Greenfertilizer
zonnemelken voor een carbo-neutrale landbouw

Hernieuwbare energie van zon en wind voor lokale carbo-neutrale kunstmest en transportbrandstof voor de landbouw

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Inhoud

1 Samenvatting

Kunstmest voor de velden en brandstof voor landbouwvoertuigen zijn belangrijke kostenposten voor de landbouw. Kunstmest en dieselbrandstof zijn energie-intensieve producten en daarmee ook een belangrijke bron van CO_2 emissies vanuit de landbouw.

Technologie voor hernieuwbare energie zoals zonne- en wind energie wordt steeds goedkoper waardoor het rendabeler wordt deze technologie ook te gebruiken. Terug leveren van geproduceerde hernieuwbare elektriciteit aan het elektriciteitsnet is echter niet altijd voordelig. De hernieuwbare energie moet hier concurreren met gesubsidieerde fossiele elektriciteit opgewekt met kolen, gas en kerncentrales.

Kleinschalige decentrale productie op het boerenbedrijf van zowel kunstmest als transportbrandstof met behulp van hernieuwbare energie levert de boer en zijn omgeving direct voordeel op:
- Inkoopkosten voor deze producten worden lager
- Vermindert de CO_2-emissie van de landbouw aanzienlijk, de carbo-footprint wordt verminderd
- Rendement op hernieuwbare energie technologie wordt hoger

Ammoniak (NH3) is zowel grondstof voor kunstmest als brandstof voor motoren. Ammoniak kan diesel voor meer dan 90% vervangen in bestaande dieselmotoren. Daarmee is ammoniak een uitstekende vervanger voor diesel in het landbouw en wegverkeer. Ammoniak is ook grondstof voor waterstof (H2) in waterstofmotoren.

De technologie om ammoniak te maken is gebaseerd op het Haber-Bosch proces uit het begin van de vorige eeuw. Deze technologie vraagt veel energie voor het creëren van de hoge druk en de hoge temperaturen. Daarom is het voordelig het Haber-Bosch proces in grote installaties uit te voeren.

Nieuwe brandstofcel-technologie maakt het mogelijk het Haber-Bosch proces (elektro-katalytisch) op kleine schaal uit te voeren. Het Kiemkracht concept Greenfertilizer onderzoekt de mogelijkheden van deze technologie voor ammoniak productie en benutting op het eigen boerenbedrijf.

Het onderzoek is uitgevoerd door TU-Delft en Hanzehogeschool. Het doel was een opgeschaald ammonia elektrolyse synthese proces te ontwikkelen waar een eerste schaal-sprong gemaakt zou worden.

Het elektrochemisch ammonia synthese proces is gebaseerd op zuurstofgeleidende elektroden, (proces figuur3. zie onder). Het voordeel van deze zuurstofgeleidende electroden boven proton geleidende electroden is dat er met omgevingslucht gewerkt kan worden in plaats van met stoom. Stoom maakt technologische ontwikkeling van het proces gecompliceerder.

Experimenteel en theoretisch onderzoek van TU-Delft laat zien dat met deze elektroden ammonia te produceren is. TU-Delft heeft met zuurstof geleidende electroden ammonia productiesnelheden behaald van $1,84 \times 10^{-10}$ mol s^{-1} cm^{-2} bij 650°C. Deze snelheden zijn een factor 100-1000 hoger dan tot nu toe gerapporteerd in literatuur (Kyriakou et al 2017). Simulatie-studies van TU-Delft laten zien dat het ammonia synthese proces met een factor 100-1000 versneld kan worden door het proces onder druk te brengen bij een temperatuur van 400-500C. Op basis van deze simulaties is een ontwerp gemaakt en uitgevoerd voor een "hoge-druk electrolyse reactor".

Technische complicaties met deze hoge druk elektrolyse reactor maakte het onmogelijk betrouwbare resultaten te verkrijgen. Met name gas lekkages bij hoge temperaturen maakten het onmogelijk ammonia massabalansen op te stellen. Bovendien was ammonia productie niet aan te tonen. Hiermee zijn de simulatie voorspellingen niet bevestigd en blijft het onduidelijk of de onderliggende hypothesen correct zijn.

De Hanzehogeschool heeft onderzoek uitgevoerd naar het concentreren van ammonia voor toepassing als vloeibare kunstmest. Uitgangspunt hierbij waren de ammonia productieniveau van de experimentele opzet en de voorspelde gesimuleerde opzet. Met de juiste technologie is het mogelijk de ammonia te concentreren voor verdere verwerking als kunstmest. Echter dit proces is economisch rendabel bij een ammonia concentratie in de uitstroom van de elektrolyse reactor die een factor 1000 hoger is dan tot nu toe is gemeten. Het feit dat de TU-Delft er niet in is geslaagd een kleine schaalsprong (factor 10) te maken met de drukreactor betekent dat commerciële toepassing van dit proces voorlopig nog niet aan de orde is.

Achteraf gezien was het wellicht beter geweest de keuze te maken voor de proton geleidende electroden die bij lagere temperaturen werkzaam zijn, hier is een schaalsprong van een factor 100 ten opzichte van de recent gerapporteerde ammonia synthese snelheden.
Een recente review door Kyriakou et al 2017 geeft als aanbeveling onderzoek te verrichten naar verbeterde elektrodematerialen en geleidende elektrolyten in de reactorcellen.

Uiteindelijk zal het elektrochemisch ammonia synthese proces er komen vanwege de vele voordelen die het beidt. Processen moeten met een factor 100-1000 verbeterd worden eer het proces economisch rendabel is. Op dit moment is het nog niet te voospellen wanneer dit moment er is

2 Inleiding

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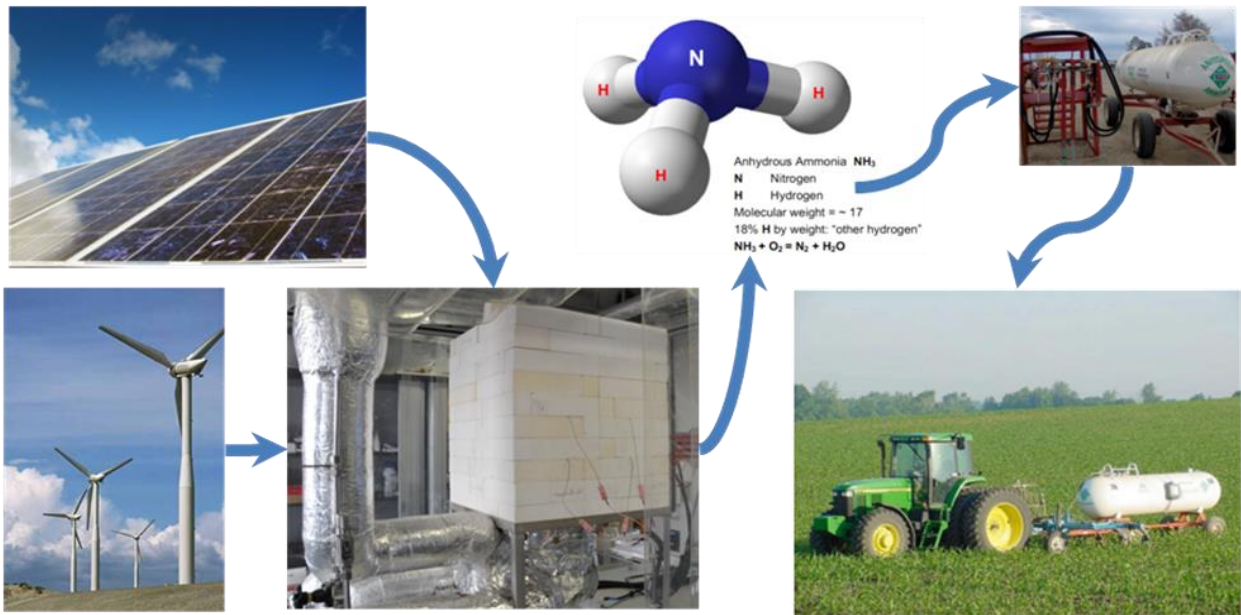
Omgekeerde brandstofcel

Brandstofcellen zijn elektrochemische toestellen die chemische energie van een doorgaande reactie direct omzetten in elektrische energie. Omgekeerde brandstofcellen zetten elektrische energie om in chemische energie en maken daarmee energie intensieve stoffen zoals waterstof. Recente ontwikkelingen met omgekeerde brandstofcellen maakt het ook mogelijk om in plaats van waterstof (H_2) ammonia (NH_3) te maken.

De technologie

Omgekeerde brandstofcellen zijn energetisch efficiënter voor productie van ammonia (NH_3). Omgekeerde brandstofcellen zijn klein en kunnen
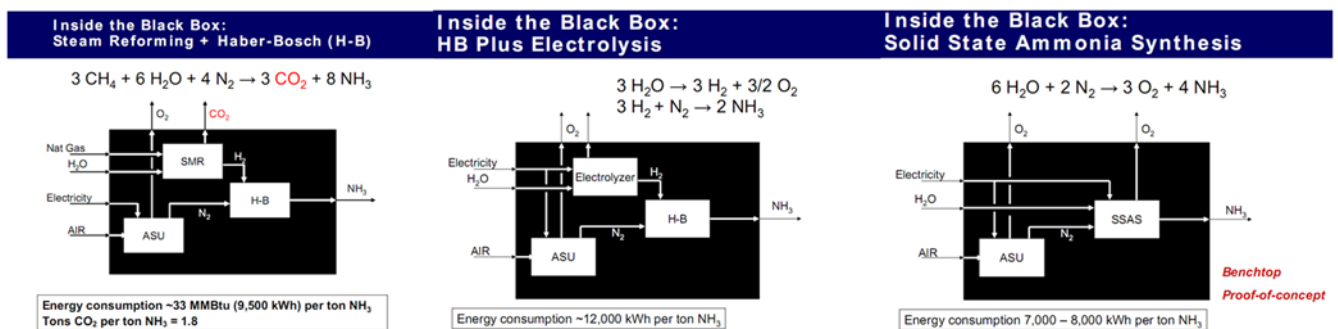
daarmee in principe op het boeren-erf geplaatst worden.

