UNIVERSITÀ DEGLI STUDI DI PADOVA

DIPARTIMENTO DI INGEGNERIA INDUSTRIALE

CORSO DI LAUREA MAGISTRALE IN INGEGNERIA CHIMICA E DEI PROCESSI INDUSTRIALI

Tesi di Laurea Magistrale in
Ingegneria Chimica e dei Processi Industriali

CONCEPTUAL DESIGN OF A GREEN-AMMONIA PRODUCTION PROCESS:
COST AND SAFETY ASSESSMENT

Relatore: Prof. Fabrizio Bezzo
Correlatori: Ing. Paolo Mocellin, Ing. Alberto Benedetti

Laureando: FABIO SALGARI

Anno Accademico 2023/2024

Un ringraziamento ai Professori Bezzo e Mocellin,
che mi hanno seguito pazientemente in questo percorso.
Ad Alberto, per il tempo sempre trovato per questo progetto.
A chi c'è sempre stato durante questi anni: la famiglia e gli amici.

A$_{lla}$ *Luci*$_{n}$*a, che mi ha sempre illuminato la strada.*

Abstract

Ammonia production accounts for about 2% of global CO_2 emissions, and there is a strong industrial interest in deploying alternative sustainable routes. The scope of the Thesis is the conceptual design of an inherently safer and more environmentally sustainable process for ammonia production. Low carbon emissions are achieved by considering the electrification of the Haber-Bosch process and the substitution of fossil-based feedstocks with water and air. Process safety issues are tackled since the beginning of the conceptual design according to the principles of inherently safe design, thus allowing for the selection of safer solutions while driving the arrangement of the process operations. A reduced plant capacity (100 ton/day) is considered. Specification on ammonia purity is set at 99.9%w. The final design is also evaluated in terms of its economic performance, considering different scenarios based on different electricity prices. The economic assessment highlights the high production costs, primarily due to the high electrical demand and capital costs necessary to retrieve the hydrogen-nitrogen mixture. The best-case scenario, with an electricity price fixed at 0.08 €/kWh, leads to an ammonia selling price of 2.30 €/kg_{NH3}, nearly five-fold the current market value (0.47 €/$kgNH_3$).

Prefazione

Per riuscire a raggiungere gli obiettivi climatici fissati al 2050, lo sviluppo di processi industriali sostenibili è un tassello fondamentale per ridurre i contributi legati al settore chimico. Questo lavoro, in particolare, si è concentrato sul contributo dell'ammoniaca, corrispondente al 35% delle emissioni di CO_2 del settore chimico e al 2% delle emissioni globali. L'ammoniaca presenta un impatto ambientale diretto, legato alla sua produzione, e indiretto, ovvero legato al suo utilizzo come materia prima per la sintesi di altre sostanze e il loro utilizzo (ad esempio la conversione di ammoniaca in urea e il suo utilizzo nel settore agricolo.

Il progetto proposto per un processo per la sintesi di ammoniaca a basse emissioni di carbonio è stato ottenuto tramite l'elettrificazione dei consumi energetici e la sostituzione delle materie prime fossili con acqua ed aria, per l'ottenimento dei reagenti necessari.

In questo elaborato, nello specifico, sono state comparate due configurazioni di processo, caratterizzate da differenti pressioni operative (200 e 300 bar) e basate su ridotte capacità di produzione rispetto agli impianti attualmente disponibili (100 ton/giorno).

Durante lo sviluppo della progettazione di processo, con l'obiettivo di incrementarne la sicurezza, i principi della progettazione intrinsecamente sicura sono stati applicati, permettendo di effettuare scelte in merito alle tecnologie da utilizzare e fornendo raccomandazioni utili per aumentare la sicurezza dell'impianto. Particolare interesse è stato rivolto agli stoccaggi, unità caratterizzate da elevati rischi intrinseci legati all'accumulo di sostanze pericolose in grandi quantità. Durante la valutazione delle performance di sicurezza del processo sviluppato, differenti tecniche sono state applicate: HAZID (*hazard identification*), necessaria ad una valutazione preliminare dei rischi e alla loro identificazione; HAZOP (*hazard and operability analysis*), per poter condurre una più dettagliata e rigorosa analisi di rischio basata sulle deviazioni che possono interessare il processo e una valutazione tramite "*TNT-equivalency*" del potenziale di esplosione nel caso di collasso meccanico dei serbatoi di stoccaggio.

In aggiunta alla valutazione di sicurezza, le proposte progettuali sviluppate sono state infine valutate in termini di prestazioni economiche, comparandole in funzione dei prezzi dell'energia elettrica. In particolare, differenti scenari che considerano la produzione di elettricità a basse emissioni di carbonio sono stati confrontati con due scenari attuali, presi come riferimento della situazione attuale del mercato elettrico.

Le prestazioni economiche del processo sviluppato, inoltre, sono state valutate in due condizioni differenti: inizialmente fissando il prezzo di vendita del prodotto ottenuto pari al

valore di mercato attuale (aggiornato a Novembre 2023) e successivamente aggiustando il prezzo di vendita con il fine di osservare le prestazioni economiche in condizioni favorevoli.
In particolare, i risultati ottenuti da queste valutazioni hanno permesso di osservare che il processo proposto soffre di costi di produzione molto elevati: nel caso migliore, il costo di vendita è risultato pari a 2.30 €/kgNH_3, ben lontano dal valore di mercato attuale, 0.47 €/kgNH_3.
A parità di prezzo di vendita, l'analisi di redditività ha evidenziato prestazioni leggermente migliori per la configurazione a bassa pressione rispetto all'alternativa a 300 bar.

Table of Contents

List of Figures

List of Tables

List of Abbreviations

Acronym		Extended	UoM
ACCR	=	Annual Capital Charge Ratio	%
AE/AEL	=	Alkaline ELectrolysis	
AIChE	=	American Institute of Chemical Engineers	
ASU	=	Air Separation Unit	
B-2050	=	*Borasio - 2050*	
BAT	=	Best Available Technology	
BFD	=	Block-Flow-Diagram	
BLEVE	=	Boiling Liquid Expansion Vapor Explosion	
BP	=	By-Product	M€
CAD	=	Cryogenic Air Distillation	
CAPEX	=	CAPital EXpenditure	€ or €/year
C_{BM}	=	Bare Module Cost	€
CCPS	=	Center for Chemical Process Safety	
CONS	=	CONSumables	M€
COM	=	Cost Of Manufacturing	M€
COP	=	Conference Of Parties	
CRW	=	Chemical Reactivity Worksheet	
DEA	=	Di-Ethanol-Amine	
DMC	=	Direct Manufacturing Cost	M€
DPPB	=	Discounted Pay-Back Period	Years
EC-LQ22	=	*European Commission – Last Quarter 2022*	
EoS	=	Equation of State	
EP	=	Economic Potential	€/year
ES-FH23	=	*Eurostat – First Half 2023*	
F_{BM}	=	Bare Module Factor	
FCI	=	Total Fixed Capital Investment	M€
FCOP	=	Fixed Cost Of Production	M€
F_M	=	Material Factor	
FMC	=	Fixed Manufacturing Cost	M€
F_P	=	Pressure Factor	
F&R	=	Fees & Royalties	M€
GE	=	General Expenses	M€
GHG	=	GreenHouse Gases	
GHS	=	Globally Harmonized System of Classification and Labelling of Chemicals	
GM	=	Gross Margin	M€
G-RES	=	*Giuliani – RES* (alternative forms with N, nuclear & H, hydrogen)	
HAZID	=	HAZard IDentification	
HAZOP	=	HAZard OPerability	
HP	=	High Pressure (often referred to steam/plants sections)	
IPCC	=	International Panel on Climate Change	
IRENA	=	International Renewable Energy Agency	
IRR	=	Interest Rate Criterion	%
ISBL	=	InSide Battery Limits	M€
ISD	=	Inherently Safer Design	

(continued on next page)

(continued from previous page)

LBR	=	cost of LaBoR	M€
LP	=	Low Pressure (often referred to steam/plants sections)	
MANT	=	MAiNTenance	M€
MAWP	=	Maximum Allowable Working Pressure	bar
MEA	=	Mono-Ethanol-Amine	
MDEA	=	Mono-Di-Ethanol-Amine	
MP	=	Medium Pressure (often referred to steam/plants sections)	
MSDS	=	Materials Safety Data Sheet	
NFPA	=	National Fire Protection Association	
NPV	=	Net Present Value	M€
NWP	=	Normal Working Pressure	bar
OPEX	=	OPerational EXpenditure	€ or €/year
Op.Lbr	=	Operating Labor	M€
OSBL	=	OutSide Battery Limits	M€
PEM/PEMEL	=	Proton Exchange/Electrolyte Memebrane (ELectrolysis)	
PSA	=	Pressure Swing Adsorption	
R&I	=	Research & Innovation	M€
RE/RES	=	Renewable Energy Sources	
REV	=	REVenues	M€
RM	=	Raw Material	M€
ROI	=	Return On Investment	%
SC	=	Start-up Capital	M€
SMR	=	Steam Methane Reforming	
SOEC/SOEL	=	Solid Oxide Electrolyser Cell / Solid Oxide Electrolysis	
SRK	=	Soave-Redlich-Kwong	
SSC	=	SuperStage Column	
SUP	=	SUPervision	M€
TCI	=	Total Capital Investment	M€
TCoP	=	Total Cost of Production	€ or €/unit
TDC	=	Total Direct Cost	M€
TdM	=	Thermodynamic Model	
T_{SL}	=	fluid super-saturation temperature at atmospheric pressure	
TNT	=	Tri-Nitro-Toluene	
UTS	=	UTilitieS	M€
UoM	=	Units of Measure	
VCOP	=	Variable Cost Of Production	M€
WC	=	Working Capital	M€
WGS(R)	=	Water Gas Shift (Reaction)	
W_{blast}	=	Work of the blast	
W_{TNT}	=	Weight of TNT	

Introduction

Net-Zero 2050 represents a key-target fixed in the near-future, that requires noticeable changes in the production processes of chemical products to achieve the sustainability goal fixed. One of the chemicals that most contributes nowadays to pollution is ammonia, accounting for about 2% of global CO_2 emissions and 35% of the chemical sector. For this reason, this work aims at developing a sustainable design for ammonia production using commercially available technologies and industrial best practices. Fossil fuels have been removed from the ammonia synthesis process, thanks to process electrification and using water and air as process feedstocks: air separation and electrolysis have been considered in order to obtain the synthesis mixture required.

The thesis is structured as follows.

After having presented the overall environmental background and the scope of the thesis in the first chapter, the method applied to simulate the conceptualized process has been presented in the second chapter of this elaborate. Two different configurations have been compared in this work, both characterized by a reduced plant capacity compared to industrial plants (100 ton/day) and that differentiate in the operative pressure used: 200 bar and 300 bar.

The third chapter presents the inherently safer design (ISD) principles applied in this work and summarizes safety-information about process risks and hazards of the chemical components. Interaction matrices, and HAZID and HAZOP analyses are discussed in this chapter, too.

The fourth chapter is concerned with the assessment of the economic performance of the proposed design configurations, taking into account several scenarios based on the price of electricity.

Some final remarks and a future work perspective conclude the thesis.

Chapter 1
State of the Art

This first chapter collects and illustrates the basis on which the work has been developed. The environmental background is firstly introduced, giving information about the concerns and challenges the chemical sector has to tackle in the near future. After a brief discussion about the chemical sector, the process considered in this elaborate and the involved species (Haber-Bosch process for ammonia production) are introduced with a resume of the technologies available to produce the required feedstocks. Concluding, the aim of this elaborate is discussed.

1.1 Global Warming

In recent years, public perception of global warming has changed, showing an increasing interest about the environment, the protection of ecosystems and, more in general, the "health" of the planet. Different associations are exhibiting their interest and feelings about the cause, in some cases also with different forms of protests.

Human activities are unequivocally responsible for the increase in greenhouse gas concentration since the industrial revolution. This increase in pollutants concentration, ascribed to "anthropogenic pollution", is responsible for the increase of the average surface temperature of the planet, that has increased by 1°C since 1850 [1]. To avoid an excessive increase in the surface temperature, which may end in rising risks of far more severe climate change impacts, at the UN Climate Change Conference held in Paris in 2016, COP21 (21st Conference of Parties), 196 Nations signed the Paris Agreement, with the common target of limiting global warming. The ambitious target fixed by the Paris Agreement is to limit the increase of global average temperatures below 2°, preferably 1.5°C, compared to pre-industrial levels [2], value indicated by the UN's Intergovernmental Panel on Climate Change (IPCC) as a limiting threshold to avoid severe consequences [3]. Paris Agreement, in addition to the mentioned temperature-increase threshold, has also set an additional ambitious target related to the amount of greenhouse gases emissions, especially of CO_2: by 2050 Net-Zero CO_2 emissions [1].

Many institutions and companies have developed, adopted and regulated both low-carbon, carbon-free and more sustainable technologies aiming to reduce human-derived pollution [4,5] with the common target of improving their environmental impact. All sectors are involved in this action, from building to transport, industry and the energy sector. *Figure 1.1* illustrates the share of CO_2 emissions pertaining to each.

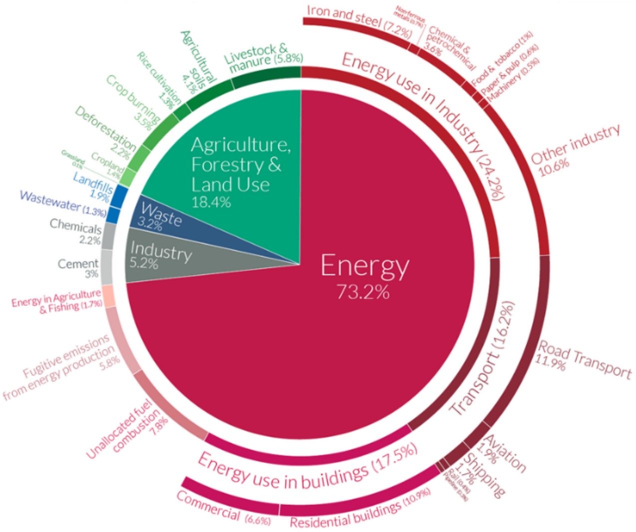


Figure 1.1 *Pie-chart showing the share of CO_2 emissions of each sector* [6].

1.1.1 Energy Sector

According to *Figure 1.1,* the energy sector covers the majority of CO_2 emissions , which are primarily associated with electricity production by power-plants, fuels for transports and even energy in the form of fossil fuels used in industrial processes. Focusing on the Italian framework and according to the data shown in *Figure 1.2,* in 2021, almost 80% of Italian primary energy supply (net energy production considering imports/exports, international bunkers and stock changes [7]) came from fossil-fuels, meaning that a relevant change is necessary for a more sustainable future.

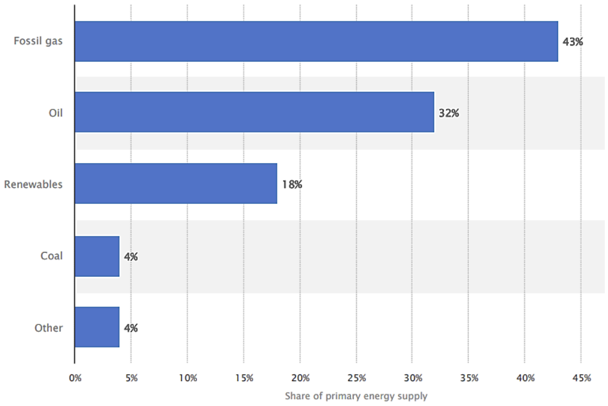


Figure 1.2 *Chart showing the share of primary energy supply in Italy by source* [8].

A significant reduction of emissions can be achieved with renewable energy sources (RES) that will undoubtedly play a relevant role in the pathway toward 2050. However, the implementation of RES will bring new obstacles to overcome, e.g. productivity fluctuations due to weather instability, local availability of natural resources (wind and solar exposure), and the need for adequate energy storage and interconnections (electricity grid improvement in transport capability). Also, a mere substitution of fossil-fuels with RES would miss the benefits of a wholesale energy transition, including energy efficiency and more sustainable and environmentally friendly practices [1].

1.1.2 Chemical Sector

The chemical sector accounts for 7% of all industrial CO_2 emissions [9], meaning that the implementation of sustainable processes can contribute significantly to the contrast of climate change. Notably, the implementation of new processes based on carbon-capture and utilization, carbon sequestration from air and green hydrogen can play a key role in the decarbonization strategy.

1.1.2.1 Electrification of Chemical Industry

Industry is the primary energy-requirement sector (*Figure 1.1*), and about one-third of the energy provided is used as feedstock [10], meaning that fossil-fuels are used to produce other products: their mass is used, not the energetic content. The remaining energy requirement is provided by fossil fuels and electricity, which account for only 20% of the overall industrial energy demand.

A central aspect to consider when discussing the decarbonization of the chemical sector is electrification, i.e. the substitution of the share of fossil fuels used for their energy content with electricity. One of the concerns of electrification of the chemical sector is the operation at high temperature: nowadays many technologies are available to provide heat up to 1000°C; above this threshold new processes must be developed to meet the final goal, as shown in *Figure 1.3*.

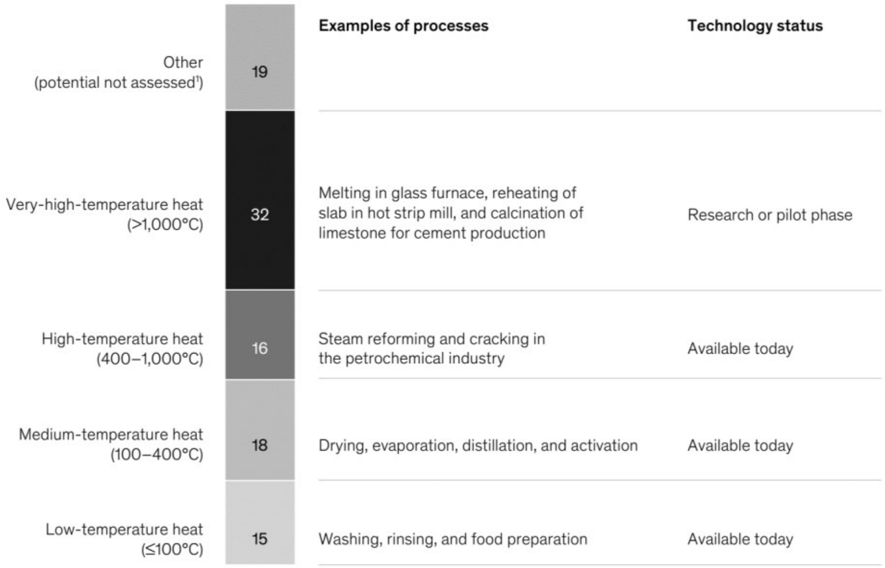


Figure 1.3 *Status of availability for technological electrically-driven alternatives to fossil-based equipment at different operative temperatures and examples of processes involved* [10].

As mentioned, electrification is a suitable strategy for the reduction of CO_2 emissions, being fossil fuels substituted with electricity, but the effect of this action is contingent by the environmental impact of the national energy mix: as higher shares of electricity are produced with fossil-fuels, as higher CO_2 emissions per kWh are produced. In such case, the direct consumption of fossil fuels in the plant rather than the electrification of the industrial process is both cheaper and more efficient (less polluting).

The practical effects of a fully electrified industrial sector with a 100% renewables-based energy system are rarely investigated. Still, compared to hydrogen-based economies (that are commonly considered as a viable substitute to the actual fossil-based market), smaller costs and higher efficiencies are obtained, leaving the hydrogen-driven equipment as a suitable option for cases where any other alternative is not suitable or available [11].

1.1.2.2 Reduction of CO_2 Emission: the Case of Ammonia Production

Ammonia is one of the "big-four" industrial processes (ammonia, steel, cement and ethylene) that requires the development of a carbon-free process because of the associated emissions [12]. As reported in *Figure 1.4*, ammonia is the process that emits more CO_2, around 500 million tons of CO_2 per year (2018), equal to 1.8% of the global CO_2 emissions [12] referring only to the chemical sector those are 35% of the overall emissions [13].

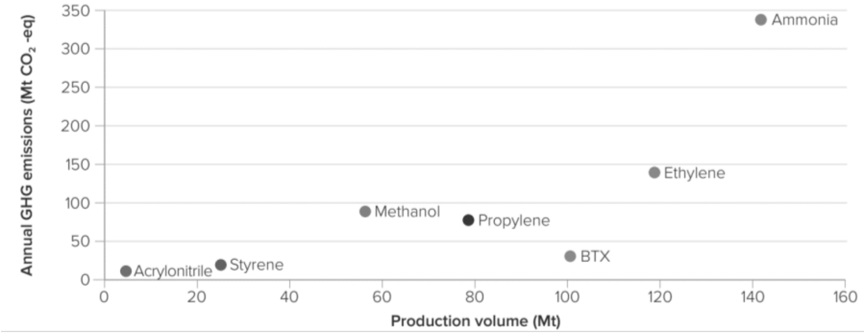


Figure 1.4 *Annual greenhouse gases emissions expressed for selected high-volume chemicals (data referring to 2010)* [12].

Interest of this work is the reduction of the environmental footprint of ammonia production. For this reason, in the following sections, both materials and processes required to develop an electrified and sustainable design for ammonia production will be introduced and discussed. This is performed considering that the two main aspects to account for achieving this goal are:

- Reactants sustainability, i.e. sustainable production of N_2 and H_2 is necessary to substitute the actual production processes used: gasification and steam-methane-reforming. This aspect is solved by retrieving nitrogen from air separation and producing hydrogen via electrolysis, both fed with low-carbon emissive electricity.
- Production process sustainability: production process electrification should be further considered, especially in terms of the energy-mix carbon-intensity used in the plant.

1.2 Air

Air is a mixture of gases, whose composition is reported in *Table 1.1*, mainly made of nitrogen, oxygen, argon and with traces of CO_2 and noble gases.

Table 1.1 *Average composition of air* [14].

Species	Concentration
Nitrogen	78.1%
Oxygen	20.9%
Argon	0.93%
Carbon Dioxide	419 ppm (0.04%)
Neon	18 ppm
Helium	5 ppm
Krypton	1 ppm

Nitrogen, oxygen and argon are commodities that are obtained by air separation units (ASU). The market size of these chemicals has increased over the years and it is expected to continue to grow [15]: after the COVID-19 pandemic, investments in oxygen production has increased noticeably, accordingly to an increasing market demand expectation, especially concerning the Asia-Pacific region. The expected growth rate of oxygen demand through 2032 is of 12.8%; the major driver of this increased demand is the healthcare industry.

1.2.1 Air Production Routes

Whenever one of the components of air is required, air separation units (ASU) are built to provide the plant the species of interest. Different techniques can be used to obtain the desired result and those are: membranes, pressure swing adsorption and cryogenic distillation of air.

1.2.1.1 Membrane Air Separation

Membrane-based air separation process can be used to separate gases via selective permeation: nitrogen (i.e. the chemical of interest) is not capable of permeate the membrane, therefore it is collected in the retentate stream leaving the unit; permeable species are instead collected in the permeate stream, that contains oxygen and impurities (mainly water and CO_2) present in the feed of pre-treated-air (without dust particles) [14].

The purity of the product can be varied by changing the operative conditions and the number of stages, but the technology is not mature enough to provide very-pure nitrogen streams. Membranes show the lowest capital and operational and maintenance costs (abbreviated in CAPEX and O&M) for production capacities smaller than 1’120 STD m^3/hour. *Figure 1.5* represents the simplified scheme of a membrane ASU.

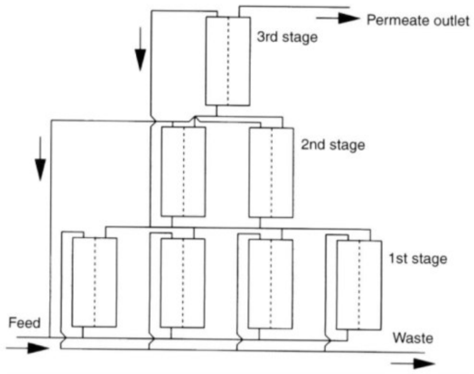


Figure 1.5 *Schematic representation of the Membrane-ASU process* [14].

1.2.1.2 Pressure Swing Adsorption (PSA)

PSA is a technology based on solid adsorption of air constituents on the surface of solid species contained in the process vessel: usually zeolites, molecular sieves; also silica gel and active carbon can be used. The adsorption mechanism is both pressure-dependent and reversible and allows to adsorb nitrogen because of its stronger interactions with solid materials used compared to oxygen and impurities. *Figure 1.6* represents a PSA unit, made of two elements that operates in parallel, allowing a continuous operation by the alternation of adsorption and desorption steps [14].

PSA could be operated also under vacuum conditions (Vacuum-PSA), approach characterized by higher capital costs but a more energetically efficient process.

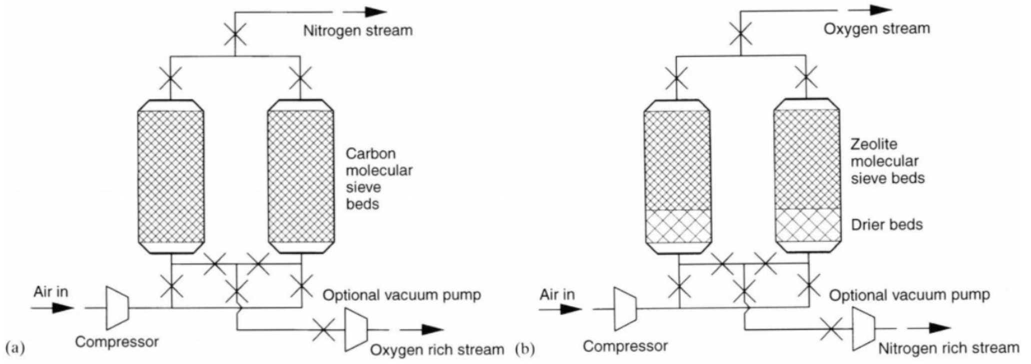


Figure 1.6 *Representations of two Pressure Swing Adsorbers for nitrogen(a) and oxygen (b) recovery* [14].

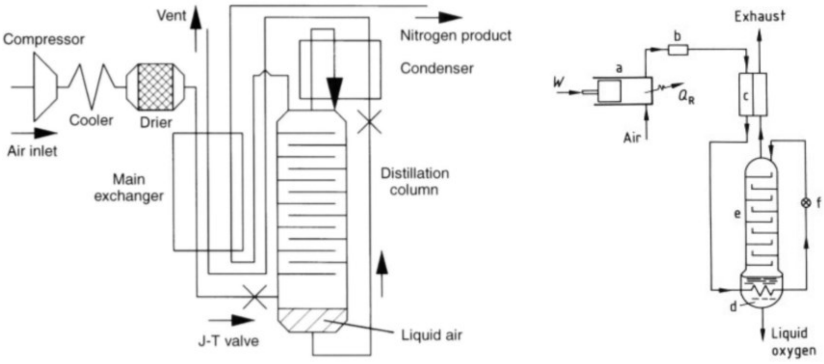
1.2.1.3 Cryogenic Air Distillation (CAD)

Cryogenic air distillation is a process performed to separate air constituents by distillation at extremely severe conditions, because of species' boiling temperatures: low-moderate pressures (10 bar) and -200°C. Because of the operative conditions a proper insulation and heat-integration are required to obtain good efficiencies [14] and to minimize costs.

To recover highly pure products, being boiling temperatures of air constituents very close to each other, minimal pressure drops are required in the two distillation columns used: 0.141 bar for the low-pressure column and 0.04 bar for the high-pressure column [16].

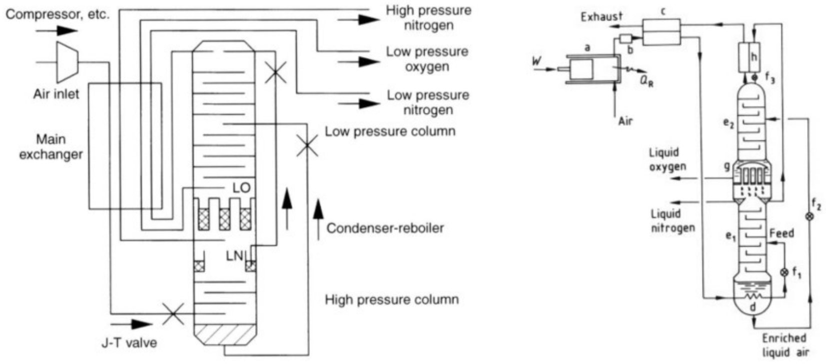
Three configurations are available for air-separation and the proper one is selected as function of the desired products and their purity, specifically:

- single-columns for oxygen/nitrogen recover at high purity, represented in *Figure 1.7;*
- double-columns for pure oxygen and nitrogen recovery, represented in *Figure 1.8;*
- triple-columns for oxygen, nitrogen and argon recovery, represented in *Figure 1.9.*



(a) (b)

***Figure 1.7** Representation of Single-Column CAD for nitrogen (a)* [17] *and oxygen (b) recovery* [18].



(a) (b)

***Figure 1.8** Representation of the Double Column CAD process for air separation (a)* [17]
and an alternative based on Linde Technology (b) [18].

