

An Investigation into the Design and Sustainability of the Ammonia Production Plant

Jean Amor-Dei-Jabo-Cyusa, Loris Baggio, Mathilde Bricteux, Étienne Chèvremont, Esra Ilhan, Nizar Imoula, Charles Ledent, Juliette Limpach, François Radoux, Antoine Rouxhet, Sylvie Thonus, Jules Zankia

Abstract

A chemical plant design for the production of 600 000 tonnes of ammonia per year through the Haber-Bosch process route is presented. It involves the simulation of an ammonia production plant with high energy efficiency and lower production cost. An iron-based catalyst is recommended if cost and safety concerns are taken into account. Process flow diagram is simulated in Aspen Plus, a pinch analysis is carried out in order to minimize the overall utility needed in the process. The optimization of the heat exchanger network design is then completed. Economic tools of the rate of return and payback period are used to determine the viability of the plant. Life cycle assessment of the process and plant location factors are considered. From the design analysis, a plant production capacity of 616 000 metric tonnes per year is obtained. The power required by the plant for ammonia production is 39.9 MW of electricity and 145.7 MW of cold utilities. The primary reforming process for syngas production is only considered for the LCA part. The plant requires a total investment cost of \$ 182.22 million with 41% rate of return on investment, and by taking into account discounted cash flows, a payback period of less than six years. Gujarat (India) is found suitable for the installation of the ammonia plant. The geographical location of Gujarat contributes immensely to the success of the ammonia business venture. Furthermore, an in-depth literature review is carried out in order to evaluate the existing technologies and provide a possible comparison to this study. Some alternative processes to a Haber-Bosh process are given, the general focus is brought to environmental-friendly production ways.

Keywords

Ammonia synthesis, Cost, Design, Haber-Bosh, LCA, Modelling

Contents			
	Introduction	1	
1	Ammonia context	2	
1.1	Market and production	2	
1.2	Main uses	2	
1.3	Hazards	2	
1.4	Haber-Bosch process	2	
1.5	Main physical properties	3	
2	Process description	3	
2.1	Thermodynamic model	3	
2.2	Kinetics and catalysis	3	
2.3	Reactor	4	
2.4	Separation	4	
2.5	Absorption and distillation	5	
2.6	Model development	5	
2.7	Heat integration	6	
2.8	Global results	7	
2.9	Comparison with literature	8	
3	Cost		8
3.1	CAPEX		8
3.2	OPEX		9
3.3	Cash flow		10
3.4	Economic evaluation		11
4	Life cycle assessment		11
4.1	Collection of data		11
4.2	Presentation of the situation		12
4.3	Environmental impacts		12
4.4	LCA conclusion		12
5	Alternatives to fossil feedstock		13
5.1	Biomass		13
5.2	Water electrolysis		14
5.3	Electrochemistry		14
6	Conclusion		15
	References		15
	Appendix		19

Introduction

Ammonia is a gas composed of one nitrogen atom bonded to three hydrogen atoms with covalent bonds. In 1774, gaseous ammonia was first isolated by Joseph Priestley, an English chemist. Then, in 1898, the first way to produce it was discovered. Today, the ammonia process is one of the biggest commodity chemicals produced by the chemical industry and thus used all around the world. Therefore, multiple models for the Haber-Bosh process exist. This study of an ammonia plant that produce 600 000 tonnes of ammonia per year from natural gas is done in this paper to contribute to these. The particularity of this one is an absorption and distillation unit of ammonia in the purge gas.

In this context, a presentation of the ammonia characteristics is first established. The market of ammonia, its uses and hazards as well as the most used process to produce NH_3 are defined. Then, the description of the modelling is established. Each unit of the process and the main flowsheet of the process are presented. The goal of this modelling is not simply to produce ammonia but to produce it efficiently and realistically. Therefore, this design also includes heat integration which is directly followed by a cost analysis and a life cycle assessment study.

1. Ammonia context

1.1 Market and production

Ammonia is the fifth most produced chemical in the world. Each year around 175 millions tonnes of ammonia are produced and this value keeps slowly growing [1]. Indeed, 80% of the production is used as fertilizer [2][3] and it needs to keep up with the growth of the population. In Europe, 1.9 tonnes of CO_2 is released by tonne of NH_3 [4] produced so, its influence on global warming is significant.

The top producing countries are China, Russia, the United States, India and Indonesia with China having four to five times the production of the others [5]. In addition, it comes as no surprise that those countries are also the biggest ammonia consumers [1].

The main producing companies are Yara international, BASF group, Airgas and Chinese companies like Baoding North Special Gases to name some of them [6]. They all compete against each other. Thus even though ammonia is more and more crucial to increase food production, its price has remained stable in the last few years for a cost of \$ 240 - 300 /tonne of ammonia [4]. This value does not concern green ammonia which cost around 3 to 4 times more with today's electricity cost and technology [4].

1.2 Main uses

As mentioned earlier, ammonia main use is as a building block for fertilizer like urea. Because the production of food crops naturally depletes soil nutrient supplies, farmers must rely on fertilizers in order to maintain healthy crops. It also

helps to increase the level of essential nutrients in food crops since it is a major source of nitrogen [2][6]. Nevertheless, it is not its only utility. Indeed, ammonia is also used in industrial refrigeration applications because of its high energy efficiency and low cost. Other applications such as nylon, explosives, fabrics or pharmaceuticals employ ammonia as nitrogen source. On a smaller scale, ammonia is found in everyday life as household cleaning product once it is diluted in water.

Finally, ammonia helps to prevent the NO_x emission of diesel vehicle in the form of Adblue [7][8]. Actually, Adblue is an aqueous solution of 32.5 %-wt urea-water that is added between the motor and the selective catalytic reduction system. Urea reacts with the CO_2 and produces ammonia that will then reacts with the NO_x transforming them up to 85% into nitrogen and water.

1.3 Hazards

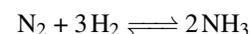
Ammonia utility is undeniable but it has also a wide range of toxicity concerning its vapor. It goes from irritation at 30 ppm to pulmonary edema at 1500 and finally death at 5000 ppm. It is because ammonia is corrosive and cause severe necrosis of mucous membrane [9]. Liquid ammonia on the other hand is very cold and therefore its main threat is severe burn due to frostbite [7][10].

Following this, ammonia needs to be stored under appropriate conditions to be kept at liquid state without leaks. The storage tank is often either refrigerated or kept at high pressure [9].

Lastly, ammonia in too big amount is toxic for the environment. Especially for the aquatic wildlife as it causes eutrophication but also for crops for which too much use of ammonia may have dramatic effects on soils and plants. For this reason, norms on ammonia emissions were put into place in Europe since 1990 [11].

1.4 Haber-Bosch process

Ammonia production at large scale mainly relies on Haber-Bosch process since the 20th century [2][4][12][13][14]. It is based on a single reaction where hydrogen reacts with nitrogen from air to give gaseous ammonia following this equation :



The reactor operates at high pressure, between 100-200 bar, and at high temperature in a range of 400-500°C [9]. High pressure promotes the reaction as the number of gas mole decreases. High temperature is needed to speed up the reaction but it is detrimental to the equilibrium conversion as it an exothermic reaction. Therefore, a compromise must be found and a conversion of 10-20% at the reactor outlet is usually achieved. Add to that, a recycling stream of nitrogen and hydrogen and a final conversion of around 97% are obtained. After that, the ammonia is condensed into liquid and separated from the other products.

The reaction needs a catalyst to accelerate the reaction rate. A lot of potential catalysts exist and have been tested but iron based catalysts (magnetite principally) are the most commonly used due to their low prices. Nonetheless, this type of catalyst can be poisoned by oxygenates, sulfur and CO/CO₂. This implies heavy purification on the feed provided to the process.

This feed contains the reagents, N₂ and H₂, for which the origin can differ between ammonia plants. For the nitrogen, it is directly taken from air but the hydrogen requires more efforts. The most common ways to obtain it is mostly from coal, widely used in China, or from natural gas. Natural gas is the most common feedstock in Europe and the United States [15] so, it is what is considered in the following article.

Natural gas is converted in hydrogen by steam reforming and coal by gasification. Those processes are not explained further as the following work focuses on the process starting with the syngas. For more information the works of Dr. M. Appl are recommended [9][16].

Other means of ammonia production exist and are discussed later in this article but those two are the main.

1.5 Main physical properties

In this section, some of the main ammonia properties are reminded in Table 1 :

Property	Value
Molar mass [g/mol]	17.0305
Boiling point at 1 atm [K]	239.81
Critical temperature [K]	405
Critical pressure [bar]	113
Enthalpy of vaporisation [kJ/mol]	23.5
Solubility in water at 24°C [mg/ml]	482

Table 1. Ammonia properties [2][17]

2. Process description

2.1 Thermodynamic model

One of the first thing that has to be thought about when designing a chemical process is what kind of thermodynamic equations are used to describe the behaviour of the different fluids present in the said process. C.Monia [18] indicates that the NRTL-HOC model is the best suited for representing ammonia mixes. The main issue is that this model cannot be used for pressure above 10-15 bar. This range is exceeded in the reactor and the separation units. For that reason NRTL-HOC is only used to model fluids in the absorption and distillation unit where the pressure is low. For the rest of the process the NRTL-RKS model is used as it is the closest to experimental data [19] for pressure above 15 bar as shown in Figure 1. It has to be precised that the comparison is done at about 10 bar because this is the only set of experimental data that could be found. At that pressure NRTL-HOC is thus still the best choice but NRTL-RKS is the second best model so this is the

reason why it is selected. The phase equilibrium in the second flash tank is represented with Henry's law in addition as the pressure is low enough compared with the first one in which only NRTL-RKS is used.

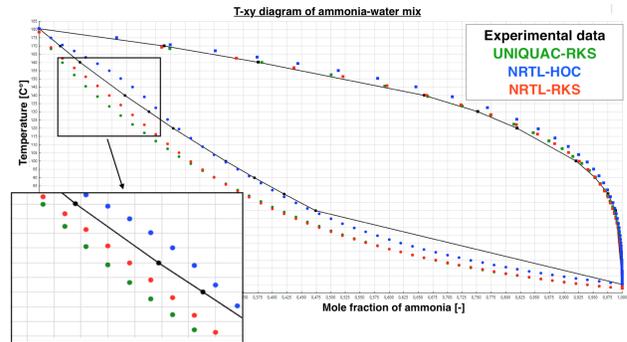
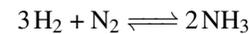


Figure 1. Comparison of binary diagrams Ammonia/Water at 1013 kPa

2.2 Kinetics and catalysis

The stoichiometric equation corresponding to ammonia production with a Haber-Bosch process is:



This reaction can be separated into its fundamental steps which are the adsorption and dissociative adsorption of reagents onto the catalyst followed by a surface reaction and the ammonia desorption. This enables to find the reaction rate equation:

$$-r_{\text{N}_2} = k_f \frac{P_{\text{N}_2} P_{\text{H}_2}^{\frac{3}{2}}}{P_{\text{NH}_3}} - k_r \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{\frac{3}{2}}} \quad (1)$$

That equation is verified by comparing it with diverse sources found in the literature [20][21][22][23] and appears to follow a Temkin-Pyzhev model. This equation is used further in the design of the reactor. In this expression the coefficients k_f and k_r are the rate coefficients for the forward and the reverse reaction, they are dependent on the temperature and can be calculated with Equations 2 and 3:

$$k_f = 5823 \times \exp\left(\frac{-17.307}{R \times T}\right) \quad (2)$$

$$k_r = 1.77 \times 10^{15} \times \exp\left(\frac{-40.765}{R \times T}\right) \quad (3)$$

in which R is expressed in cal/mol and T in K.

