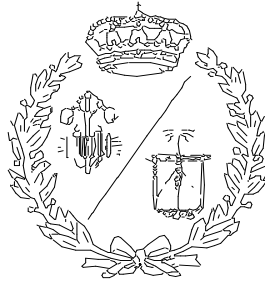


ESCUELA TÉCNICA SUPERIOR DE INGENIEROS

INDUSTRIALES Y DE TELECOMUNICACIÓN

UNIVERSIDAD DE CANTABRIA



Trabajo Fin de Grado

**SMALL-SCALE GREEN AMMONIA
PRODUCTION PLANT: PRELIMINARY DESIGN
AND SIMULATION USING ASPEN PLUS**

**(Planta de producción de amoniaco
sostenible a pequeña escala: diseño
preliminar y simulación en ASPEN Plus)**

Para acceder al Título de

**GRADUADO EN INGENIERÍA EN
TECNOLOGÍAS INDUSTRIALES**

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05-2022



Título: Planta de producción de amoniaco sostenible a pequeña escala: diseño preliminar y simulación en ASPEN Plus.

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Palabras clave: Amoniaco, pequeña escala, Aspen Plus, renovable, simulación, Haber Bosch, hidrógeno, nitrógeno.

Resumen: El presente proyecto tiene como objetivo el diseño preliminar de una planta de producción (a pequeña escala) de 25 kg/h amoniaco del 98% de pureza a partir de materias primas y energías renovables. Dicha planta permitirá el suministro de amoniaco como combustible a buques de carga desde una plataforma flotante en el puerto de Santander.

Inicialmente se realiza un análisis de alternativas comparando, principalmente, el uso de hidrogeno y amoniaco como combustibles renovables en transporte marítimo y se estudia su importancia dentro del panorama internacional a medio y largo plazo para este tipo de usos.

El análisis del estado del arte de plantas de producción de amoniaco a pequeña escala, permite seleccionar el proceso Haber-Bosch como el más adecuado en términos de accesibilidad de materias primas, condiciones de trabajo, eficiencia, costes y TRL, incluyendo la obtención de hidrógeno a través de electrólisis del agua de mar y de nitrógeno a partir de separación del aire.

Mediante simulación en ASPEN PLUS se diseña una planta de producción de 25.64 kg/h de amoniaco del 99.3% obteniéndose los requerimientos de materias primas, las características de las corrientes y las condiciones de trabajo de cada equipo. Esta información permite el dimensionado de equipos y el establecimiento de un área global para la plataforma flotante de 300 m². La estimación de costes preliminar mediante métodos modulares permite establecer un Coste Base de Capital de 2.1 MM€.

Title: Small-Scale green ammonia production plant: preliminary design and simulation using ASPEN Plus.

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Keywords: Ammonia, small-scale, ASPEN Plus, renewable, simulation, Haber Bosch, Hydrogen, Nitrogen.

Abstract: The objective of this project is the preliminary design of a plant for the production (on a small scale) of 25 kg/h of 98% pure ammonia from raw materials and renewable energies. This plant will allow the supply of ammonia as fuel to cargo ships from a floating platform in the port of Santander.

Initially, an analysis of alternative fuels is carried out, mainly comparing the use of hydrogen and ammonia as renewable fuels in maritime transport, and their importance in the medium- and long-term international panorama for this type of use is studied.

The analysis of the state of the art of small-scale ammonia production plants allows the Haber-Bosch process to be selected as the most suitable in terms of accessibility of raw materials, working conditions, efficiency, costs, and LRT, including the obtaining of hydrogen through seawater electrolysis and nitrogen from air separation.

Through simulation in ASPEN PLUS, a plant is designed for the production of 25.64 kg/h of 99.3% ammonia, obtaining the raw material requirements, the characteristics of the streams and the working conditions of each piece of equipment. This information allows the sizing of equipment and the establishment of an overall area for the floating platform of 300 sqm. Preliminary cost estimation using modular methods allows a Base Capital Cost of €2.1 MM to be established.

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ABBREVIATIONS

A, B, C= Antoine coefficients

AIST= Advanced Industrial Science and Technology

AP= Aspen Plus

Ar= Argon

ASU= Air Separation Unit

AWE= Alkaline Water Electrolysis

Ca= Calcium

Cl (-) = Chloride

CTC= Components Technology Centre

DS= Design Specifications

FREA= Fukushima Renewable Energy Institute

H₂= Hydrogen

H₂O= water

HB= Haber-Bosch

IMO= International Maritime Organization

K= Potassium

Mg= Magnesium

N₂= Nitrogen

Na (+) = Sodium ion

NH₃= Ammonia

P= pressure

PEM = Proton Exchange Membrane

Q= flow rate

SIP= Japanese Strategic Innovation Promotion Program

SO₄= Sulfate ion

SQM= Square Meters (m²)

T= Temperature

TRL= Technology Readiness Levels

V_{rev}= Reversible cell voltage

Process units: shall be named with the corresponding initial followed by a number according to the order of appearance in the flowchart:

- C= Compressor
- DESAL= Desalination Plant
- F= Flash
- HX= Heat Exchanger
- M= Mixer
- P= Pump
- R= Reactor
- SEP= Separator
- SPLIT= Splitter

Streams: the streams will be named according to the equipment from which they come; they will be named in the following way:

S (equipment name)-number (according to order of occurrence), example:

Out stream of compressor C1 would be: C1-1

1 INTRODUCTION

1.1 CONTEXT

1.1.1 Renewable fuels

It is globally known that emissions of greenhouse gases are increasing every year and fossil fuels have great impact in this phenomenon. For this reason, many countries have set out to reduce the emissions of CO₂ within the next years by decreasing the use of conventional fuels, which leave a big carbon footprint in our atmosphere. There exists also a large list of countries which depend directly on external markets to obtain products needed in the usage of fossil fuels, such as natural gas or petroleum and this entails import costs.

For these two reasons the world is experiencing a significant increase in research and development activities related to alternative fuels industry. In this context, emerging technologies that enable their obtaining and, therefore, increase their technical-economic feasibility, play an important and active role at industrial level.

At the moment many projects in search of new energy carriers can be find, defined as substances or phenomenon which contain energy that can be later converted to other forms such as mechanical work or heat (ISO 13600). A clear example of a conventional energy carrier is natural gas, which can be easily stored and afterwards it can be burnt to release energy.

As said, many development projects have settled the goal of substituting fossil fuels for other clean and renewable energy sources. Some examples of renewable fuels being investigated are hydrogen, ammonia, methanol, liquid biomethane or synthetic diesel (Sea of innovation Cantabria Cluster, 2021). Even though these are some of the most encouraging alternatives to fossil fuels, many materials and processes are being investigated and all indications are that this activity will continue to increase, showing results within the next years.

Table 1 (Sea of innovation Cantabria Cluster, 2021) shows a comparative chart between the renewable fuels above mentioned and their properties including a qualitative weighting according to the quality of each property (green=good, yellow=acceptable, red=bad).

Table 1. Renewable fuels properties

	Hydrogen	Ammonia	Methanol	Liquid biomethane	Synthetic diesel
Boiling temperature (°C)	-253	-33	65	-162	200-385
Energy density (MJ/L)	8,5	12,7	15,5	20,3	36
CO ₂ emissions (kgCO ₂ /GJ)	0	0	36-46	56	17-109
Cost (€/MWh)	110-200	70-150	120-680	60-140	130-770

Allocation of points according to the quality of the properties (2=good, 1=acceptable, 0=bad) leads to compare the five fuels in general terms and obtain a preliminary ranking as shown in Table 2.

Table 2. Renewable fuels ranking

	Points
Hydrogen	3
Ammonia	5
Methanol	4
Liquid biomethane	3
Synthetic diesel	4

According to the ranking, ammonia seems to be the best option as a renewable fuel; in addition, it doesn't present any problematic property, which makes it an easy working and transporting component.

1.1.2 Marine transport fuels

Exhaust emissions from vessels have increasingly attracted attention in the continuously growing marine transport world trade market. Although shipping has proven to be the most energy efficient mode for mass transport, according to the International Maritime Organization (IMO), emissions from ship engines are harmful to the environment at both regional and global scales (Estimation of Vessel Emissions Inventory in Qingdao, 2018). For this reason, different ways of reducing vessel’s emissions are being investigated and one the most promising solution is the substitution of conventional fuels for renewable options such as the ones mentioned in [chapter 1.1.1](#) of the present work.

When comparing ammonia to other renewable fuel options, this component is considered a balanced solution. Ammonia has a significant higher volumetric energy and has far more practical storage conditions, considering pressure and temperature in comparison to liquid hydrogen. Furthermore, ammonia requires clearly less energy for renewable synthetic production than carbon carriers. These are the main reasons to further investigate the potential of ammonia as a marine fuel (Vries, 2019).

In addition, according to a study made by the Japanese shipping line “NYK Line”, one of the biggest transport companies in the world, in the short term will be able to use electric batteries for small boats, hydrogen fuel cells in medium-sized ships sailing in relatively near-shore waters and ammonia is postulated as the main fuel for transoceanic vessels such as container ships, RORO vessels (roll on roll off) or passenger ships, as shown in Figure 1 (Hydrogen solutions for ocean-going vessels, 2020).

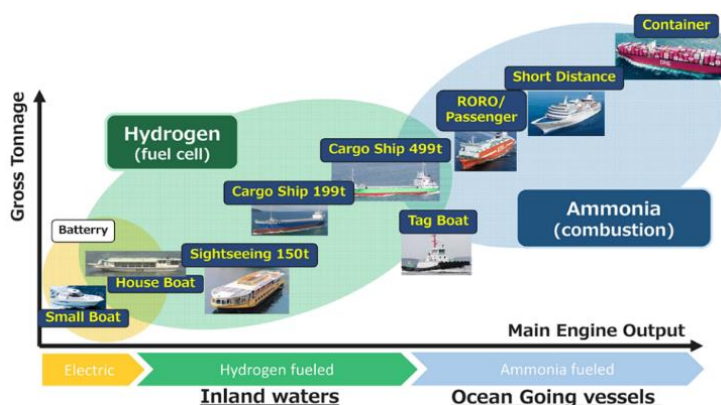


Figure 1. Renewable fuels in maritime transport

The difference in the use of hydrogen and ammonia is mainly reflected in the storage and transport capacity of both fuels. A comparison between these two energy vectors, showed in Table 3, summarize the results of NYK Line’s study.

Table 3. Comparison of Hydrogen and Ammonia

Hydrogen	Ammonia
✓ Raw material for industry.	✓ Raw material for industry and fertilizer production.
✓ Fuel for rolling vehicles.	✓ Main fuel for ships in 2050 according to IMO
✓ Electricity is produced by means of a combustion cell.	✓ Electricity produced by ammonia stacks or ammonia combustion.
✗ It is a difficult gas to store and transport.	✓ Possibility to convert back to hydrogen.
	✓ Easy to store and transport.

As indicated in Table 3, hydrogen is a difficult gas to store and transport. Therefore, according to NYK Line's study, such fuel will be valid for near-shore vessels making calls to the coast as they do not need to store fuel for an excessively long period of time and, therefore, refuelling can be carried out in smaller quantities.

However, when it comes to longer journeys, the amount of hydrogen to be stored is large and this requires a technology which, in its current premature state of development, includes substantial fuel losses; so, for this type of journey ammonia is the best option as it is much simpler to store.

An additional positive aspect of ammonia is that it can be used as an energy carrier in two different ways (Ammonia for power, 2018):

- By combustion in an adapted conventional engine. This is the most viable way to reconvert already built classical vessels into ammonia powered ships.
- By storing it in a fuel cell. For this option fuel cells must be developed for future vessels as they will be destined to be ammonia powered ships since their construction.

In this context, ammonia it is assumed as the near future best option for maritime long-distance transportation and for that reason, its production way and adaptation to this specific industry to the new energetic sources is analysed in the present work.

1.1.3 Floating energy production systems

In the last decade, technology in the floating device sector has grown rapidly. This is due to the growing energy race in the offshore wind sub-sector, which has been focusing on the development and installation of floating windmills instead of conventional windmills, which has led to the improvement of anchoring and flotation systems that can be used for windmills but also for any type of floating device.

On the one hand, most marine windmills nowadays are attached to the seabed as these designs have been implemented since the beginnings of the industry as they use technologies implemented in inland windmills (monopile, gravity base, Jacket or Tripod). This type of structures has been designed for many years and for that reason is optimized and has many available data. The disadvantage they present is that they are limited to depths above 65 meters as its cost rises exponentially for facilities in deeper areas.

On the other hand, floating devices are an alternative to this problem. Although its installation cost is still high, the development of this technology will enable windmills growth as they can be far from the coast where they have plenty of space and do not disturb the landscape. Some examples of floating devices are SPAR Buoy, Tension Leg Platform (TLP), Barge Floater and Semi-submersible platforms.

As mentioned before this technology can be used for any floating device such as platforms, ports, and artificial islands.

1.1.4 Bahia H2 offshore project

Cantabria aims to become one of the main regions in the development of green ammonia technology and therefore is committed to the innovative project "Bahía H2 offshore", a green ammonia small-scale production plant, encouraging the involvement of companies from different industrial sectors in the region (<https://www.aeh2.org/bahia-h2-el-proyecto-con-el-que-cantabria-quiere-obtener-hidrogeno-verde-en-el-mar/>).

The challenge of this project lies not only in designing an energy self-sufficient plant, but also in being a floating marine device, which increases its design complexity due to factors such as waves or corrosion inherent to the marine environment. In addition,

to obtain a completely clean device, a thorough study of the process must be carried out in order to optimize its ammonia production without gas emissions.

The "Bahía H2 offshore" project is promoted by the "Sea of innovation Cantabria cluster", counts on the participation of companies such as the Port of Santander, the National Hydrogen Centre (CNH2), ARIEMA S.L., the IHCantabria and the Components Technology Centre (CTC), among others.

In summary, the prototype to be designed under "Bahía H2 offshore" project, consists of a 500kW floating photovoltaic panel generation system connected to a 25x15 meter floating platform on which equipment for the production of ammonia by means of the Haber-Bosch process is to be installed. This plant must be capable of producing around 25kg/hr. of ammonia with a purity of over 98% in a completely clean manner, i.e., without polluting gas emissions and from renewable resources.

In order to fulfil the objective, the plant shall include the following modules (Figure 2):

- Module for obtaining H₂ from seawater.
- Module for obtaining N₂ from air.
- Haber-Bosch module for the transformation of syngas into ammonia.
- Storage tanks.

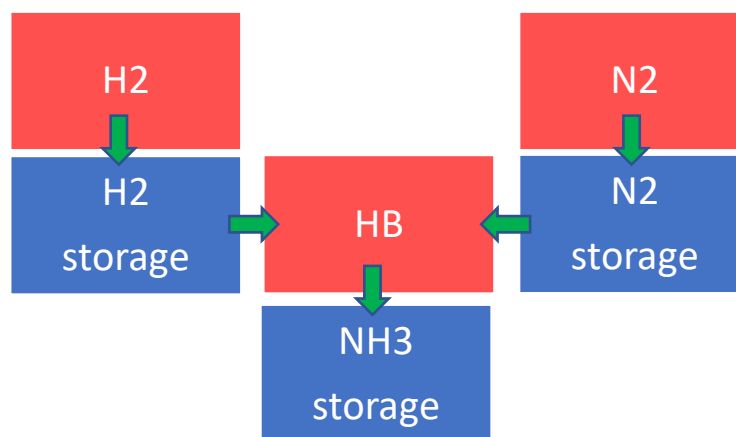


Figure 2. Modules of NH₃ manufacturing plant

The location selected for the plant is the Port of Santander (Figure 3) because it shows the following advantages:

- The bay of Santander is a sheltered place with low waves.
- It is located in one of the main logistical hubs of the region, with a third generation Port, which facilitates the transport of materials for manufacturing and the transfer of products.
- The surrounding industrial environment allows its development and continuous improvement.
- It is easily accessible for periodic inspections and maintenance.



Figure 3. Plant location

1.2 AMMONIA PRODUCTION PROCESS

Ammonia is a compound of hydrogen and nitrogen containing 17.65% by weight of H₂. It is frequently used as a fertilizer, providing nitrogen to the fields, and it is a product of great importance in agriculture. In addition, it is used as a cleaning component and in the near future it can be used as a renewable motor fuel.

Due to its many uses, ammonia is one of the most highly produced inorganic chemicals. World demand for ammonia currently exceeds 186 million metric tons per year (IFA market intelligence, 2021). The largest producer of ammonia is Asia, mainly China, which currently accounts for 27% of world production, followed by Russia (10%), the United States (9.3%) and India (8%) (Fig.4) (U.S. Geological Survey, 2021).

