) to implement control and perhaps active mixing or cooling to resolve this, and the prilling for dry products (for easier transport from a central location on a large scale) is also easier to regulate, which means no point will be deducted, resulting in a score of 3.

Ammonium phosphate: This process is essentially simple like ammonium sulphate with only a basic reaction, and scaling up can be done fairly easily as the drum-dryer and granulation process can be regulated more easily. However, one key downside as mentioned many times before is the exhaust gas post-processing. This typically consists of several stages and even a simple gas absorption column requires a pump to circulate the water, meaning that it does not scale down very easily. Even for a tiny batch (think small rural farm in a second or third world country), either a post-process is required (or more likely in the third world country case) there will not be post-processing at all, placing both the environment and humans in the immediate surrounding at a detriment. Because of this, the final score is 2 points.

A.9 Compactness

This section is on how small of a footprint the entire system of the process takes place. Farms tend to have a lot of space, which means that taking up a small amount of space is more a 'nice to have' rather than a requirement, thus worth only 2 points. However, it should be noted that even on a farm, any space that is taken up by the MEZT process could have been used for additional farming practices (e.g. an extra pig-pen for example), so one can consider taking up space to be an indirect associated cost.

Wholesale gas and aqueous ammonia: The direct process is essentially no process at all, so scores the maximum 2 points. For the higher concentrated versions, either an air conditioning unit and potentially a small heat exchanger or for tap/ground water cooling a larger heat exchanger (with 2.5 m^2 surface area) is needed. Whether it be the air-con unit or the heat exchanger (which can be placed vertically), it likely will not take much more room than 1 m^2 of floor space, so it will score the maximum 2 points.

Fuel cells: The AFC from GenCell actually has specifications on the footprint it takes up. All in all, the 4 separate machines needed for the fuel cell takes up a 2 by 4 m floor area (8 m^2 total), which is still fairly significant considering the relatively low output of the fuel cell (4 kW). For comparison, a small 4 kW petrol generator takes up less than 1 m^2. For the SOFC it will be assumed to take up a similar space. The final score will then be 1 point.

Enriched biochar: If the whole process is considered, the dryer, pyrolysis machine and adsorption column all require space. Both the dryer and the pyrolysis machine have to lay flat in order to function, which means it will take up quite some space, especially since both are relatively slow processes. The biochar enrichment process afterwards will be a vertical column, thus not taking up as much room. Do consider though that on flat ground the biochar out of the pyrolyser has to be transferred into the top of the enrichment column, which means additional space might be required for some form of transportation system (e.g. bucket elevator). Overall, although no exact value is calculated, it is estimated to take up some space similar to the fuel cells, so it will only receive 1 point.

Ammonium sulphate: Essentially the process is very simple and would not take up any noticeable space. However, one should consider that the sulphuric acid input requires a large storage tank, which does take up a substantial amount of space, although in all fairness this storage tank can be placed outside where the aforementioned "indirect cost" can be considered as significantly less. One of the supervisors also suggested that it may even be possible to fill the final storage tank with sulphuric acid beforehand to the required level so that no input storage tank is even needed. In that case it would score 2 points.

Urea: Regarding footprint, urea is the worst of all processes. For starters, it requires a CO_2 input that needs a particularly large storage tank, taking up lots of space. There are several compressors, a distillation column, a relatively large reactor (although 25 L is still not too large) and recycle streams further increasing the size. Overall then, the footprint is large and it scores 0 points.

Ammonium nitrate - 100%: This process is also quite complex with many components. However, although there are many components to this process, the air input means no input storage is required and although there are many heat exchangers, a well-designed system should be able to integrate these in a relatively compact space. Likewise, the gaseous inputs and compressors pumping these gasses around mean that it may be possible to place a lot of components on top of each other for a more compact footprint. Nevertheless, there are still a lot of components and it is still expected to take up some space, more so than the processes that score 2 points, so 1 point is given.

Ammonium nitrate - bought acid: Since in this process a lot of heat is released, it would perhaps not be such a great idea to directly mix and react everything together in the final storage tank as with ammonium sulphate. Because of this, a large storage tank for the input is required as well as a (fortunately small) reactor unit. Thus, it will score 1 point.