The catalyst used is an iron-based catalyst. Calculations are led to quantify the effect of heat and reagents diffusion in the catalyst on the reaction rate. These aspects are defined with the catalyst efficiency called η . As it is explained in Section 2.3 two reactors are used and thus two different values of η are computed. The results following the calculations prove that there is no significant thermal gradient in the catalyst.

It means that all the catalyst volume can be considered as isothermal. The second results are the coefficients η :

$$\eta_{react,1} = 0.81 \quad (4)$$

$$\eta_{react,2} = 0.73 \quad (5)$$

Those have to be used in front of the reaction rate as coefficients in order to have the apparent reaction rate in each reactor.

2.3 Reactor

The core of the process is the formation of ammonia within the reactor. First, the CRE algorithm [24] is used to model the reactor with MATLAB. This allows to determine which type of reactor is the most suitable for this process. This CRE algorithm leads to the potential choice of an adiabatic reactor. Another choice that could have been made is the reactor with heat exchange because the conversion is a bit higher than with the adiabatic one. However, a reactor with heat exchange is more expensive because it requires more equipment. The increase of conversion cannot justify its use compared to the cost increase. Therefore, the adiabatic reactor is selected. However, the conversion with a single adiabatic reactor is small. So, another implementation is made with two adiabatic reactors with a heat exchanger between the outlet of the first one and the inlet of the second one. It enables to decrease the temperature before entering in the second reactor as the reaction is exothermic. In this configuration, the conversion is increased and the decision of using two reactors instead of one is taken.

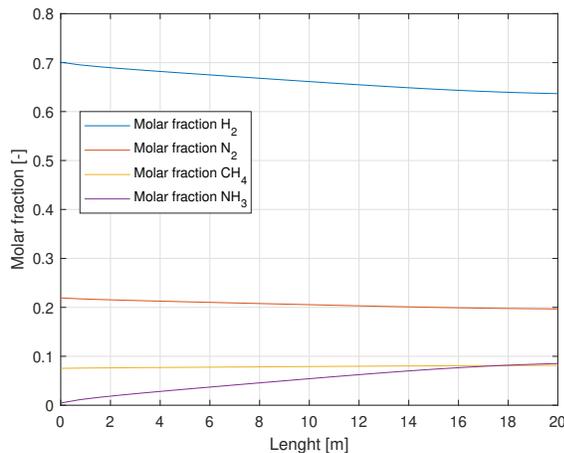


Figure 2. Molar fraction function of length - reactor 1

After the ideal modelling in MATLAB, an implementation in Aspen Plus is done. The reactor model used is a Packed-bed reactor. The catalyst bed characteristics are a void fraction of 0.44 and a catalyst density equalling 0.265 kg/m^3 . A verification between MATLAB and Aspen Plus models is carried out with an ideal model assumption to verify the correct implementation of the kinetics and catalysis. Then the thermodynamic model is updated according to Section 2.1 and

the catalyst efficiency for each reactor is taken into account in the kinetics as explained in Section 2.2. The pre-exponential factors for the forward and backward reactions are multiplied by these efficiencies.

This implementation allows to perform the different sensitivity analyses on the reactors. The key parameters are identified as the composition and flow rate of the feed stream, the pressure and the temperatures at the inlet of both reactors.

Finally, the different parameters have to be adapted in order to optimise the size of the reactors, as well as to determine the inlet temperature. In order to optimize the inlet and the inter-cooling temperatures, the optimization tool of Aspen Plus is used as well as design specifications. The goal being to get the best conversion as possible. The results of this optimization are that the optimal temperature at the entrance of the first reactor is 382.21°C and 401.73°C for the inter-cooling temperature.

	Reactor 1	Reactor 2
Length [m]	16	18
Diameter [m]	2.0297	2.8554
Ratio length/diameter [-]	7.88	6.3
Volume [m ³]	51.77	115.27

Table 2. Dimensions of reactors 1 and 2

After inspection of the reactor profiles (Figure 2), the reactor sizes were adjusted (Table 2). The final reactor sizes are then found to be equal to 51.77 and 115.27 m^3 respectively. The overall conversion obtained between the entrance and the exit of the reactor section is 22.8% .

2.4 Separation

A separation unit is required to achieve right product purity after producing ammonia in the reactors. As can be seen in the flowsheet (Figure 3), this is achieved with two flash tanks in series. In the second flash tank, Henry's law is considered in order to increase the precision of the results. Indeed, the low operating pressure of the second tank allows to use this law.

The objective of this flash tanks series is to maximize the amount of liquid product and to reach a mass purity of at least 99.9% . The outlet reactor pressure is kept to enter the first flash tank and the flux is cooled down as much as possible to maximize the liquid outlet stream (without going below an unattainable temperature). Since the other components (hydrogen, nitrogen and methane) are much more volatile than ammonia, they mostly leave the FLASH-1 as vapour. The separation takes place at -50°C and 99.3 bar . A recap of the different streams going through these flash tanks is presented in Tables 3 and 4.

The pressure of the liquid stream leaving the first flash tank is then decreased to reach two objectives. First, it increases the purity of ammonia in the liquid product. Second, it allows to reduce both CAPEX and OPEX because it prevents the use

	Inlet	Liquid outlet	Gaseous outlet
Total mass flow [kg/h]	390 426	89 037	301 389
Ammonia mass flow [kg/h]	80 267.7	76 916.7	3 351.0

Table 3. Mass flow rates of the first flash tank FLASH1

	Inlet	Liquid outlet	Gaseous outlet
Total mass flow [kg/h]	89 037	74 992.6	14 044.4
Ammonia mass flow [kg/h]	76 916.7	74 963.3	1 953.3

Table 4. Mass flow rates of the second flash tank FLASH2

of equipment to reach the required pressure at the entrance of the absorption and distillation unit. This second flash tank operates at -52.5°C and 1.6312 bar.

2.5 Absorption and distillation

A certain amount of ammonia is still present in the gaseous outlets of the flash tanks so, it is imperative to recover the ammonia that is still present in the said gaseous fluxes. In order to recover this ammonia, an absorption unit is designed as well as a distillation column to obtain a product with a high ammonia purity.

This absorption and distillation parts of the process are constituted of an absorption column and a distillation column with a recycling loop allowing the recovery of the water which is used to absorb ammonia. Indeed, water is almost pure after the distillation used to recover an ammonia product as pure as possible. The top product of the distillation column contain 97.57 wt-% of ammonia whereas the bottom product is composed of more than 99.99 wt-% of water. In order to obtain a global product with the purity required (99.9 wt-%), the top product of the distillation column is mixed with the product of the flash tanks. As the quantity obtained from the distillation is low compared to the one from the flash tanks, the influence on the high purity obtained in these later is low. From the absorption and distillation unit, a quantity of 2.2 tonnes/h is produced compared to 75 tonnes/h with the flash tanks. This leads to a global production of around 77 tonnes/h meaning a production of 616 kt of ammonia for an operating year of 8000 hours.

A crucial aspect used to design the absorption column is the potential emission of NO_x after a combustion of gaseous outlet. To deal with that, the emission of NO_x is limited at

less than 50 mg/m^3 in order to respect environmental norms [13].

The purpose of this unit is to avoid losses of ammonia. The distillation column enables to recover more than 99.9% of the ammonia entering. It is important to notice that the simulation made with Aspen Plus for the absorption and distillation are made with the assumption of equilibrium calculation. A recycle loop permits to recover 81% of the water used for the absorption. This allows to save more than 40 tonnes/h of fresh water. The recycle flux and the fresh water are mixed before entering at stage 1 in the absorption column. This column is made of 11 stages whereas the distillation column is made of 13 stages. Table 5 shows the operating conditions of the distillation column.

Condenser duty [kW]	Distillate rate [kg/h]	Reflux ratio [-]	Reflux rate [kg/h]
5 735.5	2 172	4.16	9 028.2
Reboiler duty [kW]	Bottom rate [kg/h]	Boilup ratio [-]	Boilup rate [kg/h]
15 100	67 171.14	0.37	24 929

Table 5. Operating conditions of distillation column DIST

2.6 Model development

Now that each sub-model have been described and that their best operating conditions have been determined, they can be assembled to lead to a single process gathering the reactor section, the series of flash tanks and the absorption and distillation loop. The flowsheet of this process can be found in Figure 3.

As can be seen in this flowsheet, a recycling loop is present such that a large fraction of the unreacted gases leaving the first flash tank returns to the beginning of the process where it is mixed with the fresh gas feed. The fraction of unreacted gases that is recycled is determined such that there is no accumulation of inert gas (methane in this case) in this recycling loop. This constraint leads to a recycling of 93% of the unreacted reagents, the other 7% being sent to the absorption and distillation unit. These 7% contains the fraction of the gaseous outlet of the first flash tank that is not recycled and the gaseous outlet of the second flash tank. This substantial recycle stream is in line with the desire of wasting as little as reagents as possible.