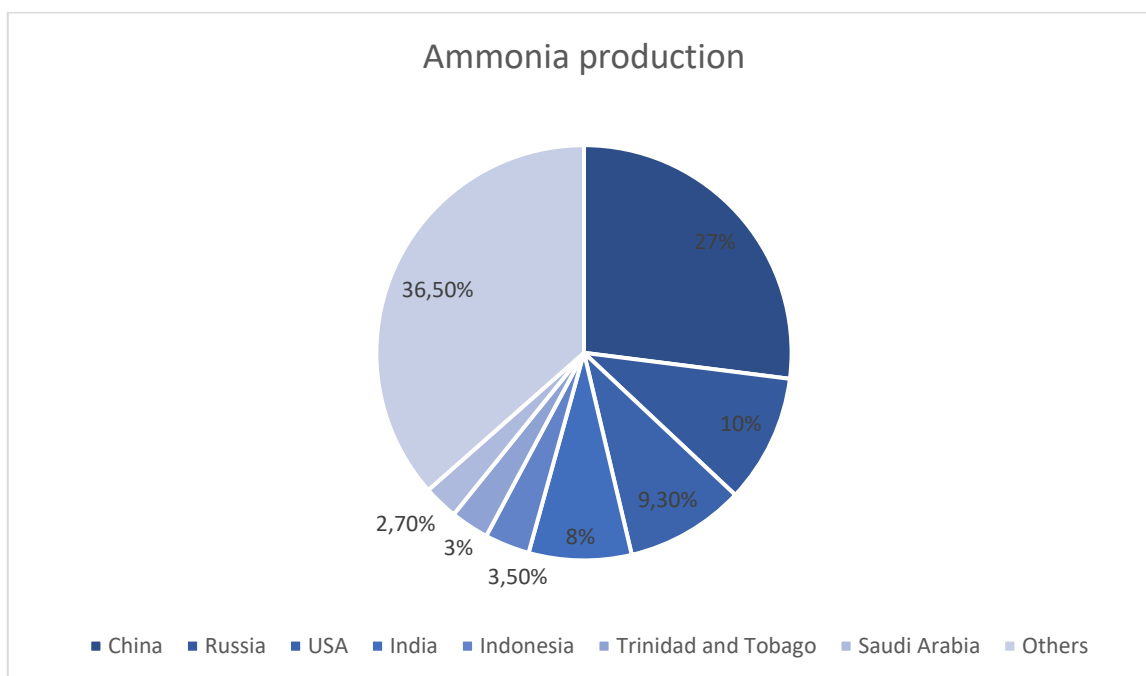


Figure 4. World ammonia production

In addition, in the coming years, the emergence of new uses for ammonia and improved manufacturing technologies are expected to boost ammonia consumption, which could reach 195 million metric tons per year by 2025 (Fig. 5)

(IFA market intelligence, 2021).

MARKET INTELLIGENCE SERVICE										
WORLD NH3 CAPACITY BY REGION IN '000 TONNES N										
REGION	WORLD NH3 CAPACITY									
	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025
West Europe	9.773	9.773	9.851	9.901	9.901	9.901	9.901	9.901	9.901	9.901
Central Europe	6.775	6.829	6.152	5.867	5.788	5.809	5.809	5.891	5.931	5.931
East Europe & Central Asia	22.828	23.843	24.565	25.608	26.097	26.354	26.434	27.141	28.085	28.250
North America	16.433	17.856	18.472	18.472	18.492	18.492	18.585	18.601	18.601	19.670
Latin America	9.653	9.980	9.911	9.896	8.952	9.292	9.292	9.292	9.292	9.307
Africa	9.368	9.368	9.368	9.368	9.622	10.871	11.495	11.857	11.857	12.215
West Asia	15.054	16.509	16.503	16.175	16.804	17.116	18.011	18.011	18.011	18.011
South Asia	17.421	18.060	18.060	18.705	18.716	19.912	21.108	21.108	21.866	22.464
East Asia	71.182	69.777	68.004	66.207	65.285	66.779	66.646	67.659	67.659	67.659
Oceania	1.838	1.838	1.838	1.838	1.838	1.838	1.841	1.841	1.846	1.846
Total World	180 323	183 832	182 723	182 037	181 495	186 364	189 122	191 303	193 050	195 254

July 2021

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Figure 5. World NH3 capacity by region

Most of the ammonia (80%) is used in the manufacture of fertilizers (Figure 6), and its main applications are (Yapicioglu, et al., 2019):

- Ammonium nitrate
- Ammonium salts
- Urea
- Explosives manufacturing
- Caprolactam, nylon
- Polyurethanes
- Cryogenic gas
- Domestic cleaning products

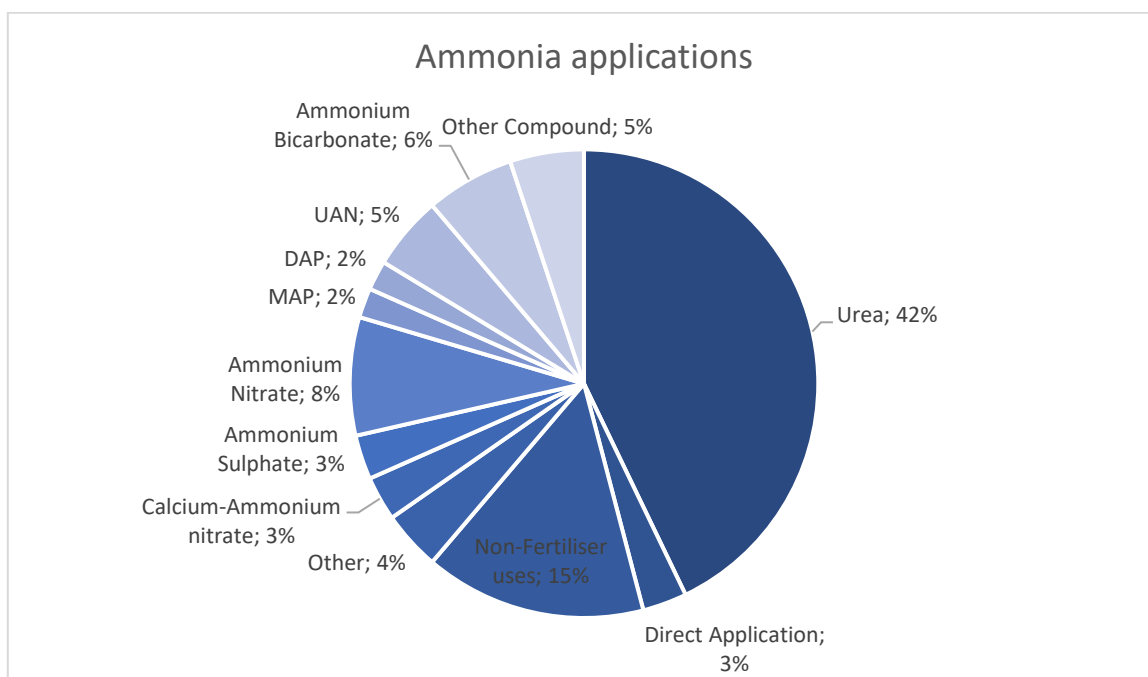


Figure 6. Ammonia applications

Due to the great importance of this product, since the beginning of the 20th century, improvements have been developed and the efficiency of its production technology has been increased, mainly the Haber-Bosch process, considered one of the greatest technological advances of the industrial era. The Haber-Bosch process has become so important that currently 90% of the ammonia produced globally is obtained in this way.

The process was initially patented by the physic-chemist Fritz Haber. In 1910 Carl Bosch, working for the chemical company BASF, succeeded in commercializing the process. Both Haber and Bosch were awarded the Nobel Prize in 1918 and 1931 respectively for overcoming the chemical and engineering problems posed by the use of large-scale, high-pressure technologies.

We must bear in mind that in today's market ammonia production plants are of industrial size and seek the highest possible production in order to gain advantage from the economy of scale, so advances in this technology have not focused on optimizing the size of the plants. However, process intensification appears last years as a promising research area that can fulfil the objectives of an offshore ammonia production.

The main technologies and projects driving the growth of this process, as well as the introduction of alternative NH_3 production technologies, will be briefly described below.

1.2.1 Ammonia production routes

Meanwhile the Nitrogen to produce ammonia is obtained by Air Separation Units (ASU), the main difference in the way of obtaining ammonia lies in the way of obtaining the hydrogen for its synthesis (Yapicioglu, et al., 2019):

- Reforming: when the raw material is natural gas or naphtha, the way to obtain ammonia is by reforming the hydrocarbons to extract hydrogen.
- Partial oxidation: the raw material used can be heavy hydrocarbons or coal.
- By product Hydrogen: hydrogen-rich gas, which is a by-product of some other process, is introduced directly.
- Electrolytic route: hydrogen is obtained by water electrolysis.
- Biological route: ammonia is obtained by conversion of biological products.

The use of natural gas as a power source has been growing over the years, while the use of naphtha and other petroleum products has been decreasing. (Kirk-Otmer, 2000)

Different ways of obtaining ammonia are shown in the block diagram below (Figure 7):

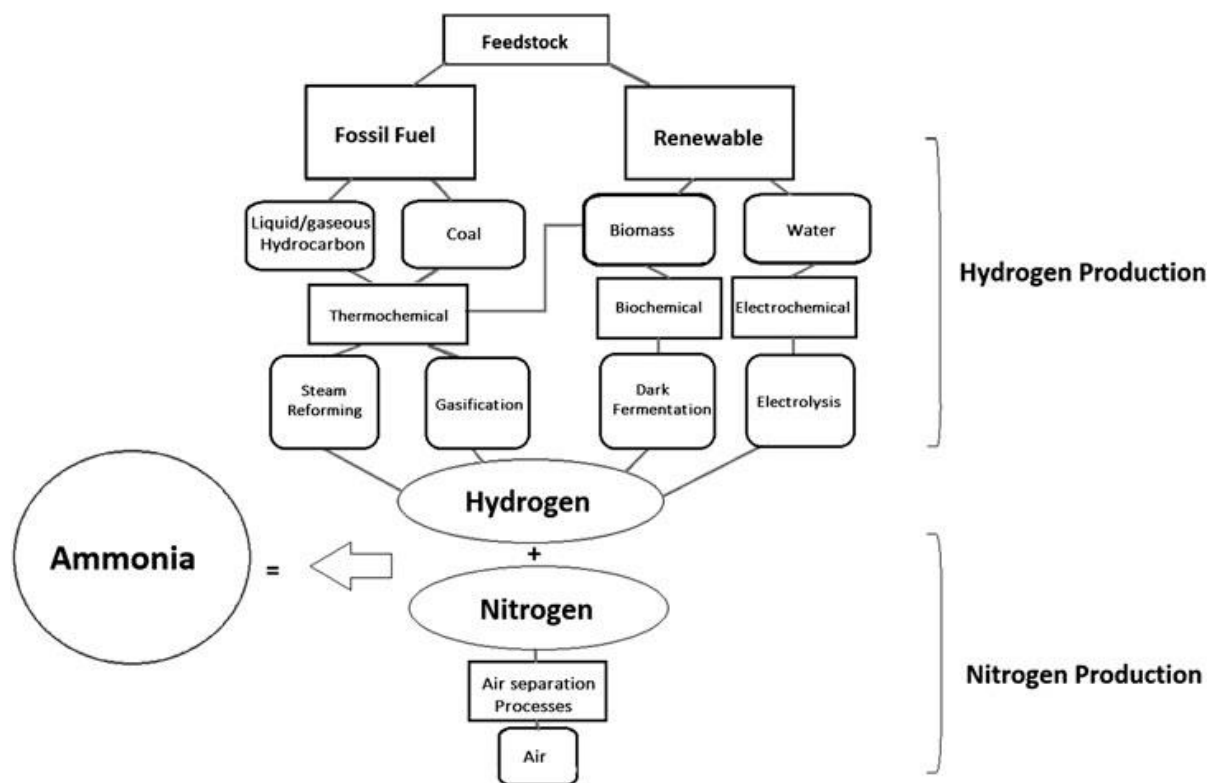


Figure 7. Ammonia production routes

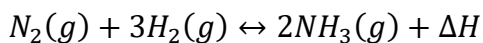
1.2.2 Conventional Haber Bosch process

Since the beginning of the 20th century, the most industrially used and efficient practice for obtaining ammonia has been the production of hydrogen by hydrocarbon reforming.

While it is true that this process is highly effective and produces large amounts of hydrogen, natural gas is a fossil fuel whose combustion results in a large amount of CO₂ emissions into the atmosphere.

In addition, since these plants are supplied with natural gas, they are totally dependent on this resource and its supply, so their installation is limited only to onshore sites with a natural gas distribution network.

The process itself consists of obtaining ammonia (NH₃) from nitrogen (N₂) and hydrogen (H₂) both in gaseous state, by means of the following reversible exothermic reaction:



In general terms, this reaction is characterized by being very slow, so it is carried out over a catalyst (commonly iron, Fe^{3+}); it also takes place under conditions of about 300 bar of pressure and a temperature of approximately $400^{\circ}C$ which avoid to reach a yield of about 20%, being mandatory a recycle loop in order to obtain industrially feasible global conversions.

Regarding the adaptation of the Haber-Bosch process to the desired size in this project, it must be initially considered that the design criteria for small plants are very different from those of large-scale ammonia production plants. For such small plants, the economic factor is more critical while the technical and operational factor is less important. This will be reflected in the process design, which will try to minimize the number of components, apply standardized equipment and design modules that minimize plant construction work.

1.2.3 Sustainable ammonia by Haber Bosch

In recent years, restrictions on pollutant gas emissions and new environmental policies have encouraged new ways of obtaining hydrogen in a clean way, based on the use of renewable resources and the design of process without emissions.

In this way, numerous advances have been made in obtaining hydrogen by alternative ways. The main options currently available are shown in Table 4, including energy inputs, technology based a short description and the associate TRL (Sustainable Ammonia Production, 2021)

Table 4. A brief description of various hydrogen production processes (Adapted from Wijers, 2011; Acar and Dincer, 2018)

Main energy inputs	Technologies	Brief description	TRL
Electrical	Water electrolysis	-Direct stream is applied in order to split water into hydrogen and oxygen.	Large
	CH4 assisted-Solid Oxide Fuel Electrolysis Cell (SOFEC)/ Natural Gas Assisted Steam Electrolysis (NGASE)	- The entire process of an CH4 assisted -SOFEC is based on substituting high value electricity with cheaper methane. In the CH4 assisted-SOFEC, methane is added to the anode side of the electrolyzer, the decomposition potential (voltage) of water is decreased, and this results in a lower energy	Medium/ small

	Plasma arc decomposition	usage and higher conversion ratio of electricity for hydrogen production. - Purified natural gas (without H ₂ S, CO ₂ , H ₂ O, etc.) is passed throughout the plasma arc in order to produce hydrogen and carbon soot.	Large
Electrical and thermal	High Temperature Electrolysis (HTE)	- Both electrical and thermal energy are utilized in order to initiate, water splitting for hydrogen production.	Large
	Hybrid thermochemical cycles	- Both electrical and thermal energy are utilized in cyclical reactions	Medium
Thermochemical	Coal Gasification	- Conversion of coal through, thermochemical process into syngas.	Large
	Fossil fuel reforming	- Fossil fuels are converted into hydrogen and carbon dioxide.	Large
	Thermolysis	- Thermal decomposition of steam at temperatures higher than 2,226.85°C.	Large
	Thermochemical processes	-Cyclic reactions (net reaction: water splitting into hydrogen) -Thermo-catalytic conversion -Biomass conversion into Hydrogen	Large
Photonic	Photo-electrochemical cells (PEC)	- A hybrid cell which generates voltage and current through absorption of light simultaneously.	Small
	Artificial photosynthesis	- Mimicking photosynthesis process for hydrogen production	Small
	Photo-catalysis	- Direct water splitting via photo-catalyst.	Small
Photonic and biochemical	Bio-photolysis	-Biological processes (microbes/bacteria, etc.) through which water dissociates into hydrogen and oxygen in the presence of light.	Small
Biochemical	Dark fermentation	- Biological processes are utilized for hydrogen production in the absence of light.	Small
	Photo-fermentation	- Fermentation process initiates through exposure to light.	Small

Among the technologies mentioned, the most widely used for sustainable hydrogen production is water electrolysis, supported by renewable technologies such as solar or wind energy.

Proton Exchange Membrane (PEM) electrolysis creates a reaction using an ionically conductive solid polymer, rather than a liquid. When voltage is applied between two electrodes, negatively charged oxygen in the water molecules gives its electron, resulting in protons, electrons, and O₂ at the anode.

The H⁺ ions travel through the proton-conducting polymer towards the cathode, where they take an electron and become neutral H atoms. These combine to make H₂ at the cathode. The electrolyte and two electrodes are sandwiched between two bipolar plates, which transport water to them, transport product gases away from the cell, conduct electricity, and circulate a coolant fluid to cool down the process.

1.2.4 Alternatives to the Haber Bosch process

Electrochemical processes

This type of processes can be divided into three major groups based on the temperatures of the electrochemical cells: low temperature (<100°C), medium temperature (100-400°C) and high temperatures (400-750°C). The advantages of this type of process with respect to the Haber Bosch process are mainly the next four (FUTURE OF AMMONIA PRODUCTION:, 2017):

- Higher efficiency allowing energy savings.
- Lower purity required.
- Lower temperatures and pressures.
- They are modular, which allows their use in small and medium-sized plants.

Non-thermal plasma synthesis

This alternative has the advantage of operating at temperatures around 50°C and atmospheric pressure conditions. This solves some of the problems posed by HB since the reduction of these conditions has a direct impact on the cost of energy and fossil fuels. However, it comprises two challenges yet to be developed (A review on the non-thermal plasma-assisted ammonia synthesis, 2018).

- Nitrogen gas fixation

- Reverse reactions

In addition, the state of conversion and efficiency still needs to be advanced, so it is in the small and medium scale development phase.