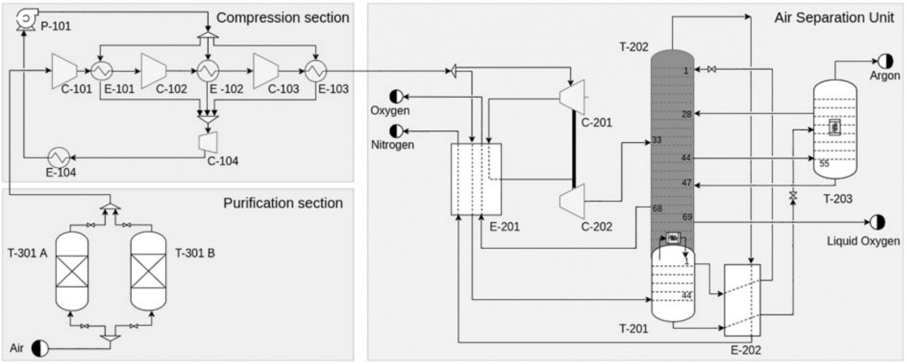


***Figure 1.9** Schematic representation of an Heylandt-type CAD-ASU with SSC for Argon recovery* [15].

In all the represented CAD alternatives, a compression-expansion process refrigerates air at the operative temperature. *Figure 1.9* explicitly represents all the steps necessary for air separation. After pre-purification, performed by PSA, air is compressed at 5/10 bar [14] by multistage compression (with three [15] or four [16] stages) with intercooling (temperature reduced at

300K after every compression-step [15]) driven by cooled water: air compression is the most expensive step in CAD [19]. Heat-integration for additional cooling of air and recovery of "cold" from products is performed with a multi-current brass-aluminum fin-plate heat-exchanger, that guarantees very small temperature gradients between fluids and allows the integration of different fluid streams, increasing process efficiency [14,16].

Once cooled, air is expanded in the distillation column with a turbine (adiabatic expansion) or by lamination (Joule-Thompson expansion), rapidly reaching the required conditions [17]. Lamination is a preferrable choice because of the high capital cost to sustain for purchasing the turbine, that operates with a to-phase flow and at arduous conditions (80K) [17]. After expansion, the two-phase refrigerated air stream is fed in the column, providing it refrigeration. In the double-column configuration, to enhance process performance, the two columns operate at different pressures and are welded together, improving heat integration: operating the bottom column at higher pressure it is possible to use its top-section as reboiler for the top-column, whose bottom acts as condenser for the low-pressure unit, as can be seen in *Figure 1.8.b*. The low-pressure column operates at 1.2-1.3 bar and the high-pressure unit at 5/6 bar: this difference allows to operate with a total condenser, exploiting the boiling temperature difference between the two fluids, that is around 3 degrees [17].

Figure 1.9 represents an alternative approach for ASU, Heylandt-type process [18]: part of the air fed (around 10% [15]) is sent to a turbine before entering the low-pressure section.

A "super stage column" (SSC) can be added to the two-column ASU to recover pure argon, with <1ppm of impurities. Without the SSC unit argon must be purged from the column to avoid its accumulation (especially in the low-pressure column), having boiling temperature between nitrogen and oxygen ones.

The main disadvantage of the SSC column is the economical impact it has on the overall process: to minimize pressure drops a suitable structured packings is required and a very high reflux is needed to increase product purity.

One final aspect related to "operation-as-usual" of CAD-ASU regards the periodic purges required: even if an SSC column is added, noble gases such as neon and helium accumulates, requiring purges to avoid an incorrect operation of the distillation unit [17].

Independently from the technology considered, nitrogen can be recovered with <2ppm of impurities [16,17], satisfying ammonia plant purity demand.

1.2.2 Comparison between Alternatives & Technology Selection

The choice of the most suitable technology is commonly performed considering the productivity demanded and the purity degree, CAPEX and OPEX of the technological alternatives. In this elaborate a very-pure nitrogen stream with a moderate-high productivity to synthesize ammonia is required. A brief comparison between the three technologies presented is reported in *Table 1.2*.

***Table 1.2** Comparison of ASU technologies: advantages and disadvantages.*

Technology	Advantages	Disadvantages
Cryogenic Air Distillation	Low electricity per unit of nitrogen Produces very pure nitrogen Generates liquid nitrogen for storage	Large space & utility requirements High capital costs Limited productivity scalability Long start-up and shut-down times
Pressure Swing Adsorption	Low to moderate capital cost Cost effective nitrogen production with Relatively high purities Quick installation and start-up	High maintenance requirement Noisy Limited scalability
Membranes	Low CAPEX Flexible productivity and product purity Quick installation and start-up	Uneconomical for high-purities or High-productivities High electrical demand

For the correct operation of ammonia synthesis unit and considering that the technology is not commercially available nowadays, membrane air separation units has not been considered for the application of interest.

Both the remaining alternatives, CAD and PSA, are suitable alternatives for the process of interest and are applied industrially nowadays. The choice of the technology to implement has been performed considering the nitrogen requirement for the ammonia plant capacity of interest, 100 ton/day [20]: the attended nitrogen demand overcome the threshold of 1’200 STD m^3/h indicated in [14] as a nitrogen productivity above which CAD is more economically convenient compared to PSA.

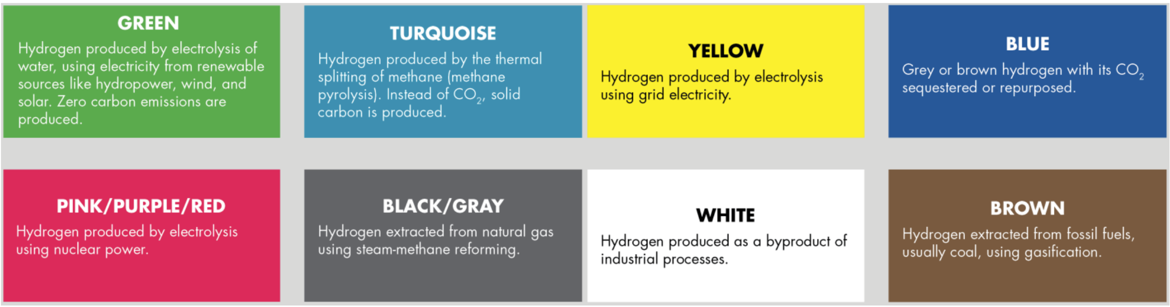
1.3 Hydrogen

1.3.1 Sustainability & Future Perspectives

In recent years, aiming to a more sustainable future, hydrogen has gained interest because of its potential in replacement of the actual hydrocarbon-based economy: hydrogen can serve as energy carrier for both transportation and chemical-related applications [21]. These applications, called "Power-to-X" approaches, consist in the conversion of power in hydrogen, that can later be converted back into energy (Power-to-Power) or chemicals, such as Gas, Ammonia or other fuels; combining this approach with low-carbon energy, the resulting green-economy can aim to achieve sustainability goals on the long-run (Net-Zero 2050 goals).

To develop this hydrogen-based scenario it must be reduced the emissions associated to hydrogen production. Presently, around 50% of hydrogen's world demand is met by steam methane reforming (SMR), 30% by oil/naphtha reforming, 18% by coal gasification, 3.9% by water electrolysis, and 0.1% from other sources [21].

NACFE has develops a color-coding technique to describe hydrogen sustainability as function of the feedstock used to produce it and this *Figure 1.10*



GREEN
Hydrogen produced by electrolysis of water, using electricity from renewable sources like hydropower, wind, and solar. Zero carbon emissions are produced.

TURQUOISE
Hydrogen produced by the thermal splitting of methane (methane pyrolysis). Instead of CO$_2$, solid carbon is produced.

YELLOW
Hydrogen produced by electrolysis using grid electricity.

BLUE
Grey or brown hydrogen with its CO$_2$ sequestered or repurposed.

PINK/PURPLE/RED
Hydrogen produced by electrolysis using nuclear power.

BLACK/GRAY
Hydrogen extracted from natural gas using steam-methane reforming.

WHITE
Hydrogen produced as a byproduct of industrial processes.

BROWN
Hydrogen extracted from fossil fuels, usually coal, using gasification.

Figure 1.10 *NACFE's (unofficial but commonly accepted) differentiation of hydrogen "types" by source* [22].

With the only exception of electrolysis-derived hydrogen, all commonly used hydrogen production technologies retrieve a gaseous mixture of H_2 and CO, called syngas (abbreviation of synthesis-gas), but for ammonia synthesis only hydrogen is of interest, therefore syngas purification and upgrading operations are necessary intermediate steps.

For the sustainable and electrified production of ammonia, the only technology to consider further is electrolysis (in its three technological alternatives, discussed in the following paragraph), therefore green-hydrogen accordingly to NACFE's color-coding. It must be noted that with green-hydrogen (or "green-X" in a wider perspective) it is commonly intended "hydrogen produced via electrolysis with electricity produced by RES". Considering in this elaborate a plant fed with electricity provided by the grid, a more correct definition of hydrogen should be "yellow hydrogen", accordingly to the presented nomenclature.

Since in this elaborate different future scenarios based on electricity produced with low carbon emissions are considered and since "green hydrogen" is a term commonly adopted to indicate hydrogen production with "low or zero carbon-emissions", in the present elaborate "green" is adopted to highlight the sustainable production of chemicals, with "low or zero" CO_2 emissions.

1.3.2 Hydrogen Production Routes

Aiming to the sustainable production of ammonia via electrified Haber-Bosch process, in the present elaborate the only technology available for hydrogen production is water electrolysis, declined in its three technological alternatives: alkaline electrolysis (AEL), proton electrolyte membrane (PEMEL) and solid oxide electrolysis (SOEL).

1.3.2.1 Electrified Production Process - Water Electrolysis

The principle of water electrolysis is the same for all the options available, the elements that differentiate the three electrolysis technologies are the electrolyte, operative conditions and materials required by the cell. In all cases water electrolysis allows to retrieve products (oxygen and hydrogen) with purities degree above 99%, but with slight differences associated with operative conditions.

It is estimated that the minimum amount of energy required to operate electrolysis is 39.4 kWh/kgH_2 at full conversion efficiency, but the actual efficiency of electrolytic cells raises this value to 55 kWh/kgH_2 [20,23,24]. The generic equation that represents the reaction occurring in the synthesis unit is reported in *Equation 1.1*.

$$2H_2O \rightleftharpoons O_2 + 2H_2 \tag{1.1}$$

Electrolysis requires demineralized water to be operated, with a cost of 1\$/m^3$H_2O_{purified}$ [25]. Accordingly to stoichiometry, 9 kgH_2O/kgH_2 are required, but demineralization and electrolysis inefficiencies increases the water intake to 18-24 kgH_2O/kgH_2 [25].

The main drawbacks of hydrogen production via electrolysis are the high CAPEX and the energy demand, but products purity degree is certainly an advantage of this approach; cell efficiencies is above 60% for all the three technologies available (AEL, PEM, SOEL) [25,26].

1.3.2.2 Alkaline electrolysis (AE/AEL)

AEL is the most mature technology available nowadays to recover H_2 and O_2 from water; the cell requires the addition of an electrolytic solution, KOH or NaOH at concentration of 20-30%. Operative temperature is between 60°C and 90°C and pressure between 10-30 bar [24].

A diaphragm is required to separate the two compartments: the anodic, where oxygen is produced and the cathodic one, where hydrogen is released, as reported in *Equation 1.2-1.3*. Water is fed in AEL in form of the electrolytic solution and it is consumed at the cathode.

$$Anode \qquad 2OH^- \rightleftharpoons H_2O + {}^1/_2\, O_2 + e^- \qquad (1.2)$$

$$Cathode \qquad 2H_2O + 2e^- \rightleftharpoons 2H_2 + 2OH^- \qquad (1.3)$$

Nickel catalysts are required and their availability and costs influence strongly the cost of the unit. Electrolyser outlets are collected in a drum that serves for separation of liquid-gas phases and it is followed by dehydration for water-removal, leading to the recovery of 99.9% hydrogen and 99-99.8% pure oxygen [24–27].

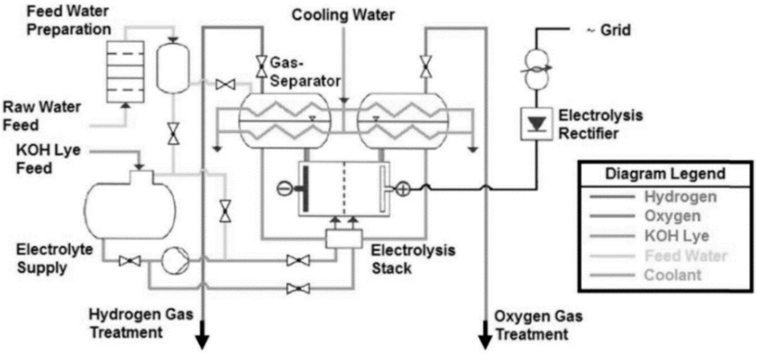


Figure 1.11 *Principle layout of a alkaline-electrolyser* [24].

1.3.2.3 Proton Electrolyte Membrane / Polymer Electrolyte Membrane (PEM/PEMEL)

PEMEL is another mature technology. Contrary to AEL, it does not require the addition of highly corrosive substances, since in this case poly-sulfonated membranes are integrated (Nafion® in most cases or Fumapem®, Flemion®, and Aciplex® [28]); the chemistry behind this technology is the same of the AEL, reported in *Equation 1.2-1.3*.

Electrodes represent another difference with respect to AEL: in this case are directly mounted on the membrane, forming the membrane electrode assembly and are made of noble metals (platinum for the cathode and iridium for the anode) covered by protective coatings, because of the acid environment. Water feed-point is also different: in PEMEL it is fed closer to the anode. Higher operative pressures compared to AEL can be achieved with PEMEL, 20-50 bar, and lower temperatures are demanded, between 50-80°C.

PEMEL advantages compared to AEL are: faster start-up (few minutes for a cold-start-up and seconds for a warm-start-up), higher hydrogen purity compared to AEL (>99.99%), higher energy conversion efficiency, lower environmental impact and smaller space occupied [24–27].

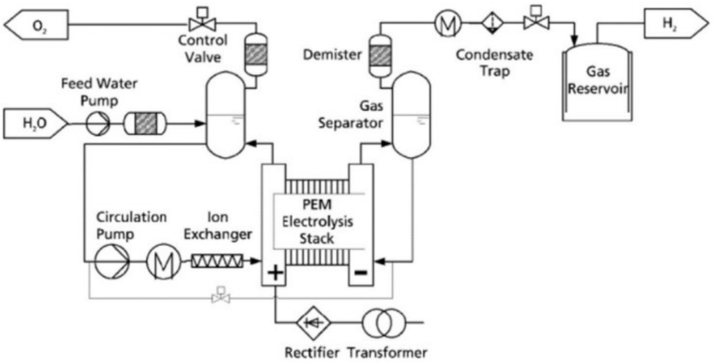


Figure 1.12 *Principle layout of a polymer-electrolyte-membrane electrolyser* [24].

1.3.2.4 Solid Oxide Electrolysis (SOEC/SOEL)

Contrary to AEL and PEMEL, SOEL is not a commercialized technology.

SOEL does not use a traditional catalyst: conductive ceramics materials are used. Different operative procedures also characterize this cell: water is fed at the cathode with some recycled H_2; air is also fed to the anode to remove the produced hydrogen.

Contrary to AEL and PEMEL, this technology requires extremely high temperatures to operate, 700-900°C, but low-moderate pressures are considered, 1 bar to 15 bar. The high temperature allows to increase cell efficiency, but introduces difficulties in materials selection because of their stability at the operative conditions; because of this, expensive materials are required and at the actual state it present a short cell-life compared to other technologies.

Relevant advantage of SOEL is the possibility of operating these units as either electrolysers or solid-oxide fuel cells [24–27].

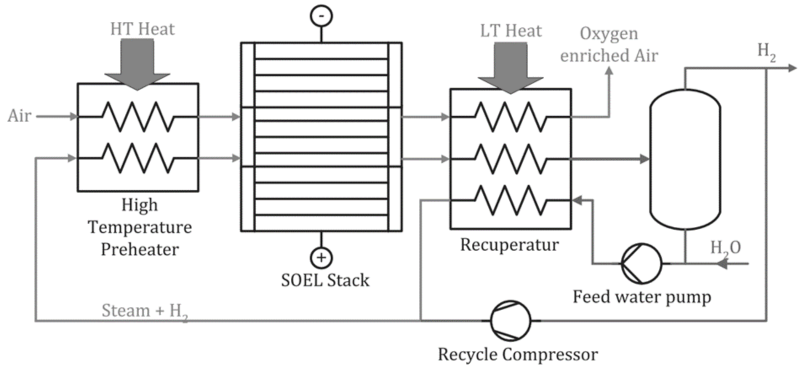


Figure 1.13 *Principle layout of a polymer-electrolyte-membrane electrolyser* [24].

1.3.2.5 Technology Selection, Plant Lifetime and Economics

Before proceeding with the selection of the technological option for electrolysis, it must be noted that only mature technologies are considered in this elaborate; this is why SOEL was excluded, because of its early degree of development.

Chemical plants are usually expected to last at least 10-15 years, 20 years on average. Therefore, the choice of the equipment and process unit operations must minimize the need to replace the equipment. In the case of electrolysis, the expected lifetime is comparable with that of chemical plants, as reported in *Table 1.3*. It must be noted that even if process-unit lifetime is comparable with the one of chemical processes, cells lifetime differs because of degradation mechanisms. In other words, after 8-15 years, cells need replacement. In the case of AEL, slightly larger degradation effects are noted compared to PEMEL, but the lifetime is comparable for both the technologies [24].

Different estimations about CAPEX and OPEX can be retrieved in the literature; in *Table 1.3* some estimations are reported for AEL and PEMEL [24].

Table 1.3 *Plant lifetime, installed and uninstalled CAPEX of AEL and PEMEL and OPEX costs* [24].

Property	Plant Lifetime	CAPEX		OPEX
		Uninstalled	Installed	
AEL	30-50 years	700-3500 €/kWh$_{el}$	800-1500 €/ kWh$_{el}$	2-3% of CAPEX
PEMEL	20 years	1300-2200 €/kWh$_{el}$	1400-2100 €/ kWh$_{el}$	3-5% of CAPEX

Being the CAPEX of PEMEL cells twice the one of AEL, the applicability can be questioned. However, the additional advantages of PEMEL compared to AEL (in addition to the ones reported in *Chapter §1.3.2.3*) are the following:

- cell load flexibility: AEL requires a minimum load of 10-40% (mainly 20-25% [24]) to avoid cross-permeation, while PEMEL does not technically requires a minimum load;
- faster (warm and cold) start-up: advantage in contexts with high RES penetrations in the energy mix. Particularly:
    - few seconds for the warm start-up of PEMEL ("stand-by" mode, kept at the operating conditions) compared to 5-10 minutes of AEL;
    - few minutes for the cold start-up of PEMEL compared to 2 hours for AEL.

It must be noted that the advantage PEMEL offers in terms of start-up times is undoubtedly an advantage in situations where RES produces electricity. Still, considering a process supplied by grid electricity and operating 24/7, PEMEL is not relevant in the decisional framework

PEMEL also show disadvantages compared to AEL, especially in terms of capacity of maintaining the operative pressure for long periods: in PEMELs the pressure decreases faster compared to AEL (few hours for PEM compared to several days in case of AEL).

Additionally, safety issues play a critical role in the selection of the proper solution: results show that the safety performances of PEMEL are worse compared to AEL [29,30].

Hence, considering pros and cons here presented, AEL can be identified both from an economical and safety perspective as the most suitable technology for the electrified and sustainable production of hydrogen.

1.4 Ammonia

Ammonia is one of the most important chemicals produced nowadays, and even if it is used in a variety of fields: over 80% of the ammonia produced worldwide is used for fertilizers [31]. It is also used as a refrigerant, and in textile and pharmaceutical industries. Ammonia future role, as valuable alternative to fossil fuels as carbon-free energy vector [12] must not be neglected. Considering the increasing interest in ammonia in different fields, its production is expected to increase in the following years, from 176 million metric tons in 2017 [12] to 270 million metric tons expected by 2050 [31].

1.4.1 Sustainability & Future Perspectives

As mentioned in *Chapter §1.3.1*, all chemicals can be classified in terms of sustainability similarly to hydrogen NACFE's classification. Particularly, in case of ammonia this classification is based on the path used to produce its synthesis, made of nitrogen and hydrogen. NACFE's classification can be applied to ammonia as follow:

- brown ammonia: hydrogen is produced through coal gasification;
- grey-ammonia: hydrogen is produced via methane steam reforming (SMR);
- blue-ammonia: grey or brown ammonia coupled to carbon capture processes;
- bio-based green ammonia: hydrogen is obtained from biomass or biogas;
- electrified (green) ammonia: hydrogen is produced by electrolysis and air separation.

As evident, nitrogen is not considered in the present classification since it can be obtained indirectly during the gasification/reforming process or via electrified air-separation, process discussed previously in *Chapter §1.2.1*.

As mentioned in *Chapter §1.1.2.2*, aiming to obtain a more sustainable ammonia synthesis, two main aspects must be considered, i.e. reactants and production process sustainability. Assessments performed on the different production routes, show that CO_2-emissions of grey-ammonia plants is about 1.6 tonCO_2/tonNH_3, that increases between 2.5-3.8 tonsCO_2/tonNH_3 in case of gasification-based plants (brown-ammonia) [12]. Also, external factors should be considered for a correct estimation of CO_2 emission from ammonia production processes. In this regard, the carbon intensity of local electricity production is a central aspect to consider when dealing with the electrification of the traditional Haber-Bosch process.

Over the time Haber-Bosch process efficiency has been improved, reducing the energy requirement from more than 100 GJ/tonNH_3 to 28 GJ/tonNH_3, considering the application of the best available technology (BAT) available nowadays, with an energy requirement that is close to the theoretical minimum of 18.6 net GJ/tonNH_3 (22.2 GJ/tonNH_3 considering also auxiliary units in the reforming section of a grey-ammonia plant), meaning that very few improvements can be performed on this design [13,32–34]. This has also led to a decrease in the CO_2 emissions related to the syngas production section, which nowadays are mainly associated with the reforming plants, which requires about 80% of the energy of a typical process [12].

Concluding, it must be noted that a practical constraint must be satisfied whenever a new proposal is developed: the economical feasibility of the process, aspect that will be addressed further in this elaborate.

1.4.2 Ammonia Production Routes

Ammonia synthesis, performed by the Haber-Bosch process, requires the H_2/N_2 mixture produced by ASU and electrolysis, part of the synthesis mixture production section [35].

The Haber-Bosch process is based on the well-known high-pressure, high-temperature catalyzed reaction, reported in *Equation 1.4*

$$3H_2 + N_2 \overset{catalyst}{\Longleftrightarrow} 2NH_3 \qquad \Delta H_r^0 = -92.4\ kJ/mol\ [36] \qquad (1.\ 4)$$

In the Haber-Bosch process, the operative conditions that allow the maximization of the conversion consider a pressure between 100-250 bar and a temperature in the reactor between 400-500°C, with suitable recycling of the unreacted species to increase process yield (single-pass conversion is around 20-30%). Low temperatures favor the process, but kinetic limitations makes inconvenient to operate below 670 K (400°C) [12,13,34,35,37–39].

Higher operative pressures can theoretically be used to increase conversion (300-1,000 bar), but because of the increased power consumption and equipment cost, pressures around 200 bar (± 50 bar) are commonly adopted [34,40].

The improvement in material and energy efficiency of the Haber-Bosch process has been followed by an increase in daily productivity, ranging from 1,000-1,500 tons $_{NH3}$/day in the early 2000s to the actual plant capacity of 600-3,000 tonsNH_3/day, with some plants producing more 3,000-4,000 tons $_{NH3}$/day [13,32,35,38].

A description of the traditional Haber-Bosch process is discussed in the following paragraphs, together with introductory concepts about the green-ammonia configuration.

The Haber-Bosch process plant layout differs among the alternative plant configurations available and depends on the way the synthesis mixture is retrieved. In general, it can be stated that after the syngas production unit (SMR, gasification or electrolysis with ASU), a cleaning and upgrading step is performed, followed by the synthesis loop, the section of the plant demanded to the conversion of the reactive mixture into ammonia. The synthesis loop involves a compression step, the reactor unit and the separation step of ammonia from the recycled unreacted mixture.

1.4.2.1 Syngas Cleaning & Upgrading Technologies

Different technologies are available to produce hydrogen in the form of a CO & H_2 mixture, and those differ in both the feedstock used and the product obtained (SMR and gasification are the two most common approaches used). Since the mixture of CO and H_2 obtained contains different poisons for the ammonia catalysts, cleaning and upgrading steps are necessary to improve the quality (and composition) of the syngas, making it viable for the Haber-Bosch process. F*igure 1.14* illustrates the steps of a grey ammonia production process.

The CO-shift step involves the water-gas-shift reaction (WGS), a catalyzed process (performed at 500K) that increase the mixture hydrogen content by conversion of CO into CO_2.

The CO_2-removal is performed by absorption-stripping driven by amines solutions and aims to remove poisoning substances for the Haber-Bosch catalysts (CO_2 and H_2S). The most common amines used are MEA (mono-ethanol-amine), MDEA (mono-di-ethanol-amine) and DEA (di-ethanol-amine); absorption is commonly operated at 40-60°C, 35 bar, while 2 bar, 120°C is the typical operating condition of the stripping unit [4,26,34,35].

Methanation, a catalyzed hydrogenation, is the last cleaning step that allows to remove the remaining traces of poisoning chemicals by their conversion in inert species: water (removed by condensation) and methane (inert species found in grey-ammonia plants) are produced.

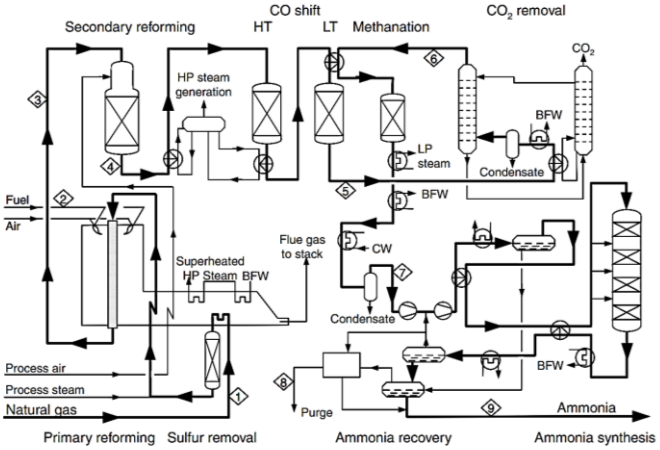


Figure 1.14 *Scheme of an integrated Haber-Bosch process for the production of grey-ammonia* [35].

Instead, considering electrified ammonia, the N_2 & H_2 mixture required is obtained ASU and water electrolysis, that produce pure streams, making the pre-purification steps not necessary.

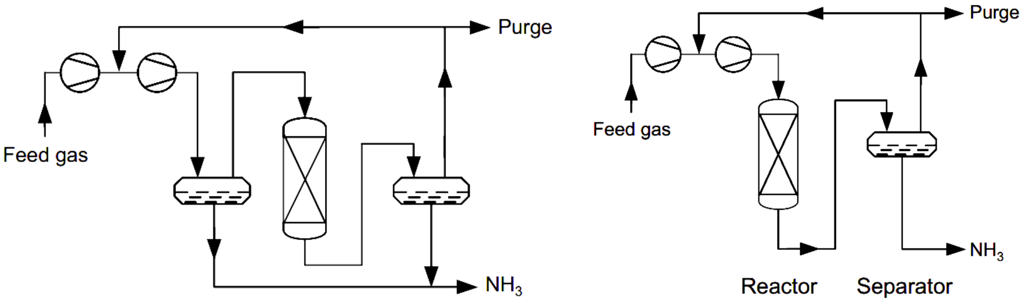
1.4.2.2 Ammonia Synthesis Loop

The present paragraph collects information regarding Haber-Bosch process units and the technological alternatives available for ammonia production.

Synthesis Loop

The Haber-Bosch synthesis loop is made of different steps: compression, to bring the reactive mixture at the reactor operative pressure, the reactor unit and the separation section of the plant, necessary to recover the produced ammonia.

Because of the low single-pass conversion, around 20-30%, the separation of the unreacted mixture from the product and its recycling is a necessary step in ammonia plants to increase the overall process conversion [35]. Because of the properties of both synthesis mixture and ammonia, depending on process operative conditions and the feedstock purity, different recycle loop designs are available to recover ammonia and unreacted reactants. *Figure 1.15* provides an overview of the best options available for both grey and electrified production processes. In *Figure 1.15.a*, the synthesis loop of a grey ammonia production plant is reported, which minimizes the ammonia concentration in the reactor feed stream and the compression cost while removing impurities that are soluble in ammonia. The configuration reported in *Figure 1.15.b*, instead, is the best option for electrified ammonia synthesis since it can be used with a high-purity feed with no poisons [35].



(a) *(b)*

Figure 1.15 *Scheme representing the simplified synthesis loop for both grey-ammonia (a) and electrified-ammonia (b) production processes*[35].

Figure 1.16 shows the main heat exchangers and compressors comprised in the synthesis loop; it is also highlights the different bed size that can be commonly found in Haber-Bosch reactors.