Kiemkracht onderzoekt samen met TU-Delft de technisch-economische mogelijkheden van *Greenfertilizer*. Met *Greenfertilizer* wordt de agrarisch ondernemer een producent van zijn eigen kunstmest en transportbrandstof op basis van hernieuwbare energie.

GreenFertilizer produceert ammonia met behulp van stoom en zuurstofgeleidende elektroden. (proces 1)
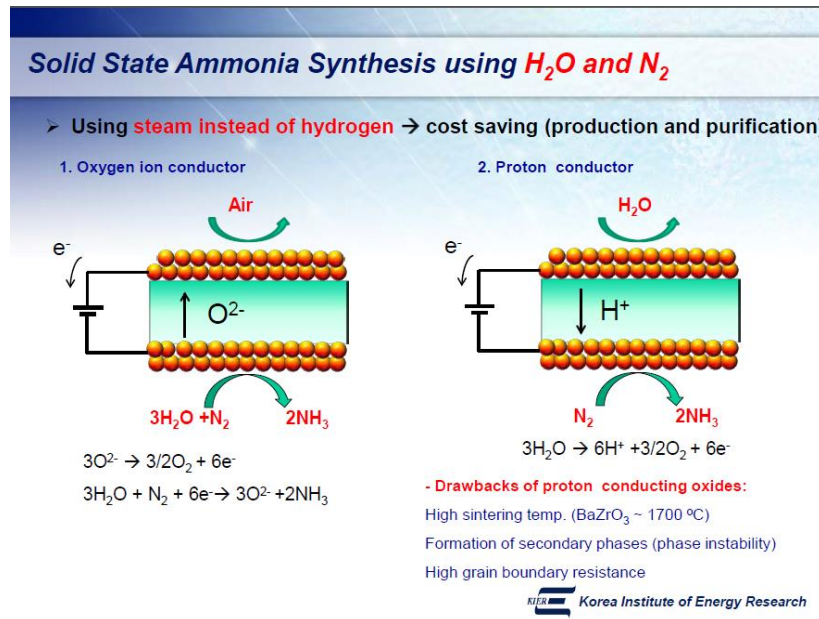
Proces 1 wordt verder uitgewerkt met TU-Delft. De resultaten tot nu toe zijn:

1) Het proces is volgens simulatiestudies thermodynamisch mogelijk
2) Met bestaande electroden zijn we in staat ammonia in het lab met proces-1 te produceren
3) De techn-econ. evaluatie voor een 100 ha akkerbouw bedrijf waar ammonia wordt toegepast voor, 100% kunstmest vervanging en 60% dieselvervanging resulteerde in
   a. Het proces is economisch niet haalbaar als de <u>volledige</u> afschrijving van zonnepanelen bij huidig prijsniveau wordt meegerekend (25ct/kWh)
   b. Het proces is economisch haalbaar als afschrijving zonnecellen niet wordt meegerekend en de stroomprijs gelijk is aan teruglevertarief aan het grid van 6ct/kWh.

Vervolgstappen zijn

1) Proces-1 onder druk (50-100 bar) en bij lagere temperatuur (400-500 ºC)
2) Ammonia-water scheidingstechnologie ontwikkelen/opschalen
3) Pre-engineering studie voor pilot faciliteit
4) Technisch economische evaluatie van het vernieuwde proces.

3 Samenvattende conclusies van het onderzoek

Het onderzoek is uitgevoerd door TU-Delft en Hanzehogeschool. Het doel was een opgeschaald ammonia elektrolyse synthese proces te ontwikkelen waar een eerste schaal-sprong gemaakt zou worden.

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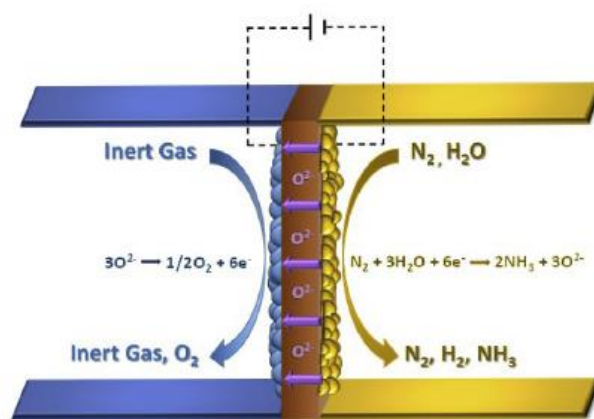
Fig. 3. A schematic of the SSAS process where an oxygen ion (O^{2-}) conductor is employed as the electrolyte.

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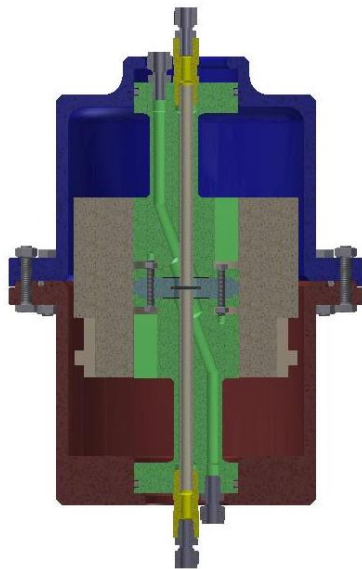
Zuurstofgeleidende omgekeerde brandstofcel in hoge-druk hoge temperatuur electrolyse reactor ontwikkeld bij TU-Delft

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4 Ammonia production

Partner: TUDELFT

4.1 *Introduction "* solid state ammonia synthesis via SSEC for fertilizer"

At this moment, the energy used by society is mostly stored within the fossil fuels (coal, oil and gas) which is converted into electricity in conventional power plants or used directly (such as in cars). There are several well known methods for sustainable energy conversion such as wind, solar and hydro power, which are playing becoming increasingly more important for the current energy challenges such as the depletion of fossil fuels and the occurrence of the greenhouse etc.

As the demand for energy is changing constantly there is need for methods to compensate

for the peaks in electricity demand and in production as well. The storage of energy

can be done in a number of ways, such as with the use of supercapacitors, hydro-storage

and electrochemical storage technologies such as batteries or chemical media. Especially

solar and wind based technologies need a method for energy storage as their electricity

production is unpredictable due to changing weather conditions and solar energy only

being available during day time. For the transportation sector it is required that the storage medium is transportable and has a high energy density. Several chemical storage media of interest have gained interest in the past years due to their applicability in the present available energy conversion systems, which increases the ease of implementation like : Hydrogen, liquid hydrocarbons, and ammonia.

It is argued that ammonia is a very suitable hydrogen carrier as its production through

Haber-Bosch as well as its storage and transportation are well understood and it has an

energy density close to that of fossil fuels[1].

Ammonia is also at this moment the only feasible carbon free chemical energy carrier solution for the transportation sector [2] and can, with some adaptations, be used in current diesel-or gasoline-powered engines
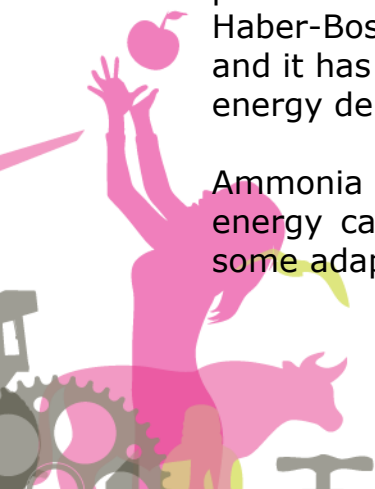
[3] [4]. Ammonia can be fed directly or indirectly into fuel cells, when the cracking of ammonia into hydrogen and nitrogen is performed internally or externally, depending on the type of fuel cell.

Ammonia is the third most used chemical and was produced for 136 million metric tons in 2011. Moreover, the global demand for agricultural nitrogen fertilizer is expected

to be 109 million metric tons in 2013, most of which is based on ammonia[5].

This increase in demand is occurring as the world-population is currently growing, and so is the amount of food required, which results in a higher request for nitrogen containing fertilizers.

The prices of fertilizer have been also increased for the past couple of years as seen in figure 1 and the use of nitrogen in fertilizers is expected to increase with 4% (within the EU with respect to now)[6] by the year 2020, increasing the attractiveness of a more economical way of fertilizer-production.

Figure 1: Prices of Fertilizer [4] in between July 2007 and July 2012.

As the demand and usage for ammonia is so high, a large infrastructure for its transportation and storage is already in place. The potential hazards have been widely studied and it is not a greenhouse gas or will damage the ozone-layer[7]. The techno-economic analysis of the ammonia-economy has been studied since the early 1970s when the concept of the "Hydrogen Energy Economy" was debated. Ammonia was then already looked at as the perfect storage medium for hydrogen.

studies were performed on the economic aspects of ammonia production methods and implementation in today's economy as an energy storage medium [8]. Having concluded that ammonia is a promising medium for energy storage as well as there being a large demand for the use in several chemical processes, its main method of production shall be investigated.

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The Haber-Bosch process was invented by Fritz-Haber and Carl Bosch, together with
the finding of the iron-based catalyst (described in section 1.1.3) found by Alwin Mittasch and made to an operational plant in 1913 [9]. The process consists of the reaction
between nitrogen and hydrogen to form ammonia, according to equation 1. The enthalpy of this reaction is negative (ΔH = -92kJ) meaning that it is an exothermic reaction. Le Chatelier's principle tells that decreasing the temperature causes the reaction to be favoured which generates more heat, which moves the reaction towards ammonia-production. The same is the case for an increase in pressure: A higher total pressure favours the reaction in the opposite (the one with the lowest number of moles) direction which is in this case ammonia. In order to achieve production rates that are economically attractive the pressure in large production plants is increased up to around 200 bar and the temperature of synthesis around 500 – 600 °C.

$$N_2 + 3H_2 \longleftrightarrow 2NH_3 \qquad (1)$$

Alternatives to the currently used Haber-Bosch method to generate ammonia could potentially have a very large impact on the transition to renewable energy sources and provide a cleaner method for fertilizer production.