Functional catalyst with nitrogenase motivated peptide

Ammonia is produced in nature by nitrogenase enzymes with an efficiency of about 75%. Since this percentage is very high, it is intended to use these enzymes for the industrial production of NH_3 . This type of ammonia synthesis is very promising but its low temperatures and working pressures present an efficiency of less than 1%, which requires catalysts to improve this efficiency (Renner, et al., 2020).

On the other hand, peptide functional catalyst has been developed and tested in anion exchange-based systems. The materials used for such a catalyst show promising results compared to conventional catalysts.

1.2.5 Discussion of the selected technology

In accordance with the previous description, different alternatives exist to carry out a complete and reliable process of ammonia synthesis being necessary to select the best one in order to suits the proposed project.

First of all, it is necessary to choose the source of the raw materials to convert them into ammonia. Considering only raw materials obtained in a renewable way and whose processing does not emit polluting gases, reforming and partial oxidation processes would be discarded. Although both of them are very efficient ways of NH_3 production, the environmental requirements of the project make them discarded.

The process to be carried out is then selected under qualitative and subjective comparing different factors that influence production. Based on different articles, research and reports, using the same weighting technique as in Table 1 and Table 2: (green=good (2 points), yellow=acceptable (1 point), red=bad (0 points)) results are obtained in Table 5 and 6:

Table 5. Ammonia production comparison

	Efficiency	Cost	P & T conditions	TRL
Haber-Bosch	Green	Green	Red	Green
Electrochemical processes	Green	Red	Green	Yellow
Non-thermal plasma synthesis	Red	Green	Green	Red
Functional catalyst with nitrogenase motivated peptide	Green	Red	Green	Red

Table 6. Production technologies ranking

	Points
Haber-Bosch	6
Electrochemical processes	5
Non-thermal plasma synthesis	4
Functional catalyst with nitrogenase motivated peptide	4

Once the process to be used has been decided (Haber-Bosch) it is necessary to determine which technology from Table 4 would be used as the hydrogen source. As mentioned above, water electrolysis remains the most viable option due to its TRL, cost and widely investigated and improved technology among the years.

At that point, the technology selected for the whole plant in the present project, as it is specified in the project objective (section 1.4), will be a Haber Bosch process obtaining H₂ from water by electrolysis and N₂ from air in an air separation unit (ASU) (Figure 8).

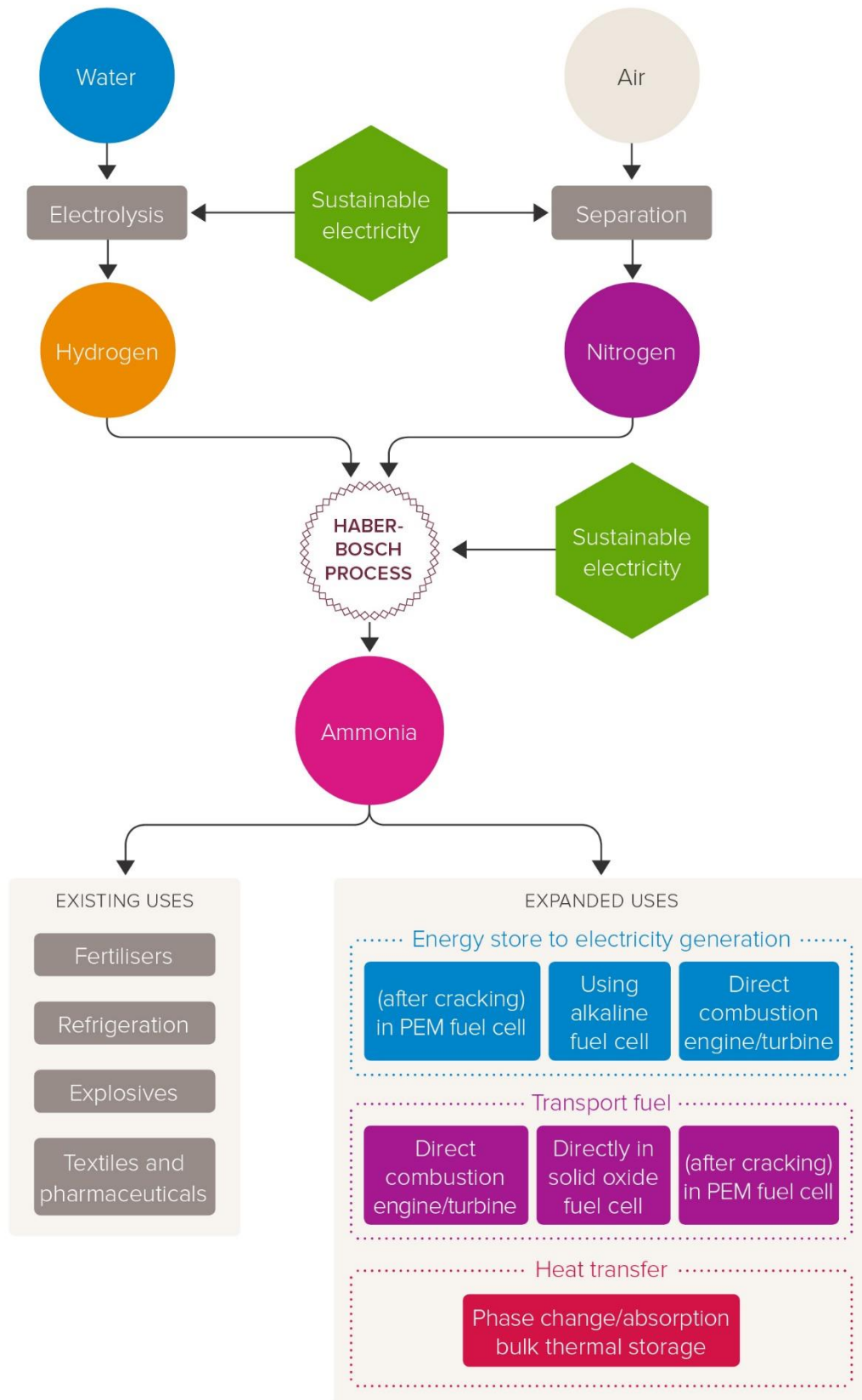


Figure 8. Ammonia production steps and uses

1.3. SMALL SCALE HABER BOSCH PLANTS AND PROJECTS USING RENEWABLE ENERGY

Manufacturing their own ammonia production plant has many advantages, especially in this case where it is a research and development project. However, it is important to know the state of the art of similar technologies, either to take advantage of its strengths for the actual project benefit or to consider the weakest points of the process in order to avoid problems or possible mistakes.

For this reason, a study of the current market and the development of similar projects has been carried out, analysing their different characteristics in order to get a global knowledge of the scope and limitations of this project.

The following are some of the small ammonia plants available on the market as well as the most promising projects for the future of the sector.

1.3.1 Proton ventures

Proton Ventures offers the possibility of manufacturing small scale ammonia plants with the named NFUEL units (Figure 10). The electricity used for this plant can come from renewable sources such as solar turbines or photovoltaic panels. This new concept allows the production of sustainable ammonia for subsequent use as fertilizer, energy carrier or fuel. (Proton Ventures, 2021).

Currently they have designed NFUEL units to produce 120kg/h NH₃ (Solar to Ammonia – via Proton's NFuel units, 2014). As can be seen in Figure 10, the unit is divided into skids that fit into 40-foot containers, which greatly facilitates transportation and logistics. Each of these skids is fully automated, remotely operated and guarantees technical integrity.

Figure 9 shows the NFUEL unit next to a wind farm, but it could also be accompanied by a photovoltaic farm or any type of energy source that allows obtaining hydrogen by electrolysis.

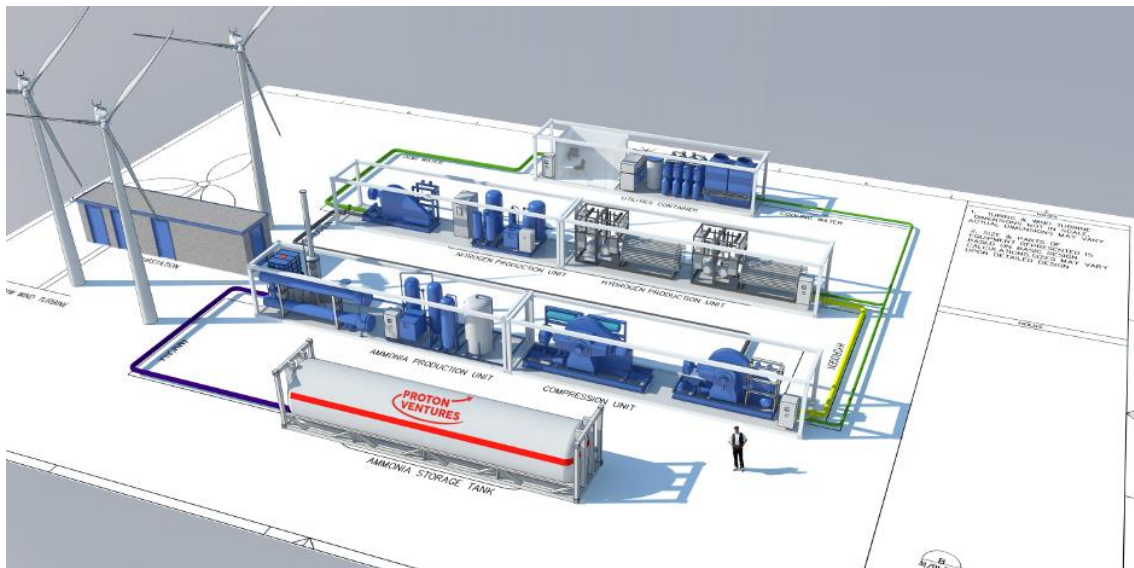


Figure 9. Proton Ventures NFUEL

The following are some of the plant's main properties:

- NFUEL units are powered by electricity from renewable energy sources and are designed to withstand rapid power fluctuations.
- Labour costs are minimal due to remote monitoring and control of the unit via a secure wireless connection.
- According to the company, NH₃ production including compressors and reactors can operate efficiently for more than 30 years. Electrolyzer and nitrogen production systems have a lifetime of around 20 years, but this can be extended by proper operation and maintenance of the system.
- All equipment operating at high pressures in the ammonia synthesis loop is designed and built to withstand fatigue due to pressurization and depressurization cycles.
- The interconnection between the different skids is designed on a site-specific basis and under the required skid layout conditions.
- The N₂, H₂ and water purification units as well as the main compression system are equipped with programmable logic controllers.
- It incorporates an emergency shutdown system into the overall control system design, along with the installation of safety valves, instrumentation and ammonia, nitrogen and hydrogen and heat detectors located at strategic points to detect any possible leaks.

- The equipment consists of the following units:
 - - Nitrogen generation skid.
 - - Hydrogen generation skid based on electrolysis.
 - - Ammonia compression skid
 - - Ammonia synthesis skid
 - - Ammonia storage tank
 - - Operations skid, control panel and motor control centre
- The service factor is 95% guaranteed and the unit's catalyst is guaranteed to last 15 years if the manufacturer's protocols are strictly followed.
- The company offers different sizes and based on these, analyses the demand and energy consumption in the market to install decentralized ammonia plants (Fig. 10).

UNIT	CAPACITY	CAPACITY	POWER CONSUMPTION
	metric ton/year	metric ton/day	Megawatt
NFUEL 1	1000	3	1,5
NFUEL 4	4000	10	5-6
NFUEL 20	20000	60	25-30

Figure 10. NFUEL size options (Proton Ventures, 2021)

1.3.2 Thyssenkrupp

According to the German company, whereas, in conventional ammonia plants, hydrogen is produced by steam reforming with natural gas, Thyssenkrupp's green ammonia concept uses AWE (Alkaline Water Electrolysis), while the nitrogen required for ammonia synthesis is produced by an air separation unit (ASU). AWE is based on the proven chlor-alkali electrolysis technology developed by Thyssenkrupp Uhde Chlorine Engineers with its EP(C) technology and execution experience gained from more than 600 plants with more than 10 GW of installed capacity worldwide.

All necessary for AWE-based green hydrogen production is energy from renewable sources and water. In addition, AWE is ideal for use in green ammonia plants, as it can be started in minutes and follows load variations in seconds (Thyssenkrupp, 2021).

Thyssenkrupp has developed two production concepts: a 50 mtpd plant based on 5 MW input power and 100% availability (Fig. 11) and a 300 mtpd production plant based on 20 MW input power (Fig. 12). As the latter approaches industrial scale, it could be an interesting refurbishment option for greening existing plants. This reduces engineering and construction costs while facilitating implementation, a fast-track solution for potential customers.



Figure 11. Thyssenkrupp 5MW

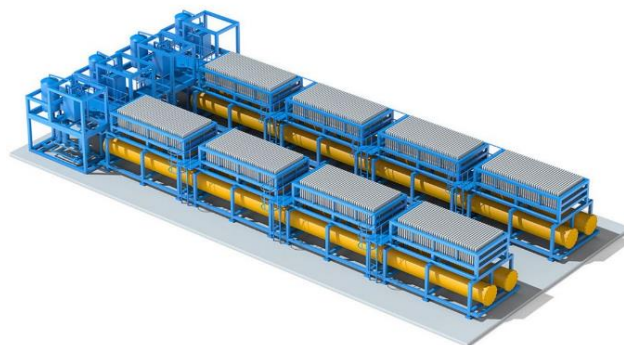


Figure 12. Thyssenkrupp 20MW

ThyssenKrupp evaluated the five key factors of feasibility:

- Capital expenditures.
- Availability and cost of renewable energy.
- Potential transportation constraints.
- The cost of ammonia.
- CO₂ emission restrictions and taxes.

The conclusion was that in landlocked locations with low energy costs, the installation of a green ammonia plant may be an interesting option, especially for the chemical or fertilizer industry. Not surprisingly, economies of scale favour conventional plants with higher production capacities. But in addition to its economically viable existence as a niche product, green ammonia is becoming increasingly interesting for renewable energy producers as a suitable energy carrier and storage medium.

1.3.3 JGC Holdings

Under the theme of “Development of ammonia synthesis from CO₂-free hydrogen” from the Japanese Strategic Innovation Promotion Program (SIP) “Energy Carriers”, JGC Holdings corporation is developing an advanced ammonia synthesis process using renewable energy, such as photovoltaic and wind turbine power generation, to be able to produce “Green” ammonia, aiming to contribute to a low-carbon society. (Demonstration of CO₂-Free Ammonia Synthesis Using Renewable Energy-Generated Hydrogen, 2018) .

Also, utilizing the catalysts developed by the Japanese National Institute of Advanced Industrial Science and Technology (AIST), National Institute of Technology Numazu College and JGC designed and constructed an ammonia synthesis demonstration plant in FREA, the Fukushima Renewable Energy Institute. From April 2018, the plant started operation to evaluate the performance of the developed catalysts and acquire the engineering data for scaling up in the future.