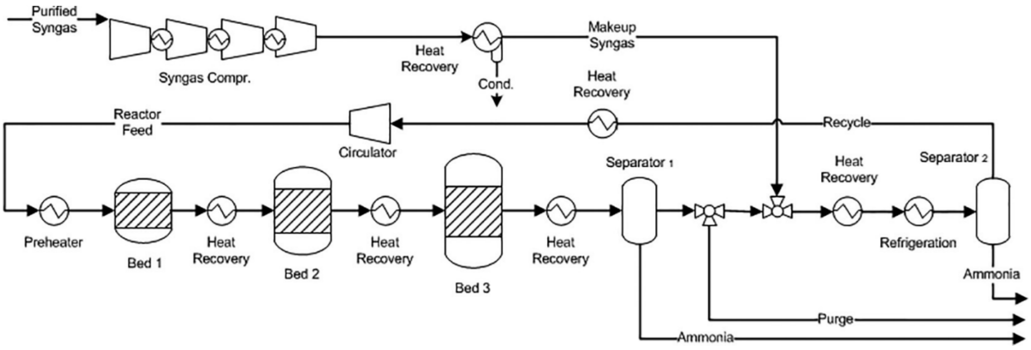


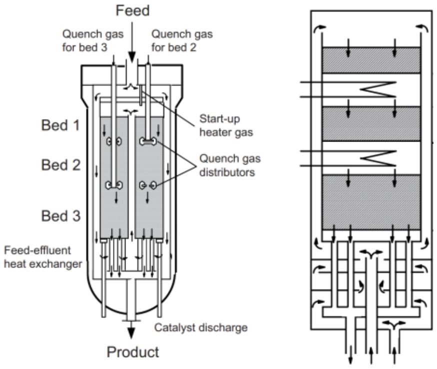
Figure 1.16 *Scheme representing the ammonia-production process including the compression-train* [34].

Multistage Compression

The starting point of the whole ammonia synthesis loop is the intercooled multistage-compressor train used to bring the make-up stream at the operative pressure. The first compressor train and the recirculation one (*Figures 1.15-1.16*) take about 45% of the overall energy requirement of the ammonia production section [34].

Reactive Section

Two reactor configurations may be found industrially, i.e. directly-cooled reactors and indirectly-cooled reactors. In the first case, a quenching process is operated in the unit, sending fresh and cold reactive mixture at different heights directly inside the catalytic bed. On the contrary, in the second configuration, intermediate heat exchangers are placed between catalytic beds. *Figure 1.17* represents these two industrially adopted configurations.

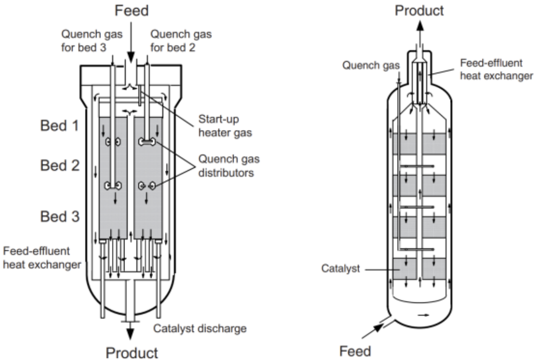


(a) *(b)*

Figure 1.17 *Schemes representing quenched (a) and inter-cooled (b) reactor configurations* [35].

Common aspect of the two technologies is the flow pattern followed by the feed of the reactor: the cold stream is firstly pre-heated with a heat exchanger embedded in the reactor head and then flows between the shell and the catalyst bed. It is further preheated using the heat produced by the reaction, avoiding issues to the metallic surface of the shell, made by carbon or alloy steels that may undergo embrittlement in the case of very high temperatures [35]. The head-heat exchanger that pre-heats the feed allows for the recovery of large quantities of heat, decreasing the temperature of the product stream (that leaves the unit at around 500K) and heats the reactive mixture to the temperature required by the process, i.e. around 670K.

In the case of quenched reactors, two different alternatives are available (*Figure 1.18*): the reactor feed can be injected directly in the catalytic bed (*a*) at different height or in spaces left between multiple-catalytic beds (*b*).



(a) *(b)*

Figure 1.18 *Schemes representing a quenched reactor with inlet in the catalytic bed (ICI) (a) and with inlet in spacers between beds (Kellogg)(b)* [35].

The second option available in terms of converter technology is the intercooled configuration (*Figure 1.17.b*), which is provided by multiple heat exchangers (explicitly represented in *Figure 1.16*). These units are interposed between the catalytic beds and are necessary to control the exothermic reaction. This approach is applied in most large-scale plants because it allows recovering heat at the highest possible temperature and increase plant energy efficiency: about 9% of the plant energy demand can be satisfied by this recovery [34]. The disadvantage of this strategy is the high investment cost compared to quenching systems because of the adoption of additional heat exchangers, which are often provided in complex configurations where each catalytic bed is accommodated in one vessel with associated heat exchangers [35].

Catalyst

Haber, Bosch and Mittasch (BASF) found the most reliable and efficient catalyst for ammonia synthesis, which is an iron oxide-based catalyst. Modern alternative noble-based catalysts have been commercialized by Kellogg/Brown & Root (KBR) [35]. To improve efficiency and resistance to sintering and poisoning, catalysts have been modified with promoters and protectors (Al, Ca and Mg in form of oxides). Critical poisons are O_2, H_2O and CO, species that react with the surface of the material, inducing irreversible bounds and, often, sintering. According to the literature and industrial experience, cumulative concentrations even below 10 ppm severely affect the catalyst activity. For this reason, the minimization of their concentration in the fed reactive mixture below 5 ppm is mandatory [41]. Moreover, the size of catalyst particles is relevant because smaller particles can increase efficiency but also increase the pressure drop across the bed, increasing compression costs [35]. A solution can be represented by radial converters (*Figure 1.19*), for example, that developed by Haldor Topsøe (radial converters can be arranged as either quenched or cooled reactors).

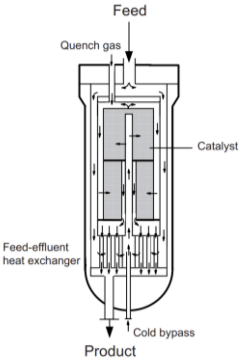


***Figure 1.19** Schemes representing a radial ammonia-converter developed by Haldor Topsøe* [35].

This approach allows for the reduction of pressure drops through the catalytic bed since a larger cross-sectional area is available for the reactive stream. In fact, by providing a larger area per unit volume, smaller pressure drops are established [35]. Since it is of primary interest in pushing the conversion based on a given catalyst volume (while minimizing pressure drops across the bed), a radial-inter-cooled converter is usually applied industrially (*Figure 1.20*). The intercooled configuration allows them to achieve better performance compared to the quenched alternative because the quenched case operates by diluting the reactive mixture with cooled-fresh mixture, decreasing the single-pass conversion.

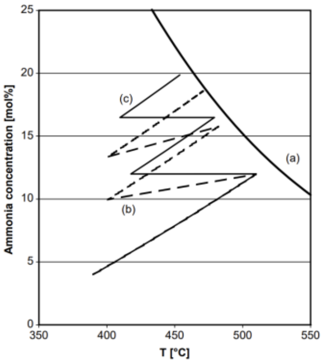


***Figure 1.20** Comparison of ammonia's concentration and temperature profiles in multibed; quenched (b) and intercooled (c) configurations with respect to equilibrium (a)* [34].

Rather than the classical iron-oxide catalyst, other alternatives have also been tested, including those based on uranium and osmium, even if unsuccessful. The ruthenium-based catalyst is 10-

20 times more active than the iron-based alternative and has been commercialized. It allows reducing the operative pressure and temperature [34,39,40]. Practical applications of ruthenium-based catalysts are limited due to the material low availability, which leads to a high cost of the metal [20]. For this reason, ruthenium-based catalysts are not considered further, even if recent studies have discussed their applicability to RES-driven processes [39,42].

Ammonia Recovery and Recycle & Hydrogen Recovery

As mentioned, after the reaction section of the synthesis loop, ammonia must be recovered and separated from the unreacted reactants. This process is performed through a refrigeration cycle at -25°C [43] to maximize ammonia recovery, a condition that changes depending on the operative pressure of the plant [42] and also depending on the ammonia recovery costs [44].

The condensed liquid stream of product contains residues of reactants, that are commonly removed from the stream by flashing down to 20 bar, retrieving almost-pure products (around 99.9 %wt.) and a stream of reactive mixture to recycle back to the reactor [20,43].

The outflow of the reactor is composed of ammonia and unreacted reactants, but impurities are also present in traces: argon, inert species produced by ASU or introduced in the hydrogen stream by SMR/gasification and methane, inert species that is produced in the syngas cleaning and upgrading steps of grey/brown ammonia plants. To avoid the accumulation of these inert in the reactor unit, a purge is necessary.

In conventional Haber-Bosch plants, to avoid the loss of hydrogen, a valuable reactant, a hydrogen recovery unit is implemented to separate it from the inert chemicals purged. Different hydrogen-recovery strategies can be applied, including a pressure-swing-adsorption process (purity of recovered hydrogen around 80-95 %vol.) [35] or membrane-based processes.

The hydrogen recovery unit is not necessary, instead, in electrified Haber-Bosch plants, where the only inert species present is argon, that is soluble in ammonia: because of this, it is removed from the synthesis-loop with the product, eliminating the need of purges [36].

1.4.2.3 Plant Configurations

A description of both the grey-ammonia and electrified-ammonia processes is here reported.

Grey-Ammonia – SMR based Ammonia Production

Figure 1.21 represents a simplified scheme of the grey-ammonia production process.

The grey-ammonia plants comprise the reactive mixture production via SMR, made of primary and secondary reformer units, that are followed by the syngas cleaning and purification section.

After syngas cleaning and upgrading steps here shown, the synthesis mixture (with a H_2/N_2 ratio of 3:1) is fed to the ammonia synthesis loop described in *Chapter §1.4.2.2*: firstly the reactive mixture is compressed at the operative condition and is later sent to the loop represented in *Figure 1.15.a*. Interest of this work is the configuration that considers an inter-cooled reactor, but *Figure 1.21* represents a quenched reactor; the purification of ammonia by flashing is also represented as the purged stream necessary to avoid inert (methane) accumulation in the reaction-loop; it is not reported the hydrogen recovery section introduced in *Chapter §1.4.2.2*.

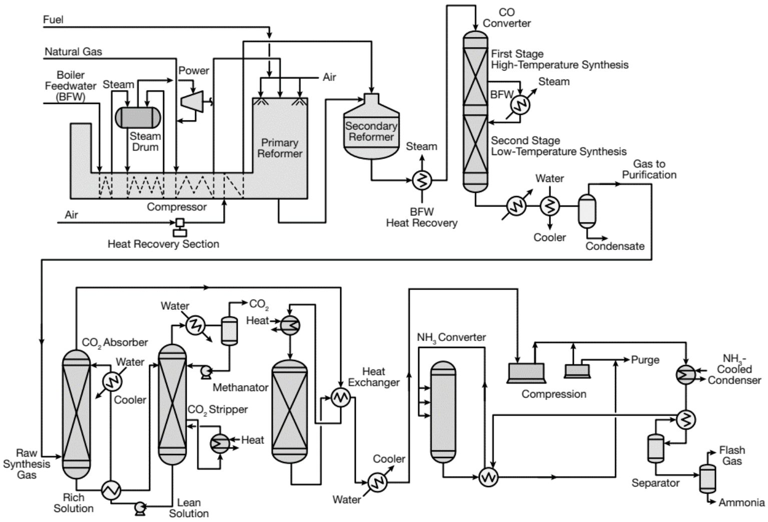


***Figure 1.21** Scheme of the Haber-Bosch process designed by KBR, one of the first single-train large capacities ammonia plants* [33].

Electrified-Ammonia

The electrified production of ammonia follows the general scheme of a state-of-the-art ammonia plant previously described in *Chapter §1.4.2.2*: the syngas production unit and the synthesis loop, made of the feed-compression-train, the reactive and separation sections. Differences compared to the grey-ammonia plant previously presented are: the processes used to retrieve the reactive mixture, the absence of the syngas cleaning and upgrading section (because of the feed purity degree) and, in the separation section of the synthesis loop the hydrogen recovery unit is not present.

In this dissertation, the electrified and sustainable production of ammonia has been considered composed by AEL as electrolysis technology for hydrogen production and CAD-ASU for nitrogen recovery; the by-product of the resulting synthesis mixture production unit, i.e. oxygen, has been assumed sold at market price.

Concerning the ammonia synthesis-loop, its feed is made of a hydrogen/nitrogen mixture in 3:1 ratio, sent directly to the Haber-Bosch synthesis loop [13] since the purity degree that respects the ammonia iron-based catalyst specifications (oxygen-content <5 ppm). The reactor unit has been considered as an inter-cooled reactor (common industrial practice) and the separation section has been considered arranged as in *Figure 1.15.b*.

An advantage offered by the electrified production of ammonia is a simplification of the process flowsheet compared to the gasification or SMR based processes [45], aspect in accordance with inherently safer designs principles.

1.4.3 Ammonia Electrified Production Considerations

In this last paragraph about ammonia, some concluding considerations about sustainability and economics of the electrified ammonia production are reported.

1.4.3.1 Electrification & CO_2 Emissions

This dissertation aims to discuss and develop a sustainable ammonia production plant based on electrified processes: in this case, electricity is the only source of energy, which has been assumed provided by the grid. This means that the process carbon intensity depends solely on CO_2 emissions of the local grid (gCO_2/kWh), which is considered based on Italy.

To assess process economic performance, different scenarios has been considered, based on both recent data and future projections; in particular, the future scenarios accounted considers low-carbon emissions associated to electricity production.

Important consideration is that, accordingly to *Figure 1.22*, nowadays fossil-fuels are a predominant source of electricity in Italy, meaning that emissions of the electrified Haber-Bosch process will be higher compared to SMR-based plants (grey-ammonia), because of the higher efficiency in the direct use of fuels compared to their use for electricity generation [13].

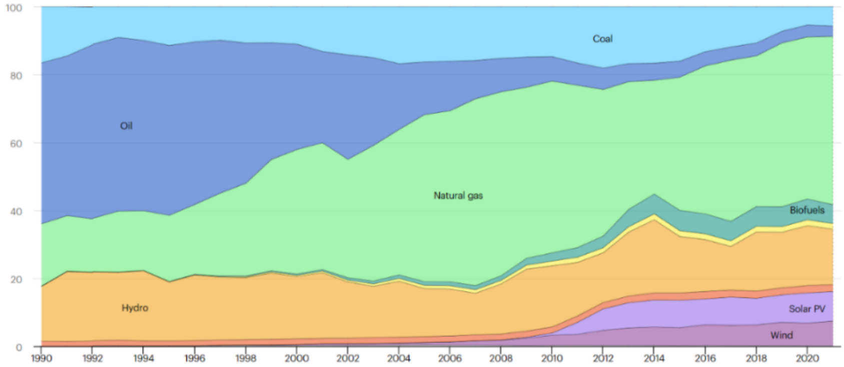


Figure 1.22 *Chart showing the evolution of the Italian electricity-generation by source* [46].

It can be estimated that to achieve a more sustainable process compared to the actual state-of-the-art grey-ammonia plant it is required a carbon-intensity of the electricity produced below 180 gCO_2/kWh, target that only few countries around the world satisfy nowadays; as European Union the average emissions related to electricity generation are 231 gCO_2/kWh [13,36].

1.4.3.2 Economical Considerations

Considering process economics, nowadays the electrified ammonia production suffers from higher costs compared to the grey alternative: electrolysis capital costs are higher compared to stem-methane-reforming and natural gas is cheaper than electricity. Similarly to classical Haber-Bosch plants, also the electrified proposal consumes most of the energy provided (95%) for hydrogen production, meaning that even with a relatively high efficiency of the apparatus required for electrolysis (that ranges 60-70% in the case of AEL [24,25]) the operative costs of this process will be high and concentrated in one single step.

1.5 Objective of the Thesis

The aim of this thesis is the development of the conceptual-design for sustainable ammonia synthesis via electrified Haber-Bosch process, based on the choice of the sustainable operations and on common industrial practices.

The resulting proposal economic performance is further assessed under different electricity-prices and the resulting ammonia cost of production is compared with its actual market-price. These assessments are performed comparing different electricity prices [47–51], based on recent data and future projections of the Italian electrical-generation for low carbon emissions. In this elaborate it has been assumed, as already mentioned, that electricity is provided to the plant by the grid, meaning that:

- the grid is capable of satisfy the plant demand continuously, 24/7;
- process CO_2 emissions are directly related to the carbon intensity of the grid.

These conclusions have a practical effect on plant performance and design: firstly, the plant must not adapt its production to energy productivity fluctuations typical of RES (i.e. plant discontinuous production is not necessary); secondly, it is not necessary to over-design the plant to obtain the same productivity of a continuous plant.

During the design development, also safety performances has been considered, aiming to implement the safer alternatives available for each process unit since the beginning of the conceptual-design, accordingly to inherently-safer-design practices. Concluding, the overall plant safety assessment has been performed, with particular attention on storage units.

Chapter 2
Process Simulation

In the second chapter of this elaborate the simulation approach is described step-by-step.
This work will consider a plant productivity that is about one-tenth of common industrial facilities, size of interest for the future development of sustainable ammonia production [20]; to discuss the economical feasibility of the process, two configurations are compared: the first one considers a pressure of 200 bar (the state-of-the-art configuration), while the second one operates at 300 bar, pressure considered also in [42].

2.1 Conceptual Design Development

The development of an industrial conceptual-design is commonly performed following a series of steps that can be summarized as follows:

- definition of customer needs: in this case the development of a sustainable-ammonia production facility capable of producing low-carbon ammonia, with a capacity of 100 ton/day and a purity degree above 99.9%w. [20];
- development of the conceptual design;
- economic evaluation of the proposal and selection of the design for the following steps (detailed design, followed by the procurement and construction phase, that anticipate the operation of the facility);

The conceptual design development starts with the definition of the process block-flow-diagram (BFD) representing schematically the process units and their arrangement, allowing to perform preliminary estimation of plant material demands. These two steps are presented in the following paragraph and are followed by plant simulation description.
During conceptual design, a very relevant aspect is cost-estimation and optimization: performing corrective adjustments to improve plant performances is both easier and less expensive during this phase compared to following design-steps (detailed design).

2.2 Block-Flow-Diagram & Preliminary Mass Balance

The developed block flow diagram representing the sustainable production of ammonia based on water electrolysis and air separation unit to recover nitrogen and hydrogen is reported in *Figure 2.1*. The steps previously described in *Chapter §1.4.2.3* are here represented, with an explicit representation of the synthesis loop.

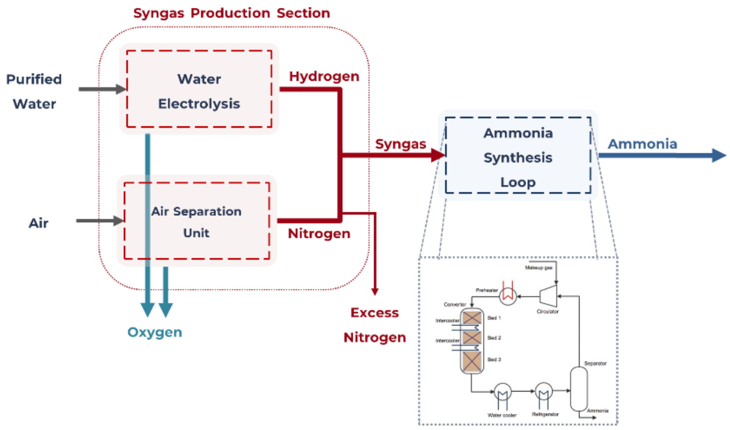


Figure 2.1 *Block-Flow-Diagram of the electrified green-ammonia production process proposed (adapted* [42]*).*

As it can be seen from the block flow diagram, the two main products of the process are oxygen (by-product) and ammonia, but depending on the technology used and the agreements with ASU contractors, also excess nitrogen could be obtained. In the present work it has been considered that only oxygen and ammonia are sold and nitrogen is produced accordingly to plant demands. The simplified input/output structure of the process considers that intermediate recycle streams have been embedded within each block (unitary conversion is assumed); the block flow diagram has been used as guide to compute the process material requirements.

Table 2.1 *Molecular Weight for the species handled in the process.*

Species	Molecular Weight	Vapor Fraction in Air
Ammonia	17.031 g/mol	-
Nitrogen	28.02 g/mol	$y_{N2} = 0.781$
Hydrogen	2.016 g/mol	-
Oxygen	31.9988 g/mol	$y_{O2} = 0.209$
Water	18.01528 g/mol	-

Table 2.2 *Reactions involved in the synthesis of ammonia from water and air.*

Species	Reaction	Stoichiometric Coefficients
Electrolysis	$2H_2O \rightleftharpoons O_2 + 2H_2$	ν_{O2}= 1 ν_{H2}= 2 ν_{H2O}= -2
Ammonia	$3H_2 + N_2 \overset{catalyst}{\Longleftrightarrow} 2NH_3$	ν_{NH3}= 2 ν_{H2}= -3 ν_{N2}= -1

Firstly, the daily productivity of ammonia is converted into molar-productivity on hourly basis.

$$100\frac{ton_{\mathrm{NH_3}}}{day} = 4'166.7\frac{kg_{\mathrm{NH_3}}}{hour} = 244.6\frac{kmol_{\mathrm{NH_3}}}{hour} \tag{2.1}$$

According to reaction stoichiometry, reported in *Table 2.2*, it is possible to retrieve the stoichiometric needs of hydrogen, nitrogen and oxygen productivity:

$$\frac{kmol_{\mathrm{H_2}}}{hour} = \frac{kmol_{\mathrm{NH_3}}}{hour} \times \left|\frac{\nu_{H_2}}{\nu_{\mathrm{NH_3}}}\right| = 366.98\frac{kmol_{\mathrm{H_2}}}{hour} = 739.8\frac{kg_{\mathrm{H_2}}}{hour} \tag{2.2}$$

$$\frac{kmol_{N_2}}{hour} = \frac{kmol_{\mathrm{NH_3}}}{hour} \times \left|\frac{\nu_{N_2}}{\nu_{\mathrm{NH_3}}}\right| = 122.3\frac{kmol_{N_2}}{hour} = 3'427.6\frac{kg_{N_2}}{hour} = 2'992.8\frac{Nm^3_{N_2}}{hour} \tag{2.3}$$

$$\frac{kmol_{O_2}}{hour} = \frac{kmol_{\mathrm{H_2}}}{hour} \times \left|\frac{\nu_{O_2}}{\nu_{\mathrm{H_2}}}\right| = 183.5\frac{kmol_{O_2}}{hour} = 5'871.4\frac{kg_{O_2}}{hour} \tag{2.4}$$

Similarly, from the nitrogen demand, ASU oxygen productivity has been computed by stoichiometry; the air intake has been derived too.

$$\frac{Nm^3_{\mathrm{Air}}}{hour} = \frac{Nm^3_{N_2}/hour}{y_{N_2}} = 3'831.95\frac{Nm^3_{\mathrm{Air}}}{hour} \;\&\; Nm^3_{\mathrm{Air}} \times y_{O_2} = 800.9\frac{Nm^3_{O_2}}{hour} \tag{2.5}$$

$$800.88\frac{Nm^3_{O_2}}{hour} = 32.7\frac{kmol_{O_2}}{hour} = 1'047.5\frac{kg_{O_2}}{hour} \tag{2.6}$$

Nm^3 corresponds to the volume of a species at normal conditions, ambient pressure and temperature: 298.15 K and 101325 Pa; *R* is the universal gas constant, taken as $8.31446\frac{J}{mol\cdot K}$.

2.3 Process Model

Ammonia process simulation has been performed in *ASPEN® Plus*, where the five sections that compose the ammonia process have been simulated: electrolysis unit, ASU unit, multi-compression, reaction and separation section (the last three compose the synthesis loop described in *Chapter §1.4.2.3* and represented in *Figure 2.1*).

2.3.1 Synthesis Mixture Production Section

The reactive mixture production section of the plant comprises electrolyser and ASU units: both have been modelled with two black-box models (calculators) to compute the electrical demand necessary to satisfy process hydrogen and nitrogen demand. CAPEX and OPEX have been added directly in *Microsoft® Excel*, where the profitability analysis has been performed.

2.3.1.1 Electrolysis

Electrolysis unit has been modelled as black-box, a calculator, with the hydrogen stream set as calculator input, necessary to compute, accordingly to values collected in *Table 2.3*: the electrical demand, water purification costs and other process costs resumed in the table.

Specifications of the hydrogen stream set in *ASPEN® Plus* are the flowrate (computed in *Chapter §2.2*) and the operative conditions, that has been fixed as the average temperature and pressure of AEL units, 70°C and 20 bar [24]. *Table 2.3* also collects simulation results for the two configurations considered in this elaborate, the synthesis performed at 200 bar and 300 bar.

Table 2.3 *Parameters used in the electrolysis black-box and simulation results.*

Parameter	Factor	Result		UoM	Ref.
		P=200 bar	P=300 bar		
H_2 Make-Up	-	778.65	739.78	kg/h	-
Purified Water	21 kgH_2O/kgH_2	16’351	15’535	kg/h	[25]
Sodium Hydroxide	Solution @ 30%w.	4’905	4’660	kg/h	-
Purification Cost	1 €/m^3	16.35	15.53	€/h	[25]
Electric Demand	55 kWh/kgH_2	42’825	40’688	kWh/h	[24]
Oxygen Produced	-	6’228	5’928	kg/h	-
CAPEX AEL (Installed)	1’150 €/kWh_{el}	4.92×10^7	4.68×10^7	€	[24]
OPEX AEL	4% $CAPEX_{PEM}$	1.48×10^6	1.40×10^6	€	[24]

2.3.1.2 Air Separation Unit

Similarly to hydrogen, also the ASU is modelled via black-box, with the nitrogen flowrate produced as input. *Table 2.4* collects both the process variables estimated to characterize ASUs and the results obtained for the two configurations considered.

The nitrogen stream has been fixed accordingly to the result of *Chapter §2.2* and the operative conditions have been fixed at 20°C and 5 bar, considering that the cold-stream of nitrogen can be heat-integrated to recover ammonia in liquid phase, decreasing refrigeration costs: this aspect has been investigated in a later-stage of process design.

Table 2.4 *Parameters used in the ASU black-box and simulation results.*

Parameter	Factor	Result		UoM	Ref.
		P=200 bar	P=300 bar		
N_2 Make-Up	-	128.75	122.33	kmol/h	-
Purified Air	-	4’033	3’832	m^3/h	-
Purification Cost	10 €/ton_{air}	52.15	49.54	€/h	[15]
Electric Demand	200 kWh/$tonO_{2(pure)}$	220.50	209.5	kWh/h	[37,52,53]
Oxygen Produced	-	1'102	1'047	kg/h	-
CAPEX (Ready-for-Start-Up)	30 M€	-	-	-	
Product Storage Costs	7.5 M€/storage-tank	-	-	-	[54]
Auxiliaries Costs	15 M€	-	-	-	

The electrical demand of CAD-ASU has been fixed at 200 kWh/$tonO_{2(pure)}$, in agreement with common ranges of 184–260 kWh/$tonO_2$ [37,52,53];

2.3.2 Ammonia Synthesis Loop

The ammonia synthesis loop is the part of the plant demanded to the conversion of the sustainable synthesis mixture obtained to ammonia and in this work it has been considered made of three sections: multistage-compression, reaction and the separation-recycle sections. The appendix collects additional information about ammonia synthesis loop modelling, *§A.1.*

2.3.2.1 Multistage Compressors

Multistage compression is the synthesis loop section demanded to bring the fresh-feed at the loop operative pressure. As commonly performed in industrial ammonia plants, one additional compressor unit is considered in the synthesis loop and treats the recycled stream of unreacted reactants; this unit, demanded to counter plant pressure-drops, has been considered part of the separation section of the facility.

To avoid compressors damages and malfunctions due to excessive temperatures caused by the increase in temperature of the gas due to normal-unit operations, intermediate cooling is performed between each compression step: shell-and-tube heat-exchangers (floating-head-type has been considered [55]) have been adopted for this scope, driven by cooling-water with final temperature fixed at 45°C. Process utilities and heat-exchangers additional information have been collected in the appendix, *§A.1.2*.

The final compression train arrangement is reported in *Figure 2.2*.

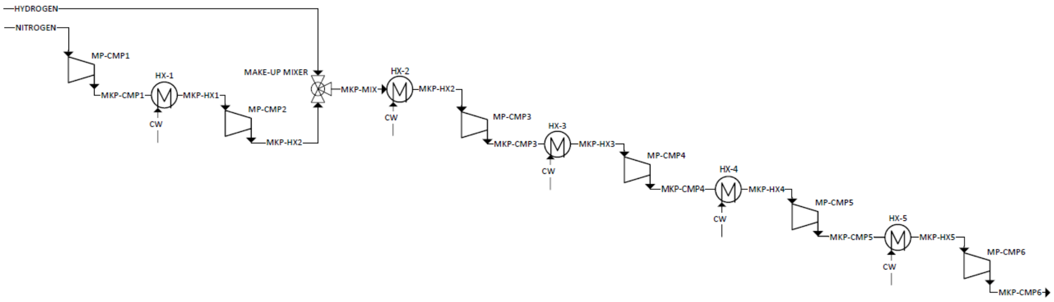


Figure 2.2 *Schematic representation of the intercooled-compression unit for the make-up stream.*

The simulation has been performed considering isentropic compressors, with an isentropic efficiency of 0.75 [20,55] and a mechanical efficiency of 0.90 [55].