Ammonium phosphate: Again, similar to ammonium nitrate, it would perhaps not be the best idea to directly mix and react the substances together due to the heat generated. However, an additional hurdle exists here as the exhaust gas post-processing also takes up space, increasing the footprint even further. However, for the final score this will not change much so it will still receive a score of 1.

B Appendix 2: Process Calculations

In this appendix the calculations are shown for the mass flows and concentrations of the final process streams. The calculations are fairly straightforward, so no formulas will be given. What is useful to note though is that all percentages are weight percentages, and that for streams with a (very) low concentration a density assumption of 1 L = 1 kg will be made.

Useful information to have ready beforehand:

Aqueous Ammonia:
24.5% concentrated solution = €210/ton, so pure NH_3 = €857/ton
Pure NH_3 = 82% N (atomically)

Sulphuric Acid:
H_2SO_4 = €194.30 /tonne (94-98% concentrated) = €200 /tonne pure
H_2SO_4 = 33% S (atomically)

Ammonium Sulphate (AS):
1kg NH_3 needs 2.88 kg H_2SO_4 and makes 3.88 kg AS
AS = 21% N
AS = €250 /tonne (pure)

Potassium Sulphate (KS):
1 kg K reacts with water to form 1.43 kg KOH. All reactions are done with KOH
1 kg KOH needs 0.874 kg H_2SO_4 and makes 1.553 kg KS and 0.321 kg H20
KS = 45% K (atomically)
KS = €481 /tonne (pure)
(KOH = €833 /tonne pure)

Tank A: Only the mineral concentrate
Input = 60-120 L/hr.
1-1.5% NH_3 and 1.2-2.4% K (or 1.72-3.43% KOH)
= 0.6-1.8 kg/hr NH_3 (0.492-1.476 kg/hr N)
and 0.72-2.88 kg/hr K (or 1.03-4.12 kg/hr KOH)
Value = (0.6-1.8)*€0.857 + (1.03-4.12)*€0.833 = €1.372-4.974 /hr

Note: Although this mineral concentrate has a high monetary value for the ingredients in it, the low concentration make it nearly impossible to sell for this value, especially due to transportation costs.

Tank B: Use all of the input to make a combined fertilizer
Input = Tank A, same as above
NH_3 needs 1.73-5.18 kg/hr H_2SO_4
KOH needs 0.90-3.60 kg/hr H_2SO_4
= 2.63-8.78 kg/hr H_2SO_4 input total (1.4-4.8 L/hr at 1.83 g/cm^3) = €0.526-1.756 /hr cost
(60+1.4)-(120+4.8) = 62-125 L/hr

For AS: 0.6-1.8 kg/hr NH_3 * 3.88 (or alternatively 1.73-5.18 kg/hr * (3.88/2.88))
= 2.33-6.98 kg/hr AS (0.49-1.47 kg/hr N) = €0.582-1.745 /hr,
with concentration 3.72-5.42% AS (0.78-1.14% N)

For KS: 1.03-4.12 kg/hr KOH * 1.553 (or alternatively 0.90-3.60 kg/hr * (1.553/0.874))
= 1.60-6.40 kg/hr KS (0.72-2.88 kg/hr K) = €0.770-3.078 /hr,
with concentration 2.56-4.97% KS (1.15-2.24% K)

Combined fertilizer concentration = 6.28-10.39%
Value = €0.582-1.745 /hr + €0.770-3.078 /hr - €0.526-1.756 /hr = €0.826-3.067 /hr

Tank C: Direct potassium-rich mineral concentrate
Input = *output* = 50-100 L/hr.
1-2% K = 0.5-2 kg/hr K (0.715-2.86 kg/hr KOH)
0.5-1% NH_3 = 0.25-1 kg/hr NH_3
Alternatively, the NH_3 is 0.41-0.82% N = 0.205-0.82 kg/hr N
Value = (0.715-2.86)*0.833 + (0.25-1)*0.857 = €0.810-3.239 /hr

