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DEN438/DENM035
Renewable Energy Sources

Designing an ammonia synthesis plant to supply a hydrogen carrier for fuel cells.

Contents

Introduction

The aim of this design is to develop a process for the production of high purity liquid ammonia while reducing the carbon footprint. The production of ammonia will be carried out via the Haber Bosch cycle (Humphreys 2021). The Haber Bosch process is a cycle where liquid ammonia is synthesised from nitrogen and hydrogen gas. The atom ratio per synthesis is 3:1 hydrogen to nitrogen, to make the ammonia molecule NH3. The gasses are mixed together and compressed to create a pressurised mixture. The pressurised mixture is then heated to high temperatures and passed through an iron-based catalyst, which is a crucial component as it reduces the energy requirement for the atoms to fuse together (Humphreys 2021). The reason being for the catalyst is due to the triple covalent bond that nitrogen gas has between its atoms, making it very strong and requiring a lot of energy to overcome. After passing through the system, hot gaseous ammonia is produced which is then passed through a condenser to cool the ammonia down to a liquid state.

This proposed design will be a Haber Bosch cycle that has a higher yield of liquid ammonia while reducing the heat and energy load required to synthesise the molecule. The excess unreacted gas will be designed to allow the unreacted and hot gaseous molecules to recycle into the system while minimising the amount of purge gas to increase the efficiency of the overall system, and the purge gas can be used for power generation applications since its discharged at a high temperature. The key aims considered is reducing the carbon footprint of the cycle, since global warming is a big issue in today's engineering world, and producing ammonia that can be utilised for applications such as fuel cells since the molecule has a high percentage of hydrogen (Lan 2014). The ammonia molecule can be cracked to release the hydrogen atoms which is used in the fuel cell to generate electricity.

Modelling

The Haber Bosch process was developed in the early 20th century (Erisman 2008), where it was a pivotal point in the advancement of synthesising ammonia. This allowed for the large-scale production of ammonia using nitrogen and hydrogen gas under high temperature and pressures (Valera-Medina 2018). The aim of this design is to replicate the Haber Bosch cycle while optimising the conditions to produce higher yield of liquid ammonia while maintaining a good purity, minimising the waste produced from the system. By minimising the waste by-product produced, the environmental impact can be reduced alongside it as well.

The system is comprised of many different components, which are; mixers, compressors, heater, synthesis reactor, cooler, two phase separator, and a stream splitter.

For the basis of design, it is assumed that there is ideal gas behaviour since its operating with atmospheric gasses, and constant reaction rates. These assumptions help simplify the model to allow a clearer understanding of the entire process. The schematic of the process is shown below.