JGC’s plant was constructed according to the flowsheet in Figure 13. Figures 14 and 15 shows the plant working under the specified properties related in (Demonstration of CO₂-Free Ammonia Synthesis Using Renewable Energy-Generated Hydrogen, 2018):

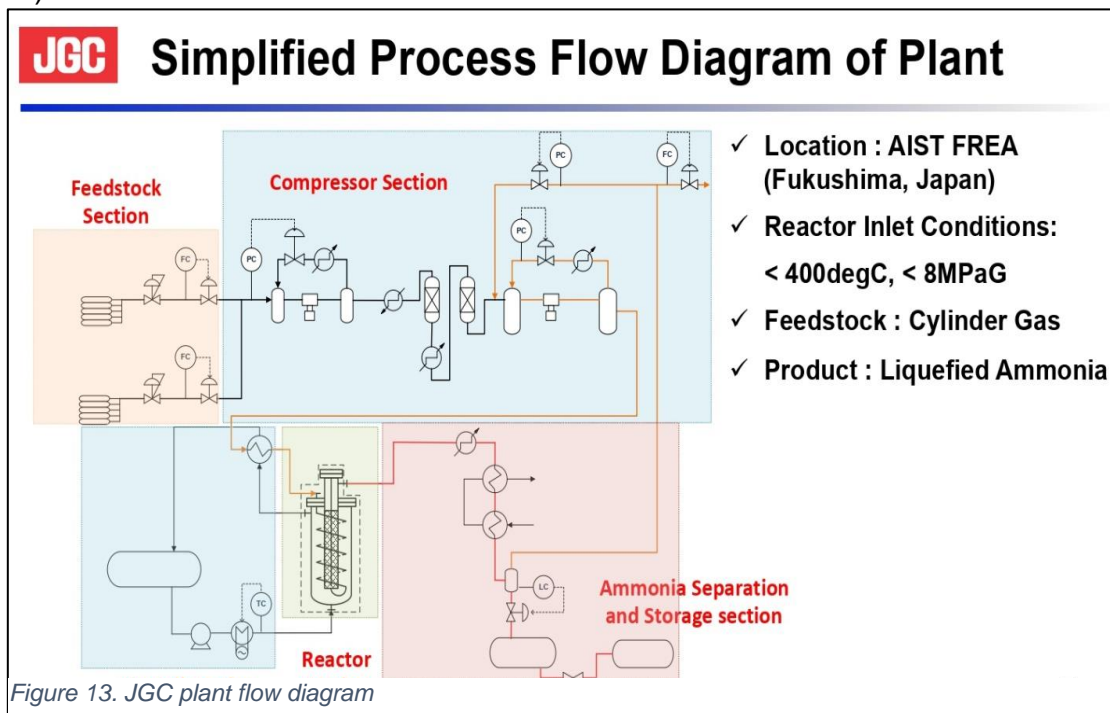


Figure 13. JGC plant flow diagram

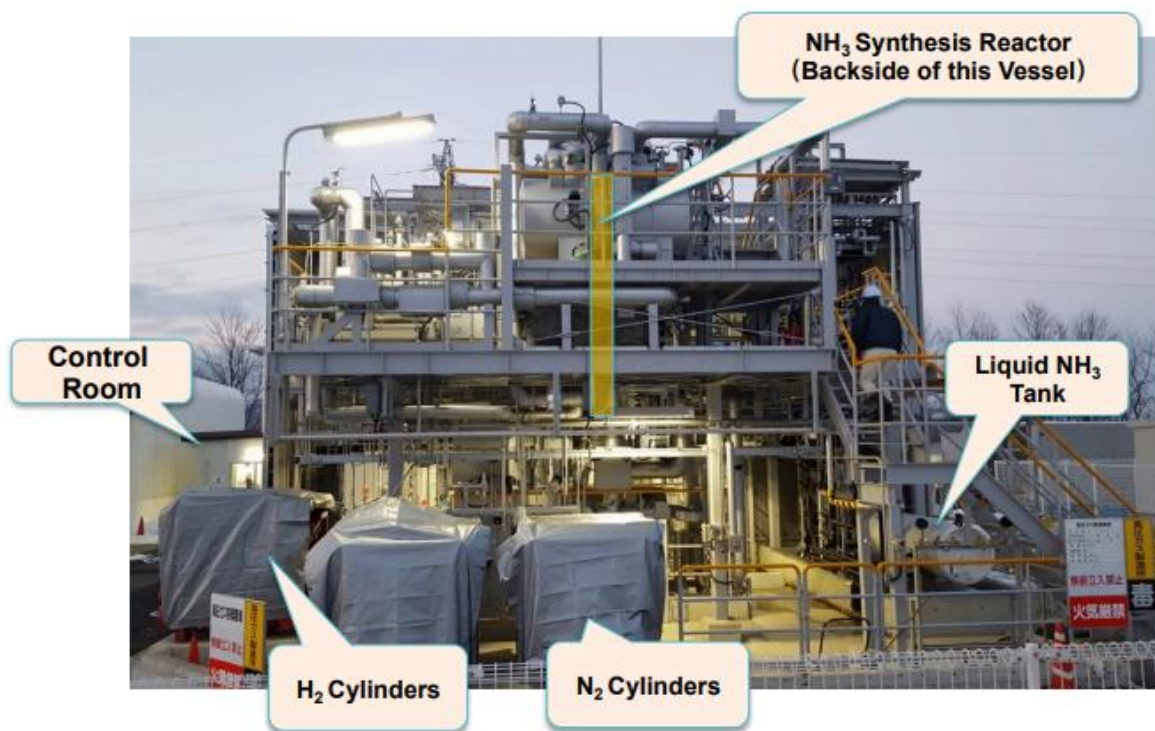


Figure 14. JGC plant



Figure 15. JGC plant

With this project launched in 2018, JGC aims to contribute to decarbonisation and to improve the energy supply chain.

1.3.4 Siemens

Following the steps of JCG, in June 2018 Siemens launched operations at its Green Ammonia Demonstrator, at the Rutherford Appleton Laboratory outside Oxford in the UK. Its aim is to provide insights into the business case for ammonia as a market-flexible energy storage vector (Green ammonia pilot plants now running, in Oxford and Fukushima, 2018).

The Siemens demonstrator includes not only storage assets but also combustion assets: an internal combustion engine adapted to generate electricity using ammonia as a fuel. The main objective of the plant is to evaluate an all-electric synthesis and energy storage demonstration system based on Green Ammonia.

Figures 16 and 17 show a scheme of the plant itself and its installation site (Hablutzel, 2019).

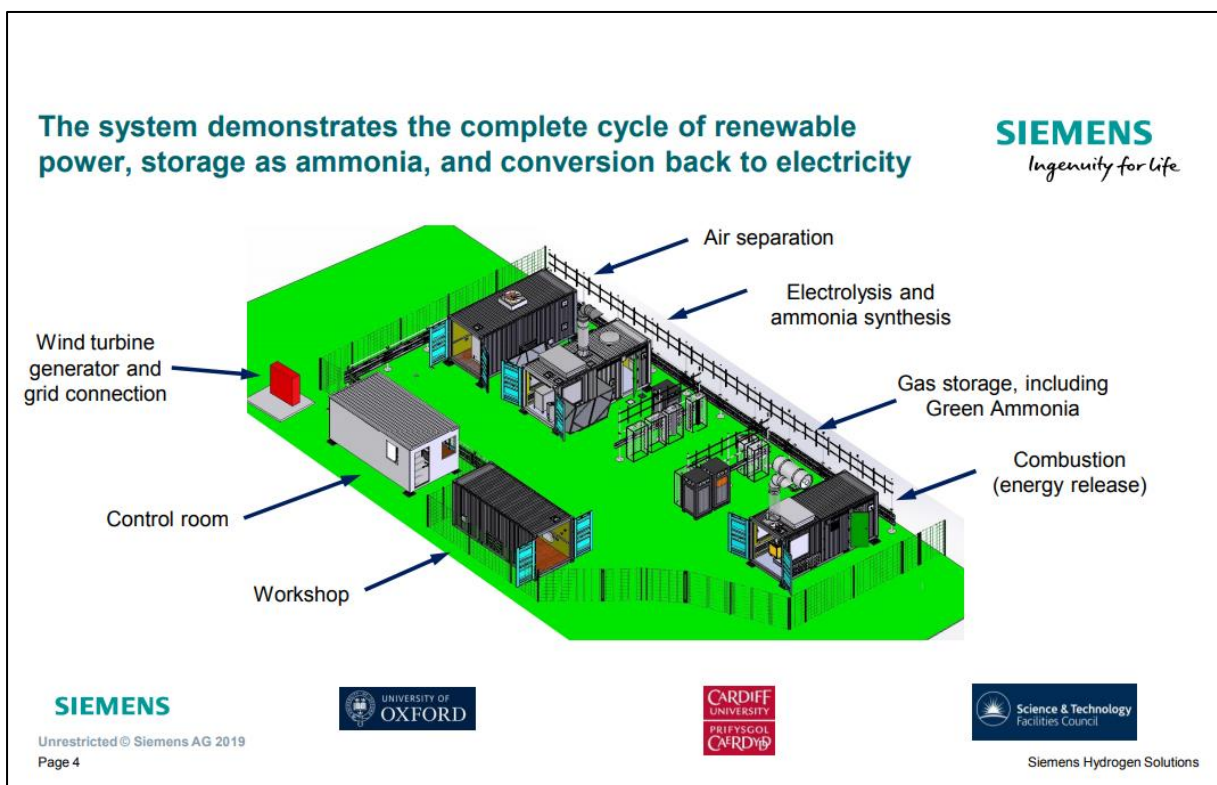


Figure 16. Siemens plant scheme



Figure 17. Siemens plant

When it comes to logistics, Siemens's plant distribution looks similar to the Proton Ventures skids and differ from JCG or Thyssenkrupp's plants which are more compact and static (Figures 15-16).

According to Siemens, the main components of this plant are the following:

- 20kW wind turbine.
- 13kW Electrolyzer, producing approx. 2.4 Nm³ /hr H₂.
- 7kW ASU (pressure-swing absorption) producing 9 Nm³ /hr N₂.
- 30kg / day Haber-Bosch synthesis capacity for NH₃ (output limited by H₂ production capacity).
- 350kg on-site NH₃ storage.
- 30kWe Generator set (reciprocating spark-ignition engine) running on ammonia.
- Siemens PCS7 Control system for unattended operation.

1.3.5 University of Minnesota

In 2013, a pilot plant was built using electricity from a utility-scale wind turbine to produce hydrogen by electrolyzing water, nitrogen is separated from air, and then these gases are combined to produce anhydrous ammonia (Figure 18).



Figure 18. Minnesota West Central Research and Outreach Centre

According to the University of Minnesota, “we envision a sustainable energy and agriculture system in which local production facilities use wind energy to produce ammonia. The ammonia is then used as fertilizer and fuel. Compared to other energy storage, ammonia is flexible and has many potential uses. Local smart-grids and utilities can use ammonia to provide short- and long-term storage to backup intermittent wind and solar generation. Farmers can produce wind-generated ammonia to significantly reduce the carbon footprint of their products” (Reese, 2020)

1.4 OBJECTIVE

This project focuses on the green production of ammonia and its use as an alternative fuel, a field of research that is gaining increasing interest. The aim of this project is to develop an ammonia production plant that can be installed on a floating platform, powered by solar panels, which produces ammonia using the Haber-Bosch process and use this product to power cargo ships in a way that is totally free of polluting emissions: obtaining hydrogen through the electrolysis of seawater and nitrogen from the separation of air. In this context, this degree final project consists of the preliminary design, by means of the process simulation in ASPEN Plus, of the equipment necessary to obtain ammonia in the aforementioned way.

Specific objectives

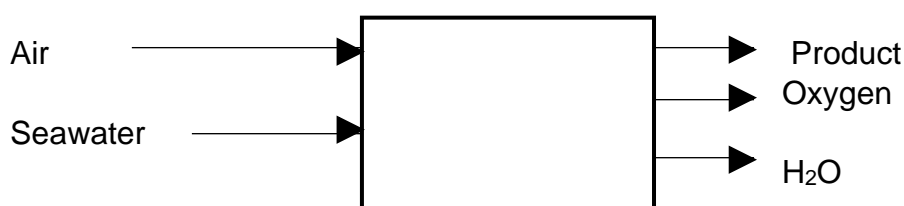
- Analyse the small-scale Haber Bosch state of art.
- Design a plant capable of producing 25kg/h of ammonia with a purity of 98%.
- Specify dimensions of the plant.
- Make a preliminary cost estimation.

2 DESIGN SPECIFICATIONS

This section shows the design specifications related to the process, energy and raw materials surplus and characteristics and the final product properties. The different subsystems or stages of electrolysis, air separation and ammonia synthesis are showed with a process flow diagram which includes material and main process conditions as well as relevant process specifications obtained from previous literature.

2.1 RAW MATERIALS AND PRODUCTS

- Haber Bosch process with the next overall input-output diagram



- Raw materials and products: based on conditions of the port of Santander and product requirements for its future use (Table 7).

Table 7. Raw materials and products specifications

	Seawater	Air	Ammonia
T (°C)	16.5	13.8	
P (bar)		1	
Q (kg/h)			25
Composition (%)			
H ₂ O	96.4		1
Cl (-)	1.98		
Na (+)	1.1		
SO ₄	0.276		
Mg	0.13		
Ca	0.04		
K	0.04		
O ₂		21	0.5
N ₂		78.05	
Ar		0.95	
H ₂			0.5
NH ₃			98

- Properties. Antoine's equation (Table 8):

Table 8. Antoine's equation coefficients

	A	B	C
Nitrogen	14.93	588.72	-6.60
Hydrogen	13.63	164.90	3.19
Argon	15.23	700.51	-5.84
Ammonia	16.95	2132.50	-32.98

2.2 AIR SEPARATION UNIT

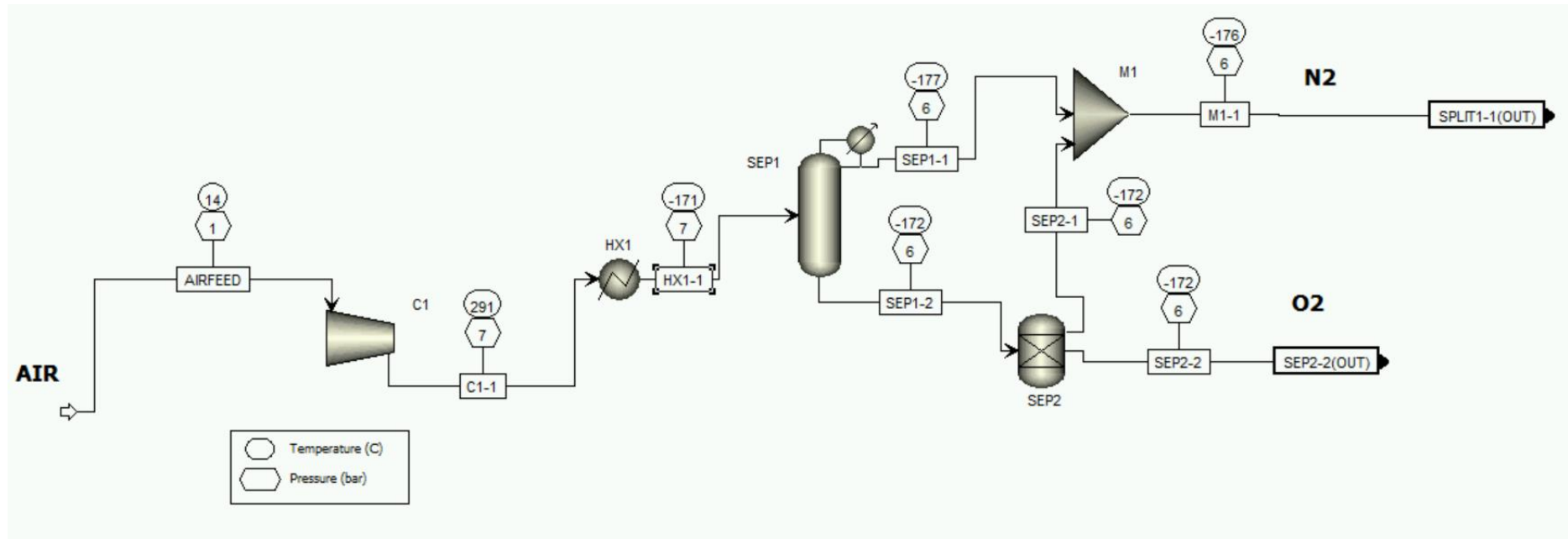


Figure 19. Air separation unit DS

- Air separators
 - Pressure= 7 bar
 - Temperature= -177°C
 - Nitrogen from air: 98%

2.3 DESALINIZATION AND WATER ELECTROLYSIS

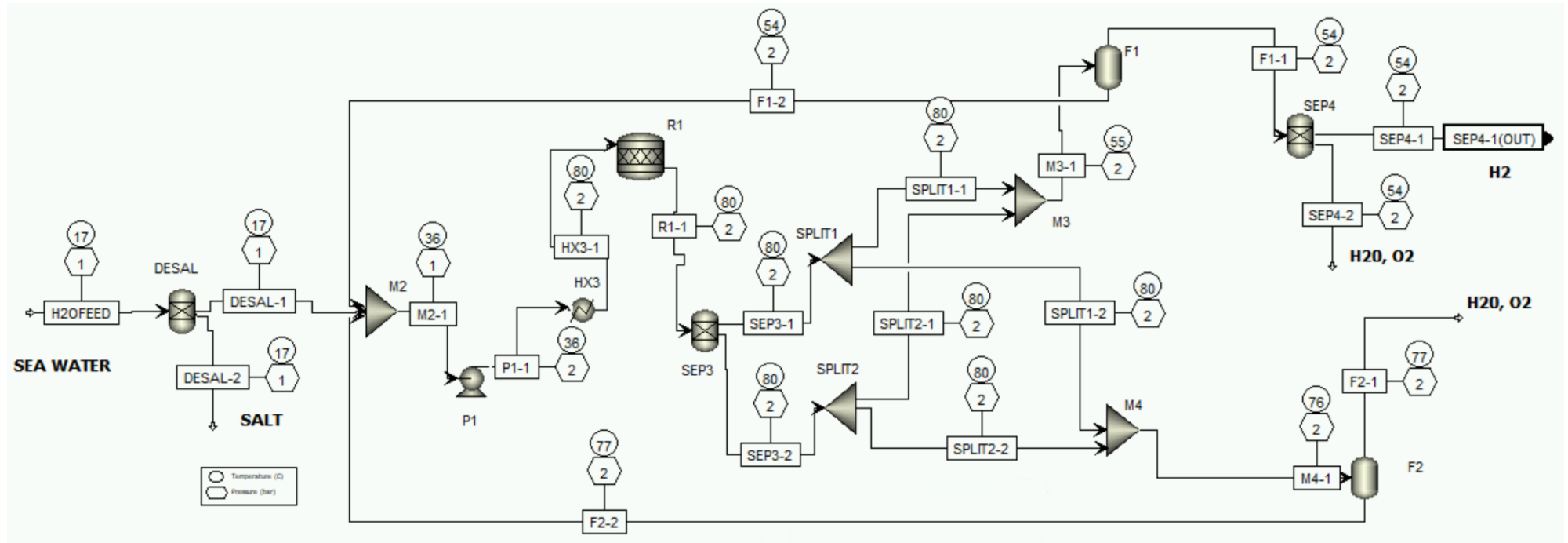
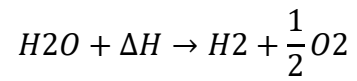