As previously stated the recycle stream is mixed with the make-up stream of reagents. This feed is composed of nitrogen, hydrogen and small amounts of methane all coming from syngas synthesis. Its composition is adapted such that once it is mixed with the recycle stream, nitrogen and hydrogen quantities are the closest as possible to stoichiometric quantities (1:3 respectively) at the entrance of the reactor section. On the other side the flow rate of this make-up stream is chosen

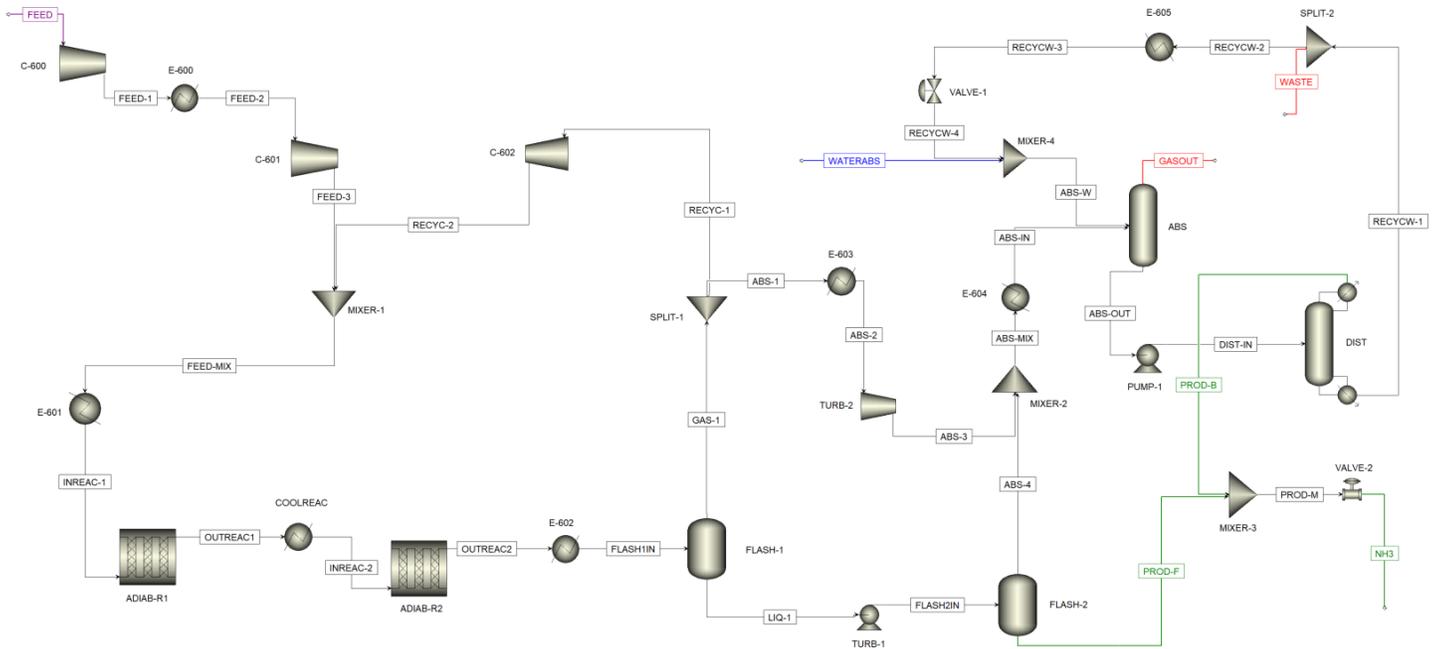


Figure 3. Process flowsheet

in such a manner that the required amount of ammonia i.e. 75 tonnes/h is leaving the series of flash tanks. This flow rate and compositions are presented in Table 6.

Compostion [%]	Feed	Recycle	Reactor inlet
N ₂	25.4	21.8	22.7
H ₂	70.6	69.6	70.0
CH ₄	4	8.0	7.0
NH ₃	0	0.6	4.3
Flow rate [kmol/h]	11 325.5	32 195.3	43 520.8

Table 6. Composition and flow rate of make-up, recycling and reactor inlet streams

As already stated high pressure is required in the reactor section while the absorption and distillation loop operates at low pressure as well as the second flash tank. It is possible to take advantage of this difference of pressure from an energy point of view. Instead of using valves to decrease the pressure, turbines can be arranged at proper places in the process in order to recover energy from stream expansion. With this in mind, two turbines are placed in the process: one between the two flash tanks being then a liquid turbine, and the other placed on the stream of unreacted gases that is sent to the absorption and distillation unit. This allows to generate a total of 2874.6 kW of electricity mostly coming from the gas turbine (TURB-2) as it develops a greater power than a liquid turbine.

2.7 Heat integration

The aim of designing such a process is to obtain a desired amount of a certain product with a desired purity while minimising the energy consumption of this process. This energy consumption gathers the electricity used for compression but also the heat that has to be supplied or removed from the process. In order to optimize the former one turbines are placed at different places in the process as just explained. Concerning the optimization of heat and cold utilities that have to be supplied, the concept of heat integration can be applied to the process. It consists in combining hot streams with cold streams. A hot stream is at high temperature and have to be cooled down such as the outlet of the reactor section for instance. Conversely, a cold stream is at low temperature and have to be heated up such as the inlet of the reactor section. This appropriate streams combination decreases the amount of hot and cold utilities that have to be supplied to the process.

The point is to determine how all these streams must be combined together such that a maximum amount of heat is recovered. The amount of energy that has still to be supplied after this combination is then known. For this purpose the so-called pinch analysis can be carried out. This analysis enables to determine the pinch temperature of the process which separates this latter in two zones: the heat sink above the pinch where only heat utilities can be supplied and the heat source below the pinch where only cold utilities can be supplied. This analysis can be graphically expressed by a characteristic curve called the Grand Composite Curve (GCC) as illustrated in Figure 5.

After carrying out this analysis it appears that the pinch temperature of this ammonia process is the highest temperature considered for this analysis. It leads to the conclusion

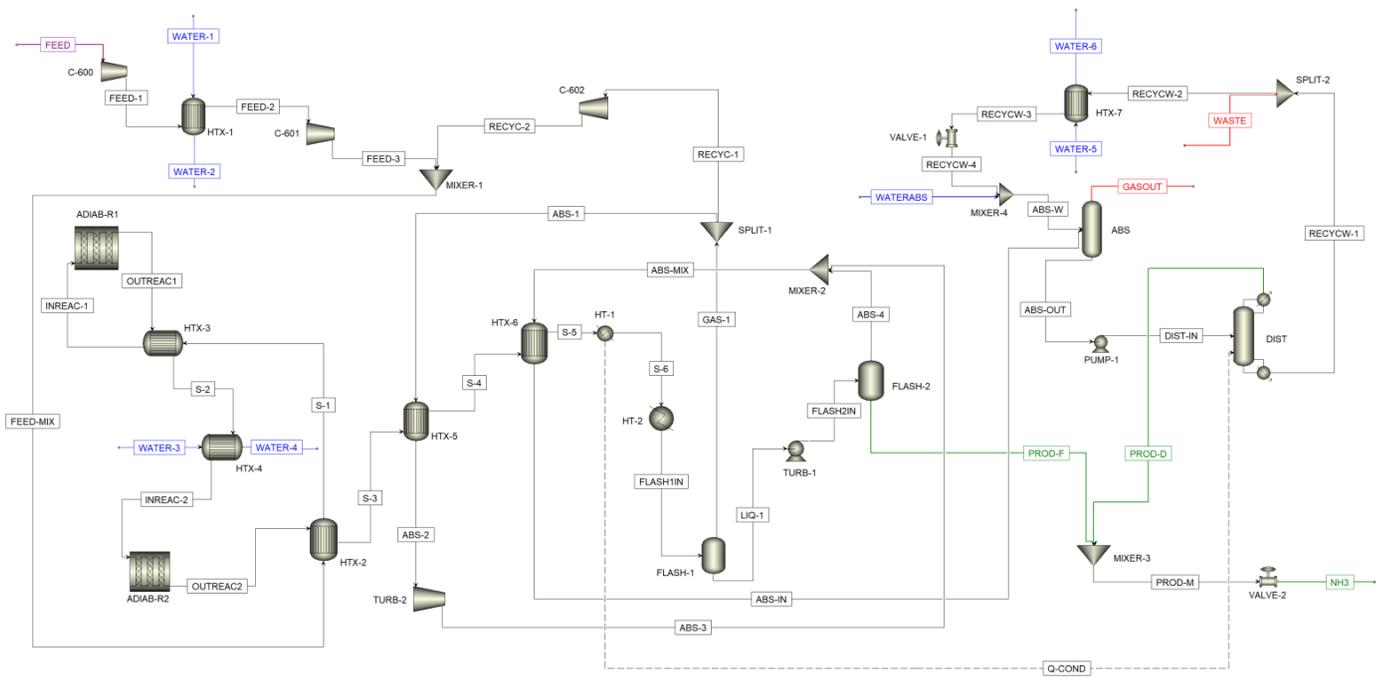


Figure 4. Heat integrated process flowsheet

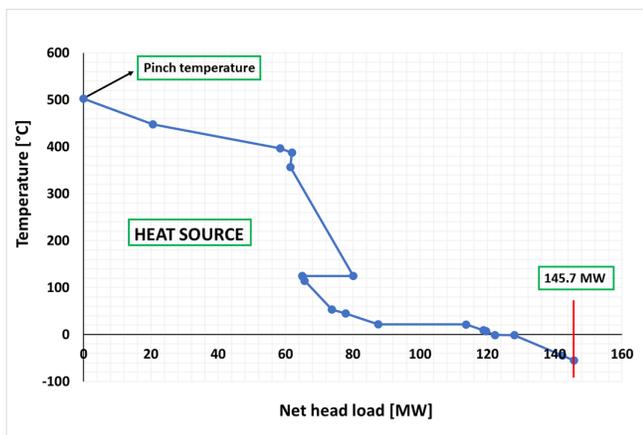


Figure 5. Grand composite curve

that this process does not present a heat sink and consequently does not require any external heat supply. Then, it means that the hot streams of the process are sufficient to heat up all the cold streams. However pinch analysis shows that there is still a need to provide 145.7 MW of cooling utilities to cool down hot streams after heat integration. After finding this minimum energy requirement, all the streams are combined through heat exchangers using the concept of heat exchangers network design. The aim of this design step is to achieve this minimum amount of energy to be provided to the process by combining the streams in a proper manner. The final heat integrated process flowsheet can be found in Figure 4 where all hot and cold streams combined through heat exchangers are visible. The different parameters concerning these heat exchangers can be found in Table 11 in Appendix. The areas

are determined according to the heat load of the considered exchanger with the design mode of Aspen Plus. This mode calculates the required area for a given temperature variation. Concerning the overall heat transfer coefficients U , they are determined for each exchanger depending on the nature of the streams involved in the exchange [25].

2.8 Global results

As presented above, using two reactors in series with an intercooling stage in between allows to reach a single-pass conversion of 22.8%. In order to get an idea of the performance of the whole process, it is convenient to calculate the process conversion. It is the conversion between the make-up stream that brings fresh reagents to the process and all streams leaving the process with unreacted reagents. In the same way as for single-pass conversion, this process conversion is calculated from nitrogen point of view and equal 78.6%. This value is discussed in the following section.

This model for the ammonia synthesis leads to the production of 77 tonnes/h. From this overall production 75 tonnes/h come from the series of flash tanks and correspond to the production goal of this process. Two additional tonnes are recovered each hour in the absorption and distillation loop. The purity of the final product is 99.9 wt-%.