4.2 Solid State Ammonia Synthesis – Problem definition

An overview will be given on electrolysis with the goal of the formation of ammonia. The first published works showing experimental synthesis of ammonia through electrochemical conversion with use of a solid electrolyte was presented by Stoukides and Marnellos [10] in 1998 when they used a SCY (H^+conducting) cell to achieve an ammonia flux rate of 3.1×10^{-9} mol cm^{-2} s^{-1} at 570°C. A higher operating temperature increased the current that could be applied to the cell and number of protons transported, however the quantity of decomposition of ammonia into N_2 and H_2 as well. After several more works published on synthesis through proton conducting cells, the research was followed up by Skodra and Stoukides in the presentation of an oxygen ion conducting cell in ammonia synthesis operation from a steam feed [11]. These two
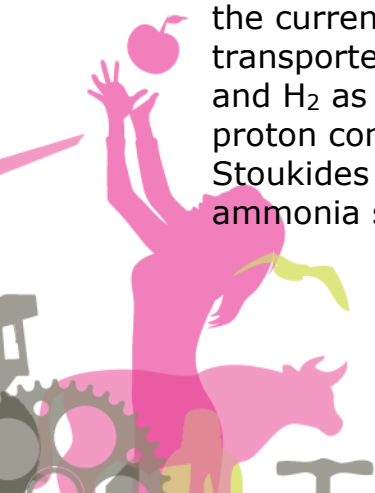
research projects indicate the two mainly used types of electrolysis cells used for the synthesis of ammonia: proton or oxygen ion conductors. The principles for both types of eletrolyzer for ammonia synthesis are shown in figure 2. For the proton conducting cell, the protons are transported through the electrolyte (by application of current) to the nitrogen containing gas where the protons react to form ammonia. In the case of the oxygen ion conducting cell the oxygen ions are transported from the fuel side of the cell to air side of the cell, allowing the hydrogen to react into ammonia with N_2.
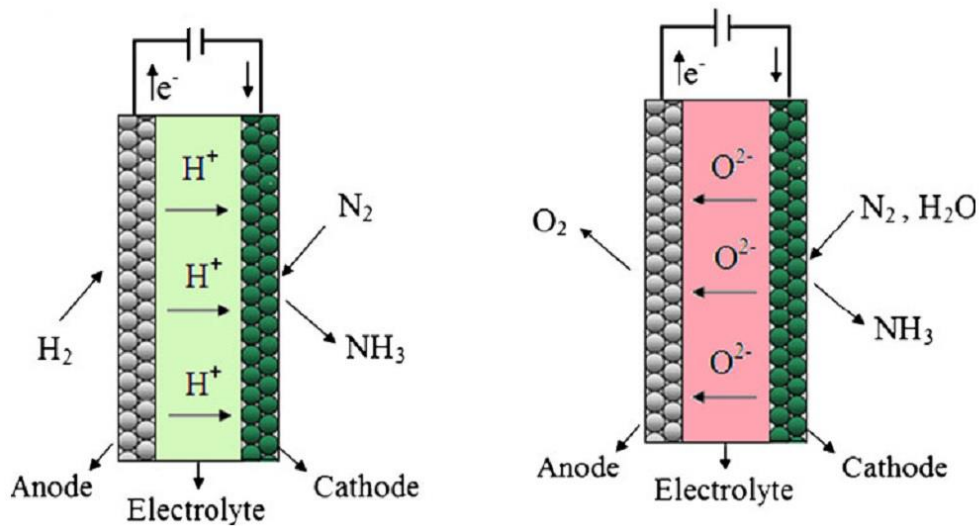
Figure 2: Workings of proton and oxygen conducting cells in process of ammonia-synthesis.

A paper presented in 2011 by Amar, Lan, Petit and Tao [12] gave an overview of the researches conducted up to that moment concerning ammonia-synthesis through Solid State Electrolyzer Cells (SSECs).
The process of ammonia synthesis with an oxygen-ion conductor is not completely understood yet, however the global reaction steps are as follows: on the fuel side, ammonia is formed according to the half cell reaction (under application of current):

$$3H_2O + 6e^- + N_2 \rightarrow 2NH_3 + 3O^{2-} \qquad (2)$$
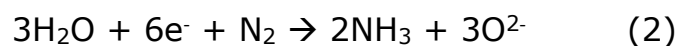
The oxygen ion is electrochemically transported to the other side of the cell through the electrolyte:

$$3O^{2-} \rightarrow 3/2O_2 + 6e^- \qquad (3)$$
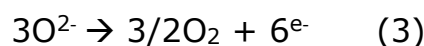
This makes the overall cell reaction:

$$N_2 + 3H_2O \rightarrow 2NH_3 \quad (4)$$
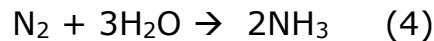
The researches mentioned performed experiments with button cells of 1-2 cm^2, whereas full scale applications most like require larger cells.
It is concluded that the two technologies, fuel cells in electricity generating and fuel generating modes, represent very promising alternatives to the currently used technologies for energy conversion. Ammonia is a promising medium for the storage of chemical energy that can later be converted into electricity as well as next to being the main chemical used for fertilizer production. The referenced papers on ammonia synthesis through electrolysis with an oxygen-ion conductor all have in common that small cell areas were used.
Thermodynamic calculations have been studied on which the experimental conditions are based to reach the following goal: Create an as high as possible flow of ammonia through the electrolysis with an oxygen-ion conducting cell.

4.3 Objectives

➢ Determine the merits of the production of ammonia through electrolysis technologies, including technical- experimental and a first economical basis.
➢ Determine the production rate of ammonia
➢ Determine the more suitable cell for the production of ammonia.
➢ Determine the operating condition that favors the production.
➢ Explore required investments, operational costs and returns of a synthetic ammonia production plant .

4.4 Review US patent 7811442 B2

The patent concerns ammonia synthesis with the use of proton-conducting electrolyzer cells and increased pressure 10 atm and 300 atm of operating pressure for the nitrogen rich side of the cell. Operating temperatures of between 400 and 800 ^{o}C are preferred for the operation of the device presented in the patent. From the literature research it is concluded that oxygen-ion conducting cells for the purpose of ammonia synthesis are not well researched and also not covered by the patent. Operation of an ammonia synthesis plant with the same operating

conditions and an oxygen-ion conducting cell should thus not be in conflict with the patent.

It is therefore recommended to perform tests with oxygen-ion conducting cells to determine the efficiency of ammonia synthesis and economic feasibility of large-scale application.

The research papers on ammonia synthesis through electrolysis with an oxygen-ion conductor all have in common that small cell areas were used. For proton conductors, research has shown that the combination of a proton conducting electrolyte, industrial ammonia catalyst and applied electricity led to an increase in catalytic activity of 1300%. The process of ammonia synthesis through oxygen ion conductors is not well understood yet, very little research information is available and no experiments have been conducted with commercially available solid oxide cells for ammonia synthesis. For fast large scale application of ammonia synthesis from SOECs, it is preferred that well-researched and developed materials are selected and therefore it is chosen that synthesis through commercially available cells is the preferred method for its synthesis.

Interfacing a commercial SOEC with an ammonia promoting catalyst has not been researched yet and for proton-conducting cells shown to be advantageous for ammonia synthesis.

Anode supported cells were found to be the most promising type of cells for ammonia synthesis due to the possibility of low temperature operation and increased performance with respect to conventional electrolyte supported cells.

4.5 Economic calculations

An economic estimation was done on the payback time required for an ammonia producing plant, producing ammonia to provide an agricultural area of 100 hectares with ammonia. This has resulted in a payback period of around 10 years with expected fuel cell prizes to drop in the coming five years and a current-efficiency of 100%. These calculations included the investment of the electrical power supply from wind and solar energy, which are expected to drop in the coming years (price-drop not taken into account).

4.6 Societal benefits

This project is aimed at the socially relevant problems related to the storage of temporary excess electrical energy from wind and solar on the one hand and the Ammonia used like a fertilizer. The availability of viable and socially acceptable storage technologies for temporary excess

electricity is key to the widespread use of renewable energy from wind and solar and reduction of greenhouse gas emissions.

Using electrolysers to convert surplus electricity from solar and wind into ammonia can really increase the wind and solar capacity . Alternately if you think to use ammonia not only like a fertilizer but also like fuel might provide a method for production of very clean fuels.

Synthetic Ammonia is a clean burning fuel. These activities are expected to help to identify and to develop efficient and viable routes for production and utilization of ammonia. This might help in reducing the total primary energy consumption.In light of the depletion of the domestic fertilizer resources within the next years, researching scenarios able to decrease the price of ammonia and its continue utilization on the farmer network is clearly beneficial to Dutch society.

4.7 Degree of innovation in international context

This project is innovative in 3 areas:

- Solid Oxide Fuel based Electrolysis Systems operating with steam and nitrogen to produce ultra clean ammonia in relatively fewer steps when compared to existing processes.
- Explore and design novel ammonia concepts based on the SSEC, focusing on experimental evaluation dynamics
- Applications of synthetic ammonia to enhance efficiency and reduce the cost of the fertilizer

This project is based on an interdisciplinary approach, which considers the interrelations between science, technology and existing infrastructure necessary to facilitate a future transition towards sustainable ammonia distribution systems.

4.8 Interdisciplinary character

The proposed project is interdisciplinary by outset since it investigates possible interrelations between technological feasibility (physical, chemical, electrochemical, thermal and material science) and technical infrastructure concepts in the gas sector.

4.9 Expected results

The project will provide insight into the technical and features of Ammonia as an energy carrier for storage and transportation of excess Renewable Energy and the production of green fertilizer .

This project aims to research the economical and technical feasibility of ammonia production and injection into the fertilizer grid. The results of this project aim to support investment decisions of Dutch Farmer.