Figure 20. Desalination and water electrolysis DS

- Electrolyzer:



$$\Delta HR = \Delta GR + T\Delta SR$$

Standard conditions: $\Delta G^\circ R = 237 \text{ kJ mol}^{-1}$

$V_{rev} = \frac{\Delta GR}{zF}$ Where z is the number of electrons transferred per hydrogen molecule produced and F is the Faraday constant

2.4 AMMONIA SYNTHESIS

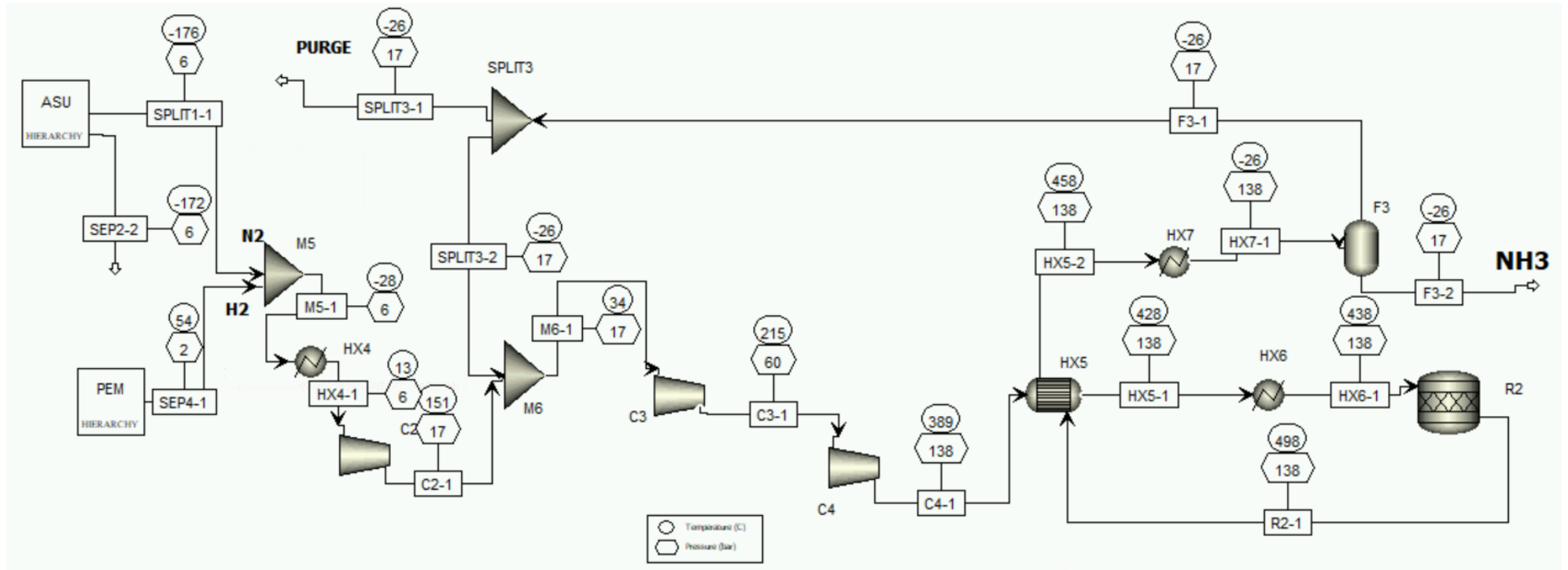
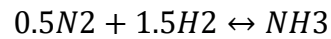


Figure 21. Ammonia synthesis DS

- Converter R2:



The ammonia production reaction has a conversion rate of $x = 0.3$

P=138 bar

T=498°C

[inert components] <12% to avoid problems in the reactor as they can affect temperatures and conversion.

- Flash F3:

T_{out}=-26°C

P_{in}= 138 bar

P_{out}=17 bar

- Separator SPLIT3:

ϵ purge= 0.1

[Inert components] <12%

3 ASPEN PLUS SIMULATION

Several authors modeled and simulated previously ammonia production plants at industrial scale using Aspen tools as Frattini et al., 2016; Lin et al., 2020; Osman et al., 2020; Verleysen et al., 2020 among others. Chehade and Dincer, 2021, proposed and developed a small modular ammonia converter by solving mass and energy balance in Matlab and Consol In the present work Aspen Plus it will be used to simulate a small ammonia plant including Nitrogen and Hydrogen obtention.

Sequential modular simulators (SMS) perform flowchart calculations in the following way:

- Executes each block of unit operations sequentially.
- Uses the output streams calculated in each block as a feed into the next block.

Flow diagrams with recirculation cycles, design specifications and optimization problems must be solved iteratively. Their solution requires:

- Choose breakthrough streams: a breakthrough stream is a circulating stream with component molar fluxes, total flux, pressure, and enthalpy determined by iterations. The breakthrough current can be any within the cycle.
- Define convergence blocks to converge breakout streams, design specifications or optimization problems. Convergence blocks determine how to update the variables for a breakthrough stream or design specification from iteration to iteration.
- Determine a sequence that includes all units and convergence blocks.

Among the possibilities offered by a process simulator, as far as convergence is concerned, the options that can be introduced by the user are, for example, the creation of different convergence blocks or the change of the order of execution of the blocks, among others.

A breakthrough stream converges when the following expression is true for all convergence variables of the breakthrough streams:

$$-tol \leq \frac{(X_{calculated} - X_{estimated})}{X_{estimated}} \leq tol$$

The default convergence variables are: total molar flux, individual molar fluxes, pressure and enthalpy.

The complexity of the simulation for the case of an ammonia production plant lies in the existence of several recycle streams, purge, different design specifications, specific thermodynamics, and high working pressures.

The simulation of the ammonia production process is then carried out with the Aspen Plus commercial simulator. As this is a complex process due to the high pressures and the need for recycling, its simulation will also be complex.

3.1 INPUT DATA

When starting the simulation, it is necessary to specify the units you are going to work with. In this case the following units were chosen due to the ease of adapting the information obtained from literature and research:

- Pressure: bar
- Temperature: degrees Celsius

Subsequently, all the components involved in the process are selected from the Aspen Plus library. The following elements were selected for this process, which are the ones that interact in the plant:

1. Hydrogen: H₂
2. Nitrogen: N₂
3. Water: H₂O
4. Ammonia: NH₃
5. Chlorine: CL-
6. Sodium: Na+
7. Sulphate: SO₄
8. Magnesium: MG
9. Calcium: CA
10. Potassium: K
11. Oxygen: O₂
12. Argon: AR

3.2 FEED AND PRODUCT STREAMS

- Feed streams

Table 9 shows the main feed streams: seawater and air, which are defined by their molar composition, pressure, and temperature.

Table 9. Feed streams

	AIR	SEAWATER
T(°C)	13.5	16.5
P(bar)	1	1
Q(kg/h)		
NITROGEN	28.45	0
OXYGEN	8.71	0
ARGON	0.48	0
HYDROGEN	0	0
AMMONIA	0	0
WATER	0	127.69
CHLORINE	0	0.6
SODIUM	0	0.5
SULFATE ION	0	0.23
MAGNESIUM	0	0.04
CALCIUM	0	0.02
POTASIUUM	0	0.02
TOTAL	37.65	129.1

- Product streams

In the air separation unit, the SEP2-2 stream, which is an oxygen-rich stream is obtained after air fractionation. The desalination unit and the PEM electrolyzer are the equipment that has the most output streams; here there are the next streams **i)** the DESAL-2 stream, that contains all the unwanted impurities in the water since the electrolyzer requires a stream of water with a high purity, **ii)** F2-1, which is a mixture of oxygen and water, and **iii)** SEP4-2, which contains water mixed with hydrogen and oxygen.

The ammonia synthesis process only has one product stream apart from the final product, this stream is SEP5-1, and it is one of the most important steps of the process as it is the purge necessary to ensure that the percentage of inert components entering the reactor is lower than 12%.

3.3 PROCESS THERMODYNAMICS

Finally, before proceeding to build the process flow diagram of the plant itself, the "Peng-Robinson" thermodynamic package is selected as the most suitable for the process to be studied and the most used in ammonia synthesis by the Haber-Bosch process.

3.4 EQUIPMENT

The equipment involved in the simulation of the ammonia production process are shown in this section following the three subsystems or units of the global process (ASU unit, Desalination & PEM electrolysis unit and Ammonia synthesis unit).

3.4.1 Air separation unit

In the nitrogen production stage by air separation, only an air stream directly from the plant's environment is introduced as shown in Figure 22.

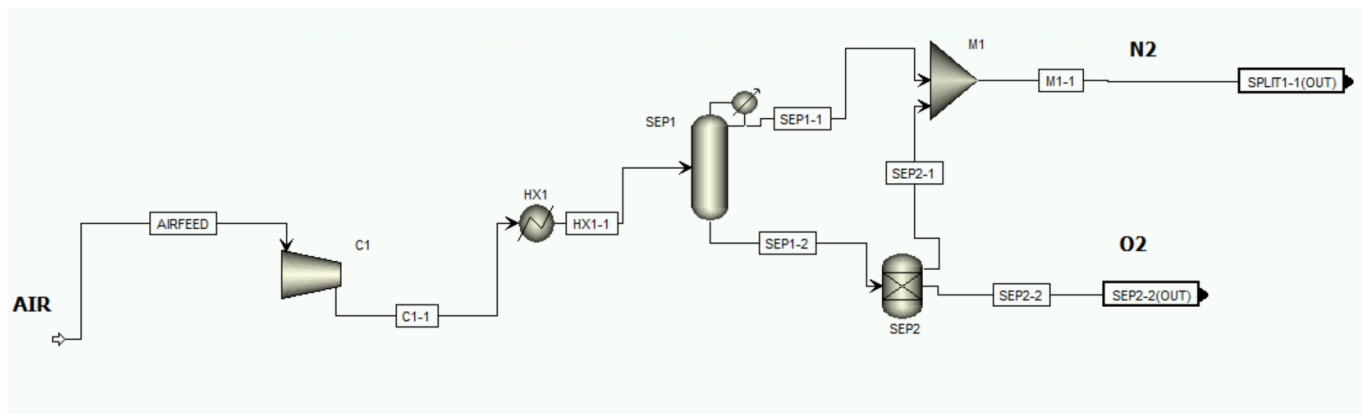


Figure 22. ASU equipment

The equipment used is:

- C1: compressor
- HX1: air feed preheater
- The core of air separation equipment is an important system for low temperature separation. High and low pressure two – stage rectification is usually adopted. In this case it's simulated with equipment SEP1 (RadFrac*) and SEP2
- M1: mixer

HX5: shell and tubes heat exchanger that heats the inlet stream by using the reactor's hot outlet stream.

HX6: electrical heater to achieve the reactor's inlet temperature.

R2: ammonia converter at high temperature and pressure.

HX7: cooler.

F3: flash separator in charge of obtaining the ammonia final product with the desired purity and separating it from hydrogen and oxygen that haven't reacted.

SPLIT3: the gas outlet of F3 stream is recycled and purged through this equipment in the appropriate amount to maintain the inert components in the reactor inlet less than 12%.

3.5 DESIGN SPECIFICATIONS

To set up the process, two specifications are implemented: N_2/H_2 ratio and reactor inlet inert components concentration.

Design specification 1: DSWATER

The electrolyzer has a water inlet, as a source of hydrogen, whose flow rate will be affected by a design specification which must be such that the reactor inlet stream has the correct nitrogen: hydrogen ratio (1:3), given by the ammonia reaction stoichiometry.

For this purpose, a design specification is created which acts by varying the flow rate of feed water entering the electrolyzer, depending on the composition of the reactor inlet stream.

Variables H20 and N20 are created as the mole fraction of the M6-1 hydrogen and nitrogen stream respectively. It is necessary to relate them by means of a Fortran sentence forcing to fix this relation in 3.0, the variable that remains free is the flow of water of entrance, since it was the hydrogen contribution to the process.

- Variable set: nitrogen : hydrogen ratio=3 in stream M5-1.
- Controllable variable: flow rate of water stream.

```

DESIGN-SPEC DS-WATER
  DEFINE H2O MOLE-FRAC STREAM=M6-1 SUBSTREAM=MIXED &
    COMPONENT=HYDRO-01
  DEFINE N2O MOLE-FRAC STREAM=M6-1 SUBSTREAM=MIXED &
    COMPONENT=N2

  SPEC "H2O/N2O" TO "3.0"
  TOL-SPEC "0.01"
  VARY MOLE-FLOW STREAM=H2OFEED SUBSTREAM=MIXED COMPONENT=H2O &
    UOM="kmol/hr"
  LIMITS "0" "30" STEP-SIZE=0.1
    
```

Design specification 2: DSPURGE

In the conversion stage, the percentage of inert components entering the reactor must be less than 12%, therefore a purge is introduced in the recirculation stream. The purge rate of which will be indicated by a design specification.

The molar flow rate of argon in the M6-1-1 inlet stream to the converter is defined, by means of a Fortran sentence this variable is related to another variable also defined by the user called "TOT" which is the total molar flow rate of the reactor inlet so that the percentage of inerts can be calculated and given a value. The variable to be left free is the fraction purged on SPLIT3.

- Variable set: mole fraction of inerts= 0.1 at converter inlet.
- Controllable variable: purge stream flow rate.

```

DESIGN-SPEC DS-PURGE
  DEFINE AR MOLE-FRAC STREAM=M6-1 SUBSTREAM=MIXED &
    COMPONENT=AR
  DEFINE OX MOLE-FRAC STREAM=M6-1 SUBSTREAM=MIXED &
    COMPONENT=O2
  DEFINE TOT STREAM-VAR STREAM=M6-1 SUBSTREAM=MIXED &
    VARIABLE=MOLE-FLOW UOM="kmol/hr"
  SPEC "(AR+OX)/TOT" TO "0"
  TOL-SPEC "0.12"
  VARY BLOCK-VAR BLOCK=SPLIT3 SENTENCE=FRAC VARIABLE=FRAC &
    ID1=SPLIT3-1
  LIMITS "0" "1"
    
```


3.6 PROCESS FLOW DIAGRAM OF THE COMPLETE PROCESS

Figure 25 represents the process flow diagram of the complete process evaluated in Aspen Plus. [Appendix 1](#) shows the ammonia synthesis process ASPEN simulation INPUT.

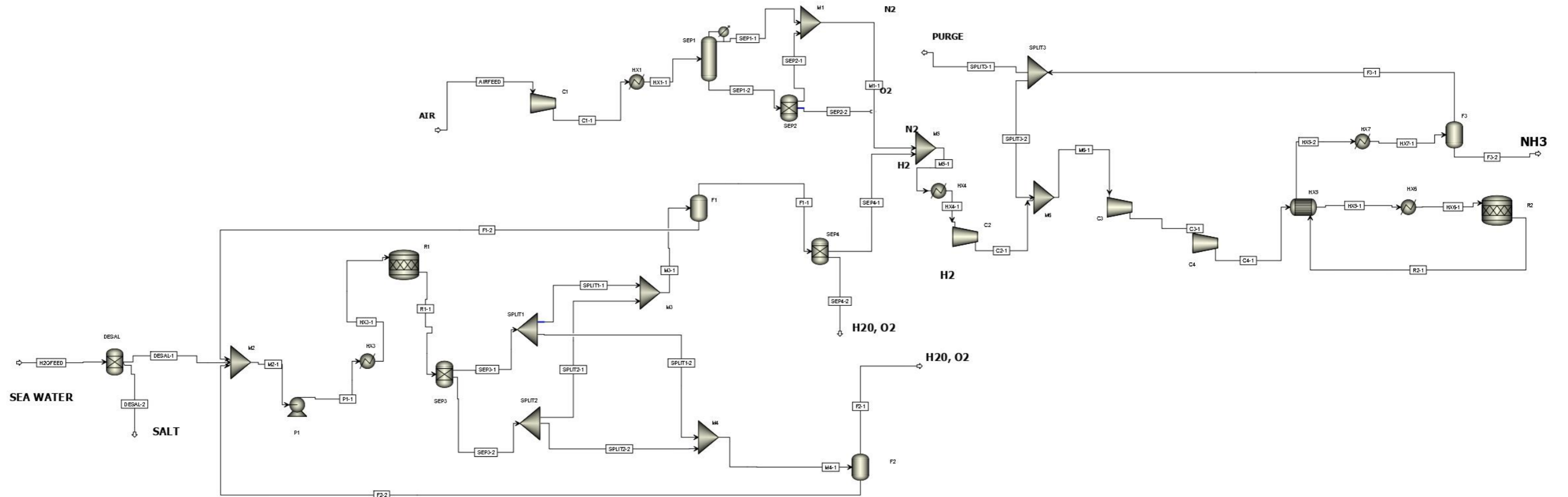


Figure 25. ASPEN Process flow diagram of ammonia production

4 RESULTS OBTAINED FROM ASPEN SIMULATION

4.1 PROCESS CONVERGENCE

The resolution of the simulation has been carried out with four "solvers" or convergence blocks, the following shows the equipment involved in them and the order carried out to calculate the flow diagram, with the breakdown streams chosen by the simulator.

- SOLVER01
- SOLVER02 (DS-WATER)
- SOLVER15 (DS-PURGE)

Table 10 shows the convergence blocks of the different design specifications, the status, the error, the tolerance, the relationship between both and the value of the manipulated variable.