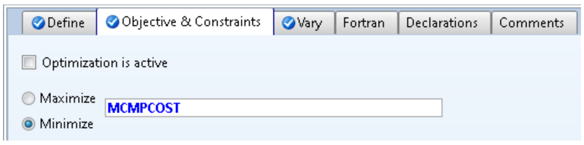
Multi-Compression Operative Condition Definition and Sizing

Compression optimal operative conditions have been defined through an optimization routine implemented in *ASPEN® Plus* aimed to minimize process costs, computed accordingly to Guthrie method, described later in this elaborate, *§4.1.1*.

The only manipulated variable set in the optimization routine has been the compression ratio, as reported in *Figure 2.4*, being the heat-exchanger duty (converted in area by a calculator) and the associated utility requirement computed autonomously by *ASPEN® Plus*.

Compression ratio has been left vary between 1 and 4, range for intercooled-multi-compression units, aiming to a ratio of circa 2, the industrial standard for ammonia synthesis [20].

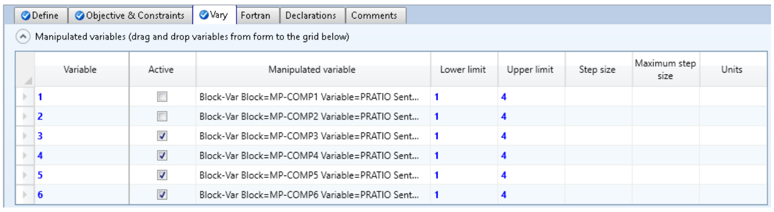
The performed optimization considered two constraints: the outlet-pressure of the final unit, necessary to define the plant pressure-requirement (200 bar, 300 bar in the two configurations) and the outlet-temperature of each unit, restrained to 145°C ± 5°C [55], necessary to avoid damages to the compression unit. Additional design constraint fixed are pressure drops of heat-exchangers, fixed to 1 bar per unit, rounding the value of 70 kPa suggested in [55].



☐ Optimization is active

○ Maximize
● Minimize
MCMPCOST

Figure 2.3 ASPEN® Plus *User-Interface for the definition of objective parameter target.*



Manipulated variables (drag and drop variables from form to the grid below)

Variable	Active	Manipulated variable	Lower limit	Upper limit	Step size	Maximum step size	Units
1	☐	Block-Var Block=MP-COMP1 Variable=PRATIO Sent...	1	4			
2	☐	Block-Var Block=MP-COMP2 Variable=PRATIO Sent...	1	4			
3	☑	Block-Var Block=MP-COMP3 Variable=PRATIO Sent...	1	4			
4	☑	Block-Var Block=MP-COMP4 Variable=PRATIO Sent...	1	4			
5	☑	Block-Var Block=MP-COMP5 Variable=PRATIO Sent...	1	4			
6	☑	Block-Var Block=MP-COMP6 Variable=PRATIO Sent...	1	4			

Figure 2.4 *Optimization routine manipulated variables and constraints definition in* ASPEN® Plus.

Units *MP-COMP1* and *MP-COMP2* have not been involved in the optimization routine since the definition of their compression ratio has been performed as preliminary step, necessary to equalize nitrogen and hydrogen feed pressures.

Sizing results for this process section has been reported in *Table 2.5*.

Table 2.5 *Sizing of the intercooled compression train.*

Process Unit	Sizing Result		UoM	Sizing Result		UoM
	P=200 bar	P=300 bar		P=200 bar	P=300 bar	
MP-CMP1	106.99	101.66	Brake Power, [kW]	2.1	2.1	Compression Ratio, [adim]
MP-CMP2	116.54	110.72		2.1	2.1	
MP-CMP3	394.55	440.01		1.882	2.077	
MP-CMP4	425.34	440.01		1.865	2.051	
MP-CMP5	367.71	428.40		1.773	1.975	
MP-CMP6	387.98	459.73		1.788	1.987	
HX-1	5.37	5.10	Area, [m^2]	-70’760	-67’230	Duty, [J/s]
HX-2	11.23	10.67		-182’610	-173’497	
HX-3	23.88	24.43		-354’344	-395’109	
HX-4	24.82	24.55		-380’449	-392’734	
HX-5	23.26	24.37		-326’996	-378’920	

2.3.2.2 Reaction Unit

The ammonia synthesis section, i.e. process reactor unit, follows the initial multi-compression train and its feed is made of the fresh-make-up and the unreacted reactants recovered in the separation section. The reactor simulation has been performed in two-steps: firstly reaction kinetic has been fixed and later the reactor model has been defined and sized.

Reaction Kinetic Description

The definition of the reaction kinetic equation is a central aspect for the correct simulation of process behavior: the first step was the choice of the catalyst, discussed in *Chapter §1.4.2.2*, being the reaction kinetic material-dependent. Considering the iron-based catalyst, the available equations are: Nielsen's kinetic expression [56] and the Temkin or Temkin-Pyzhev equation. The Temkin-Pyzhev equation [57] (reported in *Equation 2.7*) has been considered in this work: it has been directly implemented in *ASPEN® Plus* by manipulation of the equation as performed in [37,44,58–60] and reported in *Equations 2.8-2.9.*

$$r_{N_2}\rho_{cat} = -f\left(k_1\frac{p_{N_2}p_{H_2}^{1.5}}{p_{NH_3}} - k_{-1}\frac{p_{NH_3}}{p_{H_2}^{1.5}}\right)[\frac{\mathrm{kmol}_{N_2}}{\mathrm{s}\cdot m^3}] \tag{2.7}$$

$$r_{forward} = -k_1\frac{p_{N_2}p_{H_2}^{1.5}}{p_{NH_3}}[\frac{\mathrm{kmol}_{N_2}}{\mathrm{s}\cdot m^3}] \tag{2.8}$$

$$r_{reverse} = +k_{-1}\frac{p_{NH_3}}{p_{H_2}^{1.5}}[\frac{\mathrm{kmol}_{N_2}}{\mathrm{s}\cdot m^3}] \tag{2.9}$$

The Temkin-Pyzhev equation has been implemented in *ASPEN® Plus* breaking the two terms corresponding to the forward and reverse reaction, and considering a power-law model, with parameters collected in *Table 2.3*. Note that catalyst density is reported in SI units and that *f* is the catalyst efficiency, assumed unitary; the kinetic constant *k* must be implemented in SI units. As highlighted in [44], the kinetic equation implemented requires the presence of ammonia in the stream fed being its partial pressure at both numerator and denominator of the two semi-reactions: for this reason it is necessary to provide the reactor with traces of ammonia (sufficient concentration is $1 \cdot 10^{-8}$) by the implementation of a "temporary stream" during the first stages of the simulation, when the recycle (that contains few percentages of ammonia) is not closed. Once the recycle stream has been closed, this temporary stream can be removed.

Table 2.3 *Parameters of the rate of reaction used in the simulation* [44].

	Reactions	
	Forward	Reverse
Explicit Reactions	$3H_2 + N_2 \rightarrow 2NH_3$	$2NH_3 \rightarrow 3H_2 + N_2$
Kinetic Rate Parameters (Volumetric rate basis)		
k	1.54122e-07	2.27366e+15
n	0	0
E [kJ/kmol]	86'944	198'132
Concentration Exponents (Concentration in partial pressure)		
Ammonia	-1	1
Nitrogen	1	0
Hydrogen	1.5	-1.5

Reactor Representation

To simulate the adiabatic inter-cooled multi-bed reactor (commonly used in ammonia plants, described in *Chapter §1.4.2.2* and represented in *Figure 1.17.b*), both heat-exchangers and reactor blocks have been used.

Figure 2.5 represents the unit used to simulate ammonia reactor unit.

Reactor beds has been modelled by a series of RPlug blocks in *ASPEN® Plus*, that well suits their behavior: blocks have been modelled as adiabatic units, with an initial arbitrary size of 2 m in diameter and 1 m in height. Catalyst specifications have also been set to correctly estimate residence-times: 2'200 kg/m^3 of bulk density and 0.33 as bed-void-fraction [58,59,61]. The simulation of the reactor unit considers arbitrarily fixed pressure drops of 1 bar per bed; more correct estimations should be performed, for example considering the Ergun correlation.

Reactor heat-exchangers have been added to represent inter-cooling and heat-recovery units (both as the "head" heat-exchanger and the space between reactor internal and external vessels). Floating-head heat-exchangers have been considered to model the inter-cooling units necessary to decrease the mixture temperature after each bed to 400°C, while the fed mixture pre-heat has been modelled via heat-exchangers with area fixed equal to each catalytic bed external area. Also, an additional floating-head heat-exchanger has been considered to model the pre-heat of the fed mixture by recovery the heat of the reactor output stream. *B1-HINT*, *B2-HINT*, *B3-HINT* heat-exchangers have not been considered for the economical assessment of the plant.

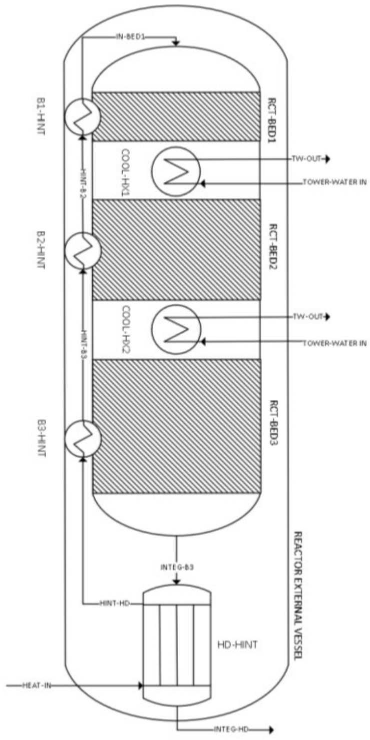


Figure 2.5 *Figure representing the reactor unit of the proposed design implemented in* ASPEN® Plus.

Reactor Unit Sizing

Reactor total size has been considered equal to the size of catalytic beds, plus a total of 1 m of additional length for heat-exchangers spacing, reactor head and bottom domes.

Beds optimal size (diameter and length) has been defined via two design specifications:

- length has been obtained constraining the bed outlet temperature at 490°C ± 5°C [42];
- optimal reactor diameter has been defined by the following procedure:
    - the height/diameter ratio for each bed has been constrained equal to 2 [44];
    - the average diameter has been fixed and the optimization of bed length has been performed again to define the optimal value for the fixed diameter.

Both diameter and length has been rounded to the closest multiple of 5 cm; design specifications considered a tolerance of 0.1°C, while final sizing the mentioned tolerance of 5°C.

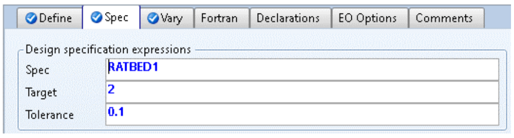
The "head" heat integrator, called *HD-HINT* in *Figure 2.5*, has been sized with a design specification: first bed T_{in}= 400°C ± 0.5°C; the manipulated variable has been its area.

Figures 2.6-2.7 represent *ASPEN® Plus* user-interfaces for the mentioned design specifications (referred to the first bed, but the same specification has been fixed for each); *Figures 2.8-2.9* represent the user-interface for the design specification of the head-heat-integrator.

Reactor unit sizing results have been reported in *Table 2.6*.

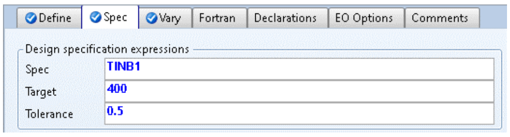
Design specification expressions
Spec TEMPBED1
Target 490
Tolerance 0.1

Figure 2.6 ASPEN® Plus *User-Interface of the parameter target of the design specification for bed length.*



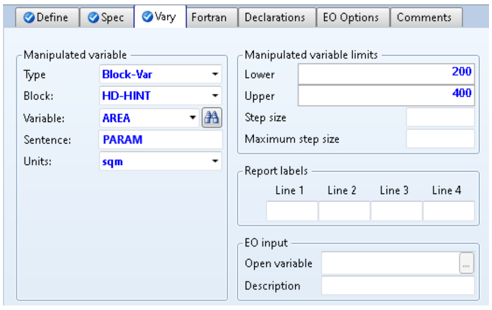
Design specification expressions
Spec RATBED1
Target 2
Tolerance 0.1

Figure 2.7 ASPEN® Plus *User-Interface of the parameter target of the design specification for bed diameter.*



Design specification expressions
Spec TINB1
Target 400
Tolerance 0.5

Figure 2.8 ASPEN® Plus *User-Interface of the parameter target of the design specification for head heat-integrator area definition.*



Manipulated variable
Type Block-Var
Block: HD-HINT
Variable: AREA
Sentence: PARAM
Units: sqm

Manipulated variable limits
Lower 200
Upper 400
Step size
Maximum step size

Figure 2.9 ASPEN® Plus *User-Interface of manipulated variables for "head heat-integrator" optimization.*

Table 2.6 *Sizing of the reactor unit.*

Parameter	Sizing Value		UoM	Sizing Value		UoM
	P=200 bar	P=300 bar		P=200 bar	P=300 bar	
BED-1	1.5	1.1	Length, [m]	0.95	0.9	Diameter, [m]
BED-2	1.5	1.1		2.95	2.7	
BED-3	1.5	1.1		7.6	5.7	
COOL-HX1	10.12	9.59	Area, [m^2]	-1'217'240	-1'151'458	Duty, [J/s]
COOL-HX2	9.13	9.40		-1'088'706	-1'127'306	
HD-HINT	267.23	296.39		-3'958'640	-4'170'943	

Considering the results of *Table 2.6* and the mentioned additional length considered, the total reactor length results in 9.3 m for the 200 bar configuration and 12.5 m for the 300 bar case.

The mass of catalyst used in the two configurations, estimated considering the fixed diameter and the total reactor length and the catalyst bulk density, results in 29.94 ton for the 200 bar configuration and 13.02 ton for the 300 bar case.

2.3.2.3 Separation Section

Separation of ammonia, as described in *Chapter §1.4.2.2*, is performed to recover liquid ammonia and is performed by refrigeration and flashing; the product resulting from this step must satisfy the specifications of productivity, 100 ton/day, and purity, > 99.9%w.

Refrigeration step is commonly performed at -25°C and is anticipated by the reduction of process stream temperature performed by a cooling-train, that aims to reduce refrigeration duty, and involves both cooling water and refrigerated water. Ammonia refrigeration temperature has been also optimized by a sensitivity analysis.

After refrigeration, the cold-two-phase stream is split in a separation vessel to recover the unreacted reactants and liquid ammonia (with traces of unreacted reactants), which is further sent to lamination, where additional unreacted species are recovered. Lamination is the last step of the process, necessary to purify ammonia and reach process specifications; an expansion tank allows to separate the two phases and recover ammonia in liquid phase and a small stream of synthesis mixture to recycle; also lamination has been optimized via sensitivity analysis.

The two streams of unreacted reactants to recycle, originating in the separation and expansion vessels, are respectively sent to: the reactor after pre-heating and compression, and the initial compression train, because of the small flowrate and low pressure.

Separation-section sizing and optimization has been performed accordingly to the procedure described in the following paragraph and the results has been collected in *Table 2.7*. The final configuration of the separation section developed has been presented in *Figure 2.18*.

Separation Optimization

Optimal refrigeration unit temperature has been defined via sensitivity analysis, aimed to maximize the ammonia recovered and minimize its molar fraction in the recycled stream, while applying the highest possible temperature to decrease refrigeration duty. Sensitivity analysis results are reported in *Figures 2.10-2.11* for the two configurations considered.

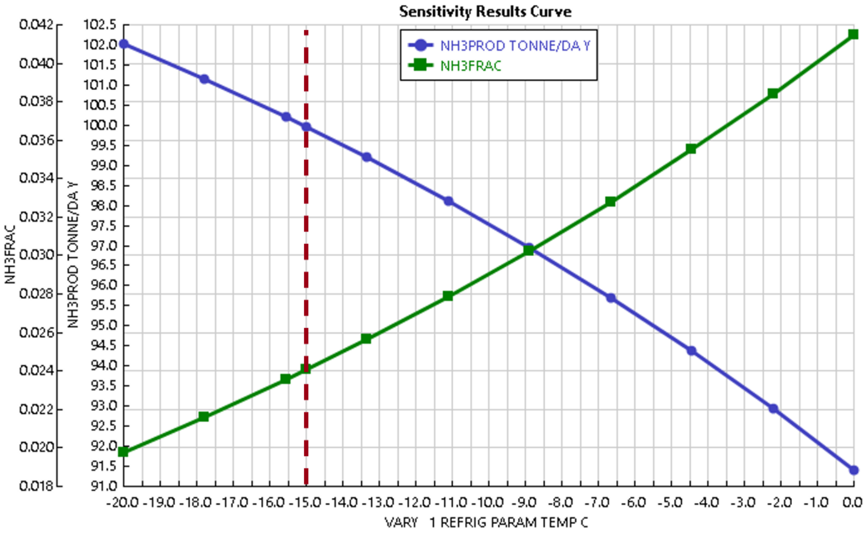


Figure 2.10 *Refrigeration temperature selection, sensitivity analysis results for the 200bar configuration.*

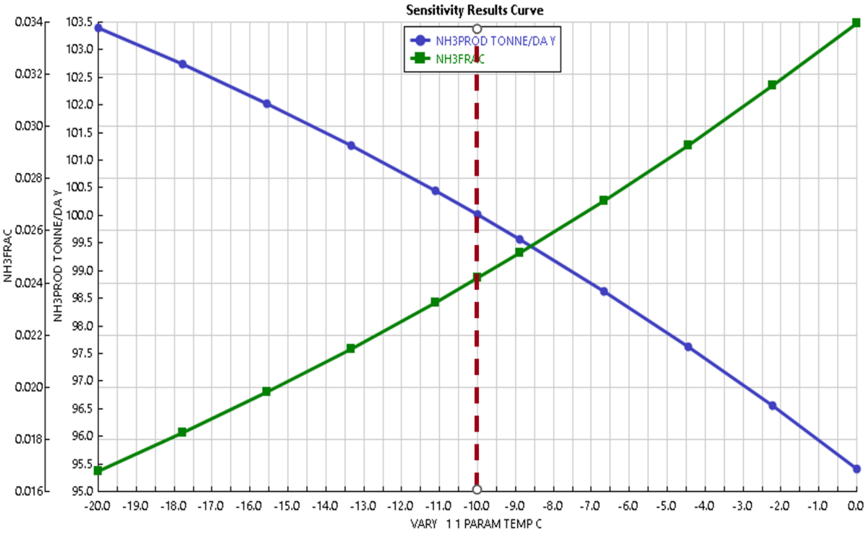
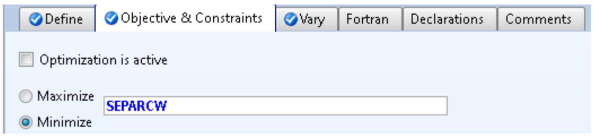


Figure 2.11 *Refrigeration temperature selection, sensitivity analysis results for the 300bar configuration.*

In *Figures 2.10-2.11* the dotted-lines represents the optimal conditions identified for the for the 200 bar and 300 bar configurations, that are -15°C and -10°C, respectively. In both configurations ammonia concentration in the recycle stream is around 2% molar and productivity is close to 100 ton/day.

Figure 2.17 show the heat-exchanger "*REF-HINT*", that has not been mentioned early: it has been added during the separation section optimization to pre-cool the process stream sent to the refrigerator, recovering "cold" of the recycled cold-gas separated in tank "*PROD-SEP*". This unit has been sized fixing the hot-inlet/cold-outlet approach-temperature equal to 15°C.

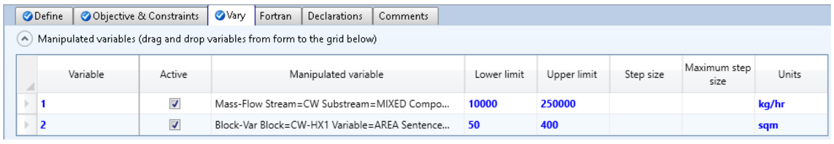
Additional optimization involves the recycle of the low-temperature vapor stream just discussed: to avoid its recycle at low temperature directly at the reactor, that leads to a decrease in the first-bed inlet temperature (catalyst requirement of 400°C is not satisfied), the stream is pre-heated by integration of an additional heat-exchanger. The additional unit, referred as "*CW-HX2*" in *Figure 2.17*, pre-heats the recycled gas stream "*INT-RCY*" with hot-cooling water leaving "*CW-HX1*" as service fluid. The optimization of this integration (i.e. coupling units "*CW-HX1*" and "*CW-HX2*" by the utility stream) has been performed via an optimization routine implemented in *ASPEN® Plus*, aimed to minimize capital and operative costs. *Figures 2.12-2.13* show the user-interfaces involved in this optimization. Manipulated variables considered has been "*CW-HX1*" area and the cooling-water flowrate, while the approach temperature in the two units (fixed at 15°C) and the maximum temperature of the cooling-water leaving the process (50°C ± 1°C) [55] have been constrained. These constraints have been fixed as either optimization constraints or design-specifications of the heat-exchangers.



☐ Optimization is active

○ Maximize
● Minimize
SEPARCW

Figure 2.12 ASPEN® Plus *User-Interface for the definition of objective parameter target.*



Manipulated variables (drag and drop variables from form to the grid below)

Variable	Active	Manipulated variable	Lower limit	Upper limit	Step size	Maximum step size	Units
1	☑	Mass-Flow Stream=CW Substream=MIXED Compo...	10000	250000			kg/hr
2	☑	Block-Var Block=CW-HX1 Variable=AREA Sentence...	50	400			sqm

Figure 2.13 *Optimization routine manipulated variables and constraints definition in* ASPEN® Plus.

Similarly to refrigeration temperature, lamination pressure has been fixed after a sensitivity analysis, aimed to satisfy both ammonia productivity and purity, while allowing an ease of recovery: lamination pressure has been selected among inlet pressures of the compression stages of the compression-train previously presented. Because of this optimization, the initial compression-train arrangement has been modified as represented in *Figure 2.16*.

Figures 2.14-2.15 show the sensitivity analysis results for the for the 200 bar and 300 bar configurations; the optimal conditions identified are, respectively: 35 bar and 38 bar (dot-lines).

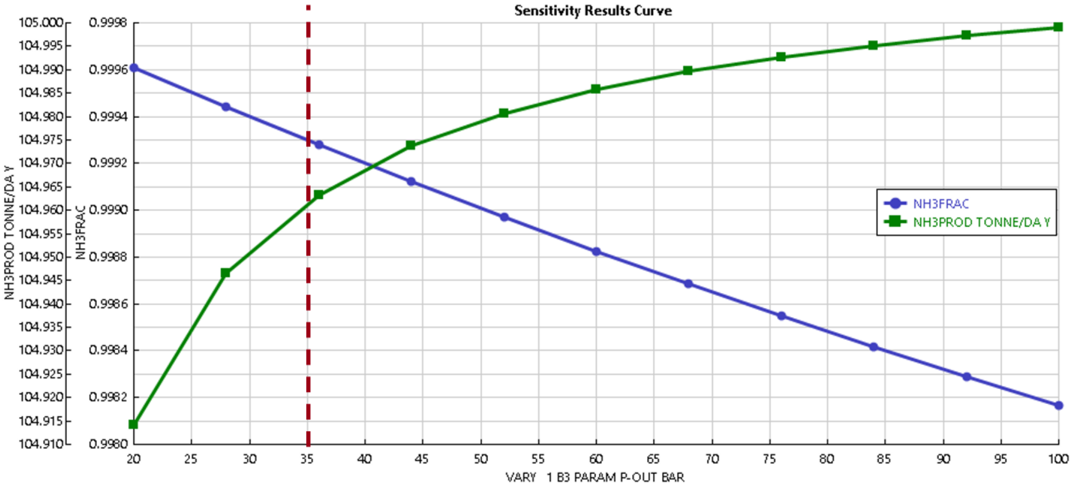


Figure 2.14 *Lamination pressure definition, sensitivity analysis results for the 200bar configuration.*

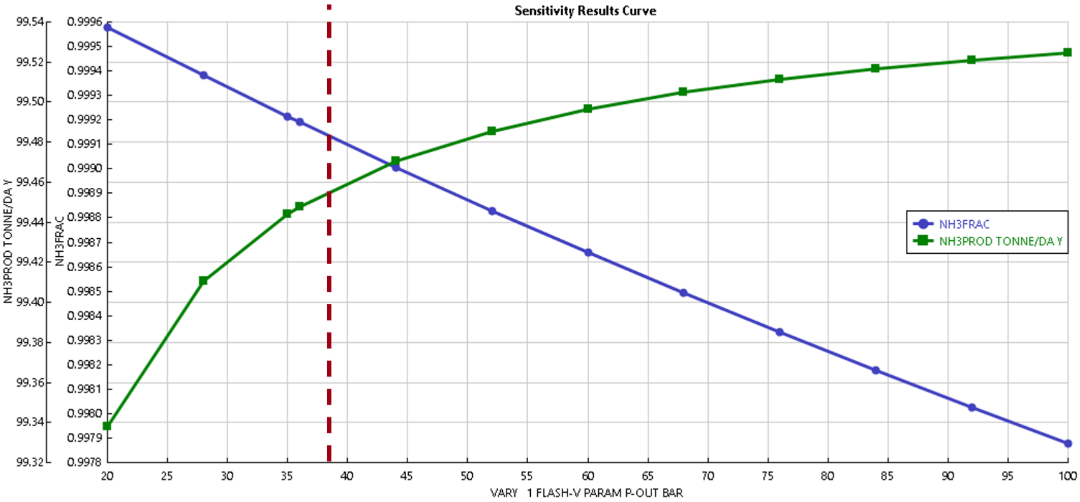


Figure 2.15 *Lamination pressure definition, sensitivity analysis results for the 300bar configuration.*

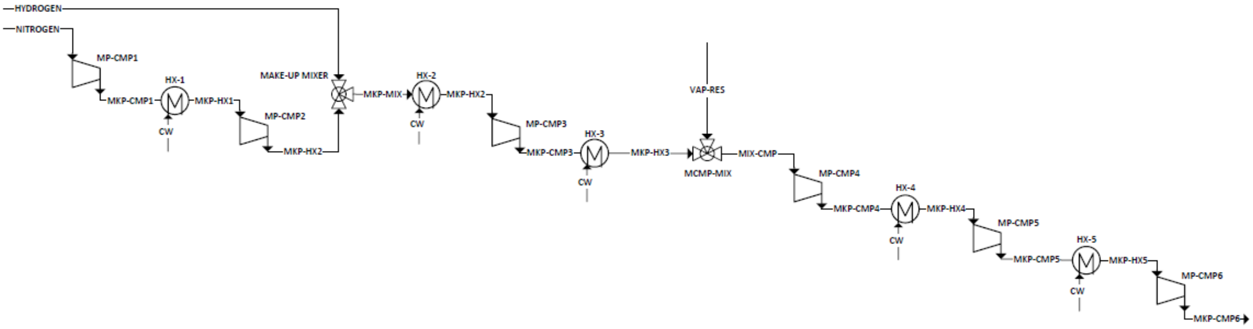


Figure 2.16 *Multi-compression train arrangement with integration of the recycled stream VAP-RES.*

From the separation section, two vapor recycle streams are obtained: "*VAP-RES*" after lamination and "*REC-VAP*" after the first vapor-liquid separation. This second stream is recycled back at the compressor after heat-integration, pre-heating and compression, step necessary to counter the synthesis loop pressure drops: specification of this unit is the same pressure of the last stage of the compression train. "*RECY*" and "*MKP-CMP6*" are mixed and sent to the reactor as "*HEAT-IN*" (*Figure 2.5*).

Figure 2.17 represents the resulting configuration of the separation section developed.

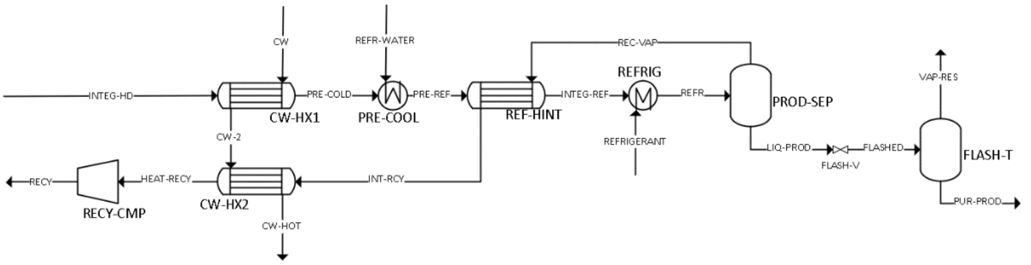


***Figure 2.17** Representation of the process separation section.*

Separation vessels implemented in this process section have been sized considering a residence time of 5 min [55] for the largest volumetric stream leaving the unit; for the purposes of the economic estimation of plant capital costs these units have been considered as process-vessels. The last optimization performed that involves the separation section regards the nitrogen stream produced by ASU: its integration in the cooling-train of the separation section has been performed to assess the economical impact on process costs. Nitrogen is produced by ASU in gas phase and after compression (necessary to counter pressure drops) it has been sent to "*NITRO-INT*", a dedicated heat-exchanger added for this purpose and shown in *Figure 2.18*. This additional heat-exchanger has been modelled considering an inlet minimum approach temperature of 15°C and a nitrogen stream in gas-phase at -175°C and 6 bar, conditions close to saturation [62]. This unit sizing results has been reported in *Table 2.7*, together with the results of the other process units involved in the separation section.