4.10 Thesis Ab Streppel

The transition from fossil fuels to renewable energy sources results in a demand for methods of energy storage. Ammonia is one of the possibilities of interest as an energy storage medium due to its well known properties and relatively high energy density to other alternatives. The currently used method (Haber-Bosch process) for ammonia synthesis is energy intensive due to high pressures and temperatures during synthesis, next to the use of fossil fuels as a hydrogen source for the synthesis reaction. Synthesis through solid state electrolysis is of interest due to reduced carbon emissions and possibly lower energy input requirements. Electrolysis experiments were performed at three temperatures and three gas compositions with five anode supported cells configurations, of which two cells were impregnated with different amounts of magnetite (Fe_3O_4), the basis for the catalyst used in the Haber-Bosch process. The highest synthesis rate of ammonia during experiments was found to be:

$$1,84 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2} \text{ at } 650^{o}C$$

with a non-impregnated cell under application of a current of 8 amperes. The cells were evaluated on required energy input and area specific resistance through Current-Voltage analysis and a comparison was made with results acquired from Electrochemical Impedance Spectroscopy. Trends for changing operating conditions were found similar for I-V analysis and EIS. Modeling was performed on the theoretical output under different operating conditions and steps for future research planned out.

4.11 Computational & System studies

Thermodynamic calculations are performed in order to determine the operating conditions for experiments and create expectations for the outcome of those experiments.
It will determine operating conditions in such a way that experimental materials are not damaged during operation and that in the end of the chapter conclusions can be drawn between different operating conditions as to which conditions were best suitable for the goals of this thesis.
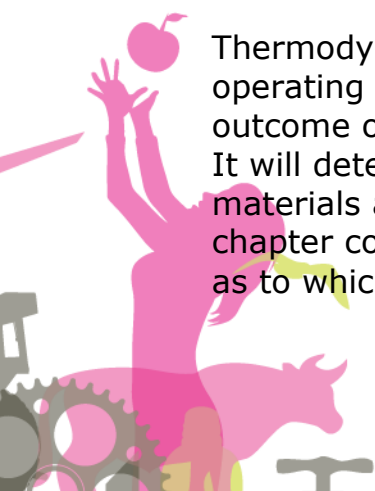
Calculations will also be performed to determine the quantities of ammonia present at equilibrium conditions for the chosen experimental conditions.

It was shown through thermodynamic calculations that the expectations are that high system pressures, low system temperatures and low quantities of water in the fuel-gas will result in the highest amounts of ammonia to be produced from the electrolyzer cell. It was shown that the change of system pressure increases the open circuit voltage, resulting in higher electricity input requirements for the electrolysis-reaction, according to the presented Nernst-voltage calculations.

The oxygen-rich side of the cell should contain as low quantity of oxygen as possible to decrease the Nernst-voltage and the hydrogen-concentration on the fuel-side should also be as low as possible. The quantity of hydrogen should however not be zero as then the possibility exist that oxidation of the nickel present in the cell and current-collector will occur. For the goal of a high quantity of ammonia production, the temperature of the cell should thus be as low as possible, however this also comes with an increased resistance to oxygen ion transport through the cell. Therefore a trade off must be made between this high ionic resistance and higher quantities of ammonia-synthesis, to be determined from experiments.

Different gas-compositions fed to the experimental cell will result in different amounts of ammonia produced: a high quantity of steam present allows for high currents to be applied and therefore higher ammonia formation. However, the equilibrium conditions for ammonia are more favourable for lower quantities of steam, therefore a balance but be found between these positive and negative aspects of steam-presence.

4.12 *Preparation of a detailed experimental plan and preliminary experiments.*

The following sections will describe the experiments that were performed in order to reach the goal : create an as high as possible flow of ammonia through electrolysis with an oxygen ion conducting elctrolyzer. The equipment for the conducted experiments shall be described as well as the methods for analysing the resulting data. This is followed by interpretation of the results and conclusions that are drawn from them. From the review of literature, performed thermodynamic calculations, the following research objectives are proposed: an increase in water content was shown to result in a lower quantity of ammonia present at equilibrium conditions, compared to high water content. A higher water

content also allows for a higher allowed current to be applied to the cell, resulting in a higher quantity of hydrogen in the outlet gas. The influence of both effects on the outlet flow of ammonia will be investigated. An increase in temperature is expected to increase the conductivity of the electrolyte material, resulting in an electrically more efficient cell operation than at low temperatures. An increase in temperature also increases the amount of ammonia decomposed into nitrogen and hydrogen.

The experimental set up consists of a gas-supply, cell holder, heating oven and gas-analysis equipment and the exhaust section for venting the exhaust gases. The gas supply lines provide reactant gases to the cell holder, in which the actual SOC is placed, where the electrochemical reactions take place.

The square ceramic cell holder is made from Alcorite (Al2O3), produced by Louwers- Hanique , and has one gas-inlet and -outlet on the fuel side of the block. The air side of the holder only contains an inlet pipe and no outlet pipe as the exhaust air is vented into the oven, surrounding the cell block. The inlet fuel gas is heated to a temperature of 180°C by tracing-wire to prevent condensation of the steam added to the gas flow. The temperature of the cell holder and the oven itself are controlled by heating elements

placed around the cell holder. Control of the temperature is done by use of a Eurotherm PLZ903P, receiving power from a Delta Elektronika Supply, model SM 120-25D.

Ceramic pipes, screwed hand-tight into the cell block, provide the gas for to the cell block, which is spread along the area of the cell through distribution channels and, after the electrochemical reactions have taken place, exhausted through a ceramic pipe.

Gas tightness between the pipes and the block is assured by use of golden sealing rings between the pipe and the block.

On top of the distribution channels there is a nickel mesh present to which platinum current collector wires are spot-welded for the current supply to the electrode. The oxygen rich side of the cell holder has a platinum mesh, platinum current collector wires and has only an inlet pipe (sealed with a golden ring) and no outlet pipe. The reacted oxygen rich gas exits by being released into the surrounding oven. Platinum wires for voltage measurements are separately spot-welded directly to the mesh.

4.12.1 Choice of the cells

Ammonia synthesis is favoured by low temperatures and therefore cells are selected that provide functionality at low temperatures. Most Electrolyte Supported Cells (ESCs) available only work well at higher temperatures due to the ionic-conductivity of the electrolyte (thickest part of the ESC) being high enough at those high temperatures[13]. Anode Supported Cells (ASC) have a thinner electrolyte and thicker anode than ESCs and as the electrolyte is generally the limiting factor for the functionality of the cell (dependent on thickness and temperature), the operating temperature can be decreased for ASCs and provide proper functionality.

4.12.2 Cell Impregnation

Literature research showed that magnetite (Fe_3O_4) together with certain additives is a
suitable catalyst for the ammonia synthesis process. Therefore, two cells were impregnated with Fe_3O_4-solutions to investigate possible
improvements to the synthesis rate due to presence of magnetite on the cell.
Two methods were chosen for the impregnation of the cell: Method 1 consists of making
a suspension of magnetite followed by impregnation of the cell.
This production method did not give satisfactory results. Therefore a commercially available Fe_3O_4 solution was chosen to perform the final impregnation with Method 2, a suspension of magnetite nano-particles from the Sigma-Aldrich corporation with an
average Fe_3O_4 particle size of 10 nm and a concentration of 5 mg/mL in H_2O was
acquired for the process of impregnation.

Electrolysis experiments were performed at 450 ^{o}C, 550 ^{o}C and 650°C with three different gas compositions. Five different cell configurations were used, of which two were with cells impregnated with an ammonia synthesis promoting catalyst.
The outlet gas was analysed for presence of hydrogen, nitrogen and ammonia using GC-analysis and Ion Chromatography.
All outlet gas measurements were performed only on the fuel-side of the cell. An overview of the layout for the gas-analysis is shown in figure3.
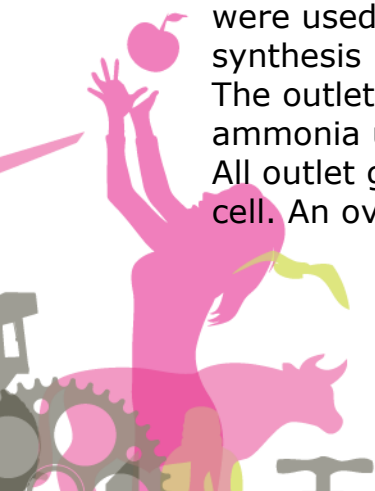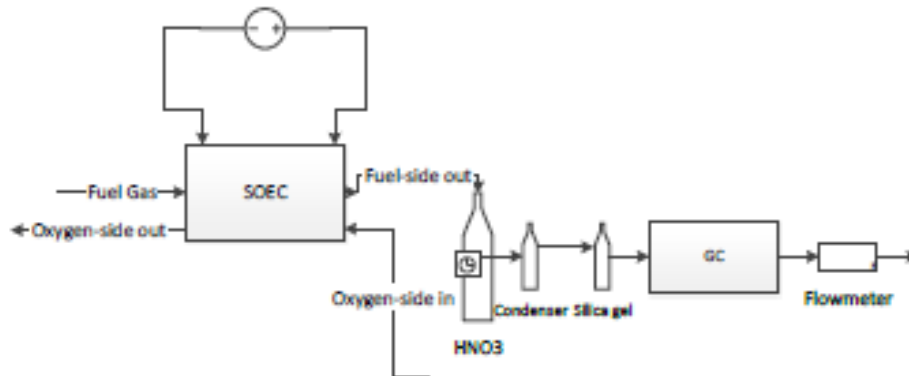
Figure 3.: Schematic drawing of the gas-analysis set-up.

4.12.3 Ammonia Quantification

Several options are available for determining the quantity of ammonia in a gas or liquid,
all of which have their positive and negative attributes.
the Ion Chromatography (in combination with HNO3 to form NH+4) was the
selected method for determining the quantity of ammonia.