Concerning the power required for this process, Figure 6 shows the evolution of the different forms of power used before and after the optimization. The optimization implies the appropriate placement of turbines and the heat integration of the process. The final process requires an electric power

of 39.9 MW and 145.7 MW of cold utilities. It is suitable to convert these powers in terms of GJ/tonne_{NH₃} for sake of comparison with literature values. It leads to a requirement of 1.9 GJ/tonne_{NH₃} of electricity and 6.8 GJ/tonne_{NH₃} of cold utilities. It has to be precised that in this case the electricity produced with the burning of the purge gases is not yet taken into account and is discussed below.

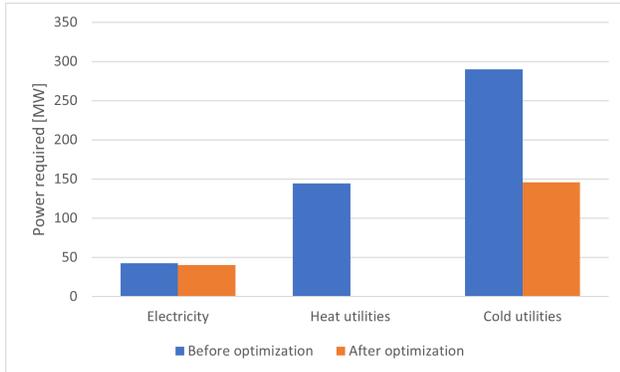


Figure 6. Evolution of electricity, heat and cold utilities power requirements before and after optimization

2.9 Comparison with literature

A typical Haber-Bosh process operates at a pressure of 100-150 bar and a temperature range of 350-550°C [15]. From a preliminary, simplified mass balance, optimal operating conditions of 58.5 bar and 420°C were found. This first estimation was out of range concerning the pressure because the thermodynamic was simplified. As a consequence, the ammonia fraction at the outlet of the reactor was 8.95%-mol, which is out of range as wemm. It should be 20-30%-mol in a typical ammonia plant [15].

In the full model described in the previous sections, operating conditions are much more realistic. Indeed, the pressure is 100 bar in the reactors and the temperatures are in range too. The inlet of the first reactor is at 382°C and the outlet of the second one at 453°C. It allows 20.55 %-mol out of the reactor unit. This difference in realism between a simplified mass balance and the full model allows to highlight the importance of a suitable thermodynamic model.

The maximum process conversion was previously announced to be around 97% for typical Haber-Bosch processes. However, the model presented in this paper only leads to a process conversion of 78.6%. It can be explained by a too large stream sent to the absorption and distillation loop even if it only corresponds to 7% of the unreacted gases leaving the reactor section. It has to be kept in mind that this purge stream is then used as it is burnt to recover energy. Moreover, this purge stream is necessary to prevent methane accumulation in the process. A better idea could be to recover unreacted hydrogen instead of burning it because of its important production price. This hydrogen recovered could then be inserted back in the synthesis loop what would lead to an increase of

the process conversion.

Once the model was established and process integration performed, the energy consumption of the process can be compared with the literature. In Europe, the newest, most efficient plants consume 28 GJ/tonne_{NH₃}. However, older plants are not this efficient so, the European mean value is rather 34.5 GJ/tonne_{NH₃} [4][15]. Not all this energy is used in the synthesis loop, out of this consumption 26.4 to 31.0 GJ/tonne_{NH₃} are from syngas production by steam reforming [26].

As stated in the previous section, 1.9 GJ/tonne_{NH₃} of electricity and 6.8 GJ/tonne_{NH₃} of cold utilities are required. To compare those results with the literature, the ideal would be to have a single value for the energy consumption of the process. However, it is not precised how this single value is obtained and how the different forms of energy are taken into account in this global value as 1 joule of electricity is different from 1 joule of cold utilities. Nevertheless it seems that if the energy requirements are removed from the global value found in literature, the energy demand for the model presented in this article looks close enough.

3. Cost

An economic analysis before building a new chemical plant allows to evaluate its profitability through the years. The capital (CAPEX) and operating (OPEX) expenditures associated with the construction and operation of the chemical plant as well as the gain due to the production are determined. These different costs associated with the production of ammonia are computed via equations extracted from the Turton book [27] and from G. Léonard's Economic Analysis Lesson [28].

3.1 CAPEX

The estimation of CAPEX i.e. the total fixed capital investment is based on 4 steps.

The first one is to determine the cost of the equipment without taking into account the pressure and material used. Equation 6 is used [27]:

$$\log_{10} C^0 = K_1 + K_2 \log_{10} A + K_3 (\log_{10} A)^2 \quad (6)$$

For each type of equipment, factors K_1 , K_2 , K_3 are given by charts [27] and A is a specific characteristic of the equipment such as its surface area, the power used etc.

The second step is to adapt the costs to the real conditions thanks to the pressure factor F_p and the material factor F_m . In the case of ammonia production, the presence of high pressure, high temperature and nitrogen environment may cause failures of the equipment due to nitridation [9][29]. One way to reduce this effect is to use chromium steel. As a result, the material used is stainless steel. Moreover, as ammonia production is a high-pressure process, this leads to a F_p varying from 1 to 20 according to the results obtained for this model.

Thirdly, the chemical engineering plant cost index (CEPCI) is used to obtain the actual cost. Indeed, the previous steps

used data from 2001 while this project is established in 2021. Therefore inflation must be taken into account thanks to the CEPCI.

Table 7 shows the cost obtained with Turton's method for each piece of equipment individually without the application of the last step. It is important to notice that the last equipment "Furnace" is not represented on the flowsheet. It is added to calculate the cost of equipment of the gaseous stream going out from the absorption column for combustion. The value is obtained in the literature [30] and the CEPCI is taken into account. Moreover, it is necessary to point out that the cost of the reboiler and condenser of the distillation column are not computed with formulas as described above but instead from an assumption of Turton's book. It is said that the reboiler and condenser costs can be estimated at 10 to 20% of the column.

Equipment	Cost [\$]	Equipment	Cost [\$]
C-600	14 657 286	ADIAB-R1	5 503 269
C-601	19 105 757	ADIAB-R2	15 175 298
C-602	889 557	FLASH-1	4 886 507
PUMP-1	23 315	FLASH-2	294 543
ABS	246 194	TURB-1	1 735 518
Internals ABS	59 352	TURB-2	3 601 795
DIST	210 883	HTX-1	104 224
Internals DIST	43 155	HTX-2	569 499
Reboiler/ Condenser	42 177	HTX-3	245 373
HT-1	1 091 045	HTX-4	75 423
HT-2	3 811 414	HTX-5	75 716
		HTX-6	75 231
		HTX-7	133 397
		Furnace	335 013

Table 7. Value of CAPEX

For the first estimation of CAPEX, Turton's method is well known and often used in the industry but in order to justify the reliability of the results, some values have been compared with the literature. The cost of compressors and columns have been confirmed by literature values [31] [32]. Then, concerning the cost of the two reactors, they have been treated as reliable although they are expensive. Indeed, the pressure inside the reactors is high as the ammonia process is a high-pressure process so it requires tougher equipment and these equipment are big (51.77 and 115.27 m³). As a result thanks to this comparison and justification, the result obtained by Turton's book is treated as reliable.

Finally, the last step of the estimation of the CAPEX is to sum all values obtained for each piece of equipment with Equation 7:

$$C_{GR} = 1.18 \times \sum_{i=1}^n C_{BM,i} + 0.5 \times \sum_{i=1}^n C_i^0 \quad (7)$$

In this sum, $C_{BM,i}$ and C_i^0 are the prices of each unit obtained respectively after the third step and the first step of the Turton

method. This equation gives the final total CAPEX cost by involving the cost of transport or installation for instance. The total cost of CAPEX is finally established at \$91 002 405.

3.2 OPEX

The manufacturing of ammonia deals with several costs: the fixed capital investment FCI, the cost of direct labour C_{OL} , utilities C_{UT} , waste treatment C_{WT} , raw materials C_{RW} , the catalyst cost C_{cata} and the depreciation d_k . They take into account the direct and fixed manufacturing costs as well as the general expenses. The general expenses are namely due to administration, distribution and research costs.

The number of particulate and non-particulate processing steps (P and N_p) of the plant, including compression and heating for N_p for example, generates a number of working positions N_{WP} (Equation 8).

$$N_{WP} = (6.25 + 31 \times P^2 + 0.23 \times N_p)^{0.5} \quad (8)$$

Then by considering that one operator makes 245 shifts per year and that 1095 shifts are made by year, the number of operators per working position is obtained. Thereafter, the number of operators is calculated by multiplying 3.26, i.e the number of working positions N_{WP} , by 4.5, i.e the number of operators needed for a working position (1095 divided by 245). In this case, the number of operators is 15 and the average salary of a chemical operator in Belgium equals \$59 600/y [33]. A Belgian salary is taken into account instead of the Indian one because in India the salary is much lower than in Belgium [34] so, it is not relevant for this first estimation. Indeed, it is due to the fact that one Indian rupee equals 0.013 dollars. By multiplying the number of operators by the average salary, C_{OL} that represents the operators' wages is obtained.

Utilities cost is determined with the cost of cooling water and electricity. As can be seen in Figure 4, heat exchangers HTX-1, HTX-4 and HTX-7 uses water to cool down streams. This water varies from 10 to a maximum of 61°C and exchange a amount of 167 GJ/h. In consequence, the cost of cooling water is directly used: \$0.378/GJ [27]. Concerning electricity, the compressors and the pump needs a total of about 42 681 kW and the price of electricity in India is considered at \$0.115/kWh [35]. As a result, the contributions of cost of cooling water and electricity are respectively of around \$ 0.5 and \$ 39.3 million per years.

C_{WT} determines the cost of the treatment of the two outlet streams leaving the absorption and distillation unit: WASTE and GASOUT. The WASTE stream is treated by neutralisation with hydrochloric acid. Indeed, the stream contains water pure at 99.99 % so, the quantity of impurities (NH₃) is low enough to use neutralisation instead of nitridation [36]. The quantity of hydrochloric acid needed to reach a pH of 7 equals 113.64 g/h. The cost is \$0.115/kg of HCl [27]. It is important to point out that this quantity of HCl dissolved in the water does not exceed the norm of 250 mg/L chlorine in water [37]. Concerning GASOUT stream, free combustion by air is established. It

leads to a decrease in the OPEX because the gain of energy is transformed into electricity and can be reused in the process or sold. The efficiency is considered to be 40% [38] [39] An amount of 655 GJ/h of energy is recovered. This value seems huge but it is relevant as around 9 tonnes/h of gas participate to the combustion. During this step, NO_x emissions must be controlled. However, as the amount of NH₃ in the volume of gases is low enough the concentration of NO_x formed is lower than any emission norm. For instance, the norm enforced in the Netherlands is 70-80 mg of NO_x/Nm³ of air [13]. While it may not be the same norm in India, it gives a first value.