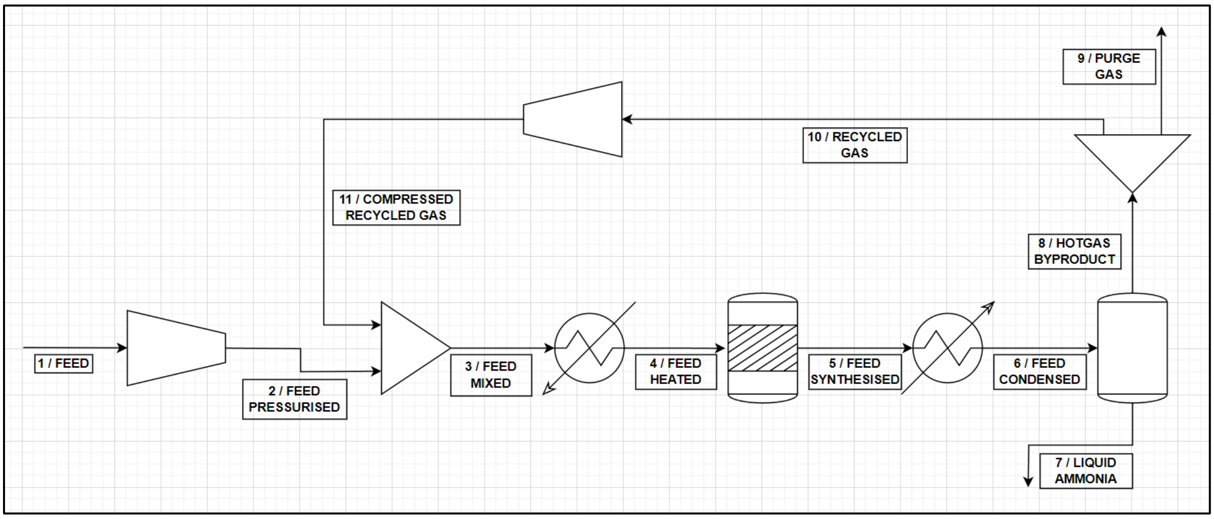

Figure 1, Proposed schematic of ammonia plant

From what is shown on figure 1, the system begins with a compressor in which the initial feed stream passes through, the compressor is set to an outlet pressure of 280 bar which pressurises the feed stream from atmospheric to a high pressure. This pressurised stream labelled '**2**' is then passed through a mixer that gets combined with the pressurised recycle stream that is formed later on. The mixed stream is then passed through a heater in which the temperature of the mixture is raised to temperatures above 400 °C, in this system the heater is set to 500 °C. This pressurised and heated stream labelled '**4**' is ready to be synthesised into ammonia, so it is now passed through the Haber Bosch reactor where there is an iron-based catalyst present to accelerate the rate in which the nitrogen and hydrogen react with each other to form the ammonia, as it lowers the activation energy needed to induce the reaction. The Haber Bosch reactor has been specified to have a conversion rate of 70% of nitrogen into ammonia, allowing some nitrogen to remain to be recycled. The synthesised stream is then transported through a cooler operating at 35 °C to condense the ammonia into a liquid state, allowing it to be separated from the gasses which is what occurs in the two-phase separator after the cooler. From the two-phase separator, the main product produced is the liquid ammonia maintained under high pressure to maintain its liquid state, as under atmospheric conditions the ammonia is in gas state. The liquid ammonia has a purity of 95.5%, containing trace percentage of remaining gasses such as nitrogen or hydrogen. However, the gas by-product is split into 2 streams where a split fraction of 0.1 is dedicated as purge gas. The reasoning behind having purge gas is to remove the build-up of unwanted inert gasses such as argon and methane, since these molecules don't form ammonia and will begin to build up within the reactor, and thus allowing more nitrogen and hydrogen to be present within the reactor which shifts the reaction equilibrium towards producing more ammonia. By doing this, the high yield percentage can be maintained. The remaining 0.9 split fraction of the gasses is re-pressurised back to 280 bar since passing through many components will create a loss in pressure since they have pressure drops. This re-pressurised gas stream is mixed back into the feed stream as stated earlier to maintain the efficiency of the cycle, minimising the amount of waste product produced from the system.

Now that the general schematic of the plant has been proposed, it is now time to begin modelling this plant into a simulation software. The software utilised is Aspen Plus V11, which is a highly operated and used tool in the chemical engineering field (Haydary 2019, Al-Malah 2022). The first step before accessing the simulation phase of the process is to list the gasses involved in the process and to specify the property method the reaction will carry out. The gasses components involved are nitrogen (N2), hydrogen (H2), ammonia (NH3), argon (Ar), carbon monoxide (CO), and methane (CH4). These gasses are then configured automatically via the aspen software once the property method has been specified, which is Peng-Robinson. The reasoning behind using Peng-Robinson over the other option is due to its ability to predict the properties of both gasses and liquids under varying temperatures and pressures highly accurately. This is effective for ammonia since it can present non-ideal behaviours under high pressures and temperatures which is what its under during the synthesis. The equation can account for the interactions between molecules and the sizes of them, proving a highly accurate model. The figure below displays the configuration of the gasses.

Component ID	Type	Component name	Alias
N2	Conventional	NITROGEN	N2
H2	Conventional	HYDROGEN	H2
NH3	Conventional	AMMONIA	H3N
AR	Conventional	ARGON	AR
CO	Conventional	CARBON-MONOXIDE	CO
CH4	Conventional	METHANE	CH4

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Figure 2, Component list for the Aspen Plus V11 software

And this figure presents the selection of the Peng-Robinson method.