4.12.4 Ion-Chromatography

Passing the outlet-gas of the cell through a Bronsted acid will cause any ammonia present in the gas to react to ammonium, according to following reaction. An Ion chromatograph can then detect the ammonium (NH4) cations present in the solution.

$$H^+ + NH_3 \longleftrightarrow NH_4^+$$
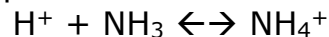
4.12.5 Experimental inaccuracy identification: Leakages

One of the problems concerning SOECs is that the experimental set-ups are hard to make completely leak-tight [13]. Three sources for leakages were identified during experiments:
1. Before the inlet of the cell-holder due to untight connectors in the gas-supply (gas-supply lines or at the contact-point between the ceramic gas-inlet pipe and the cell-holder)
2. At the cell sealing on the top or bottom-side of the cell
3. At the outlet of the cell-holder due to untight connections

4.12.6　　Analysis of Experimental results

Two economic performance indicators are of interest in this research: The quantity
of ammonia produced per electric energy input and the production rate per cell area.

Evaluation of the different operating conditions, different gas composition, and cells has resulted in the following conclusions: presence of a higher quantity of water in the inlet gas generally resulted in a lower synthesis rate of ammonia. This is the result as expected. However, the maximum rates of synthesis were achieved at the two highest concentrations of water. The non-impregnated ASC-10C cell has shown the highest absolute ammonia synthesis rates ($1.49 * 10^{-8}$ mol/s).

The highest achieved absolute production rates under load were with the ASC-10C at
8A (1.49×10^{-8} mol/s, 650°C with 15.8% H_2O) and 14A (1.46×10^{-8} mol/s, 650°C
with 39% H_2O).

Under open circuit conditions (I=0A), the highest rates were achieved with the impregnated cell ASC-10CII (1.50×10^{-8} mol/s, 650°C, 4.5% H_2O) and the other impregnated cell ASC-10C-I (1.30×10^{-8} mol/s, 550°C 4.5% H_2O). The impregnation of the cells has resulted in an increase of ammonia synthesis at open circuit (thus purely catalytic) conditions compared to non-
impregnated cells. Under conditions of electrochemical conversion (applied current), the
non-impregnated cells resulted in the highest synthesis rates.

The highest Faraday law efficiencies on an NH3-basis were achieved at 550 °C with the
10B ($\eta_{FL,NH3}$ =0.192 at 39% and 1A) and with the ASC-10C $\eta_{FL,NH3}$ =0.166 at 15.8% 1A). At higher applied currents this was with 10C at 39% and 650 °C ($\eta_{FL,NH3}$ =0.065)
and with the 10C at 7A $\eta_{FL,NH3}$ =0.042 at 550 °C, 39% H_2O).

The highest values for the Equilibrium Ratio are acquired with the ASC-10C at currents of 5 and 8 amperes, 650°C and 39 and 15.8% H_2O respectively.

All results combined, the tests with the ASC-10C have resulted in the highest synthesis rates and highest efficiencies of current use.

It is unclear how the quantified leakage of hydrogen for the ASC-10C tests can be around 30%, even though the cell resulted in the highest

production rates of ammonia of all cells. whereas the other cells generally achieved higher values for тleak.

The highest synthesis rate per current input was achieved with the ASC-10C cell with a Faradaic Law efficiency of 0.192%. On the basis of total hydrogen output (instead of purely ammonia) the ASC-10B has also resulted in the highest output of hydrogen per current input. Two ASC-10C cells have been impregnated with an ammonia promoting catalyst, which resulted in a higher area specific resistance than the non-impregnated cells, as well as an increase in synthesis rates at open circuit conditions. Under current applications the impregnated cells generally did not have higher synthesis rates than the non-impregnated cells.

Comparison of the obtained results with the results of other researched shows that the production per square cm of cell for this research was comparable to that of others. The electric energy-input per mole of ammonia produced on the other hand, was higher for this research.

4.13 Recommendations for the continuation of the work

The data obtained from experiments were used as a basis for modelling of ammonia synthesis through electrolysis at increased pressures and lowered temperatures. Analysis
of the modelling results showed that synthesis at higher pressures and lower temperatures
will result in increased synthesis rates. At these conditions, the electricity requirements
are still higher (factor 5) than the total energy input that is required by Haber-Bosch
production plants per unit of ammonia. A more detailed economic analysis must show
if this electricity input is compensated for (in terms of social and monetary value) by
added hydrogen and oxygen outputs as well as the reduce of carbon emissions.

The following recommendations are formulated for future experiments research: additional experiments with different catalysts, pressurized set ups and low temperatures must be conducted to reach higher synthesis rates.
Thinner anode supported cells and based on different materials (such as ceria based) are

recommended for analysis.

The effect of lower oxygen pressures at the air side on the operating voltage must be
researched as well as the lowering of hydrogen pressure on the steam side of the cell.

A new impregnation method must be tried in order to get a more evenly distributed de-
position of the impregnated material, such as a bath that does not completely submerge
the cell. Fabrication of cells with synthesis enhancing catalyst inside the electrode could
also be an improvement.

Further EIS experiments and modelling are recommended for understanding the behaviour
of the cell under different operating conditions. EIS measurements at high experimental
conditions are recommended as well for further understanding of the processes.

The sampling time for one current in this thesis was around 30 minutes. Different methods for analysis of the ammonia present in the gas as well as influence of a shorter sampling time on the detection of ammonia must be looked into in order to lower the time per experiment required. Extended economic modelling must be performed for a complete cost-benefit analysis and economic feasibility.

## 5 Design pressurized setup for ammonia prodcution

5.1 introduction

This project has been set-up to build on previous research done, a set-up has been designed and made to do experiments with fuel cells at high pressure and high temperature.

The set-ups consist of a sample holder at high pressure and high temperature. Attached to this sample holder are two gases that can react in the sample. This sample holder is placed in a pressure vessel and this vessel has the same pressure of inside the sample holder. This pressure vessel is filled with nitrogen/argon/helium and zero oxygen. The reason for this is that in case the sample holder is leaking that it has no chance to combust with oxygen.

A fuel cell generally consists of three layers: anode, cathode and electrolyte. To the anode side of the cell a fuel rich gas (H_2O,N_2 ….) is supplied and to the anode side an oxygen rich gas (normally air). An electrochemical reaction takes place on both sides of the cell, resulting in
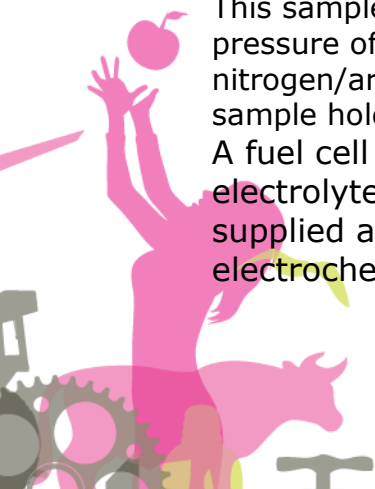
a different outlet gas and the conversion of chemical energy into electricity.

The cell is enclosed in a cell-holder that supports the cell and also makes sure that the gasses fed to the cell do not leak out to the environment by the use of sealing materials. To conduct the electricity away from the cell to the end-user, the anode and cathode have to be in contact with electronically conductive materials that guide the electricity to the outside of the pressure vessel. The operating temperatures can been changed between 450-850 degrees Celsius.

5.2 Scope

In the scope of the project at the end of the production phase:
- Design of the fuel cell holder
- Design of the pressure vessel around the fuel cell holder
- Production of the fuel cell holder
- Production of the pressure vessel around the fuel cell holder
- To test different cells
- To test different temperatures
- To prove the increasing rate of formation of ammonia with the pressurized set-up

5.3 Design
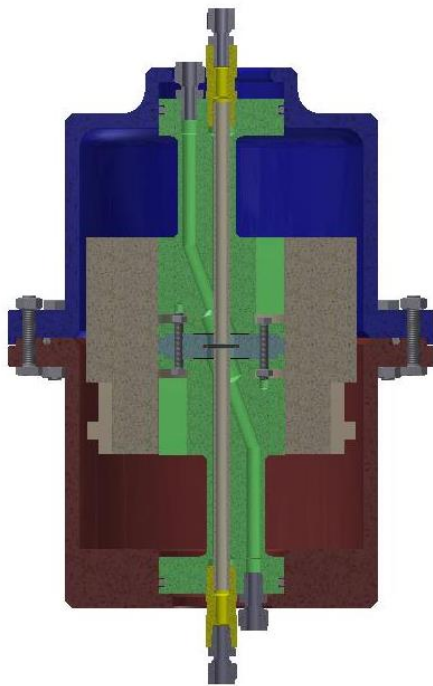
5.4 Conclusion and future prospective

Considering the latest research in the field We expect a significant increase in the rate of formation of ammonia by performing the experiments with the pressurized setup, however there is the risk that this procedure can be not sufficient to reach the goal , In this case the doping of the fuel side of the cell, with different impregnating material, will be the next challenge to get a rate of formation of ammonia that meets our expectations.

5.5 Experimental results Pressurized set-up

Ammonia production using Solid Oxide Electrolyser-Experiments and results

5.5.1 Introduction

Ammonia can be used as a sustainable fuel especially in fuel cells. With the advent of increasing renewable energy, it can also be used a medium to store energy. The Haber-Bosch for production of ammonia is well known but electrochemical synthesis of ammonia has not been discussed in detail before. In our previous experimental work we reported ammonia formation under suitable conditions under electrolysis mode. However, the amount while promising was quite small. In order to increase the ammonia yield, among the various options available it was decided to operate at higher pressures which thermodynamically favours ammonia formation (the Haber-Bosch process runs at even 150 bar). For this, a special high pressure setup was designed (Figure 1) and fabricated.

The test setup consists of a gas-supply, cell holder, heating oven and gas-analysis equipment.