C_{RM} is the money used to provide raw materials at the inlet of the process. To produce ammonia, raw materials are H₂ and N₂ with a small amount of CH₄. That's why syngas is used as feed. Syngas is provided by natural gas. The cost of this later fluctuates a lot this is the reason why it is studied in the sensitive analysis part below. The current price of syngas is about 56% of the current natural gas price [40]. The price of natural gas is equal to \$0.3/kg (0.2 €/m³) according to A. Leruth, who worked as process engineer at Yara Sluiskil [41]. Therefore, the syngas price equals \$0.168/kg. In addition, deionized water needs to be provided. Around 13 500 kg/h must be provided and the cost of this water is \$0.010569 /kg [42].

The cost of the catalyst needs to be added to the operating cost. The catalyst is an iron oxide catalyst and its price is \$0.9/kg [43]. The assumption that the catalyst is replaced every five years is taken by consulting G. Léonard, Professor at the Chemical Engineering department of the University of Liège[44]. The mass of catalyst used in reactors equals 24.79 kg.

Concerning FCI, it is equal to the CAPEX value. The depreciation is the lost of the value of material with time. Here, the project is considered to have a lifetime of 10 years and that the equipment loses 20 % of its value each year. The depreciation period is equal to 6 years. It can be estimated with the Straight Line Method (Equation 9):

$$d_k = \frac{FCI - S}{6} \quad \text{with} \quad S = FCI \times (1 - 0.2)^{10} \quad (9)$$

The value obtained for each cost is shown in Table 8. Finally, the total manufacture cost COM is calculated with Equation 10:

$$COM = 2.73 \cdot C_{OL} + 1.23 \cdot (C_{UT} + C_{WT} + C_{RM}) + 0.18 \cdot FCI + d_k + C_{cata} \quad (10)$$

OPEX	Value [\$ /yr]	OPEX	Value [\$ /yr]
FCI	91 002 405	C_{RM}	141 038 975
C_{OL}	869 707	d_k	13 538 516
C_{UT}	39 770 750	C_{cata}	4.46
C_{WT}	-66 998 367	COM	172 281 224

Table 8. Value of OPEX

3.3 Cash flow

Different steps of ammonia plant life are assumed. It is considered that at the end of year 0, only the land is bought. During the first year, the ammonia plant is built so capital investment without land cost (FCI_L) is paid. The working capital (WC) is also paid at the end of the first year then the plant is started as a startup. From the beginning of the second year until the end of the seventh year, the depreciation of equipment occurs. From startup time, there are 10 years of plant operation following by the sold of the plant. Finally, the salvage value, the land cost and the working capital are recovered at the end of 11th year. The area cost in Belgium is around 18.07 \$/m² [45]. The surface area for building the ammonia plant is obtained by measuring the Sluiskil D (Yara) plant's area since this plant was manufactured to produce the same quantity as the plant studied in this article. The surface area is about 45 000 m². The land cost C_{land} is then established at \$813 150.

Then, by considering these assumptions, the cash flow diagram can be computed thanks to the total capital investment (Land cost, Working Capital, FCI_L) and the net profit. Values are obtained with equations 11 and 12:

$$P_{net} = (R - COM_{d_k} - d_k)(1 - t) + d_k \quad (11)$$

$$TCI = FCI + C_{Land} + WC \quad (12)$$

in which R is the revenue due to the ammonia production, t is the tax rate equal to 25.17% in India [46] and COM_{d_k} are the operating cost without depreciation d_k , WC is the working capital.

Moreover, discounted cash flow (DCF) is calculated to estimate the value of an investment based on its expected future cash flows [47]. It can be established thanks to the equation 13:

$$DCF = \frac{CF}{(1 + i')^k} \quad \text{with} \quad i' = \frac{1 + i}{1 + f} - 1 \quad (13)$$

where CF value is the value of the cash flow and i' is the inflation adjusted interest rate. The interest rate i is assumed to be 10% and the inflation rate f in India is 3.75% [48].

For a first study, the current price of syngas established in previous section i.e. \$0.168 /kg is considered. It leads to a final revenue of \$217 607 313 /y for an ammonia production of around 616 661 tonnes/y . Moreover, an ammonia market price of \$0.35288/kg is taken into account [49]. In consequence, the resulting diagrams illustrated in Figure 7 are obtained. The cash flows show that the cumulative cash position is about \$ 380 million at the end of the eleventh year. The payback period ends before the end of the third year. The return on rate of investment is about 41%. Moreover, the discounted cash flow evaluate the net present value at about \$ 203 million. The payback period ends before the end of the sixth year.

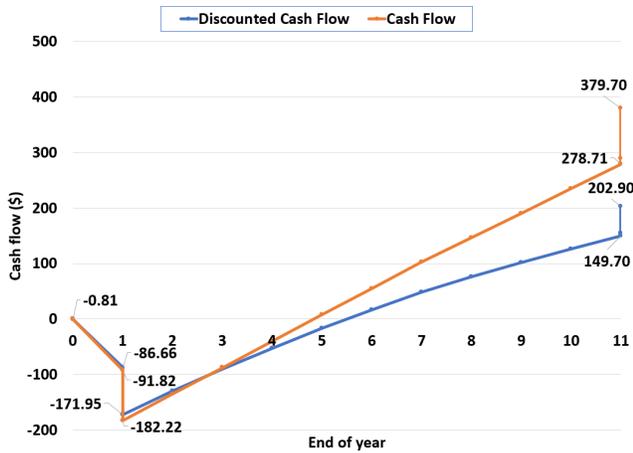


Figure 7. Cumulative cash flow and discounted cash flow diagram

CF and DCF in Equation 13 depend on the price of the raw materials and the selling price of the final product NH_3 . However, only considering the actual prices is not relevant because of the fluctuation of these prices. Therefore, in a second approach, a sensitivity study is established to determine the minimum price to sell ammonia according to syngas price in order to not be in deficit. Figure 8 shows the selling price of ammonia depending on the price of syngas in order to reach a null discounted cash flow at the end of the eleventh year. For an ammonia selling price under the blue line, profit can be made but under it, there is deficit.

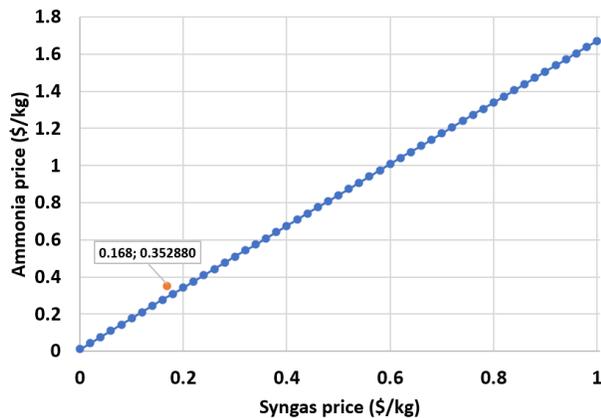


Figure 8. Price of ammonia according to the syngas price to obtain a net present value of 0\$

As it can be seen on Figure 7, the discounted cash flow is positive after the eleventh year. Indeed by entering the price in Figure 8 (Red point), it shows that it is above the blue line. Profit is done.

3.4 Economic evaluation

The analysis of the profitability of the ammonia process is more complex than just giving a positive or negative net present value. Indeed, the profitability depends on the cost

of the raw materials and the selling price of the final product. The profit will be positive when the cost of production is smaller than the foreseeable revenue and negative if it is the opposite. Currently, ammonia plant should be profitable as show by Figure 7 above. However, these results should be taken with care due to prices fluctuation. Indeed, these prices will decrease or increase through the time depending on a lot of factors that are not predictable leading to either profitability or deficit. Therefore, the profitability of the plant will vary through the time and can not be as precise as desire. In consequence, this cost must be very well discussed before investing in this process.

4. Life cycle assessment

A LCA is a cradle-to-grave analysis approach that helps to make effective and rational environmental decisions. It is used to evaluate the environmental impact of a product or process over its entire life, beginning from raw material extraction and extending to the final disposal. Furthermore, it considers all life stages of the product or process to assess the overall environmental impact. Sometimes a LCA is performed to evaluate the impact of alternative products, but it can also identify areas of major concerns and help to improve processes. However, in this project, no more than an introductory LCA is carried out, and only very approximated information is gathered. Indeed, in this project, it is decided to focus the LCA analysis on three main parts of the ammonia production: raw materials supply, the transport and the energy used in the process.

In this continuous ammonia production process, a fresh feed of hydrogen is needed. As a consequence, steam reforming of natural gas is considered. This method consists of a first reaction of methane with water vapor in a primary reformer to form carbon monoxide and hydrogen. Then the remaining methane gas is converted in the second step with oxygen to hydrogen and carbon monoxide in a secondary reformer and in a third step, carbon monoxide is oxidized to carbon dioxide. Moreover, the nitrogen needed for the process is considered to be obtained directly by air separation.

4.1 Collection of data

In this step, input raw material, energy, emissions, and waste output data are collected. These data are used to calculate the total emissions of the system. Data quality is an important aspect of LCA and during inventory analysis. These data used for the life cycle analysis can be found in Appendix (Table 12). It is important to note that in this table carbon dioxide emissions are taken into account as a input in order to consider the emissions linked to the production of hydrogen via steam reforming.

As literature gives a mean emission value in Europe of 1.9 tonnes CO_2 per tonne NH_3 [4], it corresponds to a carbon dioxide emission of around 1 170 400 tonnes CO_2 per year. The value for the process presented in this article is 1 478 958 tonnes CO_2 per year. Higher, but it is still in the same order of magnitude.

The purge stream is consisting of mainly hydrogen and nitrogen. However, it also contains a small amount of methane, ammonia, and water. There is two ways of handling this stream, recycling or burning. In this process, purge gases are considered as burned and the energy obtained will be used to generate electricity and heat via co-generation. Indeed, the assumption that 35% of the energy recovered from the combustion products is converted to electricity, 53% is converted to heat and 12% is considered as loss. The electricity produced is assumed to be directly used in the ammonia process and that the heat recovered is used for the steam reforming process as no more heat can be recovered for the ammonia production. The composition, the mass flow rate and lower heating value of the purge are exposed in Table 13.

4.2 Presentation of the situation

Several assumptions are made in order to realize this life cycle assessment. The first one is the location of the process. Finally, India is chosen. This choice is made for several reasons. The first is that India is located on a expanding market where the demand for ammonia is increasing. Actually, over a period from 2017 to 2022 the Indian market is forecasted to grow by 10.3% [50]. Moreover, an eminently important criterion is the access to primary resources at an affordable price. Indeed, in order to be competitive it is important to start from low-priced resources. In India the price of natural gas is 0.007 €/kWh which is one of the lowest available on the market [51]. Furthermore, geostrategic considerations and the availability of water resources were taken into account, this is why most of countries in the middle East were not considered.