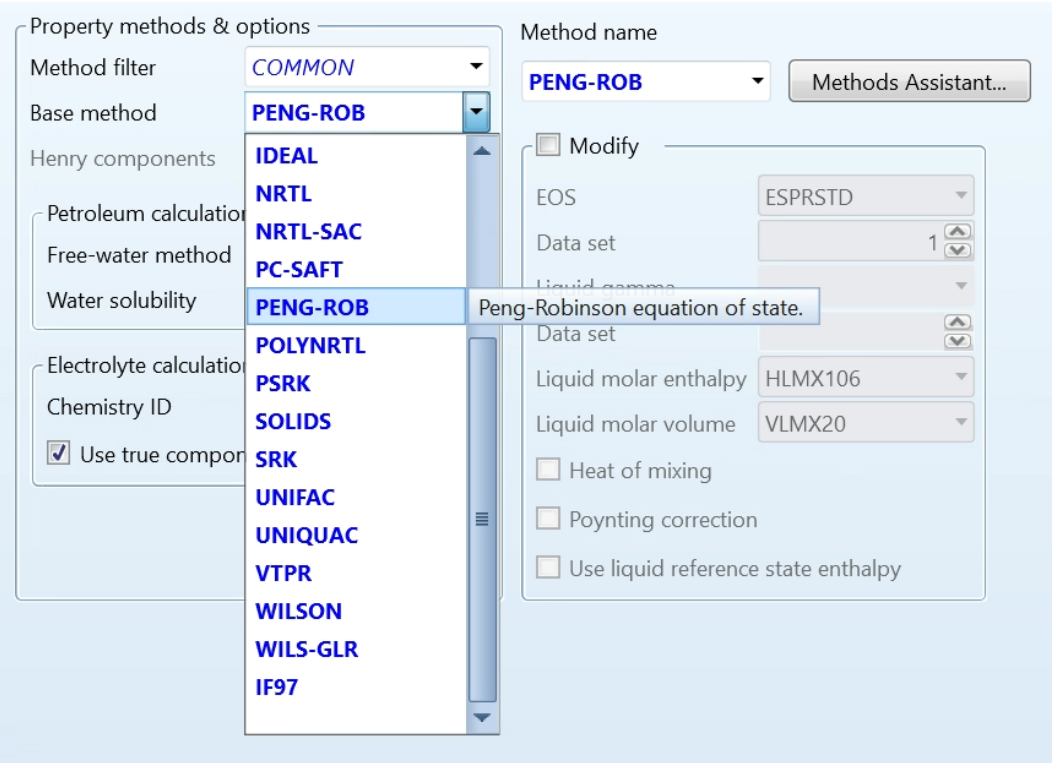

Figure 3, Method selection for reaction model in the Aspen Plus V11

Once all the property settings and gas components have been initialised, it is then ready to be simulated into the design tab. The design tab is where the main simulation occurs as it incorporates the units involved with the synthesis of ammonia as seen in the figure 1 schematic. The drawn simulation schematic is presented below.