Tank D: Use mineral concentrate to make combined fertilizer
Input = 50-100 L/hr.
1-2% K = 0.5-2 kg/hr K (0.715-2.86 kg/hr KOH)
0.5-1% NH_3 = 0.25-1 kg/hr NH_3
Alternatively, the NH_3 is 0.41-0.82% N = 0.205-0.82 kg/hr N
The NH_3 needs 0.72-2.88 kg/hr H_2SO_4
The KOH needs 0.625-2.500 kg/hr H_2SO_4
Total H_2SO_4 = 1.345-5.38 kg/hr H_2SO_4 (0.74-2.94 L/hr) = €0.269-1.076 /hr cost
Output:
51-103 L/hr
AS: 0.97-3.88 kg/hr (1.902-3.767% AS) → 0.204-0.815 kg/hr N (0.399-0.791% N)
KS: 1.11-4.44 kg/hr (2.176-4.311% KS) → 0.500-1.998 kg/hr K (0.979-1.939% K)
Value = (0.97-3.88)*€0.250 + (1.11-4.44)*€0.481 – (€0.269-1.076) = €0.507-2.030 /hr

Note: for tank E, F & G the concentration is high enough that the 1 L = 1 kg assumption does not hold true, as the deviation would be too significant. Thus, more exact densities will be used.

Tank E: Make low concentrate (10%) aqueous ammonia
10-20 L/hr of 10% NH_3 concentration (or 8.2% N concentration).
Using 1 L = 0.955 kg for the 10% NH_3 mixture... = 0.955-1.910 kg/hr NH_3 (=0.783-1.566 kg/hr N)
Value = (0.955-1.910)*0.857 = €0.818-1.637 /hr

Note: Unlike tank G, this 10% aqueous ammonia will be much more difficult to sell due to its lower concentration and increased relative transportation costs, despite equal revenues in theory.

Tank F: Use low concentration ammonia to make AS
Input: 10-20 L/hr of 10% NH_3 concentration. 1 L = 0.955 kg
= 0.955-1.910 kg/hr NH_3 =0.783-1.566 kg/hr N)
The NH_3 needs 2.750-5.501 kg/hr H_2SO_4 (1.503-3.006 L/hr) = €0.550-1.100 /hr cost
Output:
11.5-23 L/hr (total mass is 9.55-19.10 kg/hr + 2.750-5.501 kg/hr = 12.3-24.6 kg/hr = slightly more dense)
AS: 3.705-7.411 kg/hr (0.778-1.556 kg/hr N) → 30.12% NH_3 (6.325% N)
Value: (3.705-7.411)*€0.250 – (€0.550-1.100) = €0.376-0.753 /hr

Tank G: Directly store and sell high concentration ammonia
Input: 0.955-1.910 kg/hr NH_3 (due to conservation of mass. Only water is extracted)
Total mass input is then (0.955-1.910)*4 = 3.82-7.64 kg/hr
25% NH_3 concentration density: 0.905 kg/L → 4.221-8.442 L/hr
Output = the same as input:
NH_3: 0.955-1.910 kg/hr (0.783-1.566 kg/hr N) → 25% NH_3 (20.5% N)
Value = (0.955-1.910)*0.857 = €0.818-1.637 /hr*
**Note: cooling costs not included.*

C Appendix 3: MEZT Cost Check

Besides the main costs and revenues from the process described in this paper, there are also further costs and revenues from the rest of the entire MEZT process (at 300 l/hr), as given in the Excel file by the supervisors from MEZT. These are made using the help of professionals in the farming industry and should be accurate estimates. However, just as a precautionary check, a request was made by the supervisors from MEZT to double check these values, which is done in this appendix.

C.1 Capital Expenditures

A prefab urine/manure catchment basement was costed at €22,500, of which €8,000 is the prefab basement itself (of unknown size). Online, a prefab basement of 30 m^3 has been found for €9,000, which is in the same range [155]. For the other subcomponents (mixer, piping, pump and control box) the estimates weren't checked, but they appear to be around what one would expect.

The manure thick-thin separator was costed at €42,500. Online, a 'farm sized' (but unknown flow rate) unit was found at two sources for €35,000 [156] and €19,000-40,000 [157], both including installation, so the current estimate is realistic.

For the 5+ m^3/hr drum filter, €10,000 was costed. Online, prices for drum filters specifically for agricultural applications were found, being €10,000 to €30,000 for a considerably larger 10-20 m^3/hr drum filter [158]. A drum filter was also found for Koi-fish pond filtering at a similarly high flow rate of 30 m^3/hr (which is unlikely to be as suitable) for about €2,000-€2,500, with filters costing about €100 each [159]. Overall, the €10,000 estimated by MEZT appears to be in the right range for the smaller unit, including installation.