A second assumption is made for the electricity consumption of the overall process and it is assumed to come from pumps and compressors. Indeed, the hypothetical electrical consumption required to pump the cooling media from point to point are not taken into account. Additionally the last hypothesis is that the catalyst life cycle is considered as 7 years.

4.3 Environmental impacts

The environmental impacts associated with all the stages of the ammonia production are evaluated by the simulation software Simapro and are expressed for the production of 1kg of ammonia. In this analysis, hydrogen and nitrogen as raw materials, electricity consumption for pumps, compressor and the transport of raw materials is included. Furthermore the catalyst used and the recovery of the purge stream is considered. A particular European model is applied, namely CML-IA. It is a set of impact categories and characterization methods for the impact assessment steps proposed by a group of scientists under the lead of CML (Center of Environmental Science of Leiden University), in 2001 [52].

The baseline versions used of SimaPro 8 focus on 10 impact categories. The first one is abiotic depletion and its indicator is related to the extraction of minerals and fossil fuels due to inputs in the system. The Abiotic Depletion Factor (ADF) is determined for each extraction of minerals

and fossil fuels (kg antimony equivalents (Sb)/kg extraction) based on concentration reserves and rate of de-accumulation. The geographic scope of this indicator is at global scale. The other impact categories are abiotic depletion in terms of fossil fuels and global warming. For global warming emissions of greenhouse gases to the air are considered. Factors are expressed as Global Warming Potential for time horizon 100 years (GWP100), in kg carbon dioxide/kg emission while for abiotic depletion the unit is in MJ. Ozone layer depletion is given in kg trichlorofluoromethane (CFC-11) equivalent/ kg emission. For Human toxicity, fresh-water aquatic ecotoxicity, marine ecotoxicity, and terrestrial ecotoxicity sub-groups, the units are taken as 1,4-dichlorobenzene equivalents/ kg emission, while for photo-oxidant formation is kg ethylene equivalents kg emission. The units for eutrophication is kg PO₄ equivalents per kg emission and lastly for acidification is kg SO₂ equivalents/kg emission.

Figure 9 shows all the impact categories for the production of 1kg of ammonia. To normalized them, each of those impacts is divided by the corresponding impact generated by an average European resident per year. As can be seen in Figure 9, the four main impact categories are marine aquatic ecotoxicity, abiotic depletion (fuel), fresh water aquatic ecotoxicity and global warming. It can also be observed that there are four contributions for each impact: iron production, electricity consumption, hydrogen production and ammonia production among which the hydrogen production is by far the major impact in almost all the impact categories.

This is confirmed in Figure 10. That means that the main contribution to environmental impact in the ammonia production is hydrogen production. It is important to note that the ammonia production has negligible impact due to the fact that no additional external heat is needed for the production and that all the negative parts in yellow correspond to avoided impact due to an excess in electricity production with the purge.

Figure 11 highlights the life cycle analysis comparison between the ammonia production presented in this article and two reference databases provided by the software. One of them is AGRIBALYSE which is a French research program dedicated for producing life cycle inventory (LCI) of agricultural products. It provides a homogeneous and consensual LCI database to support environmental labeling policies and to help the agricultural sector to improve its practices. The other data set for ammonia is called Ecoinvent 3.3. By focusing only robust indicators such as abiotic depletion (fossil fuels) and global warming, the comparison figure allows to show that there is no big difference between the impacts intensity in both cases.

4.4 LCA conclusion

To conclude this LCA, based on the comparison between the environmental impacts between the process studied in this article and processes provided by the software Simapro, it can

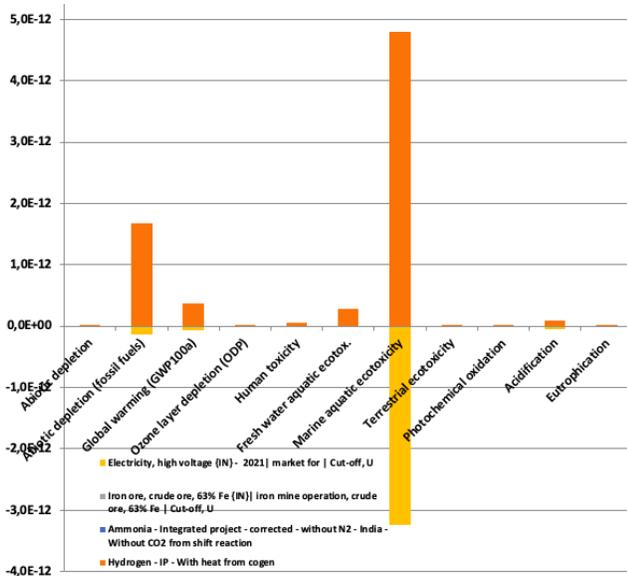


Figure 9. Normalization of LCA results

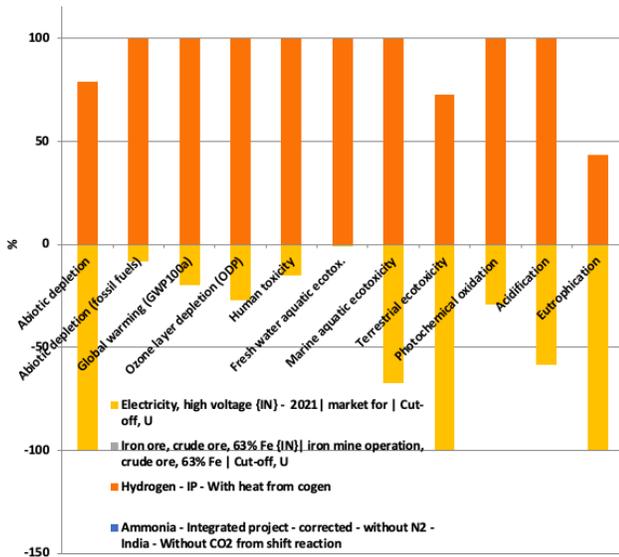


Figure 10. LCA results

be considered that the ammonia unit production developed in this project can be validated. Indeed, the results obtained for the different robust impact categories are of the same order of magnitude.

Furthermore, this analysis can be used to help decision makers to optimize the process. Indeed, it is noticed that the hydrogen production has a significant part of the overall environmental impacts. Therefore, it can be interesting to investigate possible green options of producing hydrogen rather than the steam reforming process.

5. Alternatives to fossil feedstock

As all of ammonia production nowadays is based on fossil fuel it releases a huge quantity of green house gases. Some

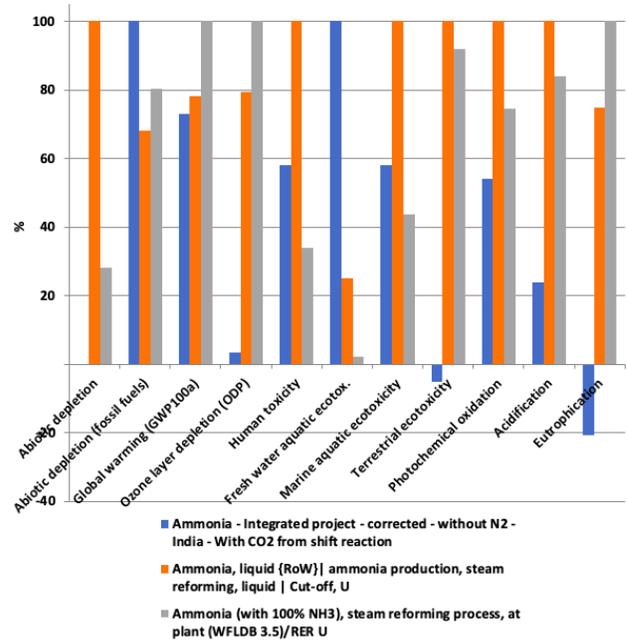


Figure 11. Comparison with the database

alternatives to a fossil fuel-based Haber-Bosh process were developed to make this crucial production less environmentally harmful. As the quasi-totality of the carbon dioxide produced comes from syngas production, changing the way it is produced is a valid path. Indeed, gas house emissions decrease while keeping the same synthesis loop than the Haber-Bosh process. It allows those modified Haber-Bosh process to be mature enough technically to build a plant. Another path is to completely change the process but it takes more research and is still at lab scale.

5.1 Biomass

Syngas can be produced by biomass gasification. Lots of different types of biomass can be used, for instance, wood, agricultural waste or domestic solid waste. Several technologies exist but all are based on the same steps.

The biomass is dried and then oxidized with oxygen deficit. The oxidation allows to produce energy for the rest of the process. Carbon monoxide is produced too. Next comes the pyrolysis. It produces hydrogen, carbon monoxide and dioxide. Around 70-90 wt-% of the feedstock becomes gas, the rest becomes tar and cinders. The last main step is the reduction step. In this part of the process, carbon monoxide reacts reversibly with water to produce hydrogen and carbon dioxide, it is called the water-gas shift reaction. It allows to produce the hydrogen needed for ammonia production. As it is an exothermic reaction, temperature should be around 800°C [53]. Once carbon dioxide is scrubbed out the syngas is sent to an Haber-Bosh process.

Biomass is interesting as it is a renewable carbon source. Moreover, it can be stored easily compared with electricity[54]. However, its price and availability depend on seasons and weather. Moreover, to diminish transport the biomass

should be produced locally. As producing 1 kg of ammonia needs almost 3 kg of biomass, it puts some serious constraints on the location and production capacity of a biomass-based ammonia plant.

A comparison with the values given by an article with the best available technologies (BAT) of the Haber-Bosh process is presented in Table 9. This article uses wood and forestry waste to produce syngas.

	BAT H-B [15]	Biomass [54]
Production [tonnes NH ₃ /day]	1000-2000	1 200
Feedstock	Natural gas	Wood
Energy [GJ/tonne NH ₃]	28	8.52
Emission [tonnes CO ₂ /tonne NH ₃]	1.6	0.67
Cost [€/tonne NH ₃]	200-250	289

Table 9. Comparison biomass with natural gas Haber-Bosh process

For the carbon balance, less emissions of carbon dioxide are released as biomass, in order to grow, need to consume this gas. Less energy is consumed per tonne of ammonia too. However the cost is bigger than natural gas based ammonia.

5.2 Water electrolysis

In order to completely eliminate onsite carbon dioxide emissions, hydrogen can be obtained by hydrolysis, preferably with renewable electricity. Several technologies are available to perform it. The conventional ones are alkaline electrolysis, polymer electrolyte membrane electrolysis and solid oxide electrolysis.

The alkaline electrolysis cell uses one anode and one cathode separated by a diaphragm. The hydrogen is produced on the cathode side and the OH⁻ pass through the diaphragm to the anode where oxygen is released. The cell operates in a temperature range of 70-90°C and has a conversion efficiency between 60 and 80% [55].