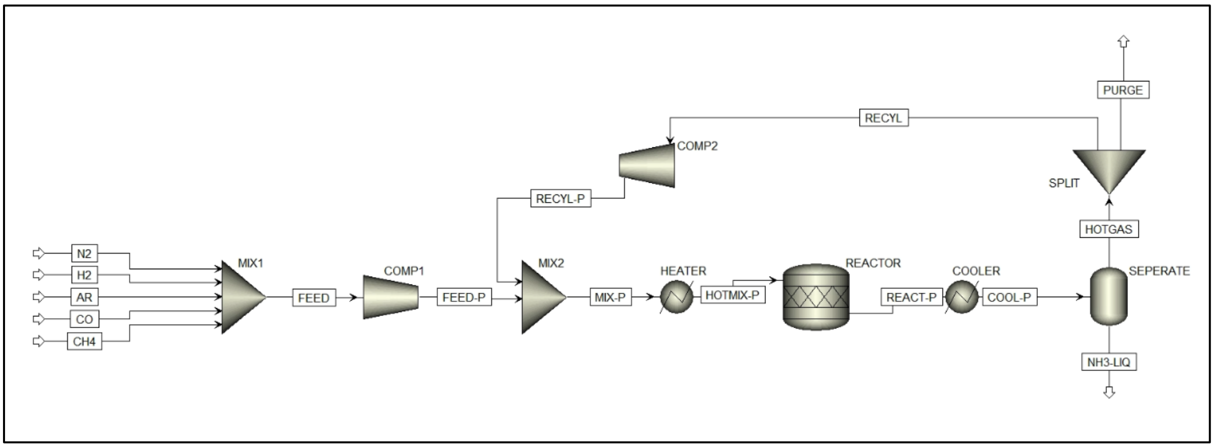

Figure 4, Simulation schematic of the ammonia synthesis plant in Aspen Plus V11

As seen in figure 4, the blueprint of the plant is almost identical to the schematic shown in figure 1, however some minor tweaks have been made to allow the simulation to work (Haydary 2019). It can be seen that the individual gasses are joined together through a preliminary mixer to incorporate all the gasses into one stream. Then as the schematic follows, the feed stream is passed through a compressor to pressurise the feed and so on. Acronyms have been given to each stream stage and unit to simplify the content displayed on the simulation.

The stoichiometry for the synthesis within the reactor is,

$$N_{2(g)} \; + \; 3H_{2(g)} \; \rightarrow \; 2NH_{3(g)}\,, \Delta H^{o} = -92\,\frac{kJ}{mol} \quad \textbf{[1]}$$

The enthalpy change from the reaction is -92 kJ/mol (Atkins 2010), meaning that the synthesis of the ammonia molecules is an exothermic reaction, releasing heat out by increasing the product stream temperature. The reasoning behind the cooler after the synthesis reactor is because it allows the ammonia to condense into a liquid state to allow it to be separated from the remaining gaseous mixture, which the two-phase separator shows. At pressures of 280 bar, the condensation transition is shifted higher to allow a less energy extensive temperature because the standard boiling point of ammonia is around -33.1 ^{o}C in atmospheric conditions. However, increasing the pressure will shift that requirement to allow the condensation of ammonia at 35 ^{o}C (Tanabe 2013), which has been specified for the cooler. This allows for easier storage and transport of the liquid ammonia.

The material chosen for the construction of the plant is grade 316 stainless steel, since it can withstand high pressures and is one the best grades in terms of temperature tolerance, as it can cope with very high temperatures since its melting point is 1400 ^{o}C. The main properties of interest on the material are listed in the table below (Elignfasteners 2023).

Table 1, Property table of 316 Stainless Steel

Grade 316 Stainless Steel	
Melting Point	1400 ^{o}C
Density	8000 kg/m^3
Youngs Modulus	193 GPa

Thermal Conductivity	16.3 W/mK
Thermal Expansion	15.9 /K

Results and Discussion

From running the simulation, the following information is presented.