The buffer basement is costed at €6,000 (2 x €3,000), which consists of partially walling off the current manure basement of the farm. Because this is custom work, this price is not checked, but it does not appear to be out of the ordinary.

For the ED, BPMED and VMS unit, a total cost of €200,000 was estimated. This is by far the largest cost, but as the technology is still very new and since the unit is custom made, this might not be out of the ordinary. Logically then, finding prices online will be very difficult, but the €200,000 cost is estimated with the producers of the unit itself (Lenntech), so this can be kept as a good estimate.

An isolated and air-conditioned container unit to store everything in was also costed at €16,000. Online, regular 20 ft containers can be bought new from €3,500 and isolated (but not air-conditioned) 20 ft containers can be had new for about €5000 [160]. Even with air-conditioning, the €16,000 estimated is perhaps a bit on the high side, but as it is unknown if this price includes transportation and installing all other equipment inside the container, this price will not be adjusted.

A fertilizer concentrate mixing unit, along with piping and sulphuric acid storage was originally costed at €3,000. Essentially there is enough residence time in each IBC that natural convection and diffusion may be sufficient for mixing, especially considering that any IBC for use on the farm will be placed on a tractor to be used and that this movement also essentially provides free mixing. Also, in the most up-to-date version, there may be several IBCs, so several mixing units would need to be costed otherwise. Thus, the mixing unit can be removed, however, since the piping and sulphuric acid storage is still required and likely to take up a good chunk of this cost, this price will not be altered.

Lastly, the storage was costed at €20,000, which as mentioned previously is in line with IBC prices for the equivalent size. The only peculiar part is that this €20,000 was costed twice, for both the watery concentrate and the final fertilizer. Since extra storage is in no way detrimental, and since the other (uninvestigated) outputs of the BPMED may also require storage, this cost is not altered or removed, but depending on how frequently the storage containers are emptied, there might be possible room for cost savings.

C.2 Operating Expenditures

For the prefab urine/manure catchment basement, €650 worth of operational costs was estimated, of which €150 is the mixer and €500 is a pump. At an electricity price of €0.065 /kWh over a year at 22 hours a day of operation, this comes to 1.245 kW in total, or 1 kW for the pump and 0.25 kW for the mixer. Considering this is all the way at the input, pumping and mixing the 300 L/hr manure, it appears to be about what one would expect.

The thick-thin separator has operational costs of €3,500, which includes electric motor power, filters, and common wear parts. It can be assumed again that the pumping likely accounts for about €500, leaving €3,000 for filters and parts. This is about 7% of the cost of the unit itself, which seems about realistic for maintenance and perishables (which is typically up to 10% of the cost annually).

For the drum filters, €500 a year is costed for 2 filters of €250 each. From the source on Koi-fish, pond filters are about €100 each, [159] which are for much lighter applications, so €250 for a heavier duty filter for the manure thin fraction is realistic.

The ED, BPMED and VMS have an annual cost of €25,000 for the expensive membranes (technically €50,000 spread over 2 years). Similarly to the capital costing, this value will not be altered as it is the best estimation available from the manufacturers of the prototype itself. It can perhaps also be considered that any (marginal/low) electricity cost of running the ED and BPMED are included in this.

The annual water usage was costed at €2,750 for 1000 m^3/yr, which results in a water price of €2.75 /m^3. This is certainly on the high side since the average water cost in the Netherlands is about €0.83 /m^3 [106] where any fixed costs are already incurred by the farmer before the MEZT system is to be implemented. Double checking this value reveals that above a usage of 300 m^3/yr, the cost may even be lower as no 'Bol' needs to be paid anymore [161]. Similarly, the volume of 1000 m^3/yr is equal to 125 L/hr at 22 hours/day operation, which is right in between the 100 and 200 L/hr needed by the larger 1000 L/hr manure operation, but twice the maximum amount for the 300 L/hr manure operation. Thus, this is changed to 500 m^3/yr at €0.83 /m^3 or €415, which is then rounded up to €500.

The air-conditioned container unit has annual operating costs of €250, which presumably is for both maintenance and to keep the container cool on very hot days. This seems to be plausible, so it is not altered.