For added safety, the assembly is placed in a pressure vessel filled with nitrogen at the same pressure as inside the sample holder.
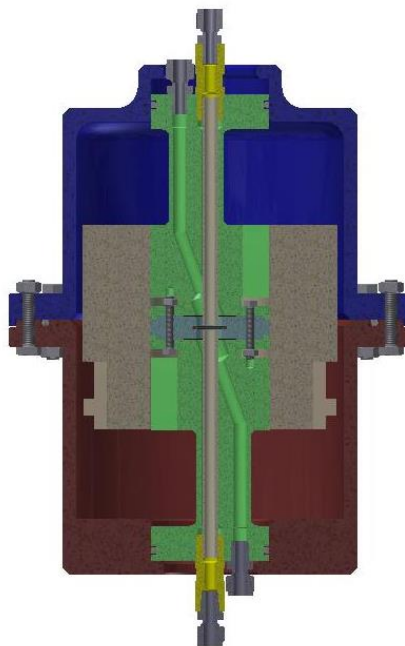

Figure 1: Test Setup

Using the above described setup, a set of experiments to produce ammonia by electrolysis were performed. Since ramping up and cooling down of this setup requires time (around 2 days) and assembly of the furnace (pressure vessel) and sample holder requires a technician half a day at least, it is possible to do only one experiment in a week. All the tests were performed at 550 ^{0}C – the temperature at which we expect maximum ammonia to form while maintaining reasonable SOEC operating conditions. The setup was operated using a traditional Ni-GDC anode, YSZ electrolyte and LSM cathode. Prior to operation as an electrolyser, the fuel electrode is reduced from NiO to Ni. This ensures catalytic activity and also electrical contact. For analysis of the outlet gas, the gas is bubbled through a hydrochloric acid solution and is further analysed using ICP-OES for ammonia. A brief description of the experiments is provided below.

5.5.2 Experiments and results

The test was performed with a new inlet tube installed (see Appendix). An OCV of close to 1V was recorded. The pressure was increased simultaneously in the anode and cathode in small steps (0.1 bar). However, it was not possible to go beyond 2.5 bar. The reason for this is not very clear – A possible explanation is the pressure of the line can be a maximum of 8 bar which after a pressure drop from the mass flow controller is not sufficient to cross 2.5 bar. However, theoretically a pressure of around 5 bar should be achieved. Rupture of the cell was ruled out as a reason as the pressure is same on both the sides of the cell. Another possibility is that a small part of the inlet tube is made from Teflon which is not usually designed for higher pressures.

However with this configuration it is possible to try to quantify if there is any ammonia formed in the system even if the current drawn is very small. For this the gas was sampled for ammonia by an impinger bottle filled with 0.01 N HCl solution. Subsequently ICP OES was performed to analyse the liquid for ammonia.
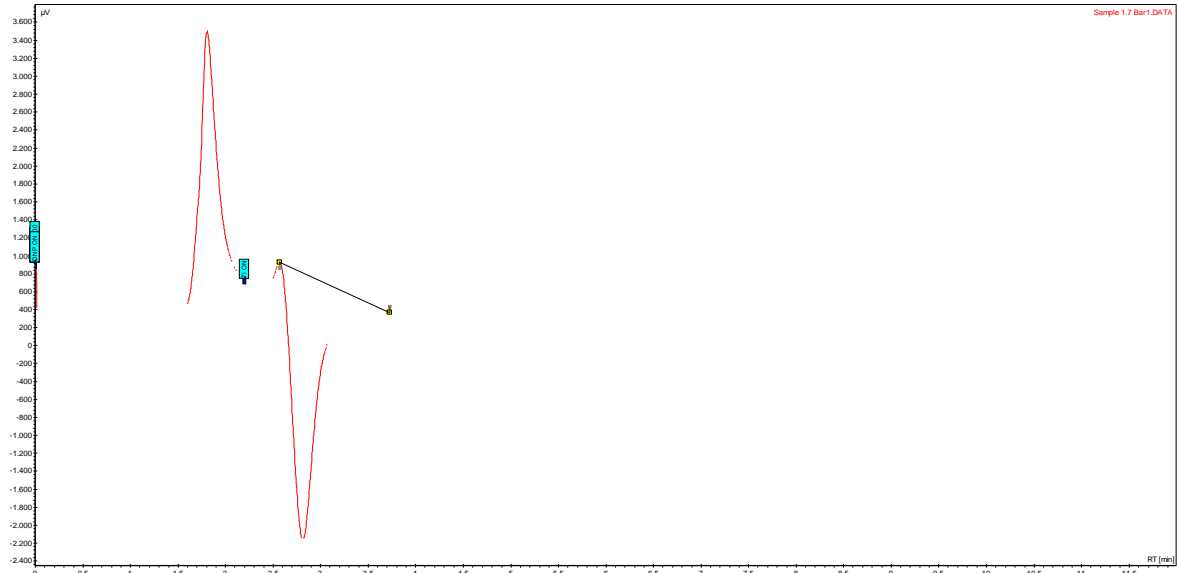
Figure 2 : ICP OES spectra of collected sample

The above graph shows the ICP OES graph for the outlet gas analysis when bubbled through HCl. The first and second peaks are ascribed to the anions (Cl⁻) in the system. The peak of ammonia is expected at around 3.5 min but is not observed here with any certainty.

5.5.3 Conclusions and future plans

A setup for potentially running high pressure electrolysis experiments was fabricated and tested for production of ammonia. Facing a number of teething problems like sealing, electrical contact, leakage etc (especially with the background of ongoing lab relocation) it was not possible to run very extensive tests within this time frame especially considering departmental and laboratory reorganisation. The tests conducted were not entirely satisfactory with respect to operation at high pressure. However, we have gained some knowledge about the requirements for operating the setup at high pressures and the modifications needed in future to operate such a setup smoothly.

We are planning to continue the work and future work will focus on making changes in the setup (inlet tube, current collector etc) for high pressure long term operation. Also, impregnation with a catalyst to promote ammonia formation will be considered.

5.5.4 Experiments

A number of experiments were performed which were abandoned because of a number of challenges such as leakage, improper reduction, improper electrical

31

contact etc. Out of around 6 experiments, the following two examples are reported for the sake of brevity

5.5.4.1 Experiment 1 :

After reduction it was found that the open circuit voltage was much lower than expected. This could be because of faulty reduction of the anode or because of insufficient contact between the current collector and electrode. After further reduction by leaving the cell to run on hydrogen for an extended time (20 hours) it was found that the contact was not improved. It was concluded that the contact was insufficient probably because of mechanical loss of contact.

5.5.4.2 Experiment 2 :

In the another iteration with a similar cell it was observed that the OCV was close to 1 V (as is expected). However we could not draw current even in small amounts. This can be because of faulty hydrogen/ water supply at the fuel electrode. The leak was traced to the inlet pipe of the setup. The reduction of the fuel electrode can be severely affected by the leakage (possibly selective leakage) of hydrogen. This was found to be the case post shutdown and removal of electrode as the fuel electrode was only partially reduced and hence was unable to carry current.

6 Technical and financial analysis ammonia production system.

Partner Hanzehogeschool

6.1 Project Description

The goal of this project is to design the technical (and financial) aspects of constructing an ammonia production system using nitrogen and water. These components are electrolysed to hydrogen using renewable energy. The system is to be housed in a container on the EnTranCe (Energy Transition Center) terrain, and should satisfy the according safety requirements.

6.2 Project Organisation

This project was commissioned by Rob van Haren to the Energy Knowledge Center (EKC), and is conducted by Mark Meerdink & Michael Barankin (EKC & Chemical Engineering), in conjunction with Lies Oldenhof (EKC). The project duration is from January through April 2014.

6.3 System Design

The system design is developed in the following sections, beginning with a process flow diagram (PFD), a description of the system's design parameters and requirements.

6.4 Process Flow Diagram

Depicted in **Fout! Verwijzingsbron niet gevonden.** is the proposed PFD, Process Flow Diagram. The PFD reveals the unit operations and general flow scheme of the system. This ammonia production system can be divided into three sections: the feed handling (nitrogen and water), reactive electrolysis, and product separation sections (on coloured blue, orange, and green backgrounds, respectively).

The feed handling system includes the nitrogen source consisting of two or more compressed gas cylinders (for continuous, uninterrupted operation), and water supply consisting of a bubbler system. An optional wing of the feed handling system provides for the addition small amounts of hydrogen to the feed (simulating a product separation and recycle system), should this become necessary for demonstration purposes.

The Solid-Oxide Electrolysis Cell (SOEC) is based on the design described by TU-DELFT. This cell is designed for high-temperature, medium-pressure electrolysis of steam to hydrogen gas, and subsequent catalytic conversion of hydrogen and nitrogen to ammonia vapour. Due to the fact that oxygen (O^{2-}) is the active diffusive charge carrier through the electrolyser (instead of H^+), the catalytic conversion is achieved on the feed side, while the sweep side may be serviced by air which is then enriched in O_2 (recombined ions emerging from
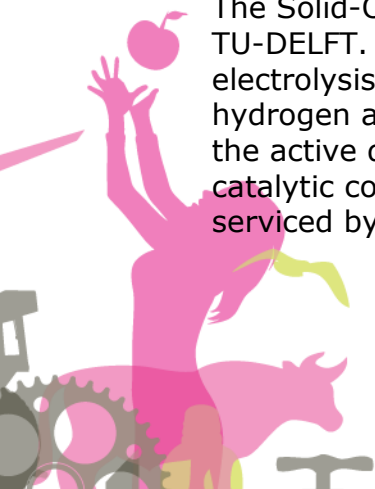
diffusion) before expulsion to atmosphere. Therefore, the following reactions are taking place in continuous operation:

<u>Feed Side</u>
$$H_2O + 2e^- \rightarrow H_2 + O^{2-}$$
$$3H_2 + N_2 \rightarrow 2NH_3$$
<u>Sweep Side</u>
$$2O^{2-} + 4e^- \rightarrow O_2$$
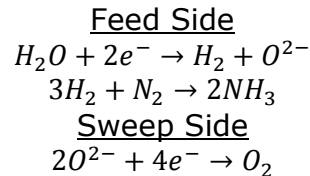
6.5 Ammonia Production: best and worse case

While the thesis of Streppel covers the feed concentrations and output of ammonia, it does not explicitly provide the water production rate. Therefore it was necessary to determine the outlet water flow rate under so-called "best case" (minimum) and "worst case" (maximum) scenarios. Toward this end, the cases are defined as follows:

- "Best Case": Here it is assumed that *all* of the hydrogen used to form NH3 (from N2) is generated by breaking water molecules (H2O), such that the hydrogen flow rate leaving the system is equal to the amount entering the system.
- "Worst Case": Here it is assumed that *all* of the hydrogen used to form NH3 (from N2) is generated by breaking hydrogen molecules (H2) only, therefore all water which is not electrolysed emerges unchanged.