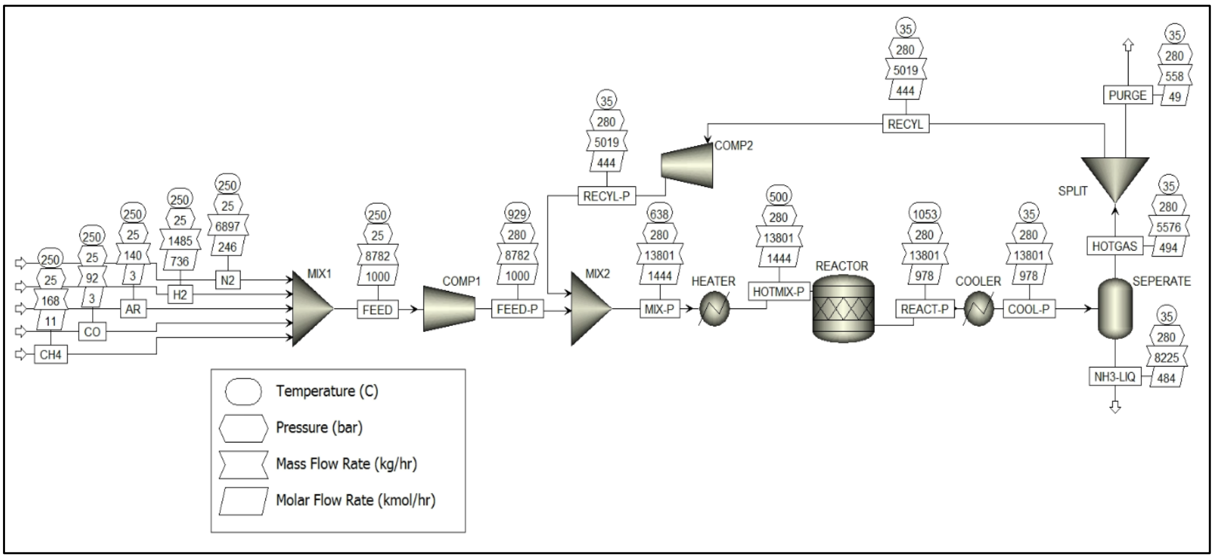

Figure 5, Running simulation of design displaying all stream data

From figure 5, the stream data can be observed at each stage of the process. The inflow of gasses shows the composition of what the feed consists of, where the nitrogen has an inflow of 246 kmol/hr, hydrogen being 736 kmol/hr, argon being 3 kmol/hr, carbon monoxide being 3 kmol/hr, and methane being 11 kmol/hr. All these streams combined together produce the inflow of 1000 kmol/hr as shown in the feed stream that comes out of the mixer. The software may not show decimals which may explain the marginal error in the addition of the streams into one. The feed stream is then fed into the system already pre-heated to 250 ^{o}C and pressurised to 25 bar. This feed stream that passed through the compressor then comes out at a pressure of 280 bar as displayed on the FFED-P stream. FEED-P is then mixed with the pressurised recycle stream at 280 bar to provide the total inflow through the reactor. MIX-P stream is then set to 500 ^{o}C via the heater to correct the stream temperature to allow the desired synthesis of the ammonia as it passed through the reactor. The reactor contains the catalyst in which allows the ammonia to be synthesised under its current condition due to it reducing the activation energy to induce the reaction, thus boosting the reaction rate. It's been set to have 70% conversion of nitrogen in the inflow into ammonia, to allow some ammonia to be recycled and maintain a good purity. Post synthesis, the REACT-P stream is formed and passed through a cooler to lower the streams temperature to a point where the ammonia can condense from its gaseous state and allow it to be separated from the other remaining gas molecules. The temperature chosen is 35 ^{o}C, as stated earlier. Then from the SEPARATE unit, the liquid ammonia is separated from the gasses each having their respective label, liquid ammonia being NH3-LIQ and gasses being HOTGAS. The NH3-LIQ that leaves the system has an outflow of 484 kmol/hr, or 8225 kg/hr in terms of mass flow. It is kept at its conditions of 35 ^{o}C and 280 bar to maintain its liquid state, as under atmospheric pressure the liquid will evaporate. The HOTGAS by-product has a mole flow rate of 494 kmol/hr, where it is passed through a splitter to allow some gas to be purged and not overwhelm the system. 558 kg/hr of gas is purged while the remaining 5019 is re-pressurised back to 280 bar and fed back into the system to reduce waste and maintain efficiency. The legend placed below the simulation indicates which numbers are related to which unit.

The figure below provides a more informative description of mains streams to be considered, displaying their composition and exact mole/mass flow.