About the polymer electrolyte membrane electrolysis, in place of a diaphragm, a polymeric membrane is used. The same gases are produced on the same electrode as for the alkaline electrolysis cell but it is H⁺ that goes from the anode to the cathode. The conversion efficiency is around 65-82% and it operates at a temperature lower than 100°C[55].

The last conventional technique is the solid oxide electrolysis. The cathode and anode are separated by a ceramic membrane through which O²⁻ pass from the cathode to the anode. It operates at high pressure and temperature around 500-850°C[55].

Regarding nitrogen, it is separated from air either by a cryogenic separation or by pressure swing adsorption. The first technologies compress the air to around 6 bar and cool it down. After distillation, almost perfectly pure nitrogen can be obtained. Pressure swing adsorption allows a high

purity too, above 99.99% [56]. Beds of granular adsorbent are used in this technology to adsorb oxygen, carbon dioxide and moisture to get pure nitrogen at the outlet [57].

The hydrogen and nitrogen produced separately are then mixed in stoichiometric amounts before sending them in the synthesis loop of an Haber-Bosh process.

Several studies have been investigated on this process and some data are available in Table 10. It is observed that this process uses a lot of electricity and that the cost of a tonne of ammonia is higher than ammonia from natural gas. Indeed, hydrolysis is both a big energy consumer and very expensive at large-scale. However, this process is worthwhile if the electricity used is renewable in terms of environment.

	BAT H-B [15]	WE [58]
Production [tonnes NH ₃ /day]	1000-2000	360
Feedstock	Natural gas	Water
Energy [GJ/tonne NH ₃]	28	36
Emission [tonnes CO ₂ /tonne NH ₃]	1.6	0
Cost [€/tonne NH ₃]	200-250	200-600

Table 10. Comparison hydrolysis (WE) with natural gas Haber-Bosh process

5.3 Electrochemistry

The electrochemical process remains based on the ammonia synthesis reaction where hydrogen is combined with nitrogen. Nitrogen comes from the separation of air in the same way as explained in Section 5.2. Hydrogen can come from natural gas, coal, biomass, water, etc. To be as carbon-free as possible, hydrolysis of water should be prioritised.

Hydrogen and nitrogen are directed to the electrodes of the reactor. Those are a porous nickel anode and cathode, respectively. At the anode, hydrogen is transferred to protons from an external source. These hydrogen ions are carried to the cathode via a proton transfer membrane where they react with nitrogen to form ammonia. The ammonia synthesized at the cathode is sent to the separation tower to obtain liquid ammonia. The stream of unreacted reagents is separated and is recycled to each corresponding electrode.

This process is a step forward as its energy efficiency is greater by 20% compared to the Haber-Bosch process [59]. It operates under mild conditions with low power requirements. It is possible to produce ammonia at atmospheric pressure. However, it uses expensive electrolytes.

An article does model ammonia production at large scale by electrochemistry. Hydrogen comes from hydrolysis and nitrogen from the cryogenic separation of air, for a production of 140 tonnes/day of green ammonia. The energy consumption has been evaluated at around 17 MWh/tonnes of NH₃. The estimated ammonia price is of 298 €/tonnes NH₃. [60]

6. Conclusion

As the global demand for ammonia increases rapidly, the optimal design of the ammonia production process is a major concern for engineers and researchers. Thus, ammonia and its production processes are investigated from several aspects. To design an ammonia synthesis, adiabatic reactors in series are used. The length of bed and the operating conditions are predicted too. Quite satisfactory model results were obtained in comparison with other plant data [13][15][4].

The energy consumption is improved by the pinch analysis performed on the process and it has shown that around 66.5% of energy can be saved if the heat integration is properly applied.

In the LCA study, the emissions are normalized in order to see the hierarchy between the relative importance of each impact category. It is evident that the ammonia process has significant impact on the global warming and abiotic depletion (fossil fuel) categories, which pushes the producer to find a possible buyer for carbon dioxide in order to reduce the emissions.

The analysis of the profitability of the ammonia process is evaluated with the Turton method and compared with literature results. By considering the current price of natural gas and the current selling price of ammonia, the study leads to a production which makes profit. The costs of production are smaller than the foreseeable revenue. A cost of production of \$279/tonne_{NH₃} is established. This value suits the range given by the literature. However, these first results cannot be considered as fully reliable to conclude that the building of the plant is profitable. The raw materials cost fluctuates a lot so only take into account the current values of them is not really representative of the profit of the plant throughout its operating. Indeed, during the plant's operating period, this type of plant will either make a profit or a deficit depending on the production period. Therefore, a sensitive analysis to determine the minimum price to sell ammonia according to syngas price has been made.

A literature review is carried out in order to evaluate the existing technologies and provide a possible comparison to this study. Some alternative processes to fossil fuel based Haber-Bosh process are given. The general focus is brought to environmental-friendly production ways which offers greener source for hydrogen, namely biomass, electrolysis.

This article has the ambition to contribute to the research on the modelling of the Haber-Bosh process. It details the different steps and assumptions that were taken and hopefully will be of interest for future works.

To go even further in this work, it could be interesting to study the process under a different point of view concerning some operating conditions. For further improvement, a process working at higher pressure and leading to maybe less cold utility could be build. Also, the potential recycling of the gaseous outlet of the absorption column into the process could also be studied in order to save feed even if this gaseous stream is recovered in term of energy.

Acknowledgement

This work was supported by professors of the chemical engineering department of the University of Liège, M-N. Dumont, N. Job, A. Léonard, G. Léonard, A. Pfennig, D. Toye and M. Philippart de Foy, teaching assistant. We, hereby, thank them for their constant supervision along the project and for all the feedback which brought critical way of thinking to this work.

We thank A. Leruth and A. Hoxha for their willingness to answer our questions from the industrial point of view.

We finally thank T. Manfredini and V. Jans for their support throughout the continuity of this project.

References

- [1] *Ammonia - Chemical Economics Handbook (CEH) — IHS Markit*. URL: <https://ihsmarkit.com/products/ammonia-chemical-economics-handbook.html>. (accessed on 15.10.2020).
- [2] *Ammonia - Wikipedia*. URL: <https://en.wikipedia.org/wiki/Ammonia>. (accessed on 15.10.2020).
- [3] *Introduction to Ammonia Production — AIChE*. URL: <https://www.aiche.org/resources/publications/cep/2016/september/introduction-ammonia-production>. (accessed on 15.10.2020).
- [4] Antoine Hoxha. *RE: Uliège : Projet intégré : production d'ammoniaque*. email. Apr. 2021.
- [5] Usgs National Minerals Information Center. *Mineral Commodity Summaries*. Tech. rep. 2020. DOI: 10.3133/MCS2020.
- [6] *Ammonia Market Size & Outlook — Industry Forecast Report, 2014-2025*. URL: <https://www.grandviewresearch.com/industry-analysis/ammonia-market>. (accessed on 15.10.2020).
- [7] Thomas Lauer. "Preparation of Ammonia from Liquid AdBlue - Modeling Approaches and Future Challenges". In: *Chemie Ingenieur Technik* 90.6 (June 2018), pp. 783–794. ISSN: 0009286X. DOI: 10.1002/cite.201700107.
- [8] *AdBlue : les explications et comment faire le plein - Moniteur Automobile*. URL: <https://www.moniteurautomobile.be/conseils-auto/a-faire-soi-meme/adblue-explications-comment-faire-le-plein.html>. (accessed on 29.04.2021).
- [9] Max Appl. "Ullmann's Encyclopedia of Industrial Chemistry". In: Wiley-VCH Verlag GmbH & Co. KGaA., 2006. Chap. Ammonia. DOI: 10.1002/14356007.o17_o02.

- [10] *Ammonia Uses and Benefits — Chemical Safety Facts*. URL: <https://www.chemicalsafetyfacts.org/ammonia/>. (accessed on 15.10.2020).
- [11] European Environment Agency. *Ammonia (NH₃) emissions*. URL: <https://www.eea.europa.eu/data-and-maps/indicators/eea-32-ammonia-nh3-emissions-1>. (accessed on 01.05.2021).
- [12] Travis P. Hignett. “Production of Ammonia”. In: *Fertilizer Manual*. Springer Netherlands, 1985, pp. 49–72. DOI: 10.1007/978-94-017-1538-6_6.
- [13] Alexandre Leruth. *RE: Uliège : Projet intégré : production d’ammoniaque*. email. Apr. 2021.
- [14] *The Haber Process for the manufacture of ammonia*. URL: <https://www.chemguide.co.uk/physical/equilibria/haber.html>. (accessed on 29.04.2021).
- [15] BERF. “Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers”. In: EUROPEAN COMMISSION, 2007. Chap. 2.
- [16] Max Appl. *Ammonia, Principles and Industrial Practice*. Wiley-VCH, 1999. ISBN: 3527295933.
- [17] *Ammonia - NIST*. URL: <https://webbook.nist.gov/cgi/cbook.cgi?ID=C7664417&Type=JANAFG&Plot=on>. (accessed on 18.10.2020).
- [18] Chatti Monia. *Propriétés thermodynamiques du mélange Eau-Ammoniac-Hélium*. 2010. URL: <https://www.yumpu.com/fr/document/view/6669310/proprietes-thermodynamiques-du-melange-eau-ammoniac-helium>.
- [19] E. J. Clifford I. I. & Hunter. *Phys. Chem.* 37. 1933. Chap. The System Ammonia-water at Temperatures up to 150 deg and at Pressures up to Twenty Atmosphere, p. 101.
- [20] P. H. Emmett and R. W. Harkness. “The Adsorption of Hydrogen by Iron Synthetic Ammonia Catalysts”. In: *Journal of the American Chemical Society* 57.9 (Sept. 1935), pp. 1631–1635. DOI: 10.1021/ja01312a037.
- [21] M. I. Temkin and V. Pyzeiev. *Kinetics of Ammonia Synthesis on Promoted Iron Catalysts*. Acta Physicochimica U.R.S.S., 1940.
- [22] A NIELSEN. “Rate equation and mechanism of ammonia synthesis at industrial conditions”. In: *Journal of Catalysis* 3.1 (Feb. 1964), pp. 68–79. DOI: 10.1016/0021-9517(64)90094-6.
- [23] Anders Nielsen, ed. *Ammonia*. Springer Berlin Heidelberg, 1995. DOI: 10.1007/978-3-642-79197-0.
- [24] H. Scott Fogler. *Elements of chemical reaction engineering*. Fifth edition. Boston: Prentice Hall, 2016. ISBN: 9780133887518.
- [25] Ian C.Kemp. *Pinch Analysis and Process Integration*. 2007. Chap. Heat exchanger network design, p. 104. DOI: 10.1016/b978-0-7506-8260-2.x5001-9.
- [26] Industrial Efficiency Technology & Measures. *Steam reforming*. URL: <http://www.iipinetwork.org/wp-content/Ietd/content/steam-reforming.html>. (accessed on 09.04.2021).
- [27] Richard Turton; Joseph A. Shaeiwitz; Debangsu Bhat-tacharyya; Wallace B. Whiting. *Analysis, Synthesis, and Design of Chemical Processes*. Fifth Edition. Pearson Education, Inc., 2018. ISBN: 9780134177403.
- [28] Grégoire LEONARD. *Introduction to economic evaluation of chemical processes*. Integrated Project University of Liège, 2021.
- [29] A. Hassan Faraji. “High temperature Nitriding corrosion in Ammonia converters”. In: *AMMONIA TECHNICAL MANUAL* (2010), pp. 183–191. URL: http://www.iffcokandla.in/data/polopoly_fs/1.2466117.1437677726!/fileserver/file/507808/filename/019.pdf. (accessed on 09.04.2021).
- [30] Umit Unver and H. Murat Unver. “Comparison of Natural Gas Fired and Induction Heating Furnaces”. In: (Mar. 2014), pp. 1009–1016. DOI: 10.1007/978-3-319-04681-5_96.
- [31] *BRAND NEW Siemens SGT 700 GAS TURBINE FOR SALE*. URL: <http://www.china-power-contractor.cn/BRAND-NEW-Siemens-SGT-700-GAS-TURBINE-FOR-SALE.html>.
- [32] Yuan Jiang et al. “Techno-economic comparison of various process configurations for post-combustion carbon capture using a single-component water-lean solvent”. In: *International Journal of Greenhouse Gas Control* 106 (2021), p. 103279. ISSN: 1750-5836. DOI: 10.1016/j.ijggc.2021.103279.
- [33] *Power Plant Operator Average Salary in Belgium 2021*. 2021. URL: <http://www.salaryexplorer.com/salary-survey.php?loc=21&loctype=1&job=12599&jobtype=3>. (accessed on 10.04.2021).
- [34] *Chemical Plant Operator Average Salary in India 2021*. 2021. URL: <http://www.salaryexplorer.com/salary-survey.php?loc=100&loctype=1&job=12174&jobtype=3>. (accessed on 10.04.2021).