Table 10. Design specifications summary

Design Spec	Status	Error	Tol	Error/ Tolerance	Variable value	Convergence block
DS-WATER	Conv	-0.0026673	0,01	-0.26673	7.088	SOLVER02
DS-PURGE	Conv	0.0019484	0,12	0.0162367	0.1	SOLVER03

Table 11 shows the convergence status of the breakdown streams and the variable checked for convergence with the highest error.

Table 11. Breakdown streams summary

Tear	Status	Variable max error	Max error/ Tol	Max relative error	Absolute error	Convergence block
M6-1	Conv	N ₂ MOLEFLOW	0.984015	-9.84 e-5	7.19 e-8	SOLVER01
HX5-1	Conv	N ₂ MOLEFLOW	0.637744	6.37 e-05	4.66e-08	SOLVER01
M2-1	Conv	N ₂ MOLEFLOW	0	0	0	SOLVER01

4.2 RESULTS OF THE PROCESS STAGES

4.2.1 Stage 1: Air separation unit

Table 12 shows the results of the streams taking part in the ASU stage:

Table 12. ASU stream results

	Units	AIRFEED	C1-1	HX1-1	SEP1-1	SEP1-2	SEP2-1	SEP2-2	M1-1
Phase		Vapor	Vapor	Vapor	Liquid	Liquid	Vapor	Liquid	Mixed
Temperature	°C	13.5	290.86	-171.34	-176.64	-172.07	-172.07	-172.07	-176.47
Pressure	Bar	1	6.5	6.5	6	6.18	6.18	6.18	6
Molar Enthalpy	kJ/kmol	-343.21	7844.33	-6024.5	-10949	-11270	-6037.7	-11986	-8988
Mass Flows	Kg/hr	37.65	37.65	37.65	16.65	20.99	11.12	9.87	27.77
N ₂	Kg/hr	28.44	28.44	28.44	16.6	11.85	10.66	1.18	27.26
O ₂	Kg/hr	8.71	8.71	8.71	1.8e-5	8.71	0.44	8.28	0.44
AR	Kg/hr	0.48	0.48	0.48	0.05	0.43	0.02	0.41	0.07

In this stage, air stream is fed to obtain nitrogen by separating it into its different components. The M1-1 outlet has a nitrogen molar flow rate of 27.77 kg/hr.

4.2.2 Stage 2: PEM Electrolysis

The results of the different streams of the PEM electrolyzer simulation are shown below in Table 13 and Table 14.

Table 13. PEM stream results 1

	Units	H2OFEED	DESAL-1	DESAL-2	M2-1	P1-1	HX3-1	R1-1	SEP3-1	SEP3-2
Phase		Liquid	Liquid	Mixed	Mixed	Liquid	Liquid	Mixed	Vapor	Mixed
Temperature	°C	16.5	16.5	16.5	35.63	35.66	80	80	80	80
Pressure	Bar	1	1	1	1	1.5	1.5	1.5	1.5	1.5
Molar Enthalpy	kJ/kmol	-28e4	-28e4	20e4	-28e4	-28e4	-28e4	-10e4	1592	-158715
Mass Flows	Kg/hr	129.1	127.69	1.41	193.35	193.35	193.35	193.35	8.65	184.7
O ₂	Kg/hr	0	0	0	4.9e-4	4.9e-4	4.9e-4	85.85	0	85.85
H ₂	Kg/hr	0	0	0	3e-6	3e-6	3e-6	10.81	8.65	2.16
H ₂ O	Kg/hr	127.69	127.69	0	139.35	139.35	139.35	96.67	0	96.67
Cl ⁻	Kg/hr	0.6	0	0.6	0	0	0	0	0	0
Na ⁺	Kg/hr	0.5	0	0.5	0	0	0	0	0	0
SO ₄ ⁻⁻	Kg/hr	0.23	0	0.23	0	0	0	0	0	0
Mg	Kg/hr	0.04	0	0.04	0	0	0	0	0	0
Ca	Kg/hr	0.02	0	0.02	0	0	0	0	0	0
K	Kg/hr	0.02	0	0.02	0	0	0	0	0	0

Table 14. PEM stream results 2

	Units	SPLIT1-1	SPLIT1-2	SPLIT2-1	SPLIT2-2	M3-1	M4-1	F1-1	F1-2	F2-1	F2-2	SEP4-1	SEP4-2
Phase		Vapor	Vapor	Mixed	Mixed	Mixed	Mixed	Vapor	Liquid	Vapor	Liquid	Vapor	Mixed
Temperature	°C	80	80	80	80	54.65	76.16	54	54	77	77	54	54
Pressure	Bar	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Molar Enthalpy	kJ/kmol	1592	1592	-15e4	-15e4	-54e3	-14e4	-20e3	-28e4	-60e3	-28e4	177	-64e3
Mass Flows	Kg/hr	6.92	1.73	36.93	147.75	43.86	149.48	31.77	12.09	95.92	53.56	6.37	25.39
O ₂	Kg/hr	0	0	17.17	68.68	17.17	68.68	17.17	1.9e-5	68.68	4.7e-4	0.34	16.83
H ₂	Kg/hr	6.92	1.73	0.43	1.73	7.36	3.46	7.36	6.6e-7	3.46	2.36e-6	5.88	1.47
H ₂ O	Kg/hr	0	0	19.33	77.33	19.33	77.33	7.24	12.09	23.77	53.56	0.14	7.1
Cl ⁻	Kg/hr	0	0	0	0	0	0	0	0	0	0	0	0
Na ⁺	Kg/hr	0	0	0	0	0	0	0	0	0	0	0	0
SO ₄ ⁻⁻	Kg/hr	0	0	0	0	0	0	0	0	0	0	0	0
Mg	Kg/hr	0	0	0	0	0	0	0	0	0	0	0	0
Ca	Kg/hr	0	0	0	0	0	0	0	0	0	0	0	0
K	Kg/hr	0	0	0	0	0	0	0	0	0	0	0	0

4.2.3 Stage 3: Ammonia synthesis

The results of the core part of the process, the ammonia synthesis, are shown in Table 15:

Table 15. Synthesis stream results

	Units	M5-1	HX4-1	C2-1	M6-1	C3-1	C4-1	HX5-1	HX6-1	R2-1	HX5-2	HX7-1	F3-1	F3-2	SPLIT3-1	SPLIT3-2
Phase		Mixed	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Mixed	Vapor	Liquid	Vapor	Vapor
Temperature	°C	-28.3	13.11	151.5	33.98	214.9	389.2	428	438	498	458.05	-26	-26	-26	-26	-26
Pressure	Bar	6	6	17	17	60	138	138	138	138	138	138	17	17	17	17
Molar Enthalpy	kJ/kmol	-2130	-842	3197	-2.6e6	-2.7e6	8.2e6	9.4e6	9.7e6	4.8e6	3.4e6	-1.4e7	-5.7e6	-7.2e7	-5.7e6	-5.7e6
Mass Flows	Kg/hr	34.14	34.14	34.14	109.77	109.77	109.77	109.77	109.77	109.77	109.77	109.77	84.02	25.74	8.4	75.62
N ₂	Kg/hr	27.26	27.26	27.26	73.72	73.72	73.72	73.73	73.73	51.62	51.62	51.62	51.61	0.006	5.16	46.45
O ₂	Kg/hr	0.78	0.78	0.78	7.66	7.66	7.66	7.66	7.66	7.65	7.65	7.65	7.64	0.015	0.76	6.88
AR	Kg/hr	0.07	0.07	0.07	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.67	0.003	0.07	0.61
H ₂	Kg/hr	5.88	5.88	5.88	15.9	15.9	15.9	15.9	15.9	11.13	11.13	11.13	11.13	0.001	1.11	10.02
NH ₃	Kg/hr	0	0	0	11.66	11.66	11.66	11.66	11.66	38.53	38.53	38.53	12.96	25.57	1.29	11.66
H ₂ O	Kg/hr	0.14	1.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	3.3e-6	0.14	3e-7	3e-6

4.2.4 General results summary

Table 16 shows the temperature, pressure and mass flowrate to the input and the final product streams.

Table 16. Stream results summary

Stream	Units	H2OFEED	AIRFEED	NH3 (F3-2)
Temperature	C	16.5	13.5	-26
Pressure	bar	1	1	17
Mass Flowrate	Kg/hr	129.1	37.65	25.64
Purity				99.3%

A flow rate of 25.64 kg/h is obtained with an ammonia richness of 99.3%. The target was 25kg/hr with a richness higher than 98%, so with the simulation this result can be achieved.

5. EQUIPMENT SIZING AND COSTING

Once the mass balances have been solved by means of simulation, the equipment sizing, and costs can be evaluated using different methods. In this case, manual short-cut equipment sizing methods were used for this purpose, followed by equipment costing estimation based on the Guthrie modular method (Biegler, et al., 1997); (Seider, et al., 2017)

Since this is a process that works under high pressure and temperature conditions, the cost estimation methods based on modular factor, show lower accuracy than when applied to estimations under mild conditions. Moreover, as the ammonia converter is a very special reactor (reactor-exchanger), commonly under proprietary information, its cost estimation will again be very approximate within this preliminary design.

The equipment to be considered will be, on the one hand, the ASU and the PEM electrolyze which are sized and estimated their cost specifically as a whole. On the other hand, the individual components of the synthesis stage, which are the following: Flash, reactor, shell and tube exchanger, heaters and cooler, three compressors, the mixer and the splitter.

5.1 EQUIPMENT SIZING

The Guthrie modular method to estimate equipment cost is based on the Williams law, which depend on the specific equipment capacity to estimate the Base Cost (C or BC) using the equations showed below and the specific parameters of each unit showed in Tables 17 and 18. Therefore, the first step would be the equipment sizing, obtaining the specific capacity that is directly related to the cost.

$$C = BC = C_o (L/L_o)^\alpha (D/D_o)^\beta \quad C = BC = C_o (S/S_o)^\alpha$$

Table 17. Base costs for pressure vessels

Base Costs for Pressure Vessels						
Equipment Type	C ₀ (\$)	L ₀ (ft)	D ₀ (ft)	α	β	MF2 / MF4/ MF6/ MF8/ MF10
Vertical fabrication 1 ≤ D ≤ 10 ft; 4 ≤ L ≤ 100 ft	1000	4.0	3.0	0.81	1.05	4.23 / 4.12 / 4.07 / 4.06 / 4.02
Horizontal fabrication 1 ≤ D ≤ 10 ft; 4 ≤ L ≤ 100 ft	690	4.0	3.0	0.78	0.98	3.18 / 3.06 / 3.01 / 2.99 / 2.96
Tray stacks 2 ≤ D ≤ 10 ft; 1 ≤ L ≤ 500 ft	180	10.0	2.0	0.97	1.45	1.0 / 1.0 / 1.0 / 1.0 / 1.0

Table 18. Base costs for process equipment

Base Costs for Process Equipment					
Equipment Type	C ₀ (\$10 ³)	S ₀	Range (S)	α	MF2/MF4/MF6/MF8/MF10
Process furnaces S=Absorbed duty (10 ⁶ Btu/h)	100	30	100-300	0.83	2.27/2.19/2.16/2.15/2.13
Direct fired heaters S=Absorbed duty (10 ⁶ Btu/h)	20	5	1-40	0.77	2.23/2.15/2.13/2.12/2.10
Heat exchanger Shell and tube, S=Area (ft ²)	5	400	100-10 ⁴	0.65	3.29/3.18/3.14/3.12/3.09
Heat exchanger Shell and tube, S=Area (ft ²)	0.3	5.5	2-100	0.024	1.83/1.83/1.83/1.83/1.83
Air Coolers S=[calculated area (ft ²)/15.5]	3	200	100-10 ⁴	0.82	2.31/2.21/2.18/2.16/2.15
Centrifugal pumps S= C/H factor (gpm x psi)	0.39 0.65 1.5	10 2.10 ³ 2.10 ⁴	10-2.10 ³ 2.10 ³ -2.10 ⁴ 2.10 ⁴ -2.10 ⁵	0.17 0.36 0.64	3.38/3.28/3.24/3.23/3.20 3.38/3.28/3.24/3.23/3.20 3.38/3.28/3.24/3.23/3.20
Compressors S=brake horsepower	23	100	30-10 ⁴	0.77	3.11/3.01/2.97/2.96/2.93
Refrigeration S=ton refrigeration (12,000 Btu/h removed)	60	200	50-3000	0.70	1.42

Next subsections present an overview of short-cut calculations for equipment sizing (Biegler, et al., 1997).

- **Pressure vessels**

Flash equipment, separators, condensers, and some single reactors are sized as pressure vessels, being the volume of the vessel the fundamental variable for their design. To calculate the vessel's volume, the following expression is applied:

$$V = 2 \cdot \frac{F_L \cdot \tau}{\rho_L}$$

Where:

V = equipment's volume [m³]

F_L = liquid outflow [kg/hr]

τ = residence time [hr] (usually taken 5 minutes if we don't have the information)

ρ_L =liquid's density [kg/m³]

For the calculation of the dimensions of the vessel, a cylindrical vessel shape is assumed and a ratio between the diameter of the tank and its length of $L=4D$, obtaining that the diameter of the equipment are:

$$D = \left(\frac{V}{\pi} \right)^{\frac{1}{3}}$$

If the diameter is less than 1.2 meters, the optimum orientation for the vessel will be vertical, thus optimizing space occupation and clamping requirements. Minimum diameter is 1 foot.

- **Heat exchangers**

To size heat exchangers, the following equation is applied, from which it is possible to obtain the required heat exchange area:

$$Q = U \cdot A \cdot LMTD$$

Where:

Q =amount of heat transfer [kW]

$LMTD$ = logarithmic mean temperature difference [°C], defined as:

$$LMTD = \frac{[(T_{inhot} - T_{outcold}) - (T_{outhot} - T_{incold})]}{\ln \left[\frac{(T_{inhot} - T_{outcold})}{(T_{outhot} - T_{incold})} \right]}$$

U =overall heat transfer coefficient [W/m^2K]

Once the exchange area is found, is necessary to calculate the number of tubes of a given dimension that together add up to that area. Normalized tube dimensions are taken. We will also decide the distribution of these tubes and the number of passages through the casing.

Note that if the area needed is over 1000 m^3 , several heat exchangers will be used, obtaining the total area as $A=A_1+A_2+\dots+A_n$.

- **Compressors**

For compressors (Fig. 26) all we need is the power needed for their use and compare it with the market's specifications of power and sizing, as they are very common products used in various industries. In the present project, this power is given by the Aspen Plus simulation, so no additional calculations are needed.



Figure 26. Industrial compressor

- **Valves**

Both the mixer and the splitter are preliminary designed as special valves (Fig. 27) that, like the equipment mentioned above, they can be easily found on the market or can be manufactured by a specialized company.



Figure 27. Industrial valve

5.2 SIZING RESULTS OF THE AMMONIA PLANT

- **Flash unit**

Table 19. Flash unit dimensions

Name	Flow (kg/hr)	ρ (kg/m ³)	τ (min)	Volume (m ³)	Diameter (m)	Length (m)
F3	109.77	86.27	5	0.21	0.41	1.63

As its diameter is less than 1.2 m, its orientation will be vertical. Vertical construction includes shell and two heads, the skirt, base rings and lugs, and possible tray supports, occupying a space of approximately 1 sqm and with a height of around 2.5 m.



Figure 28. Flash unit

- **Reactor**

Table 20. Reactor dimensions

Name	Flow (kg/hr)	ρ (kg/m ³)	τ (min)	Volume (m ³)	Diameter (m)	Length (m)
R2	109.77	21.51	5	0.85	0.65	2.59

In this case, the reactor has been modelled as a pressure vessel, but as indicated above, it is a catalytic bed reactor with heat exchange, so its sizing will depend on reaction kinetic, mass and energy transfer. To estimate its real dimensions and specifications, a complete study by a specialized company in this type of reactors

would be needed. One example of a similar reactor is the one used in the University of Minnesota’s pilot plant ([described in section 1.3.5](#)) and shown in Figure 28.



Figure 29. University on Minnesota Ammonia Reactor Skid

Considering the design of this prototype, it is assumed that the dimensions of the reactor can be around 5 sqm with a height of 2 m.

- **Heat exchanger**

Table 21. Heat exchanger dimensions

Name	T hot in (°C)	T hot out (°C)	T cold in (°C)	T cold out (°C)	LMTD (°C)	U (W/m ² K)	A (m ²)	Q (kW)	UA (J/s·K)
HX5	498	458.05	389.18	428	69.44	850	0.065	3.85	55.46

As mentioned above, the number of tubes of a given dimension must be calculated using normalized tube dimensions. Both this parameter and the tubes distribution will be designed by a specialized heat exchanger company optimizing the space to reach the mentioned exchange area (Fig. 29). It is easy to obtain a particular heat exchanger through the exchange area and by specifying some design parameters such as the maximum length and the diameter of the unit. The number of tubes is related to the exchange area by the following equations:

$$A_{Tubes} = \pi \cdot D \cdot L$$

$$N_{Tubes} = \frac{A}{A_{Tubes}}$$



Figure 30. Fluitec multitube heat exchanger with mixing elements

- **Heaters/Cooler**

Both equipment, heaters and the cooler must be electric, in line with the policy of avoiding direct emissions. They are defined by their operating temperatures and pressures as well as the inlet flow and the power required which characteristics are shown in Table 22.