Because of the constraint fixed, nitrogen leaves the integrator at about 0°C, therefore additional refrigeration can be provided by this stream. In the present work it has been assumed that the remaining heat can be recovered in other plant sections and the stream is later sent at the initial compression-train at 20°C and 5 bar.

Table 2.7 *Sizing of the separation section units.*

Parameter	Sizing Value P=200 bar	Sizing Value P=300 bar	UoM	Sizing Value P=200 bar	Sizing Value P=300 bar	UoM
CW-HX1	152.01	158.01	Area, [m^2]	2’177’596	2’236’596	Duty, [J/s]
CW-HX2	40.32	48.26		300’550	302’355	
PRE-COOL	77.17	51.59		-570’768	-467’380	
REF-HINT	39.86	34.36		267’611	211’643	
REFRIG	101.37	68.23		-850’411	-649’129	
PROD-SEP	13.40	9.18	Volume, [m^3]	1.79	1.57	Diameter, [m]
FLASH-T	0.7	0.7		0.67	0.67	
RECY-CMP	155	105	Brake Power, [kW]	200	300	Outlet P, [bar]
REFRIG	86.49	53.92	Area, [m^2]	-669’761	-468’439	Duty, [J/s]
NITRO-INT	17.72	17.80		180’441	180’876	

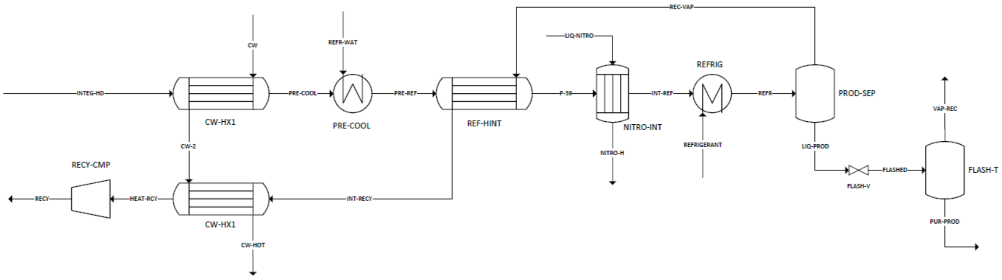


Figure 2.18 *Representation of the process separation section with nitrogen heat-recovery integration.*

2.3.3 Process Storages

2.3.3.1 Storage Generalities and Operative Conditions

Safety issues, plant operability and costs are all aspects to be considered when dealing with storage units. Two main types of storages can be distinguished: for feedstock and products (i.e. medium-long terms storage units) and “intermediate” storage units (surge tanks, at short-term). To define storage size, residence time of the unit must be defined: according to Seider et al. [63], feedstocks and products storages consider residence times from 1 week to 1 month, while intermediates between few minutes (10 min) and 1 day. In accordance to Seider et al. and considering the commercially available storage sizes and conditions for the species of interest, storage tanks have been sized for the proposal developed.

Ammonia

Ammonia is characterized by a boiling temperature of -33°C and a vapor pressure of 8.6 bar at 20°C: accordingly to these properties it can be stored in liquid phase as pressurized or cryogenic liquid, respectively at 10 bar, 25°C or -33°C, 1 atm. Ammonia can also be stored in gas phase, both as pressurized gas or in semi-refrigerated conditions: being these option not is used in large plants for products storage, these has not been considered in this dissertation [43,64–66]. In this elaborate ammonia cryogenic storage has been considered for products storage, being the preferrable choice compared to pressurized storage because of: smaller material requirement (1 tonSteel every 2.8 $tonNH_3$ in the pressurized case, 45 $tonNH_3$ in the cryogenic case), smaller cost per unit of ammonia stored (3 vs. 0.81€/$kgNH_3$) and also, due to the availability of double-walled tanks, better safety performances [67].

Considering the variation in operative conditions between synthesis-loop and storages, the electrical requirement for ammonia refrigeration has been fixed at 0.0378 kWh/$kgNH_3$ [67].

Oxygen & Nitrogen

Oxygen and nitrogen storage can be performed as either pressurized gas or in cryogenic conditions, option adopted in this elaborate. Cryogenic storage of these species can be performed at pressures ranging from 1 bar to 17 bar [68,69]. Storage cost for the scale of interest has been provided by AirLiquide [54]: 7.5M€/tank. Electrical demand for oxygen refrigeration has not been accounted, being ASU capable of producing liquid products, that can be directly stored; nitrogen has been directly fed to the ammonia synthesis loop, therefore its storage was not considered for the purpose of process economic evaluation.

Hydrogen

Hydrogen storage can be performed in both gas phase, under pressure (up to 1’000 bar and 6’000 Nm^3 [70]), or liquid, at cryogenic conditions (at about -250°C).

In this elaborate it is not considered the energetic content of hydrogen, but it is useful to notice that hydrogen storage is an energy-demanding operation that consumes up to: 40% of the energy stored at cryogenic conditions, compared to the 10% of compressed case [71].

Pressurized tanks for hydrogen storage commonly adopted in industrial plants are Type-I” or “Type-II” vessels, made of metal, with a metallic liner in case of “Type-II” vessels, that allows operations at higher pressures compared to “Type-I” tanks. “Type-I” vessels are the most widespread and cheaper option available and operates at 150-300 bar (commonly 200 bar) [72].

Liquid hydrogen storages are well-developed and widely used and has very high variability in sizes (from hundreds of liters, up to 5’000 m^3) and offers the advantage of avoiding any corrosion mechanism [73]. Liquid storages can be performed at both 1 atm, -250°C or under pressure (up to 13 bar, hydrogen critical pressure), that allows to decrease the liquefaction temperature up to about -240°C [74].

Process Stored Species

Among all the chemicals handled in the proposed design, only the necessary ones will be stored, for both safety reasons and costs.

Air and water are the two process feedstocks, which are purified and sent to electrolysis and ASU: it has been assumed that no storage is needed in this case, due to the nature of the storage necessary (surge tanks), the operative conditions (near ambient conditions) and the design step involved in this elaborate (conceptual-design), that neglects surge tank costs.

Process intermediates are hydrogen and nitrogen, whose storage has not been considered necessary being the process fed by the grid, as mentioned in *Chapter §1.5*, i.e. a steady-state production is obtained and intermediate storage is not required to balance reactants production fluctuations: the reactive mixture is assumed directly fed to the synthesis loop.

Ammonia and oxygen, the two process products, has been considered stored: oxygen tank costs has been provided by AirLiquide [54] for the scale of interest, while ammonia storage size and costs has been evaluated as discussed in the following paragraph.

2.3.3.2 Ammonia Storage Sizing

Ammonia storage size has been fixed considering the residence time suggested in [63] and the typical size of storages for this chemical, indicated in [67] as 4’550-50’000 $tonNH_3$. According to these data and considering the productivity of the plant developed (circa 100 ton/day in both configurations), the optimal solution has been identified in storage tank of 4’550 $tonNH_3$, corresponding to about 46 days of residence time. For the storage size considered and the presented costs, storage tank capital expenditure and electrical demand has been estimated.

The longer residence time considered in this case has the advantage of managing issues in the transport network and to optimize the selling of ammonia depending on contracts and market prices, while working with a single storage tank, but certainly longer residence times and storage size enhances storage safety risks and may end in excessive capital costs to sustain if tank filling is minimized during normal plant operations.

2.3.4 Reaction Kinetic Evaluation

A *MATLAB®* simulation has been performed to evaluate the correct representation of the reaction behavior of the kinetic equation implemented in *ASPEN® Plus* compared to the canonical Temkin-Pyzhev equation reported in *Equation 2.7*; results of *ASPEN® Plus* simulation have also been reported in the *MATLAB®* script, to validate the simulation.

Figures 2.19-2.20 show a comparison, expressed in percentage errors, between the results obtained accordingly to the two kinetic expressions: as reference it is considered the standard Temkin-Pyzhev equation reported in *Equation 2.7. Figures 2.21-2.22*, instead, report the profiles of temperature and conversion along the reactor volume in the two configurations.

As can be seen in *Figures 2.19-2.20*, for both the configurations the percentage errors are smaller than 1%, highlighting good consistency between the two kinetic equations. Good adherence with the results obtained in the *ASPEN® Plus* simulation can be seen by comparison of temperature and conversion profiles presented in *Figures 2.21-2.22*.

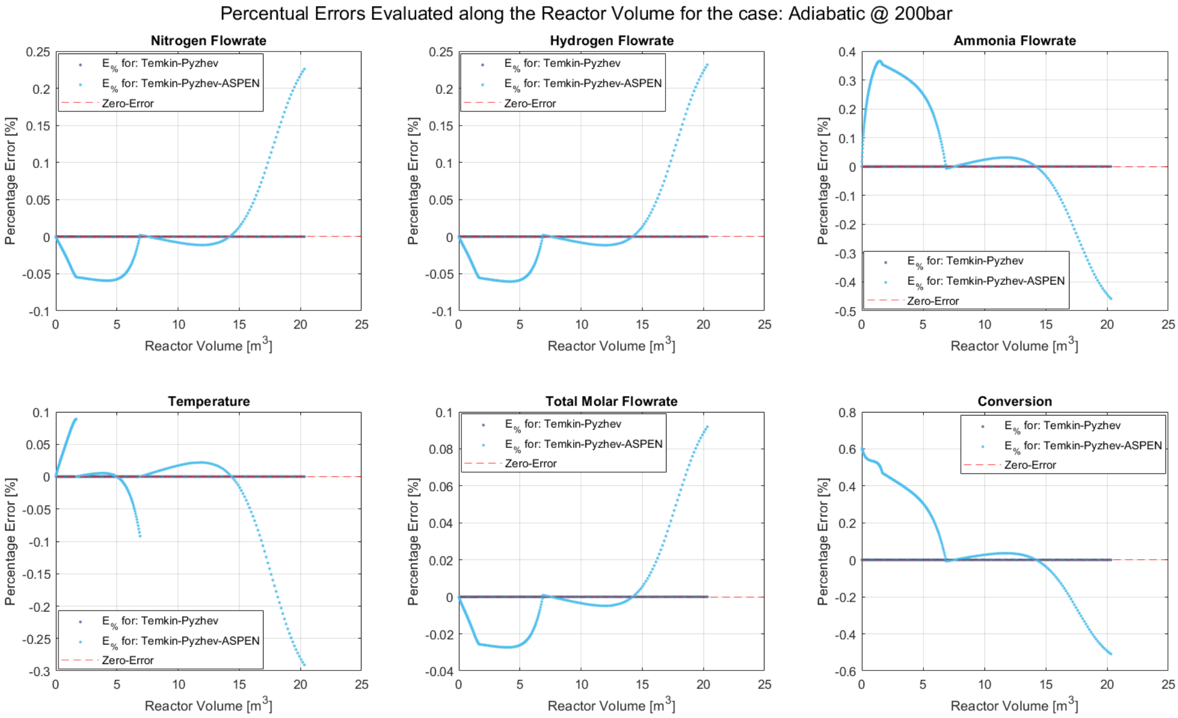


Figure 2.19 *Assessment of implemented Temkin-Pyzhev kinetic equation performance, 200 bar configuration.*

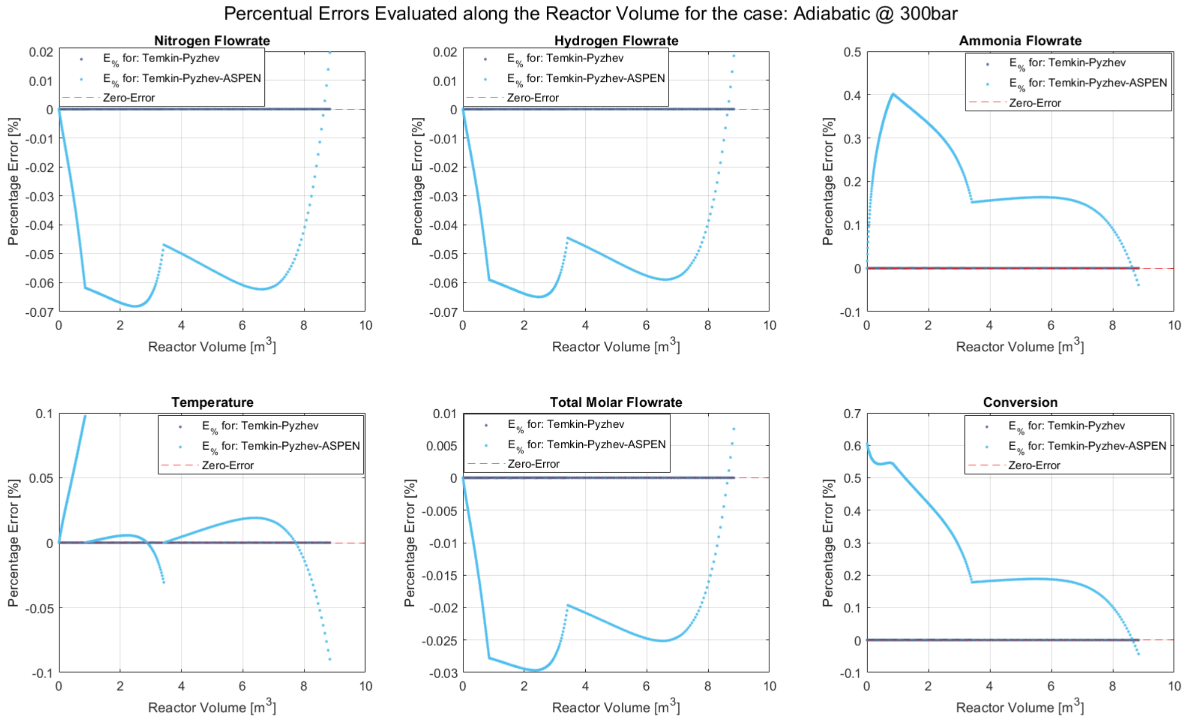
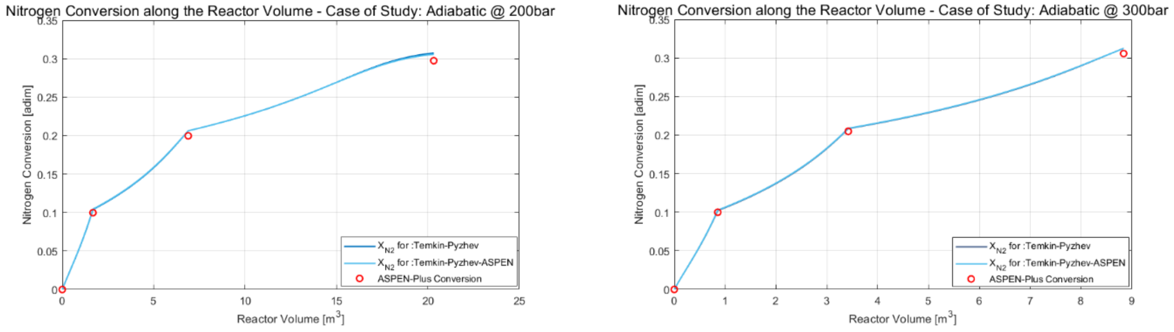
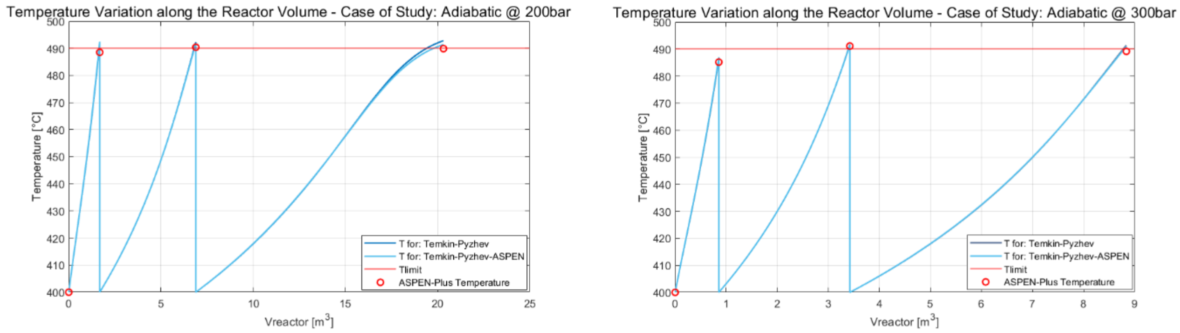


***Figure 2.20** Assessment of implemented Temkin-Pyzhev kinetic equation performance, 300 bar configuration.*



(a) *(b)*

***Figure 2.21** Nitrogen conversion profiles obtained in* MATLAB® *for the 200 bar (a) and 300 bar (b) cases.*



(a) *(b)*

***Figure 2.22** Temperature profiles obtained in* MATLAB® *for the 200 bar (a) and 300 bar (b) cases.*

2.4 Haber-Bosch Process Flowsheet

The ammonia synthesis loop modelled has been reported in the next figure as whole.

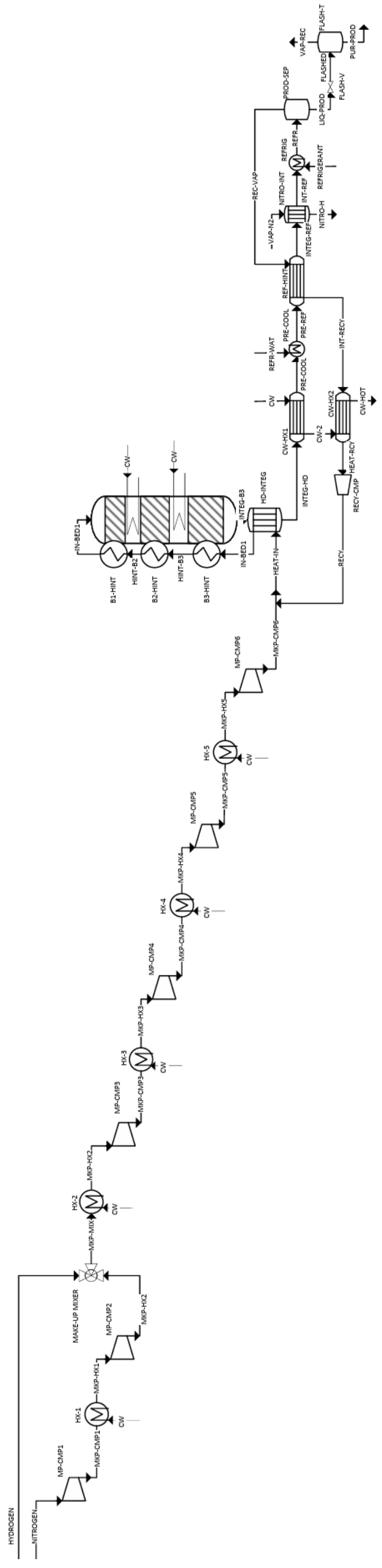


Figure 2.23 *Ammonia synthesis loop modelled in this elaborate.*

Chapter 3

Process Safety-Related Considerations

In the following paragraph, the concept of inherently safer design (ISD) is introduced, and the impact on the process safety and design and economic indicators is discussed. Concerning the developed process scheme, hazard and risk identification techniques are applied (interaction matrix, hazard identification and operability analysis). Moreover, an estimation of risks implied by the storage of chemicals involved in the process is proposed.

3.1 Safety

Process safety is a central aspect of the design of innovative production facilities, especially in light of several severe major industrial accidents that have occurred in the recent past [75].
It has been proven that safety-related costs generated by adjustments or process modifications can be reduced if inherent safety concepts are embedded early in process design (*Figure 3.1* [76]). In fact, once the process design is accomplished, the eventual implementation of safety measures may be complex or even infeasible [77].

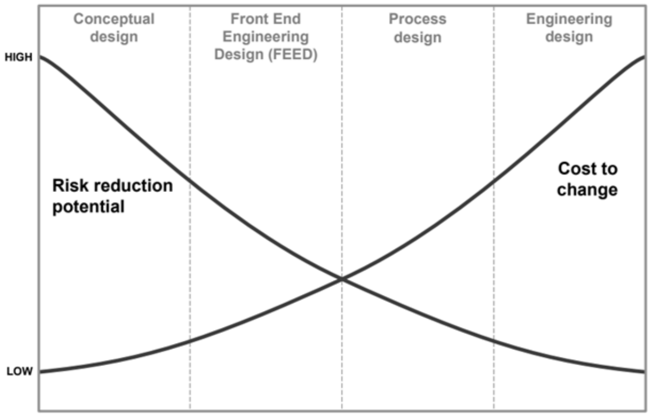


Figure 3.1 *Diagram showing variation of costs and risk reduction potential offered by safety measures during different design steps* [78].

The traditional approach to addressing process hazards (i.e. "inherent physical or chemical characteristic with the potential for causing harm to people, environment or property" [79,80]) is to identify them once the design is completed and to apply safety measures to decrease the risk. In this regard, protective layers are commonly used to manage risks due to chemical industrial processes by adopting both preventive (acting on the frequency of events) and mitigative layers (acting on the impact of events) [80,81].

This way of operating leads to the definition of *extrinsically safe processes*, i.e. processes whose safety is ensured by adding safety barriers. Alternatively, in *intrinsically safe processes*, the inherent hazards are identified, managed, and, where possible, removed since early in design. This leads to chemical processes with safety as an essential constituent or characteristic. Such processes are identified as designed according to Inherently Safer Design (ISD) principles [79,82].

3.1.1 Inherently Safer Design

Inherently safer design (ISD) is a proactive technique to minimize the risks of chemical plants [83]. It is part of green chemistry principles [84] and it is based on concepts first conceptualized by Trevor Kletz. Kletz clearly stated in the title of its most important contribution the way of addressing safety concerns via ISD: "*What you don't have cannot leak*" [85]. Inherently safer design routines differ from the standard workflow since, early in process design, hazards are identified and addressed, aiming for their elimination: the resulting process will be inherently safer and thus more reliable due to inherent safer features [85–87]. In conclusion, ISD provides more robust and reliable risk management strategies and has the potential to make the process simpler and more economical, eliminating the need for complex safety systems [79].

Inherently safer design results in a total of 14 principles. Among these, four are considered the most important and general [86] (for other authors, two more should be considered [85,88]). The remaining principles can be seen as sub-categories of the main four, and some of them are not commonly used due to high costs and complexity in practical implementation [88].

Among the four ISD principles reported here, minimization is usually the most applied approach to improve process safety [83] and the other three are commonly intended as additional measures.

Minimization (Intensification) - *"Use smaller quantities of hazardous materials."*

> Minimizing hazardous species quantities refers to both stored/processed species and process size (intensification). The economic advantage offered by this principle is the reduction of the immobilized capital: companies tend to reduce the amount of chemicals stored in plants and operate with the minimum hold-up.

Substitution - *"Replace hazardous materials with less hazardous."*

With substitution, replacing hazardous chemicals and process equipment with safer ones capable of providing similar results is advocated, guaranteeing safer and more efficient process operations. The reduction of process costs and the complexity of process safety measures implemented is achieved and can serve as an alternative approach to minimization.

Moderation (Attenuation) - *"Use less hazardous operative conditions."*

Moderation of operative conditions to work in safer ones often advocates using catalysts. Concerning storage, moderation involves dilution and refrigeration.

Simplification - *"Design facilities which eliminate unnecessary complexity and make operating errors less likely to occur."*

A less complex plant design reduces the probability of the occurrence of human errors. The practical application of simplification involves, for example, reducing the number of unit operations or substituting them with more efficient operations.

Implementing ISD principles since the beginning of design is challenging because of the lack of tools and methodologies [76] that allow a straightforward comparative assessment of different design alternatives. This requires implementing typical hazard and risk assessment techniques, including the Hazards and Operability Analysis (HAZOP) [81].

ISD principles are commonly applied after a conventional safety assessment is performed. However, such an approach cannot provide a quantitative description of process safety performance and can be applied only after a flowsheet has been developed.

Even if ISD principles are almost 40 years old and the correlated economic benefits are well known, their application is not common practice for a series of reasons (*Figure 3.2*), which involves tradeoffs during its application, lack of clear guidelines and a contrast between the degree of innovation required for its application and common project schedules [77,85].

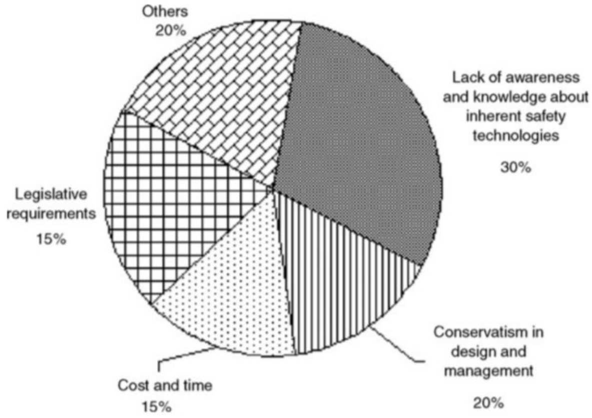


Figure 3.2 *Primary issues hindering the applicability of ISD principles* [77,87].

3.1.2 Process Design supported by Inherently Safer Design concept

ISD principles support process design operations by providing a focus on the safety performance of selected unit operations. This is not only on a techno-economic basis but also considering the role of hazardous chemicals and operations.

The selection of the appropriate technologies, based on the knowledge collected in *Chapter §1* about the sustainable synthesis of ammonia, is the first step considered in this elaborate, with particular attention to the electrolysis unit.

Once the process flowsheet has been completed, chemical compatibility (interaction) matrices and a "*What if*?" analysis have been developed to identify process hazards. Based on this, a subsequent Hazard and Operability Analysis has been performed in order to identify relevant Top Events related to the developed process.

3.2 Chemicals and Process Units Safety

3.2.1 Inherent hazards of materials

This paragraph briefly collects safety information about all the species handled in the process, i.e. nitrogen and oxygen (produced by the ASU); hydrogen produced together with oxygen in the electrolysis unit; Ammonia (the product of interest), which is obtained by conversion of hydrogen and nitrogen via Haber-Bosch process.

3.2.1.1 Nitrogen

Nitrogen safety datasheets reports the Globally Harmonized System of Classification and Labelling of Chemicals shown in *Figure 3.3* and the properties reported in *Table 3.1* [89,90].

Figure 3.3 *Pictograms for the characterization of nitrogen hazards.*

Table 3.1 *Nitrogen properties* [89,90].

Property	Nitrogen (Gas)
Vapor Density (25°C) [kg/m^3]	0.967 (Relative, air=1)
Boiling Temperature [°C]	-196
Melting Temperature [°C]	-210.01
Auto-Ignition Temperature [°C]	Not availbale
Flash Point [°C]	Do not sustain combustion
Flammability Limits	Not availbale
Explosivity Limits	Not availbale
Minimum Ignition Energy [mJ]	Not availbale
LD$_{50}$ [mg/kg] (acute oral toxicity)	Not available

Nitrogen is classified as a simple-asphyxiant, as reported in the safety diamond. Simple-asphyxiants species differentiate from chemical-asphyxiants in the process that causes suffocation: simple-asphyxiants can displace air, causing a lack of oxygen, while chemical-asphyxiants can interrupt the delivery and/or utilization of oxygen reacting in the human body. Therefore, in case of loss of containment of nitrogen, adequate safety measures must be adopted to avoid suffocation: being odorless and colorless, adequate detection measures must be defined to localize its release point and alert nearby workers.

3.2.1.2 Oxygen

Oxygen is characterized by GHS' labelling reported in *Figure 3.4* and by the properties shown in *Table 3.2* [91,92].

Figure 3.4 *Pictograms for the characterization of oxygen hazards.*

Table 3.2 *Oxygen properties* [91,92].

Property	Oxygen (Gas)
Vapor Density (25°C) [kg/m^3]	1.1 (Relative, air=1)
Boiling Temperature [°C]	-183
Melting Temperature [°C]	-218.4
Auto-Ignition Temperature [°C]	Not availbale
Flash Point [°C]	Do not sustain combustion
Flammability Limits	Not availbale
Explosivity Limits	Not availbale
Minimum Ignition Energy [mJ]	Not availbale
LD$_{50}$ [mg/kg] (acute oral toxicity)	Not available

Oxygen safety concerns are associated, as represented in *Figure 3.4*, with its oxidant property: it can enhance the flammability of other species. In the case of loss of oxygen containment, the main concerns are not associated with the species itself but with other chemicals it can react with. Similarly to nitrogen, being oxygen odorless and colorless, adequate detection methods must be implemented to increase process safety. Moreover, segregation from combustible materials is essential for preserving safety.

3.2.1.3 Hydrogen

GHS labelling for hydrogen is reported in *Figure 3.5*; *Table 3.3* collects its properties [93].

Figure 3.5 *Pictograms for the characterization of hydrogen hazards.*

Table 3.3 *Hydrogen properties.*

Property	Value
Vapor Density (25°C) [kg/m^3]	70.96
Boiling Temperature [°C]	-253
Auto-Ignition Temperature [°C]	500-571
Flash Point [°C]	Not availbale
Flammability Limits	4-76%
Explosivity Limits	18.3-59%
Minimum Ignition Energy [mJ]	0.02

Hydrogen is characterized by wide flammability and explosivity limits and by a very low minimum ignition energy (*Table 3.3*), which enhances its intrinsic hazards; because of these properties, the main risks associated with hydrogen are explosion and fires [73,93,94]. Similarly to oxygen and nitrogen, also hydrogen is colorless and odorless, meaning that it is challenging to detect whenever a loss of containment occurs, requiring the implementation of reliable sensors [71]. In addition, hydrogen fires are not easy to detect, especially when a continuous release is ignited (e.g., jet fire).