A fertilizer mixing unit has operational cost estimates of €250 /yr. As mentioned previously, this is likely to be redundant, but even if it is included, this €250 /yr alludes to a continuous (22 hr/day) electricity consumption of about 0.5 kW, which would likely provide excessive mixing. Nonetheless, testing is likely required to ensure that in practice this really is sufficient and for the prototype this cost will be kept just in case (and since it has negligible effect on the overall costs).

Sulphuric acid was costed at €1,000 /yr. Here a mistake was noticed. The costing initially mentions "€200 $/m^3$" for 99% pure sulphuric acid, but the price quota is for €194 /tonne, and the density of sulphuric acid is not close to water at a 1.83 kg/l, meaning that the real price is actually €355 $/m^3$. Checking with the newest process, the sulphuric acid usage ranges from zero to about 2.63-8.78 kg/hr for the 'worst case scenario' at 1,000 l/hr, which is equal to 0.79-2.63 kg/hr for 300 l/hr or 6,336-21,151 kg/yr or 3.46-11.5 m^3/yr, costing about €1,267-4,230. The 5 m^3/yr estimate is then still in the right range, but the cost will need to be adjusted to about €2000 to account for the error.

C.3 Revenues

The costing assumes 300 l/hr manure throughput, but the costing mentions that before this MEZT project is implemented, 5,000 m^3 manure will need to be disposed of per year. However, 300 l/hr * 22 hours * 364 days = 2409 m^3, which is approximately half of the estimated value. Also, a reduction in manure disposal cost was estimated at €30,000, as 75% of the manure entering the MEZT solution train does not need to be disposed of. This savings amount is based off of the 5,000 m^3, multiplied by 75% and the disposal fee of €10-25 $/m^3$, resulting in what should be €30,000. However, to achieve this, the manure disposal cost would need to be just €8 $/m^3$, which is very low.

Thus, these estimates need to be modified. The 5,000 m^3/yr manure is replaced with 2409 m^3/yr and if one then uses the same €30,000 in savings, a disposal fee of €16.60 $/m^3$ is achieved, which is certainly realistic and right in the middle of the range. Thus, the €30,000 is kept the same, while the manure volume is modified to 2409 m^3/yr.

The reduction of purchased fertilizer and sale of minerals was estimated separately at €5,000 each. However, with the new setup this is combined into one single 'box' as the process can be adjusted for either extreme. For 1,000 l/hr, the whole process can give revenues (excluding sulphuric acid costs) of roughly €1.5-5 /hr depending on which process is chosen. Adjusting this for 300 l/hr and a year results in 3,615-12,050 per year. Since the real concentrations and flow rates are likely in the middle, a revenue in the middle can be assumed at around €7,800.

Estimations were also made for the reduction in cattle feed, sawdust and reduced animal sickness (due to excess nutrients which would otherwise end up on the land being taken out of the cycle), at €15,000, €7,500 and €10,000 respectively. Finding estimates to check this online would be very difficult as this knowledge comes first hand from farmers which MEZT is in touch with. Thus theses values will be assumed to be accurate.

C.4 Further Costs

In the final steps of the costing file, the whole system is depreciated over 7 years. This is a typical number of years for depreciation, with many projects being spread out over (for example) approximately 10 years, so this value seems correct.

Furthermore, interest payments are set at 5%. Currently this could be considered to be a relatively high value, with some loans having repayments below 3%, but over the past few years loans have been relatively low/cheap. There is a very real chance that in the coming years the interest increases to be closer to this 5%, so it will be wise to keep this estimate in. Besides, for riskier investments (which one could consider the setup of MEZT to be due its early-adopter nature) interest tends to be slightly higher, which is another reason to keep this 5%.

Finally, an additional cost for feed-stock electricity and miscellaneous water is costed at €1,500. This is for all remaining component electricity and water usages, especially for the earlier steps. For example, the drum filter has the OPEX costed for filters, but not electricity. Those drum motors tend to be in the 50-100 W range, so it could be considered negligible (under €50 /yr), but all little parts add up. Thus, it is hard to put a solid value on this and this value is likely more than required, but it is good to take into account anyway.

D Appendix 4: NH_4Cl Fertilizer

Close to the end of this project, the supervisors from MEZT requested one final substance to be investigated: ammonium chloride (chemically known as NH_4Cl). They mentioned it could be made using aqueous ammonia and the acidic output of the BPMED. However, it was not investigated in the main paper since the acidic output of the BPMED was outside of the scope of this paper. Therefore it is only included and mentioned here for reference.