Material | Heat | Load | Work | Vol.% Curves | Wt. % Curves | Petroleum | Polymers | Solids — Sum: -2.06085

	Units	FEED	FEED-P	MIX-P	HOTMIX-P	REACT-P	HOTGAS	COOL-P	NH3-LIQ
Molar Density	mol/cc	0.000570123	0.00268032	0.00347828	0.0040561	0.00241759	0.0100192	0.0152348	0.0324531
Mass Density	gm/cc	0.005007	0.0235394	0.0332335	0.0387543	0.03412	0.113138	0.215012	0.551414
Enthalpy Flow	cal/sec	362338	1.77826e+06	1.35465e+06	930483	930483	-470848	-2.52477e+06	-2.05392e+06
Average MW		8.78232	8.78232	9.55457	9.55457	14.1132	11.2921	14.1132	16.9911
+ Mole Flows	**kmol/hr**	**1000**	**1000**	**1444.44**	**1444.44**	**977.878**	**493.81**	**977.878**	**484.068**
+ Mole Fractions									
+ Mass Flows	**kg/hr**	**8782.32**	**8782.32**	**13801**	**13801**	**13801**	**5576.15**	**13801**	**8224.84**
− Mass Fractions									
N2		0.785319	0.785319	0.676451	0.676451	0.202935	0.48595	0.202935	0.0110615
H2		0.169055	0.169055	0.145021	0.145021	0.042797	0.102965	0.042797	0.00200506
NH3		0	0	0.058326	0.058326	0.634066	0.160384	0.634066	0.955205
AR		0.0159204	0.0159204	0.0318989	0.0318989	0.0318989	0.0598583	0.0318989	0.0129435
CO		0.0105251	0.0105251	0.0432666	0.0432666	0.0432666	0.100562	0.0432666	0.0044221
CH4		0.0191805	0.0191805	0.0450366	0.0450366	0.0450366	0.0902808	0.0450366	0.0143627
Volume Flow	l/min	29233.5	6218.17	6921.23	5935.25	6741.4	821.441	1069.78	248.598
+ Vapor Phase									
+ Liquid Phase									
<add properties>									

Figure 6, Precise data and composition of streams during process

As seen, the exact value of each stream is displayed to the decimal point, and the composition of the stream is also defined. The main component of interest is the ammonia, which can be seen to be 0 in the initial feed since there is no ammonia present in the inflow of raw gasses. However, when reaching the MIX-P stream, there seems to be a presence of ammonia. This may be due to incomplete condensation of all the ammonia molecules during the separation stage. Nonetheless, the most important information to be obtained here is the mass fraction of the ammonia in the NH3-LIQ, which indicates it purity within the liquid. This tab has been highlighted to make it clearer to the reader, which is on the furthermost right side. The mass fraction of NH3 in this stream comes up to be 0.955205, which translates to 95.5%. As stated earlier in the modelling stage this is a good purity to obtain considering the conditions utilised for the process.

Since the resultant liquid ammonia produced comes to around 8225 kg/hr, this can now be used to assess how much energy can be produced when incorporated into fuel cells using ammonia has a hydrogen carrier. It is assumed that an ammonia-based fuel cell has a system efficiency of around 60%, and its energy content being 18.8 MJ/kg. these pieces of data are found from reference which is cited in the references section.

The formula to deduce the energy potential is,

$$Energy\ Potential = mass\ of\ ammonia\ \times energy\ content\ \times efficiency \quad \textbf{[2]}$$

And the calculation is as follows,

$$8225\ (kg) \times 18.8\ \left(\frac{MJ}{kg}\right) \times 0.6\ (-) = \ 92778\ (MJ)$$

The resultant value of the calculation comes to 92778 MJ of potential energy per production of ammonia per hour.

The motivation behind using the ammonia for fuel cells comes from the fact that the usage of fuel cells in electronic applications is becoming more and more popular (Jiao 2019, Stambouli 2002). What fuel cells are an energy conversion device that transforms the chemical energy from hydrogen carriers directly into electricity via electrochemical reactions (Carrette 2000). The distinction of this method from standard combustion-based devices are that the fuel cells operate more efficiently and quieter, where a combustion engine would have an efficiency of around 30%, an ammonia-based fuel cell has around 60% as stated earlier when calculating the energy potential (Jeerh 2021, Afif 2016). So about double of the fuel is used for the application rather than being wasted via heat or sound loss. The operation of the fuel cell is similar to a battery but does not have its limited storage since you can continuously feed fuel into the fuel cell. The power source is becoming more popular is application such as car, since it provides a greener alternative than the standard combustion cars, producing less greenhouse gas emissions. For stationary power generation, they can provide reliable supply of energy either in the form of electricity or heat to the grid. This can be supplied to residential homes, or industrial estates to help power the building (Lan 2014). Fuel cells are also being explored in remote applications and military purposes, providing a solution to their current energy issues. Reasoning behind this is due to fuel cells being compact, adjustable, and lightweight sources of energy (Lucia 2014).