3.2.1.4 Ammonia

Before addressing the risks related to anhydrous ammonia and a water-based solution, a recap of their properties is reported in *Table 3.4*. *Figures 3.6-3.7* represents GHS pictograms and the NFPA 704 diamond hazard of anhydrous and aqueous ammonia solutions, respectively.

***Table 3.4** Comparison of properties of anhydrous ammonia and a water-ammonia mixture* [38,95–101].

Property	Anhydrous Ammonia	Water Solution
Density (25°C) [g/cm^3]	0.6 (Relative, air=1)	0.91
Boiling Temperature [°C]	-33	38
Melting Temperature [°C]	-77	-55
Auto-Ignition Temperature [°C]	630	630
Flash Point [°C]	Non applicable	Not determined
LFL [%]	15.4%	16%
UFL [%]	33.6%	30%
IDLH [ppm]	300 ppm	
LD$_{50}$ [mg/kg] (acute oral toxicity)	350 mg/kg	

***Figure 3.6** Pictograms representing primary ammonia hazards* [38,95–101].

***Figure 3.7** Pictograms representing primary ammonia solution hazards* [99].

Ammonia is a gaseous substance at normal conditions (1 atm, 25°C), stable without any reaction-related concern under normal conditions, as reported in the risk-diamond.

Considering the process discussed in this elaborate and the species that may react with ammonia (discussed in [96]), any chemical shows potentially violent reactions. For example, the reaction between ammonia and water (process fluid or utility) can be violent, releasing large quantities of heat [97].

Anhydrous ammonia is flammable but not ignited readily [96,97]. This aspect is relevant for the Haber-Bosch process of producing ammonia, also in light of the presence of hydrogen, which can provide fires or explosions once mixed with an oxidant. Ammonia is also explosive, a safety aspect of concern, primarily when focusing on storage.

Lung damage and death are caused by ammonia inhaled at high concentrations, while burnings (on skin, mouth, lungs, throat and eyes) may arise if contact at lower concentrations occurs. Because of the strong characteristic smell, workers can easily detect leakages at concentrations far below levels that cause any health concerns [12]. Moreover, due to the high vapor pressure, ammonia risks associated with its volatility are enhanced (i.e. flammability and toxicity).

Ammonia is also a corrosive chemical (*Figure 3.6*), severely affecting the integrity of many construction materials (nickel-copper alloys, bronze and some plastic materials); for this reason the choice of the construction material has been addressed early in this elaborate via compatibility matrices.

3.2.2 Process Hazards

In the following paragraphs, an overview of hazards due to process units is reported.

3.2.2.1 Electrolysis

Electrolysis is a well-known technology that demands the conversion of water into oxygen and hydrogen. It is characterized by inherent hazards in handling pure streams of hydrogen and oxygen under medium-high temperatures and pressure. Water demineralization is the pre-purification step of electrolysis, but its safety has not been addressed in this elaborate. Indeed, the associated process hazards can be neglected compared to electrolysis hazards.

Major process hazards of electrolysis are associated with oxygen-hydrogen flammable mixtures that may be formed because of cell membrane degradation or failure in process operations. An uncontrolled contact between the two generates a strong potential explosive mixture that can be easily ignited.

In the case of AEL, additional process hazards are due to the corrosivity of the caustic solution (NaOH or KOH at 20-30% concentration), handled at moderate to high temperatures and pressures [25–27].

To select the proper electrolysis technology to implement, as mentioned in *Chapter §1.3.2.5*, safety performances of AEL and PEMEL have been compared. Moreover, similar safety-related performances have been demonstrated [29,30]; the assessment highlighted that AEL has obtained slightly better performances because of the lower operative pressures compared to PEM. Hence, as presented in *Chapter §1.3.2.5*, AEL has been identified as the most suitable technology for the electrified production of hydrogen.

In large plants, electrolysis stacks are commonly allocated inside containers or buildings, increasing risks due to hydrogen accumulation and confined explosions. In addition, because of the demand of the plant considered in this elaborate, many stacks will be required, increasing risks of domino effects in case of failure. Not less significant is the potential harm to operators in case of accidents while working in nearby active modules [102].

3.2.2.2 Air Separation Unit

Cryogenic air distillation is operated at low pressures and cryogenic temperatures. It is used to obtain the nitrogen required for producing ammonia. Similarly to electrolysis, a pre-treatment is necessary. In fact, air must be separated from water and carbon dioxide because of their freezing point at column operative temperatures. Also, hydrocarbons must be separated from the air to avoid accumulation in oxygen-pure streams. Historical analysis has shown this to be a recurrent cause of major accidents [17].

Safety concerns associated to oxygen and nitrogen have already been presented in *Chapter §3.2.1*, and in addition to those, safety concerns associated to ASU operative conditions must be considered: because of the temperatures involved, to avoid material failures, a proper material selection is necessary.

3.2.2.3 Ammonia Synthesis Loop & Storage

The Haber-Bosch process has been considered to convert nitrogen and hydrogen into ammonia via a catalyzed process conducted at high temperatures and pressure (400-500 °C and both 200 bar and 300 bar). Safety concerns about the synthesis loop are mainly associated with fires, the most alarming scenario [103] caused by the loss of containment of the hydrogen/ammonia mixture, that in this process is handled at high pressure and temperature, operative conditions that enhance dramatically the safety risks of the process. The reactor unit, therefore, can be addressed as the most alarming unit because of the large hold-up of hazardous chemicals in extreme conditions. Even if at low temperatures, the separation section of the ammonia synthesis loop is characterized by similar hazards: hold-ups associated with the separation tanks and the hydrogen/ammonia mixture handled at high pressure. In addition, it must be remembered that a refrigeration step is required to separate and purify ammonia, introducing safety concerns associated with the handling of two-phase streams involving refrigerated and pressurized liquids. The most common accident involving ammonia plants is the release of the product from the synthesis loop or the storage section of the plant [38,103]: storages contain high quantities of hazardous materials, therefore are characterized by a relevant inherent risk. Storage units have been addressed in this elaborate being critical units, with a dedicated assessment of the potential hazards in case of mechanical failure.

3.3 Hazards and Risk Assessment

3.3.1 Assessment Adopted Procedure

This work considered, for the assessment of plant safety performance, the combination of different safety techniques: compatibility matrices, hazard identification and operability analysis. In *Figure 3.8* it has been reported a flow-chart representing the decision-making process considered for the development of the inherently safer design developed.

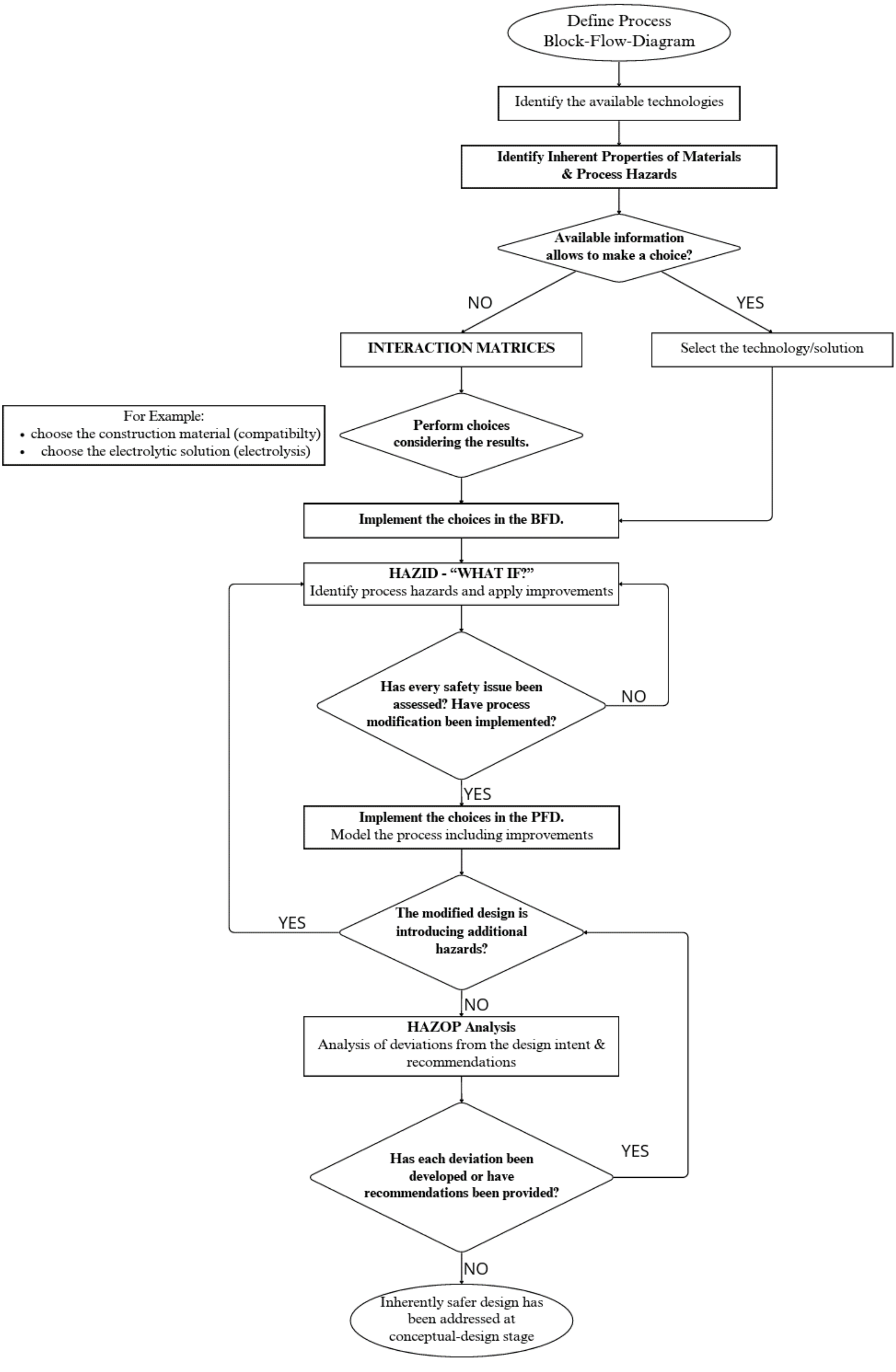


Figure 3.8 *Flow-chart representing the decision-making process for the development of the proposed design.*

3.3.2 Interaction Matrix

The first step adopted is based on the interaction matrix. This allows analyzing the chemical interaction while focusing on potential causes and consequences of undesired incompatibility issues [104]. The interaction matrices have been developed based on the MSDS (Materials Safety Data Sheet) of the chemicals involved and using the CRW® 4.0.3 (Chemical Reactivity Worksheet) software developed by CCPS (Center for Chemical Process Safety) and AIChE (American Institute of Chemical Engineers) [105]. Moreover, the CAMEO-Chemicals compatibility charts have been used [106].

An example of an empty interaction matrix is reported below in *Table 3.5*.

Table 3.5 *Structure of an Interaction Matrix for investigating compatibility issues among chemicals.*

Information	Reference Number	Health	Flammability	Reactivity	Special		*Chemical A*	*Chemical B*	*Chemical C*
-	1	-	-	-		*Chemical A*			
	2	-	-	-		*Chemical B*	N		
	3	-	-	-		*Chemical C*	C	Y	

The advantage offered by this technique is the immediate understanding of possible incompatibilities among different chemicals involved in the process. However, additional information must be provided separately to framework the reasons for compatibility issues. This tool allows for analyzing the interaction of a couple of chemicals and does not always consider process conditions in the evaluation.

3.3.3 HAZID - "What if?" Analysis

HAZID (hazard identification) techniques can be performed at any stage of process design and allow the retrieval of information about safety risks, allowing them to be fixed at early stages of process development. HAZID are, in conclusion, design-enabling tools that fit the ISD workflow well. Different techniques are grouped under the HAZID category. In the present work, the "*What if?*" analysis has been used. It is a safety tool that consists of brainstorming that tackles potential process deviations or failures and their consequences, aiming to suggest suitable actions to counter them. Being a brain-storming technique, the main drawback is the time dedicated to it; an additional disadvantage is the ease of "overwriting", an aspect that makes the identified issues less reliable, especially when the working team is not expert enough to deal with all safety issues. *Table 3.6* is an example of table collecting results of the "*What if*?" analysis conducted.

Table 3.6 *Example of a "What if?" table*
to retrieve information about process safety risks..

What if	Consequences	Recommendation
Possible accident	Consequences of the accidents	List of recommendations

3.3.3 HAZOP Analysis

HAZOP (hazard operability) analysis is an identification technique that assesses possible process malfunctions and provides recommendations to avoid their occurrence or protect the plant from the consequences of the events. Contrary to HAZID, HAZOP analysis cannot be performed at every stage of process design, requiring, at least, a basic plant flowsheet: the layout is necessary since the method involves the identification of "nodes", i.e. process sections characterized by the "change in process stream path". Process deviations are accounted for on each node, and their outcomes are systematically discussed, addressing each process stream and event. For each node, deviations are found, and recommendations are provided and collected in tables like *Table 3.7*, which represents an example of HAZOP analysis. The HAZOP analysis, therefore, helps identify Top Events of interest based on the data and process diagram under analysis.

Table 3.7 *Example of an HAZOP analysis table*
for investigating process deviations from normal operations.

ID-NUMBER	GUIDE-WORD	ELEMENT	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	COMMENTS	ACTION REQUIRED
0.0	more, less, no	flow, temperature	more temperature, less flow, no pressure	List of causes	List of consequences	Prevention or protection elements	Comment	Suggested recommendations to avoid the deviation

3.4 Safety Analysis

3.4.1 Interaction Matrix

3.4.1.1 Electrolysis Unit

In this elaborate it has been considered an AEL unit for conversion of water into hydrogen and oxygen, operated at 20 bar and 70°C. Sodium and potassium hydroxides have been included in the matrix since one of them is necessary for the correct unit operation. Additional information regarding incompatibility between pairs have been reported in the appendix, *§A.2.1.1*.

Table 3.8 *Interaction matrix for the electrolysis unit (AEL) with NFPA safety indices reported in CRW4.*

Information	Reference Number	NFPA - Health	NFPA - Flammability	NFPA - Reactivity	NFPA - Special		*Demineralized Water*	*Hydrogen*	*Oxygen*	*Sodium Hydroxide*	*Potassium Hydroxide*	*Stainless-Steels*
Species	1	0	0	0		*Demineralized Water*						
	2	0	4	0		*Hydrogen*	Y					
	3	3	0	0	OX	*Oxygen*	N	N				
AEL	4	3	0	1		*Sodium Hydroxide*	C	Y	N			
	5	3	0	1		*Potassium Hydroxide*	C	Y	N	-		
S-S	7	-	-	-		*S-S AISI 304*	Y	Y	Y	Y	C	
	8	-	-	-		*S-S AISI 316*	Y	Y	Y	C	C	

Safety Notes

The construction material is stainless steel, which must be chosen carefully due to corrosion caused by caustic materials (NaOH and KOH) and hydrogen attack. Materials compatibility tables [107,108] show optimal compatibility with all the chemicals handled for AISI 304, except for KOH; similar results are obtained with AISI 316, which is characterized by worst performance with respect to sodium hydroxide (tables report 20% and 50% NaOH solutions; to be conservative the worsening scenario is considered, i.e. light-attack).

Safety issues are comparable for the two caustic solutions; therefore, the cheapest is considered further in the present work for the AEL operation [109,110].

In conclusion, according to data reported in the compatibility matrix and economic information about the chemicals involved, the selected construction material was stainless-steel AISI 304, and the electrolysis was operated with NaOH, resulting in the best configuration in terms of safety performance and economic indicators.

3.4.1.2 Air Separation Unit

ASU aims to separate air into its components, and in this elaborate, a cryogenic unit has been considered; it operates at 1.5-5 bar of pressure and cryogenic conditions (about -200°C). Due to extreme operative conditions, its material selection is critical. In the appendix, additional information about pairs compatibility have been collected, *§A.2.1.2*.

Table 3.9 *Interaction matrix for the cryogenic-ASU with NFPA safety indices reported in CRW4.*

Additional Information	Reference Number	NFPA - Health	NFPA - Flammability	NFPA - Reactivity	NFPA - Special		*Water*	*Nitrogen*	*Oxygen*	*Argon*	*Carbon Dioxide*	*Stainless-Steels*
Species	1	0	0	0		*Water*						
	2	3	0	0	SA	*Nitrogen*	Y					
	3	3	0	0	OX	*Oxygen*	N	Y				
	4	0	0	0	SA	*Argon*	Y	Y	Y			
	5	2	0	0	SA	*Carbon Dioxide*	Y	Y	Y	Y		
S-S	6	-	-	-		*S-S AISI 304*	Y	Y	C	Y	Y	
	8	-	-	-		*S-S AISI 316*	Y	Y	C	Y	Y	

Safety Notes

The compatibility matrix shows excellent compatibility with stainless steels for all the species [107,108], except for oxygen in cryogenic conditions, with "acceptable" compatibility.

In *Table 3.9*, both water and carbon dioxide are reported, representing two chemicals removed from the air in the pre-treatment. However, they can enter the column in case of failure. Argon has also been included being an impurity of the produced streams and safety information has been recovered from its material safety data sheet [111].

3.4.1.3 Ammonia Synthesis

Ammonia synthesis, performed with the Haber-Bosch process, is the central step considered in this elaborate; it is performed as described in *Chapter §1.4.2*, at 200-300 bar and 400-500°C. In the matrix reported in *Table 3.10*, in addition to the chemicals involved in the synthesis, construction materials and the catalyst (magnetite, whose information have been retrieved from its MSDS [112–114]), also argon and oxygen have been considered, being the only two relevant impurities present in the unit. The appendix collects additional information about binary compatibility, *§A.2.1.3*.

Table 3.10 *Interaction matrix for the ammonia synthesis unit with NFPA safety indices reported in CRW4.*

Additional Information	Reference Number	NFPA - Health	NFPA - Flammability	NFPA - Reactivity	NFPA - Special		*Hydrogen*	*Nitrogen*	*Ammonia*	*Argon*	*Oxygen*	*Magnetite*	*Stainless-Steels*
Species	1	0	4	0		*Hydrogen*							
	2	0	0	0	SA	*Nitrogen*	Y						
	3	3	1	0		*Ammonia*	Y	Y					
	4	0	0	0	SA	*Argon*	Y	Y	Y				
	5	3	0	0	OX	*Oxygen*	N	Y	N	Y			
Materials	6	1	0	0		*Magnetite*	Y	Y	C	Y	N		
	7	-	-	-		*S-S AISI 304*	Y	Y	Y	Y	Y	-	
	8	-	-	-		*S-S AISI 316*	Y	Y	Y	Y	Y	-	

Safety Notes

The incompatibility of oxygen and hydrogen is well-known, and similar considerations can be stated for ammonia-oxygen mixtures. The incompatibility of oxygen and magnetite is another well-known interaction, making oxygen a poison for the catalyst. *Table 3.10* shows a "caution" indication for ammonia-magnetite since ammonia may decompose via a magnetite-catalyzed reaction, according to the analyzed safety database (CAMEO Chemicals).

Anhydrous ammonia is a corrosive species (as mentioned in *Chapter §3.2.1.4*) for some metals, and the correct choice of construction materials is necessary to avoid safety issues due to material degradation. Moreover, the effect of hydrogen must be considered. It can be concluded that two main corrosion-related mechanisms are involved in this process [40], in particular:

Nitriding

Corrosion mechanism caused by a nitrogen-donor (ammonia) at temperatures higher than 400°C. Nitriding causes the superficial hardening of the steel; in the case of ammonia plants, this mechanism lasts for an extended period (plant life, around 20-25 years), causing severe in-depth embrittlement, and fatal failure can follow.

Hydrogen attack

> The embrittlement caused by hydrogen is similar to nitridation and, for a prolonged period (plant lifetime), may lead to catastrophic failure of the equipment.

Because of the corrosion concerns and according to material compatibility tables [107,108], [20] and [115], AISI 316 is the best choice because of the addition of CrNi(Mo), which increases the resistance to nitriding and hydrogen attack. Concerning ammonia storage tanks, a reduction in corrosivity can be achieved by adding small quantities of water (0.1-0.2%) [116].

3.4.2 Hazard Identification and Operability Analysis

HAZID - “What if?” Analysis

Once information about chemical compatibility has been collected and organized in matrices, the “*What if?*” analysis has been performed.

The complete analysis performed on the design developed is reported in the appendix, *§A.2.2*; an extract of it have been reported in *Table 3.11*.

HAZOP Analysis

Following the “*What if?*” analysis, the HAZOP technique has been applied to the developed design, identifying major deviations from the design intent.

HAZOP has been performed by dividing the obtained flowsheet into five nodes (i.e. process sections), specifically: electrolysis unit, nitrogen-hydrogen make-up mixing, compression train and the recycle stream, the reaction synthesis loop and the separation section.

Similarly to the “*What if?*” analysis, the resulting HAZOP has been reported in the appendix, *§A.2.3*; *Table 3.12* collects some examples of the deviations formulated during the analysis.

Table 3.11 *Table collecting examples of the "What if?" analysis performed on the developed layout.*

What if	Consequences	Recommendation
Reactor Unit		
reactor collapse	Same as above Mechanical rupture	- Check the material of construction degradation degree during maintenance (reactor and support elements / reactor internals), cover it with protective paintings - Maintain a suitable distance between process units to avoid chain effects
bed support breaks	Bed collapses inside the reactor, creating a chain-effect with potential catastrophic failure of the unit and release of the entrained materials (flammability and toxicological concerns)	- Adequate choice of construction material and sizing are necessary - To avoid a failure associated to improper operative conditions (material degradation) a suitable control of reactor temperature is necessary - During catalyst substitution a revision of material degradation is advised, eventually a substitution of support elements is suggested
reactor outlet is blocked	Reaction proceeds inside the unit reaching equilibrium conditions, with increasing beds temperature; due to poor fluid movement cooling provided by heat-exchangers is not enough. Temperature increase can overcome the auto-ignition temperature of hydrogen and also cause sintering of catalyst.	- By-pass that can deviate the flux avoiding the plugged section - Flow meter to control the flowrate along the pipe and block the fed stream to the reactor if the situation is prolonged in time to avoid repercussions on the compression train (outlet stream excessive temperature)
Separation Section		
flash vessel leaks (no catastrophic failure)	Release of the material contained at high pressure and low temperatures (-4°C or -10°C): made of flammable species, it may be ignited readily; the contained materials have toxicological concern; the released flashing stream may affect nearby workers	- Frequent maintenance operations for control of external vessel integrity - Implement sensors for detection of releases and loss of pressure - Alert workers and plant emergency operations should begin when the scenario occurs - A back-up vessel can be considered for emergency operations
accidents in flash vessels' nearby units occurs	Chain effects involving the flash may occur, e.g. units that inadvertently hit the vessel creating a leak of a cold stream that may affect safe operation of nearby process units (chain effect propagation)	- Emergency shut-down operations should begin when reactor integrity is questioned or at risk - If possible reactor feed should be stopped and the contained materials discharged

(continued on next page)

(Table 3.11, continued from previous page)

What if	**Consequences**	**Recommendation**
Compression Section		
compressor unit breaks	Unit is not capable of increasing stream pressure (reactor feed pressure decreases, with repercussions on reaction kinetic behavior)	- By-pass of the broken unit and back-up compressor is necessary, increased maintenance frequency is suggested
	Unit output flow is blocked (increase in output temperature of previous compressors due to blocked stream that may damage the unit integrity)	Same as above - Temperature control for each compressor to avoid integrity damages
Electrolysis Unit		
membrane degrades	O_2/H_2 permeate through the membrane and mix, creating an easily ignitable mixture	- Frequent maintenance and substitution of the membrane when degradation signs are present on its surface - Control of the quality of the outlet streams to detect early possible degradation and proceed with preventive maintenance operations
Process Issues		
a black out occurs	Process control is lost	- An emergency generator or accumulation system (in the worst case scenario a fuel cell that uses either the ammonia produced or part of the hydrogen stored) is necessary to satisfy the minimum plant demand to bring operations in a safer condition - Emergency shut-down operations are required - Valves that avoid backflows and that are closed when black-out occurs are necessary (especially between process sections, e.g. electrolysis, storage and compression sections)
incident involving pipelines occurs	Flammable and toxicological concerns regards the spills from process pipelines since are involved gaseous H_2, N_2 and NH_3 in different purities. If the incidents involves the product stream (liquid ammonia) the release will create a boiling pool and a flashed stream of toxic species.	- An adequate piping location must be chosen to minimize incidents due to chain-effects from other unit failure - Protective elements should be placed near pipelines at height where those may be hit by machinery (e.g. forklift) - Process sensors capable of detecting leakages (e.g. pressure losses or flow decrements) may be installed with emergency operations for isolate a section of the plant and if possible bypass the leak

Table 3.12 *Extract of the HAZOP analysis performed on the layout developed.*

ID-NUMBER	GUIDE-WORD	ELEMENT	DEVIATION	POSSIBLE CAUSES	CONSEQUENCES	SAFEGUARDS	COMMENTS	ACTION REQUIRED
Electrolyser – Node Zero *Design Intent: Production of H_2 and O_2 from water electrolysis* *Operative Conditions: P=20 bar, T=70°C*								
0.1	More	Flow	More Flow	- Faulty instrumentation and controls - Faulty valves (excessive opening) -Wrong operation of the electrolysers stacks	- Wrong reactants ratio, variation in rate of reaction and reactor residence times (may damage the catalyst) - Higher hydrogen content in the downstream mixture enhances safety risks in case of loss of containment	- Flow meters	- Redundancy of the control systems and valves - By-pass of most important valves in case of failure - Control and manage downstream compressors to operate the plant properly	- Control redundancy of flow-meters - Safety interlock to avoid reactor irreversible damages (current density) - Maintenance
Reactants Mixer – Node One *Design Intent: Mixing of Pure Hydrogen and Nitrogen streams* *Operative Conditions: P=20 bar, T_{max}=150°C*								
1.5	Reverse	Flow	Reverse Flow	- Faulty valves	- Backflow may affect the upstream sections (ASU, Electrolysis, Storages)	- NRVs	- Proper maintenance	- Install flow control systems and NRVs - Maintenance

(continued on next page)

(Table 3.12, continued from previous page)

Recycle Mixer – Node Two *Design Intent: Mixing of compressed reactants with recycled unreacted species from the separation section* *Operative Conditions: P=35 bar, T_{max}=45°C*								
2.6	More	Flow	More Flow	- Variation in separation efficiency - Reaction efficiency variation and cascade effect on separation	- Variation in reactor residence times and conversion per-pass - Compressor-train capacity varies	- Flow meters	- Adequate control system to manage and minimize deviations from steady-state - Control and manage compressors power	- Flow control systems redundancy - Maintenance
Reaction Section – Node Three *Design Intent: Catalytic conversion of hydrogen and nitrogen into ammonia* *Operative Conditions: P=200 or 300 bar, T_{range}=70-490°C*								
3.17	No	Cooling	No Cooling	- Blockage of pipelines of coolant - Coolant upstream damages/failure	As Deviation *3.16*	- Temperature and flow meters	None	- Emergency shut down of the plant procedures - Alarms for workers
Ammonia Purification – Node Four *Design Intent: Recovery of pure ammonia in liquid phase and recycle of unreacted reactants* *Operative Conditions: P_{range} =200 or 300-35 bar, $T_{average}$=-10 or -5°C*								
4.2	More	Temperature	More Temperature	- Lack of cooling-capacity in the separation section	- Separation is inefficient: ammonia purity is not on specification at the operative temperature (at constant pressure)	- Temperature and pressure meters	- A variation in temperature at constant pressure leads to a variation in flashing efficiency - Chain effect on temperature of the recycle must be considered (see Deviation *2.1*)	- Control redundancy - Maintenance

3.4.2.1 Top Events & Safety Considerations

Reactive Mixture Production

Electrolysis, as already mentioned, is characterized by top events associated with handling the chemicals involved in the process unit, i.e. oxygen and hydrogen. The pre-purification step of water (i.e. demineralization) has not been considered in the safety analysis due to negligible safety-related events.

As highlighted in the safety analysis performed and mentioned in the description of general process hazards, cross permeation is identified as one of the most impactful events because of the potential risk associated with forming an easily ignitable mixture of hydrogen/oxygen in a confined environment and under pressure. This may be due to either malfunction of the unit and material degradation of the membrane or wrong unit operations that may cause cross-permeation. In particular, AEL requires a minimum load during normal operations and a complete purge of the entrained gases after prolonged shut-down [24].

From a wider perspective, loss of containment from the electrolysis unit that involves the release of hydrogen will end, if ignited, in fires or explosions, depending on the surrounding conditions. Electrolysers are commonly placed in containers or buildings (*Chapter §3.2.2.1*); therefore, in case of loss of containment and delayed ignition, hydrogen may accumulate in the closed environment, leading to explosions. To avoid such a scenario, proper ventilation must be adopted to reduce the accumulation of hydrogen. An alternative approach could be the separation of electrolysis stacks into different buildings or containers with adequate spacing, avoiding/limiting domino effects.

Additional safety concern involves the electrolytic solution required by the unit to operate; NaOH has been considered so far, but KOH is also involved in this consideration for completeness. In the case of leakage, damages to nearby equipment and related construction materials may occur due to the corrosivity of the species involved. Therefore, maintenance and the correct construction materials are advised to avoid consequences.