Table 22. Heaters and cooler dimensions

Name	Pin (bar)	Pout (bar)	Tin (°C)	Tout (°C)	F (kg/hr)	W (kW)
HX4	6	6	-28.3	13.11	34.14	1.41
HX6	138	138	428	438	109.78	1
HX7	138	138	458	-26	109.78	5.7

According to the market, this equipment with the aforementioned characteristics may have dimensions of around 1sqm and 1.5 m height.

- **Compressors**

This equipment is defined mainly by its power, although its size and cost also vary depending on the working pressures and the materials used to withstand high temperatures.

Table 23. Compressors dimensions

Name	Pin (bar)	Pout (bar)	Tin (°C)	Tout (°C)	F (kg/hr)	W (kW)
C2	6	17	13.11	151.46	34.14	4.41
C3	17	60	33.99	214.9	109.78	17
C4	60	138	214.9	389.18	109.78	17

In this case the power of the compressors C3 and C4 is very high (Table 23), reason way the simulation is carried out by a compressors train, composed by more compressors with less power.

As a guideline, the size of the three compressors will be around 3 sqm and 1 meter high.

- **Mixers/Splitter**

The mixers will be static mixers without moving components, as the one shown in Figure 30 and will have the following requirements shown in Table 24:

Table 24. Mixers and splitter dimensions

Name	F (kg/hr)	P (bar)	T(°C)
M5	34.14	6	-28.3
M6	109.78	17	33.99
SPLIT3	84.03	17	-26

The size will depend on the desired flow, but all these devices are about 0.5 square meters in size.



Figure 31. Static mixer

- **Air Separation Unit (ASU)**

This system consists of separating the air by means of a cryogenic distillation process. It involves cooling the air until it liquefies and then obtaining the air components to their corresponding boiling temperature by distillation. It is a relatively simple and tested process, and there are several products on the market that allow us to perform this function at different capacities, depending on the volume of nitrogen to be obtained.

For the requirements of the present project (25 kg/h and a purity of 98.5 % N₂) the size of one of this units designed for other projects are usually around 4 sqm like the one showed in Figure 31.



Figure 32. Air Separation Unit prototype

- **PEM Electrolyzer**

This equipment consists of a stack of cells assembled under pressure that support the high pressures generated inside and that, by means of collectors, collect gas products in the anode (water and oxygen) and cathode (water and hydrogen) which are later processed according to the final application of these gases (in this case to obtain hydrogen).

Some specialized companies such as ARIEMA S.L. offer different variants depending on the real needs of their customers: from large industrial electrolysis plants to medium or small plants adapted to the needs of each case, as is the designed ammonia plant in the present project.

According to the previously observed in other similar plants and projects, as well as in small hydrogen production plants, it has been shown that the size of this equipment for the specifications desired in the process (6.3 kg/h and a purity of 99.1 %H₂) is around 4 sqm. Figure 33 shows an example of this type of equipment.



Figure 33. Ariema PEM Electrolyzer

- **Storage tanks**

Additionally, different storage tanks must be included, each one with its own design requirements depending on its content and the amount stored. The tanks to be placed in the plant are the following:

- Hydrogen feed tank. Tank designed to store the hydrogen feedstock at a pressure of 1.5 bar, coming from the PEM electrolyzer and connected directly to the first mixer of the ammonia synthesis step.
- Nitrogen feed tank. Tank designed to store the nitrogen feedstock at a pressure of 6 bar, coming from the Air Separation Unit and connected directly to the first mixer of the ammonia synthesis step.
- Ammonia storage tank. This tank will store the desired product until it is transported to bigger tanks or directly to the ships to be used as a renewable fuel
- Purge tank. Since the purge stream contains pollutant components, it must be stored for subsequent treatment by a company that collects and recycles toxic waste.

Initially in this previous design, all storage tanks will be assumed to have dimensions of 9 sqm.

5.3 REQUIRED AREA AND PLANT LAYOUT

As a summary, the estimated total area of the plant has been calculated as the sum of the area of all its equipment obtaining a value of 60 sqm to which should add space for pipes, pumps, valves, control and safety systems and space between equipment in case access to them is necessary. Thus, being conservative it would be possible to install the plant on a platform with a surface of around 300 sqm.

APPENDIX 2: AUTOCAD PLANE shows a plan drawn in the AutoCAD program and represents what could be the floor plan layout of the designed equipment. For convenience, when making repairs it has been decided to place all similar equipment in the same area, so that compressors, tanks, and separators are grouped into separated areas.

5.4 COST ESTIMATION OF EQUIPMENT

The cost estimation method of Guthrie is used to estimate the updated base module cost of each equipment. This is a “Preliminary” category of cost estimation, which could have errors higher than 50%.

The Base Cost of equipment is obtained through the Williams law expression to pressure vessels, $C = BC = Co (L/Lo)^\alpha (D/Do)^\beta$, or $C = BC = Co (S/So)^\alpha$ to the rest of the equipment (Biegler et al., 1997) (Biegler, et al., 1997); Values of base cost and size as well as exponents are shown in Tables 17 and 18. Purchase costs of other industrial processing equipment are shown in Process Design bibliography (Seider, et al., 2017); (Douglas, 1988); (Sinnot, y otros, 2020); (Martín, 2016); (Viguri, et al., 2017). To update cost from mid-1968 (Co and So), an Update Factor UF , to account for inflation, is applied.

$UF: (Present\ Cost\ Index / Base\ Cost\ index) = (CI_{actual}) / (CI_{base})$, with $CI_{2021} = 708$ and $CI_{Base} = 115$. $UF = \frac{708}{115} = 6.16$

Updated bare (simple) module cost: $BMC = UF(BC) (MPF+MF-1)$, where

MF is the Module Factor, affected by BC , taking into account labor, piping instruments and accessories among others and are $MF\ 2$; $MF\ 4$; $MF\ 6$; $MF\ 8$; $MF\ 10$ from Tables 17 and 18. The MPF factor is the Materials and Pressure correction Factors F (F_d , F_m , F_p , F_o , F_t) which are empirical factors that modified BC and evaluate particular instances of equipment beyond a basic configuration. This correlation factors are shown in the Tables 25-29. (Viguri, et al., 2017)

Table 25. Material and pressure factors for pressure vessels

Materials of Construction for Pressure Vessels								
High Temperature Service					Low Temperature Service			
Tmax (°F)		Steel			Tmin (°F)		Steel	
950	Carbon steel (CS)				-50	Carbon steel (CS)		
1150	502 stainless steels (SS)				-75	Nickel steel (A203)		
1300	410 SS; 330 SS				-320	Nickel steel (A353)		
1500	304,321,347,316 SS. Hastelloy C, X Inconel				-425	302,304,310,347 (SS)		
2000	446 SS, Cast stainless, HC							
Guthrie Material and pressure factors for pressure vessels: MPF = Fm · Fp								
Shell Material		Clad (Revestimiento), Fm			Solid (Macizo), Fm			
Carbon Steel (CS)		1.00			1.00			
Stainless 316 (SS)		2.25			3.67			
Monel (Ni:Cr/2:1 alloy)		3.89			6.34			
Titanium		4.23			7.89			
Vessel Pressure (psig)								
Up to	50	100	200	300	400	500	900	1000
Fp	1.00	1.05	1.15	1.20	1.35	1.45	2.30	2.50

Table 26. Material and pressure factors for Heat Exchangers

Heat exchanger: Countercurrent, steady state

Guthrie Material and pressure factors for Heat Exchangers: MPF: Fm (Fp + Fd)									
Design Type	Fd	Vessel Pressure (psig)							
Kettle Reboiler	1.35								
Floating Head	1.00	Up to 150 300 400 800 1000							
U Tube	0.85	Fp 0.00 0.10 0.25 0.52 0.55							
Fixed tube sheet	0.80								
Shell/Tube Materials, Fm									
Surface Area (ft ²)	CS/ CS	CS/ Brass	CS/ SS	SS/ SS	CS/ Monel	Monel Monel	CS/ Ti	Ti/ Ti	
Up to 100	1.00	1.05	1.54	2.50	2.00	3.20	4.10	10.28	
100 to 500	1.00	1.10	1.78	3.10	2.30	3.50	5.20	10.60	
500 to 1000	1.00	1.15	2.25	3.26	2.50	3.65	6.15	10.75	
1000 to 5000	1.00	1.30	2.81	3.75	3.10	4.25	8.95	13.05	

Table 27. Materials and pressure factors for Direct Fired Heaters

FURNACES and DIRECT FIRED HEATERS (boilers, reboilers, pyrolysis, reformers)

Guthrie MPF for Furnaces: $MPF = F_m + F_p + F_d$

<u>Design Type</u>	<u>F_d</u>
Process Heater	1.00
Pyrolysis	1.10
Reformer	1.35

Vessel Pressure (psig)

<u>Up to</u>	500	1000	1500	2000	2500	3000
F_p	0.00	0.10	0.15	0.25	0.40	0.60

Radiant Tube Material, F_m

Carbon Steel	0.00
Chrome/Moly	0.35
Stainless Steel	0.75

Guthrie MPF for Direct Fired Heaters

MPF: $F_m + F_p + F_d$

<u>Design Type</u>	<u>F_d</u>
Cylindrical	1.00
Dowtherm	1.33

Vessel Pressure (psig)

<u>Up to</u>	500	1000	1500
F_p	0.00	0.15	0.20

Radiant Tube Material, F_m

Carbon Steel	0.00
Chrome/Moly	0.45
Stainless Steel	0.50

Table 28. Materials and pressure factors for Refrigeration

Guthrie MPF for Mechanical Refrigeration

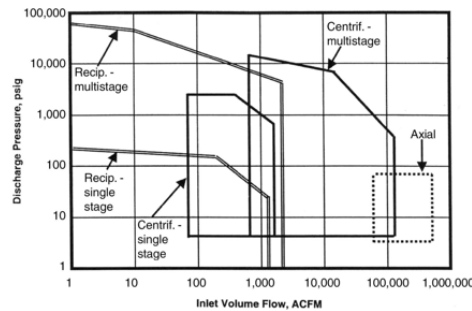
MPF: F_t

<u>Evaporator Temperature, F_t</u>	
278 K / 5 C	1.00
266 K / -7 C	1.95
255 K / -18 C	2.25
244 K / -29 C	3.95
233 K / -40 C	4.54

Table 29. Materials and pressure factors for Compressors

Guthrie MPF for Compressors	
MPF: Fd	
Design Type	Fd
Centrifugal/motor	1.00
Reciprocating/steam	1.07
Centrifugal/turbine	1.15
Reciprocating/motor	1.29
Reciprocating/gas engine	1.82

Compressor selection. Areas indicate regions of best performance (<http://www.dresser-rand.com/>).



All the calculations were made using American units as shown in Table 17 and Table 18. The main equivalences we will need are the following: 1m=3.28ft; 1sqm=10.76sqft; 1\$=0.92€.

- **Pressure vessels**

For this cost's estimation, the flash unit and reactor will be considered as pressure vessels to simplify calculations, but we must take in account that the real price will increase when talking about the real equipment.

- **Flash unit F3 (Vertical):**

$$BC = 1000 \left(\frac{5.35}{4}\right)^{0.81} \left(\frac{1.35}{3}\right)^{1.05} = 547.23\$$$

MF=2

From Table 25 the MPF:

Tmin=-14.8F so the material used will be Carbon Steel. Fm=1

P=231.87psig so Fp=1.20

MPF=Fm·Fp=1.20

$$BMC = 6.16 \cdot 547.23 \cdot (1.2 + 2 - 1) = 7416.06\$$$

- **Reactor R2 (Vertical):**

$$BC = 1000 \left(\frac{8.5}{4}\right)^{0.81} \left(\frac{2.13}{3}\right)^{1.05} = 1285.23\$$$

MF=2

From Table 25 the MPF:

Tmax=928.4F so the material used will be Carbon Steel. Fm=1

P=1986.82psig so Fp=2.5

MPF=Fm·Fp=2.5

$$BMC = 6.16 \cdot 1285.23 \cdot (2.5 + 2 - 1) = 27709.56\$$$

- **Heat exchanger HX5**

$$BC = 0.3 \cdot 10^3 \left(\frac{7}{5.5} \right)^{0.024} = 301.74\$$$

MF=1.83

From Table 26 the MPF:

We will suppose that the design type will be Kettle reboiler so
Fd=1.35

P=1986.82psig so Fp=0.55

Shell and tube will be made of carbon steel according to their
temperature and according to the exchanger area Fm=1

MPF=Fm·(Fp+Fd)=1.9

$$BMC = 6.16 \cdot 301.74 \cdot (1.9 + 1.83 - 1) = 5074.3\$$$

- **Direct fired heaters**

- **HX4:**

$$BC = 20 \cdot 10^3 \left(\frac{4.8}{5} \right)^{0.77} = 19381.12\$$$

MF=2.23

From Table 27 the MPF:

The heater is cylindrical so Fd=1

P=72.18psig so Fp=0

Radiant tube material is made of Carbon Steel so Fm=0

MPF=Fd+Fp+Fm=1

$$BMC = 6.16 \cdot 19381 \cdot (1 + 2.23 - 1) = 146845.96\$$$

- **HX6:**

$$BC = 20 \cdot 10^3 \left(\frac{3.39}{5} \right)^{0.77} = 14827.81\$$$

MF=2.23

From Table 27 the MPF:

The heater is cylindrical so Fd=1

P=1986.83psig so Fp=0.2

Radiant tube material is made of Carbon Steel so Fm=0

MPF=Fd+Fp+Fm=1.2

$$BMC = 6.16 \cdot 14827.81 \cdot (1.2 + 2.23 - 1) = 130615.21\$$$

- **Refrigeration. HX7**

$$BC = 60 \cdot 10^3 \left(\frac{195.25}{200} \right)^{0.7} = 58998.91\$$$

MF=1.42

From Table 28 the MPF:

Evaporator temperature is -26°C so MPF=Ft=2.25

$$BMC = 6.16 \cdot 58998.91 \cdot (2.25 + 1.42 - 1) = 970366.87\$$$

- **Compressors**

- **C2:**

$$BC = 23 \cdot 10^3 \left(\frac{15.03}{100} \right)^{0.77} = 5345.47\$$$

MF=3.11

From Table 29 the MPF:

This first compressor will be a reciprocating- single stage so according to the Table: MPF=Fd=1.07

$$BMC = 6.16 \cdot 5345.47 \cdot (1.07 + 3.11 - 1) = 104711.34\$$$

- **C3:**

$$BC = 23 \cdot 10^3 \left(\frac{59.18}{100} \right)^{0.77} = 15356.86\$$$

MF=3.11

From Table 29 the MPF:

This compressor will be a reciprocating- multistage so according to the Table: MPF=Fd=1.29

$$BMC = 6.16 \cdot 15356.86 \cdot (1.29 + 3.11 - 1) = 321634.08\$$$

- **C4:**

$$BC = 23 \cdot 10^3 \left(\frac{59.15}{100} \right)^{0.77} = 15350.87\$$$

MF=3.11

From Table 29 the MPF:

This compressor will be a reciprocating- multistage so according to the Table: MPF=Fd=1.29

$$BMC = 6.16 \cdot 15350.87 \cdot (1.29 + 3.11 - 1) = 321508.62\$$$

Table 30 summarize the sizing parameters related to the cost as well as the estimated cost of the equipment list of the ammonia plant.

Table 30. Cost and size parameters summary

Type (Unit)	Cost. BMC (€)	Layout Area (sqm)	Other specifications
ASU	20,000	4	To obtain 27.8 kg/h of 98% N ₂
PEM Electrolyzer	500,000	4	To obtain 8.7 kg/h of 99.1% H ₂
Ammonia Synthesis to obtain 31.4 kg/h of 99.1% NH₃			
Flash F3	6,804.46	2.5	
Reactor	25,424.35	5	
Heat exchanger HX5	4,655.82	2	
Heater HX4	134,735.57	1	
Heater HX6	119,843.37	1	
Cooler HX7	890,340.71	1	
Compressor C2	96,075.80	3	
Compressor C3	295,108.92	3	
Compressor C4	294,993.80	3	
Ammonia synthesis plant	1,541,218.06	21.5	
TOTAL Plant	2,061,218.06	29.5	

6. CONCLUSIONES / CONCLUSIONS

En el presente proyecto se ha evaluado y diseñado una planta de producción de amoníaco (a pequeña escala) de 25 kg/h y 98% de pureza a partir de materias primas y energías renovables. Dicha planta se diseña con el objetivo de suministrar amoníaco como combustible a buques de carga desde una plataforma flotante situada en el puerto de Santander.