The table below was constructed based on the data listed on page 77 in Streppel's thesis by using the following best and worst case calculation methods for the water flow rate out of the electrolyser:

Best Case $\quad P_{water}\left[\frac{mol}{min}\right] = F_{water} - \frac{3}{2}P_{NH3}$ **or,** Zero (0) if F_{water} < (3/2)P_{NH3}

Worst Case $\quad P_{water}\left[\frac{mol}{min}\right] = F_{water} - \left(\frac{3}{2}P_{NH3} - F_{H2}\right)$ **or,** F_{water} if F_{H2} > (3/2)P_{NH3}

Finally, the concentration of ammonia in the effluent (neglecting gaseous components such as H_2 and N_2) is computed by dividing the ammonia production rate, provided in Streppel's thesis, by the water flow rate out of the electrolyser, under each case scenario.

Cell	Temp	H2O	Voeding		Output	Water debiet (mol/min)		NH3 concentration		Bron
			Debiet (mol/min)	NH3 (mol/min)	Best Case	Worst Case	Best (ppm)	Worst (ppm)	
3A/10B	550	4,5%	1,0518E-03	6,7200E-07	1,0508E-03	1,0518E-03	639	638	Streppel p. 77
3A/10C	650	4,5%	1,0518E-03	4,5960E-07	1,0511E-03	1,0518E-03	437	437	Streppel p. 77
1A/10C	450	4,5%	1,0518E-03	2,8080E-07	1,0514E-03	1,0518E-03	267	267	Streppel p. 77
14A/10C	650	39,0%	1,4271E-02	8,7600E-07	1,4270E-02	1,4271E-02	61	61	Streppel p. 77
7A/10C	550	39,0%	1,4271E-02	7,3200E-07	1,4270E-02	1,4271E-02	51	51	Streppel p. 77
8A/10C	650	15,8%	4,1886E-03	8,9400E-07	4,1872E-03	4,1886E-03	213	213	Streppel p. 77
5A/10B	550	15,8%	4,1886E-03	8,3400E-07	4,1873E-03	4,1886E-03	199	199	Streppel p. 77

The highest concentration of ammonia in the aqueous effluent is 639 ppm, or 0,064 mol%. Needless to say, this is a very low concentration of ammonia in water, and hence difficult to concentrate/extract.

6.6 Ammonia Separations

The separations section is crucial for the economic feasibility of this system. While it is trivial to separate the product stream (ammonia) from the remaining non-condensable reactants such as hydrogen and nitrogen, by means of flash or thermodynamic phase separation, the separation of ammonia from water can be much more difficult to achieve (in an economically efficient manner). There are two general approaches to this problem: (1) thermodynamic separations (usually flash or low temperature and vacuum distillation); or (2) conversion to a non-volatile product and subsequent separation/concentration. These will be handled separately below.

6.6.1 Thermodynamic Separations

The most cost-efficient manner of separating ammonia from an aqueous mixture is flash vaporization. Liquid is brought into a flash tank in which a significant pressure drop is obtained to "flash" convert a portion of the liquid into the vapour phase, as depicted below. With careful thermal control (constant temperature), a precise and continuous concentration of ammonia, y_{NH3}, can be produced in the vapour phase. Flash vaporisation is, at its heart, simply a single-stage distillation unit operation. Because it only involves one stage, it is generally much cheaper—both in terms of capital and operating expenses—than an alternative distillation tower. The downside to having only one-stage is, of course, the fact that some ammonia will be inevitably lost in the raffinate or liquid stream, L. The amount of waste (inefficiency) of the flash vaporisation process is determined by two factors: the ammonia concentration at the inlet (x_F, the feed concentration) and the temperature of the flash vessel. The quantitative graphical analysis of the flash process is described below.
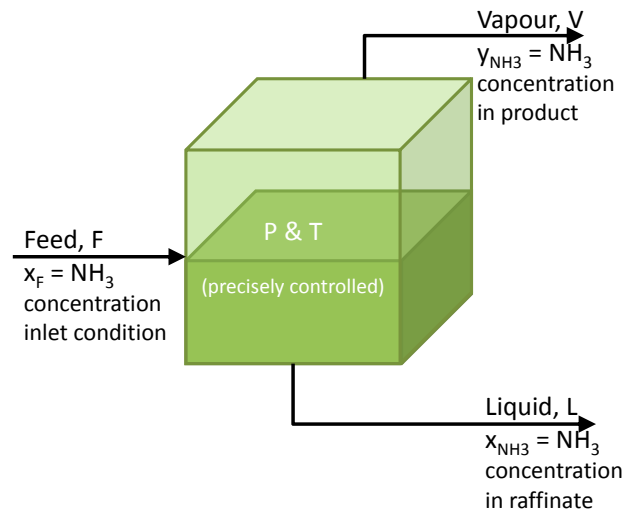
Figure 3. Diagram of the flash vaporization process where a liquid feed, F, is vaporized to produce a stream of ammonia-rich vapor and ammonia-poor liquid (relative to the feed).

Figure 4 presents the vapour-liquid equilibrium lines of an ammonia-water mixture at 1.2 atm, generated by ChemSep, a substituent of the CoCo simulator environment. In order to determine the equilibrium vapour concentration of ammonia, a flash temperature is selected and the feed point is identified on the graph at the corresponding coordinates (x_F, T_{flash}). As an example, a 50% mixture is flashed at 1.2 atm and 300 K, which defines the black circular feed point drawn roughly in the middle of the figure. Since the (ideal) flash tank operates isothermally, a horizontal line is drawn at the flash temperature to the vapour and liquid lines in order to determine the (ideal) equilibrium ammonia concentration in these outgoing streams, respectively. Thus, it can be seen that the feed concentration determines the range of allowable flash temperatures (for a 50% mixture, this is roughly between 260 and 350 K), as selecting a temperature above this range would result in no separation, with all of the product going to the vapour phase (a temperature below this range would retain all materials in the liquid phase).
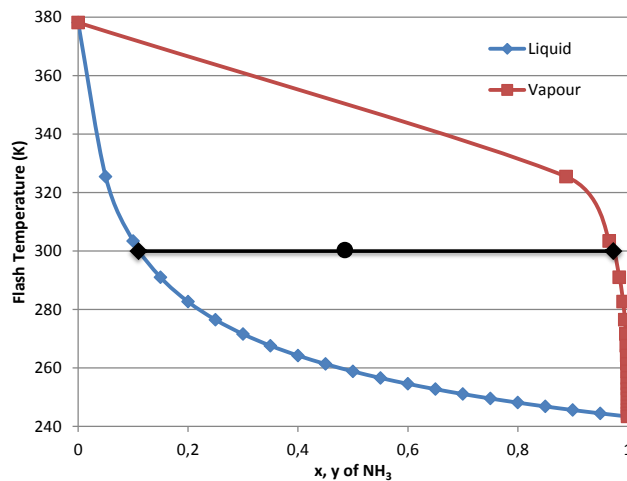
Figure 4. Txy diagram for an Ammonia-Water mixture at 1.2 atm, with an operating line drawn from a feed point at 50% ammonia and 300 K.

The separation efficiency, defined as the amount of ammonia in the vapour stream divided by the amount in the feed, may be derived using a continuous process mass balance as:

$$Efficiency = \left(\frac{y_{NH3}}{x_F}\right)\left(\frac{x_F - x_{NH3}}{y_{NH3} - x_{NH3}}\right)$$

Assuming a fixed feed composition, determined by the outlet of the electrolyser, the first component of this equation (y_{NH3}/x_F) can only be maximized by increasing the equilibrium vapour concentration of ammonia, which in turn is determined by the flash temperature. The second component of this equation may be seen as the ratio of the left-hand side of the horizontal feed line to the full length of this horizontal line, as shown below in the higher pressure (10 atm) equilibrium curve for an ammonia-water mixture in Figure 5. In order to maximize this ratio for a given feed concentration, it is clear that the flash temperature should be increased such that the feed point falls closer to the vapour line (than to the liquid line). This, in turn, reduces the maximum obtainable vapour fraction of ammonia (y_{NH3}), so these two factors must be optimized simultaneously in order to obtain the highest efficiency.
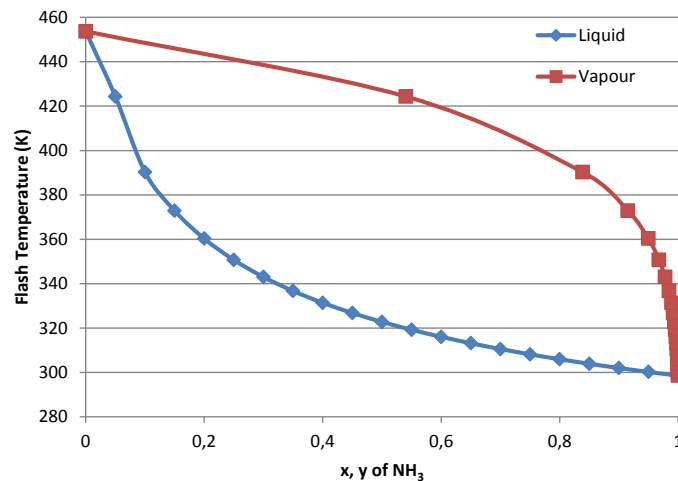
Figure 5. Txy diagram for Ammonia-Water mixture at 10 atm.