The ASU is characterized by cryogenic operations involving oxygen and nitrogen. In the case of accidental releases of these two species, a relevant effect is associated with the cold leakage on nearby units, which may cause domino effects [17,117,118] because of both low-temperatures that brings to malfunctions or construction materials failure to abnormal operations, or the result of the oxygen capacity of enhancing flammability of other chemicals.

In particular, this last event occurred in 2019 in China's Henan Province during a major accident involving an oxygen cryogenic release as an intermediate event [117,118].

The effect on nearby workers regarding exposure to cold leakage and toxicological concerns must not be neglected: nitrogen is asphyxiant and may accumulate, provoking suffocation.

An additional scenario addressed is air pre-purification, whose performances have been enhanced to avoid the accumulation of hydrocarbons in the oxygen-rich stream [17].

Ammonia Synthesis Loop

Results of the safety assessment on the synthesis loop highlight that the loss of containment in this process section may result in different outcomes depending on the conditions because both flammability and toxicological concerns are involved. If any ignition source sets on fire the released cloud, the result of the leakage is the dispersion of both asphyxiant and toxic compounds that constitute a severe risk for workers' health; otherwise, depending on process surroundings and ignition source, different outcomes associated with the flammable and explosive properties of hydrogen and ammonia will result, scenarios that represent the most critical hazards in ammonia plants [103]. Important consideration involves, in the same terms, the separation section of the plant, where two phases are present, particularly ammonia in the liquid phase as both refrigerated and compressed liquid.

The most critical unit in the Haber-Bosch process is the reactor, which is operated at both high temperature and pressure and involves a considerable hold-up of hazardous chemicals. This unit, which represents the core of the plant, has been assessed during the "*What if?*" analysis, including accidental scenarios such as the mechanical failure of reactor internals, scenarios with catastrophic consequences on unit integrity, and potentially resulting in an immediate release of the reactor content. To avoid this scenario, the correct choice of construction materials, sizing, and effective maintenance can significantly reduce risk.

An additional scenario involving reactor internal failure is the blockage of the reactor output, e.g., due to the accumulation of catalysts, which may result in an insufficient cooling capacity and loss of control of the reaction. This scenario may determine alarming temperatures above the threshold fixed for hydrogen concerning auto-ignition temperature (510°C) and catalyst integrity, which may bring severe consequences if oxygen is present due to upstream malfunctions. A similar consideration can be considered in the scenario involving insufficient cooling or no cooling of the reactor unit.

Regarding the separation section of the plant, particular attention must also be given to the separation vessels used because of their hold-up, which involves hazardous chemicals handled at significant flow rates at low temperatures. Leakages from the separation vessels have been assessed. Still, their catastrophic failure may also be investigated. The expected scenario involves the formation of boiling pools (because of liquid ammonia) and releasing a toxic and flammable mixture.

Also, some general concerns about the overall process operability have been considered, such as the case of blackouts, which lead to emergency generators' need to compensate for the missing energy. Accidents involving forklifts have been considered concerning pipelines damaged by human error or misoperations. Still, similar accidents may also involve major process units (e.g., reactor) during maintenance (e.g., plant equipment maintenance while the process is under operation), causing severe consequences on both plant safety operations and workers' health.

3.5 Storage Safety

3.5.1 Storage Safety Generalities

Information about storage types for the handled species are reported in *Chapter §2.3.3.1*, while the safety framework is discussed in the present section.

Ammonia

Ammonia is lighter than air, but when a loss of containment occurs, a heavier-than-air toxic white cloud (ammonia-humidity mixing) that follows the ground is generated due to the partially vaporized (flashing) release. As the dispersion proceeds and the cloud’s temperature increases, it will spread upwards due to its buoyancy [43,96,97,116].

Nitrogen

If stored under pressure, a loss of containment may cause burns or frostbites during expansion, while cryogenic burns may be caused by a leak from cryogenic storage [89,90]. Nitrogen leakages are difficult to detect, being colorless and odorless; for this reason, localized accumulation and increased concentration may occur near the release point, with a consequent displacement of air and risk of suffocation.

Oxygen

Oxygen is both odorless and colorless. Therefore, a loss of containment may be challenging to locate. Safety scenarios associated with oxygen releases differ depending on the type of storage: leakages from pressurized storage may cause burns or frostbites. In contrast, a cryogenic storage release may cause cryogenic burns and worker injuries [91,92].

To avoid severe consequences in case of oxygen leakages, asphalt must not be used in the proximity of storage areas; a flammable solid due to oxygen enrichment will be obtained in this scenario [119].

Hydrogen

Liquid hydrogen storages are provided by a vacuum jacket, which increases safety, reliability, and protection from severe malfunctions caused by low temperatures and may lead to damage to the nearby equipment in case of leakages [21,71,72].

Hydrogen can diffuse through materials faster than other gases, increasing the risk of loss of containment [73]. Interactions between hydrogen and the construction material of tanks may lead to severe consequences and loss of containment because of embrittlement: stainless steel or aluminum are the materials of choice for constructing hydrogen storages [71,73,120].

3.5.2 Storage Tank Burst Evaluation

The storage units considered in this assessment involve all the chemicals involved in this process: ammonia and oxygen (i.e. process products), nitrogen and hydrogen (process intermediates). In particular, the cryogenic storage of all these chemicals has been assessed considering the catastrophic mechanical failure of the vessel. In addition to the cryogenic storage, the pressurized case (at 350 bar and 700 bar) has also been assessed for hydrogen.

For oxygen and ammonia, a comparable storage size has been considered. In this regard, the same residence time for both the chemicals has been selected and corresponding to the higher residence times among the two process configurations investigated (200 and 300 bar), corresponding to 46 days (derived from the ammonia storage size and the productivity of the two proposals). Concerning hydrogen and nitrogen cryogenic storage, size has been derived assuming the maximum residence time suggested for intermediate species in [63] and considering the higher productivity obtained between the configurations developed. For hydrogen pressurized storage, instead, the maximum tank size allowed by regulations (6’000 Nm^3) has been considered [70].

Storage safety has been investigated considering the catastrophic explosion of the vessel: its mechanical failure, that occurs after generation and propagation of a crack on tank walls. At the same time, this dissertation has not accounted for the thermal effect associated with species flammability.

Results of the mechanical failure of the vessel are the generation of vessel fragments (projectiles) and a pressure wave, whose energy depends on the conversion efficiency of the blast, an aspect regulated by the type of vessel breakage: for a ductile failure, 40-50% of energy is converted into shock-wave, while 80% in a fragile failure [121]. In this assessment, the ductile breakage of the vessel has been considered.

The comparison has been performed based on the energetic content of a potential bursting event leading to the release of the energy stored in the associated tank. A TNT equivalency approach was then used to compare the different events, with a conversion factor to convert the blast energy into the equivalent mass of trinitrotoluene (W_{TNT}) considered equal to 4'680 J/g_{TNT}. *Equation 3.1* reports the conversion of blast energy into W_{TNT} considering the vessel breakage.

$$W_{TNT} = \frac{W_{blast} \times 0.5}{4'680} \tag{3.1}$$

For all the considered scenarios, results of the assessment, together with a resume of normal, burst and final conditions have been collected in *Table 3.13*.

Hydrogen Compressed Storage

Considering compressed hydrogen storage, the energy derived from the vessel's blast is evaluated according to *Equation 3.2*. Storage conditions considered are the pressurized storage at 350 bar and 700 bar, both at 0°C and 25°C: a comparison between two different storage conditions has been performed.

Initial and final states (of *Equation 3.2*) are considered as the blast condition and a moment after the explosion when the gas volume has expanded [122]. Burst conditions consider a burst pressure (storage maximum allowable working pressure, MAWP) fixed according to industrial common practice at 5 times the normal working pressure (NWP) of 350 and 700 bar [80,121,123]. Final and burst temperatures have been computed assuming an isentropic process (expansion or compression) according to *Equation 3.3*. Accordingly to *Equations 3.1-3.3*, the equivalent mass of trinitrotoluene (W_{TNT}) has been computed.

$$W_{blast} = M \times \left[\hat{U}_f\left(P_{amb}, T_f\right) - \hat{U}_i\left(P_{burst}, T_i\right)\right] \tag{3.2}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \tag{3.3}$$

M is the initial fluid mass in kg; thermodynamic information has been retrieved from [81].

Cryogenic Storage

Cryogenic storages mechanical failure has been based on the BLEVE mechanism, defined as: a Boiling Liquid Expanding Vapor Explosion (BLEVE) is "an explosion resulting from the failure of a vessel containing a liquid at a temperature significantly above its boiling point at normal atmospheric pressure" [121], i.e. after the vessel breakage conditions.

Two different scenarios can be discerned depending on the blast conditions: if the burst temperature of the fluid exceeds the "superheat limit temperature" ($T_{SL} = 0.895 \cdot T_C$), a "hot-BLEVE" is recalled, otherwise the event is named "cold-BLEVE" [121]. T_{SL} is the fluid super-saturation temperature at atmospheric pressure (immediately after the burst), that cause fluid instantaneous vaporization (instantaneous depressurization) due to homogeneous nucleation. In cold BLEVEs, this mechanism will not take place, and a mild scenario is expected.

The energy release by the blast has been computed accordingly to *Equation 3.4*, an internal energy balance analog to *Equation 3.2*. Initial and final conditions are fixed with respect to pressures at the burst and ambient conditions: temperatures are considered as the saturation temperatures at the two mentioned pressures [122]. The base-case NWP has been fixed at 1 bar for all cryogenic storages. Still, higher pressures have also been compared, i.e. 5 bar in the case of ammonia (not common practice), 17 bar for nitrogen and oxygen and 13 bar for hydrogen (equivalent to its critical pressure).

Equation 3.5 allows to retrieve w_f (final liquid vaporized fraction), unknown of *Equation 3.4*. In all scenarios with 1 bar as storage pressure (and ammonia at 5 bar), saturated conditions are met at burst ($w_i = 0$). At higher pressures, because of the pressure increase above the critical point, super-critical fluid conditions are retrieved ($w_i = 1$), and burst temperature has been computed with *Equation 3.3* (assuming ideal gas conditions). Under this scenario, the final temperature has been calculated by the same approach and compared with boiling temperature at ambient conditions, being $T_f < T_{boil}$ in all cases, the isentropic balance of *Equation 3.5* has been applied to compute w_f.

$$W_{blast} = M \times \left\{ \left[w_f \widehat{U}_f^V \left(P_{amb}, T_f \right) + (1 - w_f) \widehat{U}_f^L \left(P_{amb}, T_f \right) \right] - \left[w_i \widehat{U}_i^V (P_{burst}, T_i) + (1 - w_i) \widehat{U}_i^L (P_{burst}, T_i) \right] \right\} \tag{3.4}$$

$$w_i \hat{S}_i^V (P_{burst}, T_i) + (1 - w_i) \hat{S}_i^L (P_{burst}, T_i) = w_f \hat{S}_f^V \left(P_{amb}, T_f \right) + (1 - w_f) \hat{S}_f^L \left(P_{amb}, T_f \right) \tag{3.5}$$

M is the initial fluid mass in kg; thermodynamic information has been retrieved from [81].

Table 3.13 *Resume of information about the assessment of the blast performed work.*

Chemical	*Storage Conditions*			*Blast Conditions*		*Final Conditions*			$\Delta\widetilde{U}$	*Work Performed*	W_{TNT}
	T [°C]	P [bar]	*Size*	T_{burst} [°C]	P_{burst} [bar]	T_f [°C]	P_{atm} [bar]	w_f	[kJ/mol]	[GJ]	[kg]
NH_3	-33	1	4'550 ton	3.85	5	-33.68	1	0.115	-0.432	115.30	12'317
		5		58.06	25			0.265	-1.654	441.80	47'199
N_2	-196	1	606 ton	-179.18	5	-195.93	1	0.158	0.440	9.53	1'018
		17		-108.3	85			0.328	-0.896	19.40	2'070
O_2	-183	1	8'093 ton	-164.47	5	-183.10	1	0.137	-0.194	49.12	5'248
		17		-93.13	85			0.482	-1.853	468.64	50'068
H_2	-253	1	1'850 m^3	-246.03	5	-252.94	1	0.158	-0.047	3.05	327
		13		-220.27	64			0.389	-0.340	22.08	2'359
	25	350	6'000 Nm^3	201.55	1750	-218.41	1	0	-7.960	1.95	209
	25	700		201.55	3500	-228.36		0	-8.374	2.05	219
	0	350		161.71	1750	-223.00		0	-7.143	1.75	187
	0	700		161.71	3500	-232.11		0	-7.538	1.85	198

3.5.3 Storage Safety Assessment

According to the results reported in *Table 3.13*, significant outcomes are associated with catastrophic failures of ammonia and oxygen storages for the scales of interest (i.e., the two storages effectively implemented). Nitrogen shows the highest variation in internal energy due to the burst, but the smaller quantity decreases the final outcome noticeably.

Following the ISD minimization principle, avoiding the storage of hydrogen and ammonia positively affects the overall plant safety performance, given that a severe TNT equivalency characterizes them. It must be noted that this crucial consideration applies to the proposed layouts, thanks to an assumption, i.e. the grid can satisfy continuous plant energy demand. If dynamic ammonia productivity were considered, the plant would probably need the integration of storages for intermediate species to decouple the three processes (ASU, electrolysis and Haber-Bosch) and better integrate their different dynamic behaviors.

ISD principle of moderation effects is also shown in the obtained result: a relevant variation in the energy released by the blast is met whenever the NWP increases, highlighting that reducing operative pressure improves process safety performance.

Hydrogen storage allows additional observations about process storage safety: cryogenic hydrogen storage allows for better safety performances because of the smaller internal energy variation associated with the vessel burst. Limiting the size of hydrogen storage under pressure, which has higher damaging potential than the cryogenic case, allows a comparable effect in terms of pressure wave between cryogenic and pressurized scenarios (excluding the cryogenic storage at 13 bar). It must be noted that, on the other hand, the variation in storage capacity is significant: a numeric comparison highlights that to store the same amount of hydrogen (7 days), 264 pressurized tanks are necessary, while one medium-size cryogenic storage tank (1’850 m^3 compared to 5’000 m^3 of maximum size) is demanded for the application considered.

Concluding, it can be stated by observing the results obtained, that accordingly to inherently-safer-design practices and the results obtained in the performed assessment, storages performed under moderate conditions (lower pressure) and in cryogenic conditions (with reference to the hydrogen-case assessment), represents the inherently safer storage conditions.

Chapter 4

Process Economic Analysis

This chapter illustrates the economic analysis performed on the developed flowsheet for electrified ammonia production.

Evaluation of process costs is an essential step to carry out as early as possible during process design development, minimize costs via design adjustments, and assess the developed proposal's economic feasibility. The method applied to estimate equipment costs and the results obtained are described first in this paragraph; afterwards, the profitability analysis performed is presented, together with estimations of each cost contribution. Finally, the economic effect arising from the cold-nitrogen stream integration is briefly presented.

4.1 Cost Evaluation Practice

A “study-estimate” approach is commonly applied to estimate equipment costs during conceptual design. The method only requires information (sizes) for the most expensive pieces that contribute most to total process capital costs. The accuracy of the “study estimate” applied is approximately 20-30%, a sufficient degree of approximation for the conceptual design stage of development. More accurate and detailed cost estimations will be performed as the design process proceeds.

At intermediate design stages, the assessment of the plant's “Potential Profitability” (also called “Economic Potential”, EP) is commonly performed. This metric is used to give the engineer an indication about plant economics while the proposal is developed, allowing the operator to apply corrective measures from the beginning. In this elaborate, this approach has been applied to describe the composition of process CAPEX and OPEX, and it is outlined in the appendix, *§A.1.3.1.*

4.1.1 Equipment Cost Estimation

The method considered in this work to estimate equipment costs has been widely described in Turton et al. [124] and it is based on a method developed by Guthrie in the 70s; the disadvantage of the technique reported in Turton et al. is that it is based on not up to date estimations that have been “eventually updated using cost indices or data points” [125].

The method considered is based on estimating equipment costs, knowing their sizes, and applying corrective factors to adequacy the base cost of the purchase to the operative conditions and the material considered. The base-conditions purchased costs of the equipment, estimated with *Equation 4.1*, assume the unit is made of carbon steel and operated at atmospheric conditions; factors required are reported in *Table 4.1* and "*A*" is the equipment capacity size.

$$\log C_p^0 = K_1 + K_2 \log A + K_3 (\log A)^2 \tag{4.1}$$

Table 4.1 *Factors for estimating the base-purchase cost of equipment* [124].

Equipment	Parameters			Capacity		
	K_1	K_2	K_3	Capacity	Min. Size	Max. Size
Compressor, Centrifugal	2.2897	1.3604	-0.1027	Fluid Power, kW	450	3000
Drives, Electric, Exp-Proof	2.4604	1.4191	-0.1798	Shaft Power, kW	75	2600
Heat-Exch, Floating Head	4.8306	−0.8509	0.3187	Area, m^2	10	1000
Process Vessel, Vertical	3.4974	0.4485	0.1074	Volume, m^3	0.3	520

Once the base purchased cost of equipment has been estimated, it is corrected accordingly to *Equation 4.2*, which includes factors that assess the effect of the construction material (F_M) and the operative conditions (pressure, F_P): in this way, the bare module cost (C_{BM}) is retrieved.

F_P is estimated according to *Equation 4.3* and *Equation 4.4*, where the last one is applied to process vessels (e.g. flash units) and the first to the other equipment elements; *Table 4.2.* collects the parameters needed for the estimations of the pressure contribution.

F_M has been fixed accordingly to the corrective value proposed by Towler and Sinnott [125], being not available in Turton an estimation for stainless-steels (AISI 304 and 316); a material factor equal to 1.3 has been considered in this elaborate [126]. For some process equipment, the material factor has been reported in Turton in graphical form and collected in *Table 4.2*.

$$C_{BM} = C_p^0 \cdot F_{BM} = C_p^0 (B_1 + B_2 F_M F_P) \tag{4.2}$$

$$\log F_P = C_1 + C_2 \log P + C_3 (\log P)^2 \tag{4.3}$$

$$F_{P,vessel} = \frac{\frac{PD}{2SE - 1.2P} + CA}{t_{min}} = \frac{\frac{PD}{2[850 - 0.6P]} + 0.00315}{0.0063} > 0.0063m \tag{4.4}$$

In *Equation 4.3*, “*P*” is the operative pressure of the unit expressed in bar gauge (barg). In *Equation 4.4*: “*D*” is the diameter of the tank, “*P*” is its pressure (in barg), “*S*” and “*E*” are two parameters of carbon-steel, t_{min} is the minimum allowable vessel thickness and “*CA*” is the corrosion allowance; the second term already considers the parameters for carbon-steel. If $F_{P,vessel}$ results in being smaller than one, it is taken as 1; more conditions are stated in [124].

***Table 4.2** Corrective factors and parameters for calculating the base purchase cost of equipment* [124].

Equipment	Parameters				Pressure Factor Coefficients			
	F_{BM}	F_M	B_1	B_2	C_1	C_2	C_3	Range (barg)
Compressor, Centrifugal - SS	2.75	-	-	-	-	-	-	-
Drives, Electric, Exp-Proof	1.5	-	-	-	-	-	-	-
Heat-Exch., Floating Head - SS	-	1.3	1.63	1.66	0.03881	-0.11272	0.08183	$5<P<140$
Process Vessel, Vertical	-	3.10	2.25	1.82	-	-	-	-

After the estimation and correction of the bare-module cost, C_{BM} (capital cost to purchase the unit) is obtained and must be updated to account for inflation, parameters referred to a specific time-instant. The inflation adjustment is performed according to *Equation 4.5*, where I_1 and I_2 represent two cost indices that refer to the year when the cost is known (I_2, 2001 [124]) and the year when the cost is to be estimated (I_2, 2023 in the case of the work). According to Chemical Engineering Plant Cost Index (CEPCI), the values for 2001 and 2023 are, respectively, I_1=397 and I_2=808.8 [127].

$$C_{BM,2023} = C_{BM,2001} \cdot \frac{I_2}{I_1} \; also \; as: C_{BM} = C_{BM}^0 \cdot \frac{I_2}{I_1} = C_p^0 \cdot F_{BM} \cdot \frac{I_2}{I_1} \tag{4.5}$$

A resume of each process equipment bare-module cost and inflation-adjusted purchase costs have been collected in *Table 4.3*.

It must be noted that, as reported in *Table 4.1*, the correlations proposed in Turton et al. have ranges of validity that, in some cases, could not be respected, as in the case of floating-head heat-exchangers, whose capacity is limited to a range of pressures between 5-140 barg. The correlations described have been retained since no alternative estimation equations are available. According to the data collected about unit sizing in *Chapter §2*, a similar conclusion can be stated for a few heat exchangers.

Table 4.3 *Resume of equipment bare-module cost and inflation-adjusted cost of purchase; reference is Fig. 2.23.*

Equipment	P=200 bar		P=300 bar		
	C_{BM} [€]	C_{BM}^{0} [€]	C_{BM} [€]	C_{BM}^{0} [€]	
			Multi-Compression Train		
MP-CMP1	359212	176319	343745	168727	1st Compressor Unit
MP-CMP2	386381	189656	369902	181567	2nd Compressor Unit
MP-CMP3	1016214	498809	1100977	540415	3rd Compressor Unit
MP-CMP4	1074013	527180	1100988	540421	4th Compressor Unit
MP-CMP5	964452	473402	1079660	529952	5th Compressor Unit
MP-CMP6	1003673	492653	557943	558943	6th Compressor Unit
HX-1	185997	91297	189774	93151	1st Heat-Exchanger Unit
HX-2	155229	76194	156734	76933	2nd Heat-Exchanger Unit
HX-3	152888	75045	154355	75765	3rd Heat-Exchanger Unit
HX-4	162662	79843	166344	81650	4th Heat-Exchanger Unit
HX-5	174738	85770	183257	89952	5th Heat-Exchanger Unit
			Reactor Section		
REACTOR$_{vessel}$	7412273	3638319	4710409	2312107	Reactor Vessel
COOL-HX1	206614	101416	226474	111165	1st Inter-Bed Cooler
COOL-HX2	210826	103484	227045	111445	2nd Inter-Bed Cooler
HD-HINT	460523	226048	536253	263220	Reactor Head Heat-Integrator
			Separation & Recycle Section		
RECY-CMP	491454	241231	352882	173213	Recycle Compressor Unit
CW-HX1	321091	157608	174708	31663	Refrigeration Train 1st Cooler
CW-HX2	199012	97685	109969	20016	Recycle Pre-Heater
PRE-COOL	236896	116263	112003	20328	Refrigeration Train 2nd Cooler
REF-HINT	199380	97866	103915	18860	Refrigeration Train – Heat Integrator
REFRIG	246775	121130	230526	113154	Refrigeration Train – Refrigeration
PROD-FLASH	5621488	2759311	6439578	3160871	Product Phase Separator Tank
SEP-T	97101	47662	103202	50657	Product Lamination Tank
NITRO-INT	190369	93443	206597	101408	Nitrogen Heat-Integrator

4.1.2 Scenarios Considered

As mentioned in *Chapter §1.5*, the assessment of the economic performance of the proposal is done by comparing scenarios with different electricity prices [47–51] based on recent data (EuComm - LQ22, Eurostat - FH23) and future projections of the Italian electrical-generation with low carbon emissions (Giuliani, Borasio). *Figure 4.1* collects electricity prices for each scenario considered, highlighting the four that have been considered further: *EuComm – LQ22*, the case with extremely high electricity prices; *Eurostat – FH23*, the most recent data available; *IRENA*, cheaper estimation available and *Giuliani-RES*, representing the average price of the scenarios described in [49].

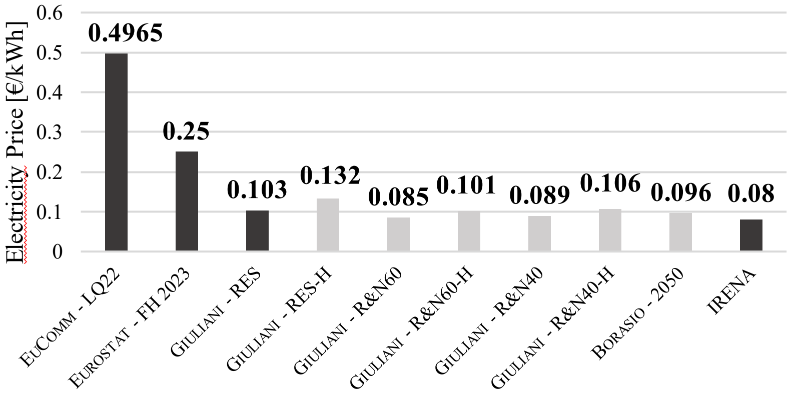


Figure 4.1 *Electricity prices in the scenario considered* [47–51].

4.2 Cost Contribution Assessment

The analysis of plant profitability was performed after collecting and estimating all the cost contributions of the process. Because of the early degree of development, some assumptions have been made to estimate unknown contributions. In the following paragraphs, the different cost contributions will be presented.

4.2.1 Total Capital Costs

The evaluation of the total capital (TCI) consists of the definition of three main contributions: Total fixed capital cost (FCI), Start-up capital (SC) and Working capital (WC). In fact, TCI considers, in addition to the cost to sustain the purchase of the equipment, the investment necessary to start up and operate the plant until an income is earned.

Fixed capital costs consider all the purchased that must be sustained to build the plant, both in terms of core (e.g. compressors, reactors) and auxiliary equipment (e.g. laboratories, utility sub-stations), that compose the total direct cost (TDC) and indirect costs that consist of feed and contingencies, that is estimated commonly as a function of TDC's contributions.

The two elements composing TDC are ISBL, inside-battery-limits, and OSBL, offsite-battery-limits, respectively. ISBL have been assumed equal to the sum of the time-updated purchase-cost of equipment (C_{BM}) estimated via Guthrie's method (*Chapter §4.1.1*). In the case of OSBL, instead, the contribution has been assumed proportional to the sum of the bare-module cost of equipment (C^0_{BM}) previously estimated. This approach follows the evaluation of the "grass-roots costs", i.e. the necessary cost to build the plant ex-novo, that considers OSBL equal to 50% of the total C^0_{BM}. The evaluation of ISBL and OSBL involves a location factor necessary to capture the differences in labor cost among different countries: the obtained estimation of ISBL and OSBL is then multiplied by this factor, which for Italy has been considered equal to 1.14. Indirect FCI's cost contributions (i.e. fees and contingencies) have been assumed respectively: 3% and 20% of C_{BM}. Working ad start-up capitals are assumed to be SC=10% TDC and WC=3% FCI. The sum of the three cost-contribution leads to the recovery of TCI. *Table 4.4* collects all the results obtained and the assumptions used to estimate the missing contributions. The resume of equipment costs has been previously reported in *Table 4.3*.

ASU capital costs have been provided by AirLiquide [54], both in terms of columns, auxiliaries and storages, whose cost has been assumed to cover the size of interest for the plant. Electrolysis capital cost contribution has been obtained according to data reported in *Chapter §1.3.2.5* Ammonia, cryogenic storage tank cost, has been evaluated as previously discussed in *Chapter §2.3.3.2*, where also its sizing has been discussed.

***Table 4.4** Plant Capital Cost, with explicit cost contributions.*

Cost Element	Additional Information	Cost Estimated [M€]	
		P=200 bar	P=300 bar.
	Capital Cost Estimation		
Air Separation Unit	ISBL (Column Ready-for-Start-Up)	30	30
	OSBL (Utilities+O_2 Storage)	22.50	22.50
Electrolysis	Installed Cost	49.25	46.79
Storage Unit	Ammonia	3.69	3.69
Plant ISBL	100% of C_{BM}	24.54	22.84
Plant OSBL	50% of C^0_{BM}	6.02	5.61
Total Direct Costs (TDC)		**136.00**	**131.42**
Fees	3% of C_{BM}	0.65	0.60
Contingencies	20% of C_{BM}	4.31	4.01
Fixed Capital Investment (FCI)	Fees + Contingencies + TDC	**140.95**	**136.03**
Working Capital (WC)	15% of TDC	**20.40**	**19.71**
Start-Up Capital (SC)	9% of FCI	**12.69**	**12.24**
Total Capital Cost (TCI)		**174.04**	**167.99**

4.2.2 Manufacturing Costs

As described in the previous chapter, capital costs involve only the cost of building and operating the plant for a restricted period. Still, at regime, different expenses must be sustained: the cost of raw materials, the utilities demanded, and labor, in addition to maintenance and administration of plant operations. These contributions are all summed to obtain the cost of manufacture (COM), which, according to Turton et al., can be expressed as:

$$COM = DMC + FMC + GE \tag{4.6}$$

In *Equation 4.6,* cost contributions to COM are DMC, direct manufacturing costs (also VCOP, variable cost of production), FMC, fixed manufacturing costs (or fixed cost of production, FCOP) and GE, general expenses. DMC includes all the variable costs of production: raw materials, utilities and labor; FMC includes taxes, maintenance and plant overhead; instead, GE considers administrative costs, marketing and research and development (R&I) contributions. In the following paragraphs, the breakdown of cost contribution is performed, and the results obtained have been collected for each element.

4.2.2.1 Direct Manufacturing Cost - Variable Cost of Production

In this section, the variable cost of production is assessed, considering each contribution independently: the cost of chemicals, utilities and the terms associated with labor, concluding with additional cost terms.