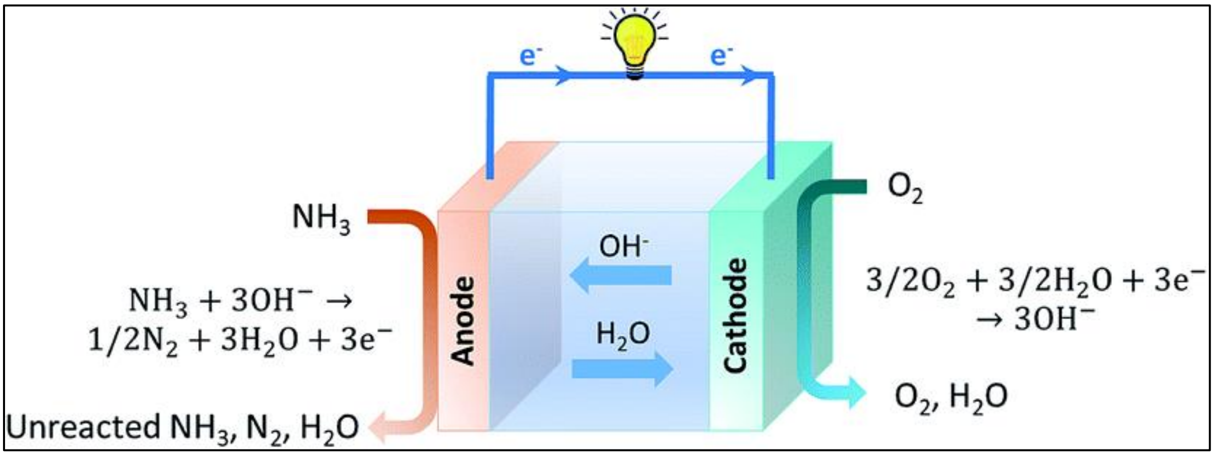

Figure 7, Diagram of ammonia fuel cell and function

The current price of liquid ammonia based on literature sources comes to around \$0.45 per kg of liquid ammonia (BusinessAnalytiq 2023, Wijayanta 2019). Since the designed plant has an outflow of 8225 kg of liquid ammonia per hour, it can be expected that per hour the ammonia can potentially be sold for \$3701.25, which would give an income of \$88830 per day if 24-hour production was to be carried out. The general costing of the plant can be determined using the Aspen Plus V11 software.

Table 2, CAPEX and OPEX of designed ammonia synthesis plant

Unit	Cost / $
CAPEX	
Instruments and Installation	3,020,590
Total	***3,020,590***
OPEX	
Operating cost	1,709,410 / year
Electricity	36,178.80 / year
Cooling water	349,348.80 / year
Total	***2,095,145 / year***

Conclusion

To summarise, this purpose of this design was to provide a suitable hydrogen carrier for fuel cell powering, where the chosen molecule was ammonia. A plant was then developed that would carry out ammonia synthesis via the Haber Bosch cycle producing enough liquid ammonia to supply to consumers. The initial schematic was first designed on a drawing software to obtain the general layout of the plant, where it was then transferred to the Aspen Plus V11 software for exact construction schematic. The software presented that from a 1000 kmol/hr inflow of gaseous mixture, consisting mainly of nitrogen and hydrogen, passing through the system at specified temperature and pressure to obtain a desired amount of around 484 kmol/hr, having a feed to desired product conversion rate of 48.4%. The discussion of how the ammonia is distributed and the costing of liquid ammonia per kilogram is also touched upon, where it was estimated that an income of $88830 would be made depending on whether the system was running for 24 hours a day. A description of what fuel cells are and their function, alongside their potential applications and benefits compared to typical methods of energy production. The future of fuel cells was also touched upon, about the idea of being incorporated into cars, and its prospects for military/remote applications.

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