D.1 Chemical Information on Ammonium Chloride

The dominant application of ammonium chloride is as a nitrogen source in fertilizers (corresponding to 90% of the world production of ammonium chloride), with the remainder use mostly consisting of using it as a flavouring agent [45]. However, although 90% of all NH_4Cl is used as a fertilizer, NH_4Cl usage overall remains extremely low, not even showing up as a major ammonia fertilizer during the main analysis of this paper. Commercially, it's made by combining NH_3 with HCl (or chlorine gas) through the following equation.

$$NH_3 + HCl \Longrightarrow NH_4Cl$$

Although the composition of the acidic output of the BPMED is unknown, for this quick analysis it will be assumed that HCl or another similar substance is present. Once reacted, it is useful to note that it is quite stable. It requires heating of over 300 °C before it decomposes to NH_3 and HCl gas, but because diluted versions will be mixed at ambient temperatures, this is not a problem.

D.2 Usage on a Farm

The Cl ions in ammonium chloride are particularly good for rice, coconut, oil palm, and kiwi fruit [162]. However, the Cl ion means that its use is limited to Cl tolerant crops. Because of this, $2/3^{rd}$ of all NH_4Cl is used in Japan and the remainder $1/3^{rd}$ in China and India [162]. Purely based off of this, there is unlikely to be a huge demand for it in Europe.

Additionally, ammonium chloride is slightly acidic, but so is the current chosen ammonium sulphate, so for that there is no major difference. However, farmers usually still prefer to use ammonium sulphate or urea as nitrogen fertilizer, because heavy rainfall can more easily leach nutrients away from ammonium chloride fertilizers [163]. That is why it is predominantly be used in Japan: during the growing season it rarely rains heavily in Japan for long periods and the weather is quite predictable on an annual basis. Also, it was noted that using ammonium chloride as a fertilizer for wheat results in higher Cadmium (Cd) concentrations, which can have adverse health effects [163]. Overall then, although cases can certainly be made in parts of Asia, ammonium chloride does not appear to be an ideal fertilizer to use in Europe.

D.3 Price/Profitability

What is perhaps even more important is the profitability, since the MEZT system only creates a limited amount of ammonia, which should be used optimally. Thus, the wholesale price and profitability is determined.

Unsurprisingly, due to its more popular usage in Asia, most prices found are from Asia. On Alibaba, the price varied, mostly being between 90-160 USD/tonne (about €75-135 /tonne). According to Echemi, the Q2 2021 price averages around 122 USD/tonne (about €102 /tonne) [164], whereas CEIC Data noted an average price of around €90 /tonne [165]. One supplier was also found on Alibaba located in France (Sarl SB Holding), which sold it at a range of €77-127 /tonne. A roughly average price of €102 /tonne can then be assumed.

Atomically speaking, ammonium chloride is 26% Nitrogen by mass, meaning that converting this wholesale price to a nitrogen price results in a price of €394/tonne N.

To compare this to some of the other investigated fertilizers (and their Nitrogen contents) from this paper:

- Ammonium sulphate: €250 /tonne at 21% N = €1,190 /tonne N
- Pure (or aqueous) ammonia: €857 /tonne at 82% N = €1,045 / tonne N
- Urea: €275 /tonne at 46% N = €597 /tonne N
- Ammonium Nitrate: €255 /tonne at 34% N = €750 /tonne N
- (Di)ammonium phosphate: €440 /tonne at 18% N = €2440 /tonne N (unrealistic, since it is mostly phosphate accounting for the price, not Nitrogen)

Clearly then, this places the profitability of ammonium chloride very low and close to that of some of the worse alternative fertilizers investigated. Upon further investigated, ammonium chloride is commonly made as a side-product of the ammonia-soda process for making sodium carbonate [166], thus explaining its relatively low price, since it is essentially a waste stream. Also, with its low price per nitrogen compared to other fertilizers, it would seem that it would be lucrative (cheaper) for farmers to use, and yet it is rarely used in Europe. This means that there might even be further downsides to this fertilizer than was identified in this brief analysis.

Nonetheless, ammonium chloride can reasonably safely be discarded as a chemical product to create in the MEZT system.