After a detailed literature analysis (see **Fout! Verwijzingsbron niet gevonden.**) it became evident that, even under the best conditions, the concentration of ammonia in the outlet stream of the electrolyser is less than 700 ppm (0.07 mol%, or 700 mg/L in a condensed stream). At this low concentration of ammonia, not only is the VLE space very narrow (giving a temperature range of only about 2 K, and limiting the accuracy of the foregoing ideal theoretical analysis) but the maximum obtainable vapour concentration of ammonia is roughly 2.5 mol% for a flash pressure of 1.2 atm. If the flash pressure is increased, the slope of the vapour line is brought closer to zero, slightly increasing the operating window and the maximum obtainable vapour concentration. However, the compression costs of increasing the effluent from 1,2 atm to 10 atm would be prohibitively expensive. Flash separation is therefore not advisable, unless the ammonia concentration can be increased (or water concentration significantly decreased) in the effluent, by means of improved catalytic efficiency.

The question remains: What are the obtainable yields as the ammonia concentration is increased in the water stream being fed to the flash tank? As described above, the flash pressure and feed concentration determine together the achievable temperature window in which separation can be achieved by single-stage flash. Furthermore, it is a trivial exercise to derive the yield (percentage of fed ammonia retained in the vapour stream) and the concentration of ammonia (mole fraction NH3 in the vapour stream) for a given temperature. These conditions were modelled using ChemSep software using a Wilson thermodynamic package (G. Wilson's modification of Raoult's Law) for an ammonia-water mixture based on ideal volumes in solution. The flash pressure was held constant at 1,001 atm and the obtainable temperature range was determined manually (by trial-and-error) to within ±0,1 K. A parametric study was then performed within ChemSep to study the effect of varying the temperature within the separations-achievable range, consisting of no less than

30 data points. The resulting yield and vapour phase mole fraction of ammonia are plotted in the graphs below:
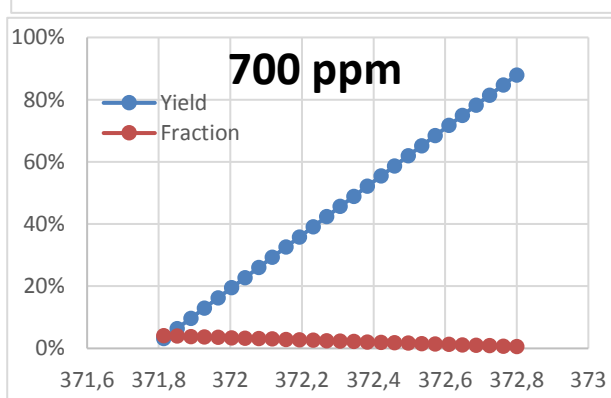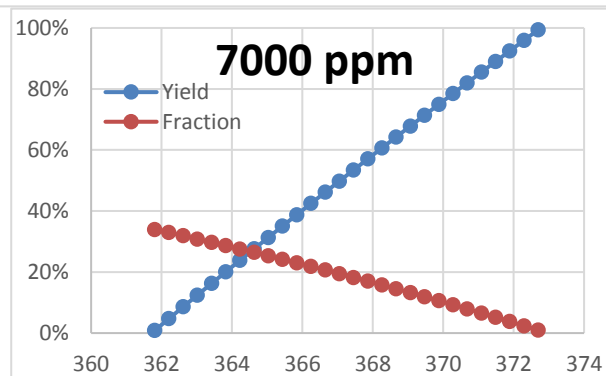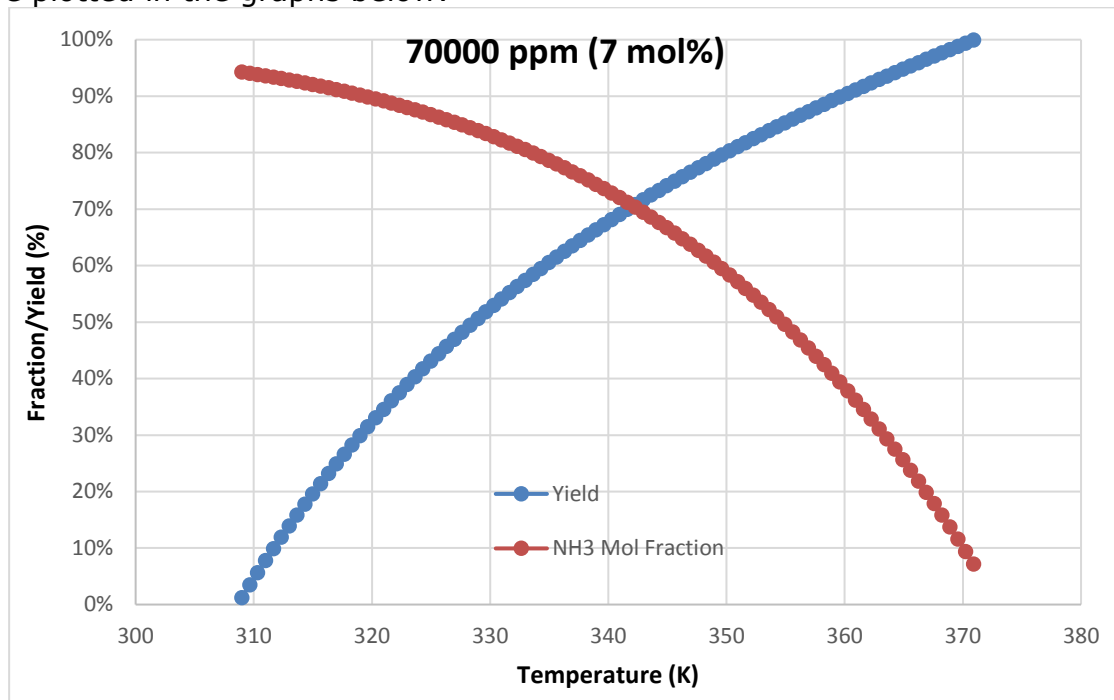
From these graphs it is evident that using a flash tank on a stream of 700 ppm NH3 in H2O will never result in a vapour phase concentration higher than a few

percent—and if a concentration greater than 1%, is desired the yield will be less than 75%. As the feed concentration increases by orders of magnitude, not only does the maximum achievable vapour phase concentration increase, but the separations-achievable temperature range increases dramatically—for 700 ppm the range is between 371,8 and 372,8 K, whereas for 70000 ppm this range is between 305 and 370,9 K. This is a temperature window of 1 degree Kelvin versus that of nearly 66 degrees K—clearly the 70000 ppm will produce more reliable and consistent streams.

Another way to quantify this effect is to determine what the vapour phase concentration of ammonia in water will be for a given target yield. If we aim for at least around an 80% yield, the 700 ppm feed emerges in a fraction of 0,86 mol% (with 81% yield); the 7000 ppm feed produces a vapour-phase fraction of 7,9 mol% (with 82% yield), and the 70000 ppm feed produces a 51% ammonia vapour stream (with a yield of 85%).

6.6.2 Reactive Separations

The most common form of fertilizer is ammonium nitrate, NH_4NO_3, which is produced by reaction with nitric acid. Ammonium nitrate is a solid, highly soluble in water, with a melting point of 443 K and a (theoretical) boiling point above its decomposition temperature (approx. 480 K). While the capital expenses of a reaction system may be held in check, the operating expenses are largely determined by the cost of nitric acid (materials) and subsequent concentration by evaporation of water (energy).

Considering the fact that this technology is intended to be implemented in a distributed manner, the production rate of ammonia (and therefore ammonium nitrate) is relatively low. This combined with the low concentration of ammonia makes it conceivable to implement a passive-evaporation system in which large shallow pools are constructed which allow for the evaporation of water through a check-valve (a low pressure-drop, one-way valve) through solar thermal energy, thereby minimizing the operating costs of separations. In such a case, the operating costs would be almost completely determined by the cost of nitric acid.

The commercial indicative costs of nitric acid, and ammonium nitrate are given in the table below.(source: http://www.icis.com/chemicals/channel-info-chemicals-a-z/).

Component	Indicative cost $/kg
Nitric acid (100% basis)	0.225
Ammonium nitrate 33.5 %	0.175

Converting ammonia into ammonia nitrate will result in added value (ammonium nitrate 100% basis appox 0.52 $/kg), but will costs about 0.83 $ per kg ammonia converted, as can be seen in the table below.

	NH₃ +	HNO₃ →	NH₄NO₃
Molar mass (g/mol)	17	63	80
Mass (mol)	58.8	58.8	58.8
Weight (kg)	1	3.7	4.7
Price ($)		0.83	2.46

The concept of using solar energy in order to evaporate the excess of water concentrate ammonium nitrate making it applicable for use as a fertilizer is calculated. In this calculation the following assumptions have been made.
Final concentration of ammonium nitrate 33.5 %
Solar energy usable is approx. 5 kWh per day per m^2.
The system needs to produce (on average) 0.27 kg ammonium nitrate per dag..
This represents the own production of 100 kg ammonium nitrate per year. For a farmer having 10 hectares of land to be fertilized the total demand of fertilizer is for corn about 500 kg (see table below) . This means that the 100 kg of ammonium nitrate fulfills 20% of the demand.

	Ammonium nitrate use kg per hectare per year
Potatoe	150-250
Corn	50

The required area is calculated for different ammoniam nitrate concentrations.

Concentration (ppm)	Concentration (%)	Evaporated water per day (kg)	Area required (m2)
700	0.07	390	50
7000	0.7	38	4.9
70000	7	3.1	0.40

A evaporating system having about 1 -2 m3 is assumed to be feasible. The corresponding concentration of ammonium nitrate (ammonium) is calculated to be 32000 ppm (3.2%) respectively 17000 ppm (1.7%).

6.7 Conclusions

This analysis has shown that the current ammonia production of TU-Delft of about 700 ppm are a factor of 100 to low for development of an economic feasible ammonia production and separation process. This economical analysis has not incorporated depreciation of investments costs yet. A conservative estimate there is that the ammonia production rate must be at least a factor of 1000 higher then current production rates. The failure of TU-Delft to increase

the ammonia production rate with a factor of 10 in a pressurized set-up because of technical difficulties (leakages) is with that respect disappointing. The overall conclusion. The processes are possible but there re major technological issues to be solved before a commercial setup is possible.

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