- [35] GlobalPetrolPrices.com. *Inde prix de l'électricité*. Sept. 2020. URL: https://fr.globalpetrolprices.com/India/electricity_prices/. (accessed on 01.04.2021).
- [36] Suez. *Élimination de l'ammonium*. 2021. URL: <https://www.suezwaterhandbook.fr/procedes-et-technologies/traitement-des-eaux-potables/traitements-specifiques/elimination-de-l-ammonium>. (accessed on 09.04.2021).
- [37] in BW. *PARAMÈTRES ET NORMES*. 2021. URL: <https://www.inbw.be/parametres-et-normes#chlorures>. (accessed on 09.04.2021).
- [38] *Energy conversion efficiency*. URL: https://en.wikipedia.org/wiki/Energy_conversion_efficiency. (accessed on 29.04.2021).
- [39] *Evaluer le coût économique de la production d'électricité*. URL: <http://www.energy-alternatives.eu/2020/08/20/decomposition-lcoe.html#annexe-3--d%C3%A9mant%C3%A8lement-et-gestion-des-d%C3%A9chets-nucl%C3%A9aires->. (accessed on 29.04.2021).
- [40] Peng Pei et al. "Cost comparison of syngas production from natural gas conversion and underground coal gasification". In: *Mitigation and Adaptation Strategies for Global Change* 21 (June 2014). DOI: 10.1007/s11027-014-9588-x.
- [41] Alexandre Leruth. *Re: Production ammoniac*. email. Apr. 2021.
- [42] *De-ionization 101 - USWATER System*. URL: <https://www.uswatersystems.com/blog/de-ionization-101>.
- [43] businesswire. *Worldwide Catalyst Fertilizers Market Forecast to 2023 - Strong R&D Activities to Reduce the Cost of Catalysts - ResearchAndMarkets.com*. 2021. URL: <https://www.businesswire.com/news/home/20190225005456/en/Worldwide-Catalyst-Fertilizers-Market-Forecast-to-2023---Strong-RD-Activities-to-Reduce-the-Cost-of-Catalysts---ResearchAndMarkets.com>. (accessed on 01.04.2021).
- [44] Grégoire Léonard. informal discussion. Apr. 2021.
- [45] *Industrial plots - Belgium*. URL: <https://invest-hub.org/ads/industrial-plots-belgium>. (accessed on 19.04.2021).
- [46] Trading economics. *India Corporate Tax Rate*. 2020. URL: <https://tradingeconomics.com/india/corporate-tax-rate>. (accessed on 10.04.2021).
- [47] Jason Fernando. *Discounted Cash Flow (DCF)*. Mar. 2021. URL: [https://www.investopedia.com/terms/d/dcf.asp#:~:text=Discounted%5C%20cash%5C%20flow%5C%20\(DCF\)%5C%20is,will%5C%20generate%5C%20in%5C%20the%5C%20future..](https://www.investopedia.com/terms/d/dcf.asp#:~:text=Discounted%5C%20cash%5C%20flow%5C%20(DCF)%5C%20is,will%5C%20generate%5C%20in%5C%20the%5C%20future..) (accessed on 12.04.2021).
- [48] Statista. *India: Inflation rate from 1985 to 2025*. Mar. 2021. URL: <https://www.statista.com/statistics/271322/inflation-rate-in-india/>. (accessed on 10.04.2021).
- [49] *Black Sea Urea Spot Price*. URL: https://ycharts.com/indicators/black_sea_urea_bulk_spot_price. (accessed on 20.04.2021).
- [50] The Economic Times Market. *Natural Gas Rate*. URL: <https://economictimes.indiatimes.com/commoditysummary/symbol-NATURALGAS.cms>. (accessed on 04.04.2021).
- [51] Global petrol prices. *India's ammonia capacity is expected to witness double digit growth over the next six years, says GlobalData*. URL: <https://www.globaldata.com/indias-ammonia-capacity-is-expected-to-witness-double-digit-growth-over-the-next-six-years-says-globaldata/>. (accessed on 01.04.2021).
- [52] SimaPro Database Manual. *Methods Library*. URL: <https://simapro.com/wp-content/uploads/2020/06/DatabaseManualMethods.pdf>. (accessed on 01.04.2021).
- [53] Antonio Molino; Simeone Chianese; Dino Musmarra. "Biomass gasification technology: The state of the art overview". In: *Journal of Energy Chemistry* 25.1 (2016), pp. 10–25. DOI: 10.1016/j.jechem.2015.11.005.
- [54] Paul Gilbert; Sarah Alexander; Patricia Thornley; John Brammer. "Assessing economically viable carbon reductions for the production of ammonia from biomass gasification". In: *Journal of Cleaner Production* 64 (2014), pp. 581–589. DOI: 10.1016/j.jclepro.2013.09.011.
- [55] Prabhu Saravanan;Maksudur Rahman Khan; Chin Sim Yee; Dai-Viet N.Vo. "New Dimensions in Production and Utilization of Hydrogen". In: Elsevier, 2020. Chap. 7 - An overview of water electrolysis technologies for the production of hydrogen, pp. 161–190.

- [56] Stefanie Tesch; Tatiana Morosuk; George Tsatsaronis. “Comparative Evaluation of Cryogenic Air Separation Units from the Exergetic and Economic Points of View”. In: *IntechOpen* (2019). DOI: 10.5772/intechopen.85765.
- [57] Mira Dobрева. *How Do PSA Nitrogen Generators Work? - Pressure Swing Adsorption*. URL: <https://www.peakscientific.com/discover/news/how-do-nitrogen-generators-work-pressure-swing-adsorption-psa/>. (accessed: 02.05.2021).
- [58] C. Fúnez Guerraa; L. Reyes-Bozob; E. Vyhmeisterc; M. Jaen Caparrosd; Jose Luis Salazare; C. Clemente-Jul. “Technical-economic analysis for a green ammonia production plant in Chile and its subsequent transport to Japan”. In: *Renewable Energy* 157 (2020), pp. 404–414. DOI: 10.1016/j.renene.2020.05.041.
- [59] Tim Lipman; Nihar Shah. “Ammonia as an alternative energy storage medium for hydrogen fuel cells: scientific and technical review for near-term stationary power demonstration projects, Final Report”. In: (2007). URL: <https://tsrc.berkeley.edu/publications/ammonia-alternative-energy-storage-medium-hydrogen-fuel-cells-scientific-and-technical>.
- [60] Yusuf Bicer; Farrukh Khalid; Amro M.O. Mohamed; Mohammed Al-Breiki; Moiz Maroof Ali. “Electrochemical modelling of ammonia synthesis in molten salt medium for renewable fuel production using wind power”. In: *international journal of hydrogen energy* 45 (2020), pp. 4938–34948. DOI: 10.1016/j.ijhydene.2020.03.085.

Appendix

Heat exchangers Heaters	Area [m ²]	Heat load [kW]	U [W/m ² K]
HTX-1	152.2	29478.6	1500
HTX-2	996.4	95 289.4	650
HTX-3	405.2	30 353.6	600
HTX-4	16.8	9 643.6	1500
HTX-5	29.5	2 463.2	600
HTX-6	17.3	1 287.2	355
HTX-7	248	7 062.3	2500
HT-1	/	15 100	/
HT-2	/	93 755.5	/

Table 11. Heat exchangers - Operating conditions

		Aspen values [tonnes/year]	In Functional Unit
Input	Methane	561 484	0.91
	Nitrogen	645 699	1.05
	Water (for separation)	360 000	0.58
	Water (for water-gas shift)	1 234 985	2.00
	Carbon dioxide emissions	1 478 958	2.40
		Aspen Value [kWh/year]	In Functional Unit
ELECTRICITY	Compressor	341 429 920	0.56
	Turbine	-22 208 336	-0.035
	Pump	22 640	0.4e-4
	Cold utilities	1 132 000 000	1.83
		Aspen value [kg/year]	In Functional Unit
OUTPUT/ Waste Water Stream	Ammonia	324	0.5e-6
	Water	355 060 800	0.57

Table 12. Data collected from the ammonia process

		Mass flow [kg/year]	Functional unit	LHV [GWh]	LHV [GWh/ kg ammonia per year]
OUTPUT/ Purge Stream	Hydrogen	19 413 200	0.0315	652.85	1.1 e-6
	Nitrogen	138 004 000	0.2235	92.07	7.5e-6
	Methane	57 963 200	0.0939	806.17	3.2e-6
	Ammonia	12 926	0.00002	0.067	0
	Water	5 244 800	0.0085	0	3 e-7

Table 13. The LHV of the purge stream