Del desarrollo de este trabajo se han obtenido las siguientes conclusiones:

1. Se ha realizado un análisis de la obtención de diferentes combustibles alternativos y su uso en buques de carga seleccionando el amoníaco como principal candidato bajo un enfoque de fabricación sostenible utilizando energía y materias primas renovables.
2. Tras analizar diferentes alternativas de fabricación de amoníaco de pequeño tamaño, se ha considerado que el proceso Haber-Bosch, con fuentes de materias primas renovables como el agua de mar y el aire, es la opción más adecuada en términos de recursos accesibles, eficiencia, coste, condiciones de presión y temperatura, así como TRL.
3. Se ha realizado un diseño preliminar y una simulación de una planta de producción de amoníaco mediante el proceso Haber-Bosch a pequeña escala. Esta simulación se ha realizado mediante la herramienta de modelización ASPEN Plus, obteniendo los siguientes resultados concretos: caudal de producto de 25,64 kg/h con una riqueza de amoníaco del 99,3%.
4. El producto amoníaco se obtiene totalmente libre de emisiones contaminantes debido a la utilización de energía renovable a través de paneles solares y a la obtención de hidrógeno a través de la electrólisis del agua de mar y de nitrógeno a partir de la separación del aire.
5. En base a los resultados anteriores, se realiza un estudio preliminar de la necesidad de superficie para ubicar los equipos que componen la planta. Siendo conservadores, sería posible instalar la planta en una plataforma con una superficie de unos 300 m². Por lo tanto, se comprueba que es lo suficientemente pequeña como para ser instalada en un área reducida como una plataforma flotante.
6. Bajo el mismo enfoque conceptual, se han aplicado a la planta de amoníaco métodos abreviados para el dimensionamiento de los equipos principales y métodos modulares para la estimación preliminar de costes, obteniendo un Coste del Módulo Base de 2,1 MM€.

This project has evaluated and designed an ammonia production plant (small scale) of 25 kg/h and 98% purity from raw materials and renewable energies. This plant is designed with the aim of supplying ammonia as fuel to cargo ships from a floating platform located in the port of Santander.

The following conclusions have been drawn from this work:

1. An analysis has been carried out on the production of different alternative fuels and their use in cargo ships, selecting ammonia as the main candidate under a sustainable manufacturing approach using renewable energy and raw materials.
2. After analysing different small size ammonia manufacturing alternatives, the Haber-Bosch process, with renewable raw material sources as seawater and air, was considered the most suitable option in terms of accessible resources, efficiency, cost, pressure, and temperature conditions as well as TRL.
3. A preliminary design and simulation of an ammonia production plant using the Haber-Bosch process on a small-scale basis have been made. This simulation has been carried out by the ASPEN Plus modelling tool, obtaining the following specific results: product flowrate of 25.64 kg/hr with an ammonia richness of 99.3%.
4. The product ammonia is obtained totally free of polluting emissions due to the use of renewable energy through solar panels and obtaining hydrogen through the electrolysis of seawater and nitrogen from the separation of air.
5. Based on the previous results, a preliminary study of the area need to allocate the equipment that make up the plant is done. Being conservative, it would be possible to install the plant on a platform with a surface of around 300 sqm. Therefore, it is verified that it is enough small to be installed in a reduced area such as a floating platform.
6. Under the same conceptual approach, short-cut methods to sizing the main equipment and modular methods to the preliminary cost estimation have been applied to the ammonia plant, obtaining a Base Module Cost of €2.1 MM.

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APPENDIX 1: SIMULATION INPUT

DYNAMICS

DYNAMICS RESULTS=ON

IN-UNITS SI MASS-FLOW='kg/hr' MOLE-FLOW='kmol/hr' &

VOLUME-FLOW='cum/hr' PRESSURE=bar TEMPERATURE=C DELTA-T=C &

PDROP-PER-HT='mbar/m' PDROP=bar SHORT-LENGTH=mm

DEF-STREAMS CONVEN ALL

MODEL-OPTION

DESCRIPTION "

Air Separation Simulation with Metric Units :

C, bar, kg/hr, kmol/hr, Watt, cum/hr.

Property Method: PENG-ROB

Flow basis for input: Mole

Stream report composition: Mole flow

"

DATABANKS 'APV110 PURE28' / 'APV110 AQUEOUS' / 'APV110 SOLIDS' &

/'APV110 INORGANIC' / NOASPENPCD

PROP-SOURCES 'APV110 PURE28' / 'APV110 AQUEOUS' / &
'APV110 SOLIDS' / 'APV110 INORGANIC'

COMPONENTS

N2 N2 /

O2 O2 /

AR AR /

HYDRO-01 H2 /

AMMON-01 H3N /

H2O H2O /

CL- CL- /

NA+ NA+ /

SO4-- SO4-2 /

MAGNE-01 MG /

CALCI-01 CA /

POTAS-01 K

SOLVE

RUN-MODE MODE=SIM

FLOWSHEET

BLOCK M6 IN=SPLIT3-2 C2-1 OUT=M6-1

BLOCK C4 IN=C3-1 OUT=C4-1

BLOCK HX5 IN=R2-1 C4-1 OUT=HX5-2 HX5-1

BLOCK HX6 IN=HX5-1 OUT=HX6-1

BLOCK R2 IN=HX6-1 OUT=R2-1

BLOCK HX7 IN=HX5-2 OUT=HX7-1
BLOCK F3 IN=HX7-1 OUT=F3-1 F3-2
BLOCK C2 IN=HX4-1 OUT=C2-1
BLOCK M5 IN=SEP4-1 M1-1 OUT=M5-1
BLOCK SPLIT3 IN=F3-1 OUT=SPLIT3-2 SPLIT3-1
BLOCK HX4 IN=M5-1 OUT=HX4-1
BLOCK C3 IN=M6-1 OUT=C3-1
BLOCK HX1 IN=C1-1 OUT=HX1-1
BLOCK SEP1 IN=HX1-1 OUT=SEP1-1 SEP1-2
BLOCK M1 IN=SEP1-1 SEP2-1 OUT=M1-1
BLOCK C1 IN=AIRFEED OUT=C1-1
BLOCK SEP2 IN=SEP1-2 OUT=SEP2-1 SEP2-2
BLOCK SEP3 IN=R1-1 OUT=SEP3-1 SEP3-2
BLOCK SEP4 IN=F1-1 OUT=SEP4-1 SEP4-2
BLOCK F1 IN=M3-1 OUT=F1-1 F1-2
BLOCK M3 IN=SPLIT2-1 SPLIT1-1 OUT=M3-1
BLOCK F2 IN=M4-1 OUT=F2-1 F2-2
BLOCK M4 IN=SPLIT1-2 SPLIT2-2 OUT=M4-1
BLOCK SPLIT2 IN=SEP3-2 OUT=SPLIT2-2 SPLIT2-1
BLOCK SPLIT1 IN=SEP3-1 OUT=SPLIT1-2 SPLIT1-1
BLOCK R1 IN=HX3-1 OUT=R1-1
BLOCK HX3 IN=P1-1 OUT=HX3-1
BLOCK P1 IN=M2-1 OUT=P1-1
BLOCK M2 IN=F2-2 F1-2 DESAL-1 OUT=M2-1
BLOCK DESAL IN=H2OFEED OUT=DESAL-1 DESAL-2



PROPERTIES PENG-ROB

USER-PROPS PRKIJ 1 2 1

PROP-DATA PRKBV-1

IN-UNITS ENG SHORT-LENGTH=in

PROP-LIST PRKBV

BPVAL N2 O2 -.0119000000 0.0 0.0 -459.6700000 1340.330000

BPVAL O2 N2 -.0119000000 0.0 0.0 -459.6700000 1340.330000

BPVAL N2 AR -2.6000000E-3 0.0 0.0 -459.6700000 1340.330000

BPVAL AR N2 -2.6000000E-3 0.0 0.0 -459.6700000 1340.330000

BPVAL O2 AR .0104000000 0.0 0.0 -459.6700000 1340.330000

BPVAL AR O2 .0104000000 0.0 0.0 -459.6700000 1340.330000

BPVAL N2 HYDRO-01 .1030000000 0.0 0.0 -459.6700000 &
1340.330000

BPVAL HYDRO-01 N2 .1030000000 0.0 0.0 -459.6700000 &
1340.330000

BPVAL N2 AMMON-01 .2193000000 0.0 0.0 -459.6700000 &
1340.330000

BPVAL AMMON-01 N2 .2193000000 0.0 0.0 -459.6700000 &
1340.330000

BPVAL AR AMMON-01 -.1800000000 0.0 0.0 -459.6700000 &
1340.330000

BPVAL AMMON-01 AR -.1800000000 0.0 0.0 -459.6700000 &
1340.330000

BPVAL AMMON-01 H2O -.2589000000 0.0 0.0 -459.6700000 &

1340.330000

BPVAL H2O AMMON-01 -.2589000000 0.0 0.0 -459.6700000 &

1340.330000

PROP-SET GASPROPS ZMX VMX VVSTDMX CPCVMX UNITS='cum/hr' &

SUBSTREAM=MIXED PHASE=V

; "Compressibility, volume flow, heat capacity ratio"

STREAM AIRFEED

SUBSTREAM MIXED TEMP=13.5 PRES=1. MOLE-FLOW=1.3

MOLE-FRAC N2 0.78118 / O2 0.2095 / AR 0.00932

STREAM H2OFEED

SUBSTREAM MIXED TEMP=16.5 PRES=1. MOLE-FLOW=1.2

MOLE-FRAC H2O 0.964 / CL- 0.0198 / NA+ 0.011 / SO4-- &

0.00276 / MAGNE-01 0.0013 / CALCI-01 0.0004 / &

POTAS-01 0.0004

BLOCK M1 MIXER

PARAM

BLOCK M2 MIXER

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr' &

HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C &

VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum' &

MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol' &
MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' &
PDROP=bar SHORT-LENGTH=mm

PARAM

BLOCK M3 MIXER

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr' &
HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C &
VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum' &
MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol' &
MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' &
PDROP=bar SHORT-LENGTH=mm

PARAM PRES=1.5

BLOCK M4 MIXER

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr' &
HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C &
VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum' &
MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol' &
MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' &
PDROP=bar SHORT-LENGTH=mm

PARAM PRES=1.5

BLOCK M5 MIXER

PARAM PRES=6.

BLOCK M6 MIXER

PARAM PRES=-0.01 NPHASE=1 PHASE=V T-EST=0.

BLOCK-OPTION FREE-WATER=NO

BLOCK SPLIT1 FSPLIT

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr' &
HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C &
VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum' &
MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol' &
MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' &
PDROP=bar SHORT-LENGTH=mm

FRAC SPLIT1-1 0.8

BLOCK SPLIT2 FSPLIT

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr' &
HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C &
VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum' &
MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol' &
MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' &
PDROP=bar SHORT-LENGTH=mm

FRAC SPLIT2-2 0.8

BLOCK SPLIT3 FSPLIT

FRAC SPLIT3-1 0.1

BLOCK DESAL SEP

PARAM

FRAC STREAM=DESAL-1 SUBSTREAM=MIXED COMPS=H2O CL- NA+ &
SO4-- MAGNE-01 CALCI-01 POTAS-01 FRACS=1. 0. 0. 0. &
0. 0. 0.

BLOCK SEP2 SEP

PARAM

FRAC STREAM=SEP2-1 SUBSTREAM=MIXED COMPS=N2 O2 AR FRACS= &
0.9 0.05 0.05

BLOCK SEP3 SEP

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr' &
HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C &
VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum' &
MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol' &
MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' &
PDROP=bar SHORT-LENGTH=mm

PARAM

FRAC STREAM=SEP3-1 SUBSTREAM=MIXED COMPS=HYDRO-01 FRACS= &
0.8

BLOCK SEP4 SEP

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr' &
HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C &
VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum' &
MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol' &

MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' &
PDROP=bar SHORT-LENGTH=mm

PARAM

FRAC STREAM=SEP4-1 SUBSTREAM=MIXED COMPS=O2 HYDRO-01 H2O &
FRACS=0.02 0.8 0.02

BLOCK HX1 HEATER

PARAM PRES=6.5 VFRAC=1. DPPARMOPT=NO

BLOCK HX3 HEATER

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr' &
HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C &
VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum' &
MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol' &
MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' &
PDROP=bar SHORT-LENGTH=mm

PARAM TEMP=80. PRES=1.5 DPPARMOPT=NO

BLOCK HX4 HEATER

PARAM PRES=-0.01 VFRAC=1. DPPARMOPT=NO

BLOCK HX6 HEATER

PARAM TEMP=438. PRES=-0.01 DPPARMOPT=NO

BLOCK HX7 HEATER

PARAM TEMP=-26. PRES=-0.01 DPPARMOPT=NO

BLOCK F1 FLASH2

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr' &
HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C &
VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum' &
MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol' &
MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' &
PDROP=bar SHORT-LENGTH=mm
PARAM TEMP=54. PRES=1.5

BLOCK F2 FLASH2

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr' &
HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C &
VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum' &
MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol' &
MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' &
PDROP=bar SHORT-LENGTH=mm
PARAM TEMP=77. PRES=1.5

BLOCK F3 FLASH2

PARAM TEMP=-26. PRES=17.

BLOCK HX5 HEATX

PARAM T-COLD=428. CALC-TYPE=DESIGN TYPE=COUNTERCURRE &
PRES-HOT=0. U-OPTION=PHASE F-OPTION=CONSTANT &
CALC-METHOD=SHORTCUT

FEEDS HOT=R2-1 COLD=C4-1
 OUTLETS-HOT HX5-2
 OUTLETS-COLD HX5-1
 HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
 COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
 TQ-PARAM CURVE=YES

BLOCK SEP1 RADFRAC

PARAM NSTAGE=60 ALGORITHM=STANDARD MAXOL=25 DAMPING=NONE
 COL-CONFIG CONDENSER=TOTAL REBOILER=NONE
 FEEDS HX1-1 60 ON-STAGE
 PRODUCTS SEP1-2 60 L / SEP1-1 1 L
 P-SPEC 1 6.
 COL-SPECS D:F=0.4 DP-STAGE=0.003
 SPEC 1 MOLE-FRAC 1E-006 COMPS=O2 STREAMS=SEP1-1 &
 SPEC-DESCRIP="Mole purity, 1E-006, PRODUCT"
 VARY 1 D:F 0.3 0.7

BLOCK R1 RSTOIC

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr' &
 HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C &
 VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum' &
 MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol' &
 MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' &
 PDROP=bar SHORT-LENGTH=mm
 PARAM TEMP=80. PRES=1.5

STOIC 2 MIXED H2O -2. / HYDRO-01 2. / O2 1.

CONV 2 MIXED H2O 0.5

BLOCK R2 RSTOIC

PARAM TEMP=498. PRES=138.

STOIC 1 MIXED HYDRO-01 -3. / N2 -1. / AMMON-01 2.

CONV 1 MIXED HYDRO-01 0.3

BLOCK P1 PUMP

IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='Gcal/hr' &
 HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE=bar TEMPERATURE=C &
 VOLUME=cum DELTA-T=C HEAD=meter MOLE-DENSITY='kmol/cum' &
 MASS-DENSITY='kg/cum' MOLE-ENTHALP='kcal/mol' &
 MASS-ENTHALP='kcal/kg' HEAT=Gcal MOLE-CONC='mol/l' &
 PDROP=bar SHORT-LENGTH=mm

PARAM PRES=1.5

BLOCK C1 COMPR

PARAM TYPE=ISENTROPIC PRES=6.5 SB-MAXIT=30 SB-TOL=0.0001

BLOCK C2 COMPR

PARAM TYPE=ISENTROPIC PRES=17. NPHASE=2 SB-MAXIT=30 &
 SB-TOL=0.0001 MAXIT=100

BLOCK-OPTION FREE-WATER=NO

BLOCK C3 COMPR

PARAM TYPE=ISENTROPIC PRES=60. NPHASE=1 SB-MAXIT=30 &
 SB-TOL=0.0001
 BLOCK-OPTION FREE-WATER=NO

BLOCK C4 COMPR

PARAM TYPE=ISENTROPIC PRES=138. NPHASE=1 SB-MAXIT=30 &
 SB-TOL=0.0001
 BLOCK-OPTION FREE-WATER=NO

DESIGN-SPEC DS-PURGE

DEFINE AR MOLE-FRAC STREAM=M6-1 SUBSTREAM=MIXED &
 COMPONENT=AR
 DEFINE OX MOLE-FRAC STREAM=M6-1 SUBSTREAM=MIXED &
 COMPONENT=O2
 DEFINE TOT STREAM-VAR STREAM=M6-1 SUBSTREAM=MIXED &
 VARIABLE=MOLE-FLOW UOM="kmol/hr"
 SPEC "(AR+OX)/TOT" TO "0"
 TOL-SPEC "0.12"
 VARY BLOCK-VAR BLOCK=SPLIT3 SENTENCE=FRAC VARIABLE=FRAC &
 ID1=SPLIT3-1
 LIMITS "0" "1"

DESIGN-SPEC DS-WATER

DEFINE H2O MOLE-FRAC STREAM=M6-1 SUBSTREAM=MIXED &
 COMPONENT=HYDRO-01
 DEFINE N2O MOLE-FRAC STREAM=M6-1 SUBSTREAM=MIXED &

COMPONENT=N2

SPEC "H2O/N2" TO "3.0"

TOL-SPEC "0.01"

VARY MOLE-FLOW STREAM=H2OFEED SUBSTREAM=MIXED
COMPONENT=H2O &

UOM="kmol/hr"

LIMITS "0" "30" STEP-SIZE=0.1

EO-CONV-OPTI

CONV-OPTIONS

WEGSTEIN MAXIT=300

STREAM-REPOR MOLEFLOW MOLEFRAC PROPERTIES=GASPROPS

PROPERTY-REP PCES

PROP-TABLE PTENV-1 PTENVELOPE

PROPERTIES PENG-ROB FREE-WATER=STEAM-TA SOLU-WATER=3 &

TRUE-COMPS=YES

STREAM AIRFEED

ENVELOPES VFRAC=1

PARAM MAXPT=50

TABULATE

APPENDIX 2: AUTOCAD PLANE