Process Stream Factor

Plant operative costs and revenues generated by selling the obtained products are assessed yearly, particularly considering the number of hours of plant operability (operative year). A metric represents the time the plant operates each year and is called an on-stream factor (or simply stream factor).

By its definition, it is possible to make explicit the relation to evaluate the stream factor as:

$$Stream\ Factor = \frac{Number\ of\ plant\ hours\ of\ operation\ per\ year}{365\frac{day}{year} \times 24\frac{hours}{day}} \tag{4.7}$$

In the present elaborate, the stream factor has been considered equal to 0.93, a common value for chemical plant operations. This stream factor corresponds to 8146.8 hours of operation per year.

Chemicals & Consumable Costs

The contribution to process operative costs associated with raw materials and consumables and the revenues generated by selling the produced main and by-products are collected and considered in this paragraph.

In the present section, as cost, it has been considered also the sodium hydroxide necessary for the correct operation of the electrolysis unit (electrolytic solution at 30%w.), a chemical with a relevant impact on the overall process costs.

In *Table 4.5*, all the information about productivity and demands of the configurations considered in this elaborate; the price of chemicals or purification steps have been collected. Market prices have been retrieved from literature and available online sources. It must be noted that market-price fluctuation occurs, which may change plant economics dramatically; for this reason, more in-depth observations and estimation of raw materials and product costs must be performed in later design stages.

***Table 4.5** Productivity and demands of the two plant configurations and market prices of chemicals.*

Feedstock/Product	P=200 bar	P=300 bar	UoM	Costs	Ref.
Purified Air	4’033.28	3’832.07	m^3/h	10€/ton	[15]
Demineralized Water	16’351	15’535	kg/h	1€/m^3	[25]
Sodium Hydroxide	4’905.5	4’660.6	kg/h	0.25€/kg	[109]
Hydrogen	778.65	739.78	kg/h	-	-
Nitrogen	3’605.08	3’425.22	kg/h	0.5€/kg	[37]
Oxygen	7’331.48	6’965.55	kg/h	0.177€/kg	[37]
Ammonia	4’358	4’167	kg/h	0.47€/kg	[128]

Table 4.6 collects the results obtained for the estimation of chemicals and consumables costs.

Table 4.6 *Economic assessment of chemicals and consumables costs and revenues.*

Cost Element	Additional Information	Cost Estimated [M€]	
		P=200 bar	P=300 bar.
Chemicals & Consumable Costs			
NH_3 Revenues (REV)	0.47 €/kg	16.79	15.95
O_2 Revenues (BP)	0.177 €/kg	10.57	10.04
Air Purification (RM#1)	10 €/ton	0.42	0.40
Water demineralization (RM#2)	1 €/m^3	0.13	0.13
Gross Margin (GM)	Revenues – Costs	**26.81**	**25.47**
Sodium Hydroxide (CONS)	0.25 €/kg	9.99	9.49

Process Utilities

Process utilities contribution to plant operative costs has been evaluated by retrieval of the consumptions computed in the *ASPEN® Plus*, applying the presented stream factor and prices reported in the appendix (*§A.1.2*), where the method for assessing the cost of refrigeration is also presented. The resume of the demand for each process utility is reported in *Table 4.7*.

Table 4.7 *Utilities demand in the two configurations proposed.*

Utility	P=200 bar	P=300 bar
Electricity [kW]	45'167	43'140
Tower-Water [kg/h]	198'494	196'154
Cooling-Water [kg/h]	283'811	300'293
Refrigerated-Water [kg/h]	98'015	80'261
Refrigerant [GJ/s]	0.00067	0.000468

Being this elaborate based on the electrified production of ammonia, as mentioned in *Chapters §1.5* and *§4.1.2*, the effect of electricity prices on plant economics has been assessed, and different scenarios effects on process economics have been considered. It must be noted that electricity prices affect refrigeration costs, which has been considered in this dissertation.

Electricity is mainly consumed in the plant's electrolysis unit and also by compressors and the cryogenic air separation unit. It constitutes the most expensive contribution to plant utilities, as shown in *Table 4.8*, which reports a resume of utilities costs. Cooling water is demanded for refrigeration in the initial multi-compression train and in the first units (*CW-HX1*, *CW-HX2*) after the rector. Tower water, instead, has been considered applied to the reactor unit for inter-bed refrigeration of the reactive mixture due to reduced costs compared to cooling water.

Refrigerated water has been considered in the refrigeration train of the reactor outlet stream to minimize the refrigeration duty that has been assumed to be sustained by an ammonia-driven single-stage refrigeration train.

Table 4.8 collects the results of estimating utilities impact on process costs in the different scenarios considered in this elaborate.

Table 4.8 *Economic assessment of utilities cost contribution in the different scenarios.*

Cost Element	Additional Information	Cost Estimated [M€]	
		P=200 bar	P=300 bar.
	Utilities Costs		
Tower-Water	$2.5 \cdot 10^{-5}$€/kg	0.04	0.04
Cooling-Water	$5 \cdot 10^{-5}$€/kg	0.12	0.12
Refrigerated Water	$3.13 \cdot 10^{-4}$€/kg	0.25	0.20
Refrigeration	*EC – LQ22* @ 63.72 €/GJ	1.25	0.88
	ES – FH23 @ 32.66 €/GJ	0.64	0.45
	G – RES @ 14.14 €/GJ	0.28	0.19
	IRENA @ 11.24 €/GJ	0.22	0.15
Electricity	*EC – LQ22* @ 0.4965 €/kWh	182.69	174.50
	ES – FH23 @ 0.25 €/kWh	91.99	87.86
	G – RES @ 0.103 €/kWh	37.90	36.20
	IRENA @ 0.080 €/kWh	29.44	28.12
Utilities Costs (UTS)	*EC – LQ22*	**184.35**	**175.74**
	ES – FH23	**93.04**	**88.68**
	G – RES	**38.58**	**36.76**
	IRENA	**30.06**	**28.64**

Cost of Labor

The labor cost estimation as an additional contribution to direct manufacturing costs has been performed following the method proposed by Turton et al.; as a function of the labor costs, overhead and supervision costs have been later derived.

To evaluate the cost of labor, Turton et al. suggest an approach based on the number of process units, considering that each requires a certain number of operators. *Equation 4.8* allows an estimate of the number of workers needed in the plant and requires the number of processing steps, distinguished between particulate (P) and non-particulate (N_{np}) steps that differentiate in solid-species handling. The number of positions obtained is multiplied by a factor of 5, the number of operators per shift-position (ratio between the total number of shifts per year and the number of shifts that an operator works a year), to retrieve the total number of workers needed.

$$N_{OL} = 5 \cdot (6.29 + 31.7 \cdot P^3 + 0.23 \cdot N_{np})^{0.5} \tag{4.8}$$

N_{OL} is the number of work positions per shift needed; P is the number of non-particulate steps N_{np} is the number of non-particulate steps and are both computed as the sum of particulate/non-particulate process operations ($P = 0$ in this work, while $N_{np} = 34$).

Once the total amount of workers needed has been obtained, the labor cost can be computed considering the yearly wage of workers, fixed at 45’000€/year per operator in this elaborate.

In *Table 4.9,* a resume of the information used to assess the cost of labor has been collected, while in *Table 4.10,* the resulting assessment of labor cost has been reported.

Table 4.9 *Data for estimating the cost of labor.*

Parameter	Value
Operator per Shift-Position	5
Process Step – Particulate (Solids)	0
Process Step – Non-Particulate (Non-Solids)	35
Operator Wage	45’000 €/year

As mentioned early, from the cost of labor can be derived the supervision and direct-overhead costs, that in this elaborate have been considered, respectively: 25% of the cost of operative labor and 33% of the total cost of labor (operative and supervision).

Table 4.10 *Economic assessment of labor cost contribution.*

Cost Element	Additional Information	Cost Estimated [M€]	
		P=200 bar	P=300 bar.
	Cost of Labor		
Operating Labor (Op.Lab)	45’000 €/operator-year	0.86	0.86
Supervision (SUP)	25% of Op.Labor	0.21	0.21
Direct Overhead	33% of Supervision + Op.Labor	0.35	0.35
Cost of Labor (LBR)		**1.42**	**1.42**

Additional Contribution & Variable Cost of Production Estimation

VCOPs have been estimated accordingly to *Equation 4.9*, where in addition to previously presented contributions (resumed in *Table 4.11*) it has been accounted also the contribution of fees and royalties associated to licenses and patents: being the process innovative, but based on commercially available technologies, patents have been assumed accounting for 0.5% REV.

$$VCOP = (RM_1 + RM_2 + CONS - BP + UTS + F\&R + LBR) \tag{4.9}$$

Table 4.11 *Contributions to Total Variable Costs of Production.*

Cost Element	Additional Information	Cost Estimated [M€]	
		P=200 bar	P=300 bar.
	Variable Costs of Production		
NH_3 Revenues (REV)	0.47 €/kg	16.79	15.95
O_2 Revenues (BP)	0.177 €/kg	10.57	10.04
Raw Materials (RM)	-	0.56	0.53
Sodium Hydroxide (CONS)	0.25 €/kg	9.99	9.49
Utilities Costs (UTS)	*EC – LQ22*	**184.35**	**175.74**
	ES – FH23	**93.04**	**88.68**
	G – RES	**38.58**	**36.76**
	IRENA	**30.06**	**28.64**
Fees & Royalties (F&R)	0.5% of REV	0.08	0.08
Cost of Labor (LBR)		**1.42**	**1.42**
Variable Cost of Production (VCOP) (RM+CONS-BP+UTS+F&R+LBR)	*VCOP-EC*	**195.82**	**186.71**
	VCOP-ES	**104.51**	**99.65**
	VCOP-G	**50.06**	**47.73**
	VCOP-I	**41.54**	**39.61**

4.2.2.2 Fixed Cost of Production

FCOP comprise different contributions, from maintenance to taxes and insurance and the rent of land and buildings. Similarly to the previously presented cost contributions, in this case, different assumptions have been made to estimate the involved costs.

Maintenance has been considered based on ISBL costs, equal to 3% of ISBL, while taxes and insurance have been considered 1% of ISBL; the plant overhead has been considered as 65% of the sum of the cost of labor and maintenance. The cost of rent of land and buildings has been considered to be 1% of TDC. Accordingly, to the presented assumptions, FCOP has been evaluated for the two configurations considered and reported in *Table 4.12*.

Table 4.12 *Contributions to Total Fixed Cost of Production.*

Cost Element	Additional Information	Cost Estimated [M€] P=200 bar	 P=300 bar.
	Fixed Operating Cost of Production		
Maintenance (MANT)	3% of ISBL	3.11	2.99
Plant Overhead	65% of LBR + MANT	2.95	2.87
Taxes & Insurance	1% of ISBL	1.04	1.00
Rent	1% of TDC	1.36	1.31
Fixed Cost of Production (FCOP)		**8.46**	**8.17**

4.2.2.3 General Expenses

GE represents the costs associated with company administration, marketing and R&I departments. Commonly assumed factors of 65% of labor plus supervision have been assumed for administrative costs, while 2.5% of DMC+FMC has been considered for marketing and sales. R&I, instead, has been assumed to account for 0.5% of revenues. It must be noted that in *Table 4.13*, where the results for the estimation of general expenses have been collected, different results have been obtained about the marketing department costs because VCOP has been estimated for different scenarios.

Table 4.13 *Contribution of General Expenses.*

Cost Element	Additional Information	Cost Estimated [M€] P=200 bar	 P=300 bar.
	General Expenses		
Research & Development	1% of REV	0.08	0.08
Sales & Marketing	3% of FCOP + VCOP-EC	5.11	4.87
	3% of FCOP + VCOP-ES	2.82	2.70
	3% of FCOP + VCOP-G	1.46	1.40
	3% of FCOP + VCOP-I	1.25	1.19
Administrative Costs	65% of LBR+SUP	0.69	0.69
General Expenses	*GE-EC*	**5.89**	**5.65**
	GE -ES	**3.60**	**3.47**
	GE -G	**2.24**	**2.17**
	GE -I	**2.03**	**1.97**

4.2.3 Estimation of the Total Cost of Production

The total cost of production (TCoP) has been computed for each scenario considered as the sum between the total cost of manufacturing (COM), obtained as the sum of the previously presented contributions (the resulting COM has been reported in *Table 4.15*) and the annual charge associated to the purchase of equipment and catalysts. The resulting cost is divided by the amount of product obtained to retrieve the value per unit of product sold, representing the minimum selling price to cover all expenses.

The annual charge, i.e., the cost to sustain until the nth year to cover the cost of the equipment, is computed by multiplying the cost of equipment by ACCR, and the annual capital charge ratio is computed accordingly to *Equation 4.10. n* represents the year of plant lifetime/depreciation (assumed 10 for the plant equipment and 14 as catalyst lifetime), and *i* is the interest rate.

$$\mathrm{ACCR} = \frac{i \cdot [1+i]^n}{(1+i)^6 - 1} \tag{4.10}$$

In the present elaborate, catalyst cost has been fixed at 23 €/kg and its expected lifetime is 14 years [37], slightly longer than [42].

Instead, the interest rate has been estimated considering the assumptions reported in *Chapter §4.3. Table 4.14* collects all assumptions used to estimate ACCR and the estimations obtained.

Table 4.14 *Annualized capital charge evaluation.*

Cost Element	Additional Information		Cost Estimated [M€] P=200 bar	 P=300 bar.
	Annualized Capital Charges			
Total Fixed Capital Investment	10 years & 11% Interest Rate	ACCR=0.170	23.93	23.10
Catalyst #1	14 years & 11% Interest Rate	ACCR=0.143	0.10	0.04
Catalyst #2	14 years & 11% Interest Rate	ACCR=0.143	0.10	0.04
Total Annual Capital Charge			**24.13**	**23.18**

Table 4.15 collects the total cost of production (equal to COM) for each scenario and the resulting total cost of ammonia production.

Table 4.15 *Cost of production and Total cost of production estimations.*

Parameter	Scenario	Costs [M€/year]		Cost [€/kgNH$_3$]	
		P=200 bar	P=300 bar	P=200 bar	P=300 bar
Cost of Production	*EC-LQ22*	210.17	200.52	5.89	5.90
	ES – FH23	116.57	111.29	3.27	3.26
	G-RES	60.76	58.07	1.70	1.70
	IRENA	52.03	49.74	1.46	1.45
Total Cost of Production	*EC-LQ22*	234.30	223.71	6.56	6.58
	ES – FH23	140.71	134.47	3.94	3.95
	G-RES	84.89	81.26	2.38	2.38
	IRENA	76.15	72.93	2.13	2.13

4.3 Profitability Analysis

The profitability analysis was the last step performed to assess the design economic feasibility. It took advantage of the economic results obtained and presented in the previous chapter. Its role is to evaluate process economic performance and compare different solutions to identify the best alternative. Similar to the economic assessment previously performed, a series of assumptions has been made in the profitability analysis case. The main assumptions are collected in *Tables 4.16-4.17* regarding the estimation of the interest rate, the approach used to estimate plan depreciation, and both cost distribution and plant capacity profiles considered.

Table 4.16 *Economical assumptions in the profitability analysis.*

Economic Parameter	Value
Straight Line Depreciation	10 years
Cost of Equity	25%
Cost of Debt	5%
Debt/Equity Proportion	50-50
Taxable Income [129]	59.1%
Cost of Capital (Interest Rate)	11.0%

Table 4.17 *Profiles of plant productivity evolution over plant lifetime and fixed cost impact on plant economics.*

Economic Parameter	Profile (year)					
	0	1	2	3	4	5+
Productivity	-	-	60%	90%	95%	100%
Fixed Cost Impact	60%	30%	10%	-	-	-

The profitability analysis performed over a time interval of 25 years in total (comprising construction, considering two batches of catalysts), time-value-of-money has been considered by discounting the cash-flows and actualizing them to "year 0", corresponding to 2023. The time required to build the plant has been assumed to be three years, among which FCI costs impact differently, as reported in *Table 4.17*, which also shows the expected profile of plant productivity variation over the years. At the end of the process lifetime, it has been assumed possible to recover 10% of FCI and the working capital initially allocated.

4.3.1 Profitability Analysis Results

The profitability analysis performed in this dissertation started by considering an ammonia selling price equal to the actual market value. This condition was expected to result in poor performance by comparison of the ammonia TCoP computed and reported in *Table 4.15* with the market price reported in *Table 4.5*. Later, the ammonia selling price was fixed arbitrarily for each scenario to allow the description of plant profitability under different conditions.

4.3.1.1 Base-Case – Ammonia Sold at Market-Price

As mentioned, considering ammonia selling price at market conditions, the presented plant shows poor economic performance, with highly negative discounted NPVs (net-present-values, discounted sum of cash-flows during process operations) at the end of the process lifetime. *Figures 4.2-4.3* represent the mentioned process performance for both configurations in each scenario with ammonia sold at market price.

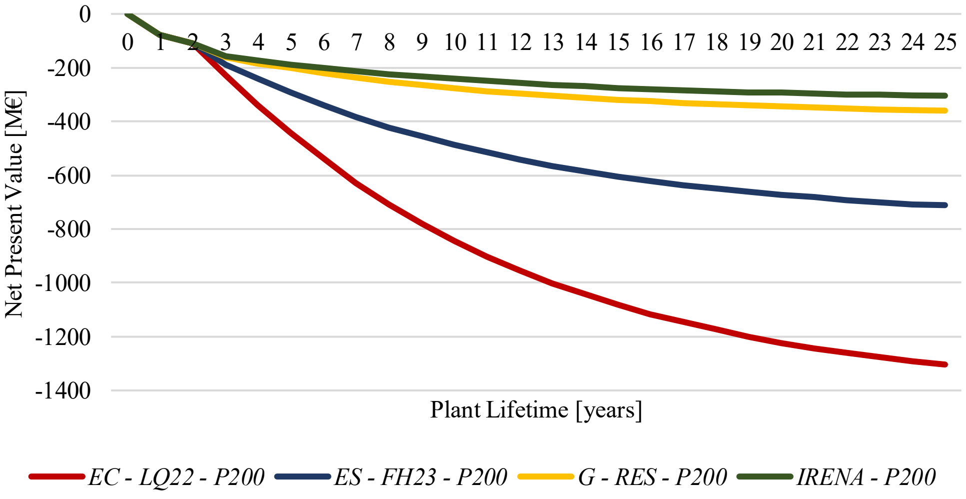


Figure 4.2 *NPV comparison in different scenarios for the 200 bar configuration.*

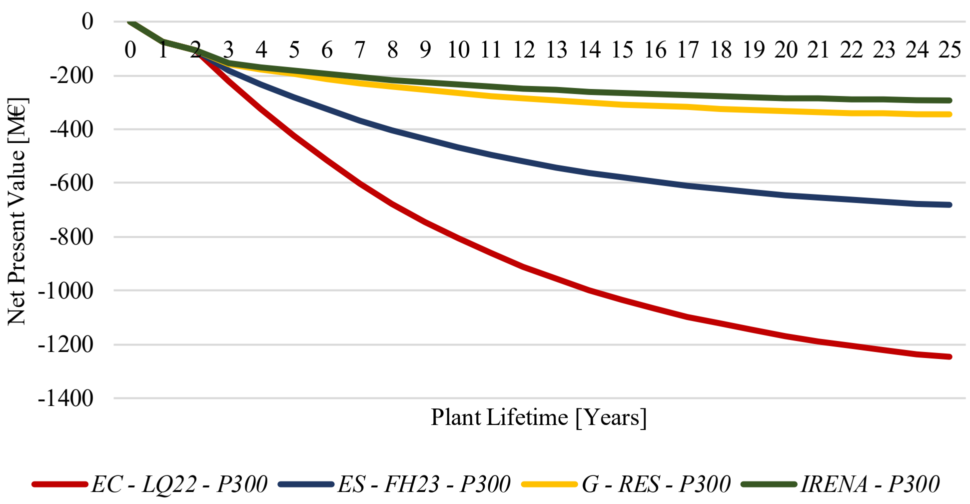


Figure 4.3 *NPV comparison in different scenarios for the 300 bar configuration.*

Under the present conditions, the process is not economically sustainable. Therefore, different selling prices must be considered to make the process feasible, guaranteeing positive NPVs. To understand the impact of the different cost contributions on plant economic performance, the composition of plant CAPEX and OPEX has been analyzed in both configurations and for all scenarios; this has been reported in *Figures 4.4-4.5*. It must be noted that costs here represented have been estimated and reported in *Chapters §4.1.1-§4.2.2.1*.

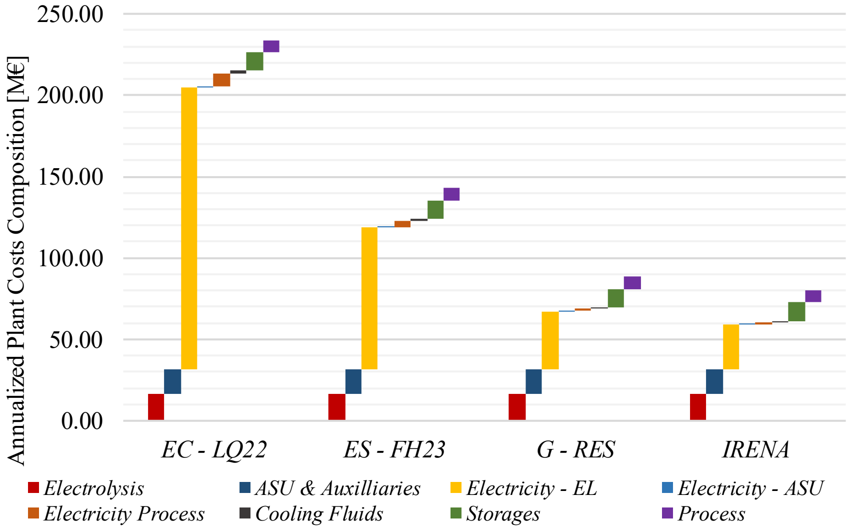


Figure 4.4 *Plant CAPEX and OPEX composition in the 200 bar proposal design.*

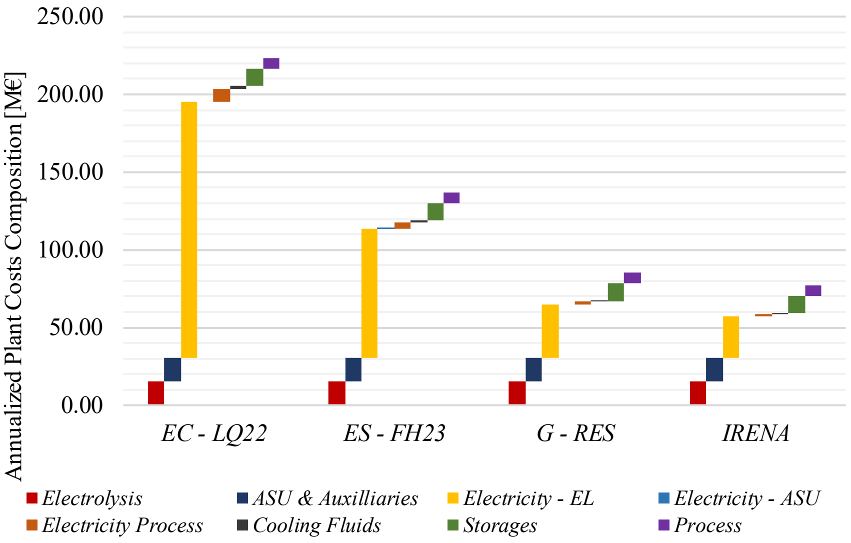
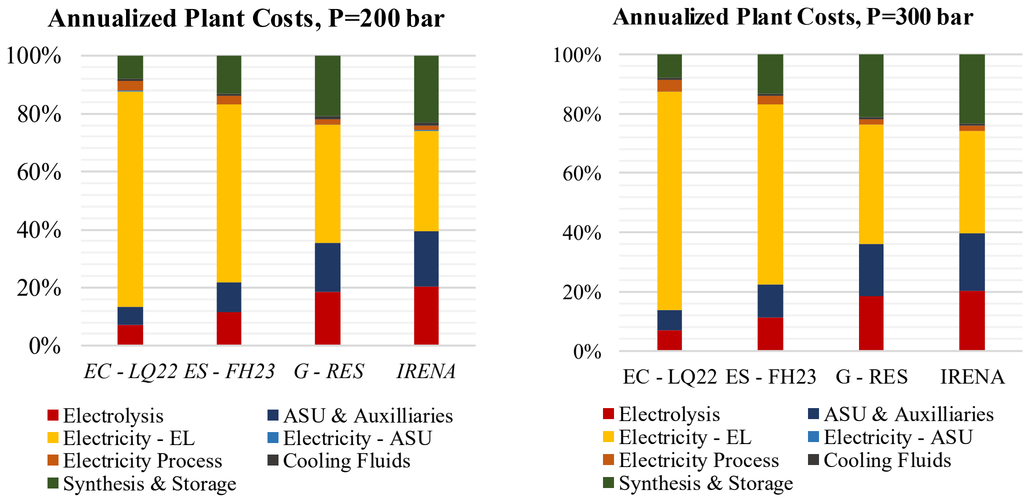


Figure 4.5 *Plant CAPEX and OPEX composition in the 300 bar proposal design.*

As can be noticed, the most relevant contribution in both configurations is associated with electrolysis and air separation, especially the first one. Also, the effect of electricity prices can be seen clearly in the above figures, with annualized costs about one-third in the cheapest scenario compared to the most expensive. The comparison of normalized costs composition can also observe this conclusion.



(a) *(b)*

Figure 4.6 *Composition of annualized plant costs for the 200 bar (a) and 300 bar (b) cases.*

Figure 4.6 shows that for both configurations, reactant production accounts for the vast majority of plant costs, about three-quarters in the best-case scenario, associated with the lowest electricity prices.

4.3.1.2 Optimized Scenario – Arbitrary Ammonia Price

As the second step, the ammonia selling price was fixed arbitrarily in the four considered scenarios to achieve, simultaneously for both configurations assessed, positive NPVs at the end of the project lifetime. In *Figure 4.7,* the TCoP for both configurations in all scenarios considered are reported, and the selling price of ammonia assumed is obtained via manual multiple-shooting.

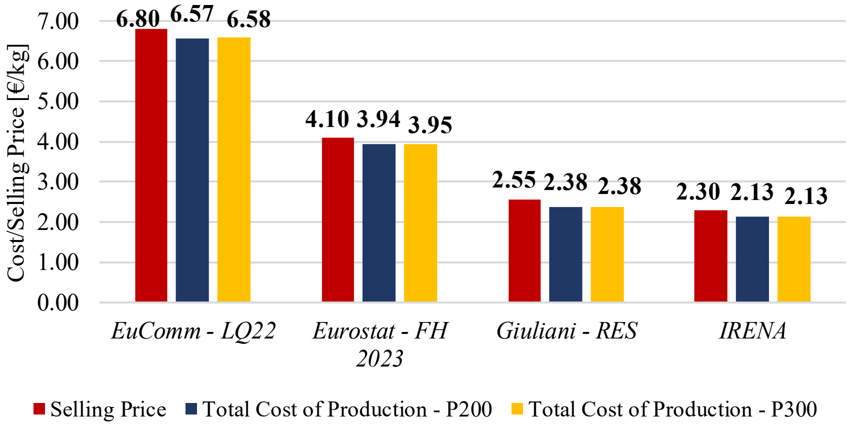


Figure 4.7 *Comparison of fixed ammonia selling prices and total costs of productions in different scenarios.*

The resulting plant cash flow has been compared for both configurations in the extreme scenarios (i.e. the two scenarios with highest and lowest electricity prices), with the highest and smallest electricity prices, respectively, represented in *Figures 4.8-4.9*. Economic results for the reported configurations have been collected in *Table 4.18*.

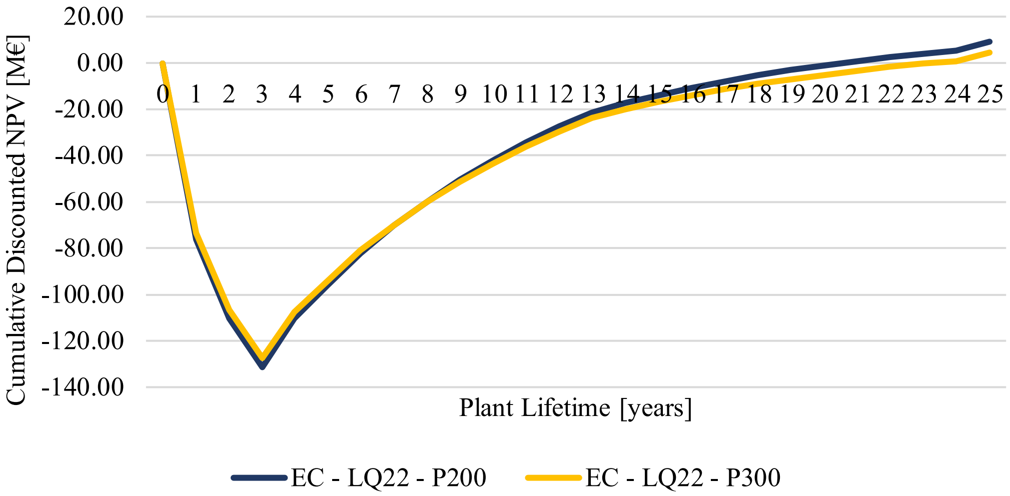


Figure 4.8 *NPV representation for the EC-LQ22 scenario of 200 bar and 300 bar configurations.*

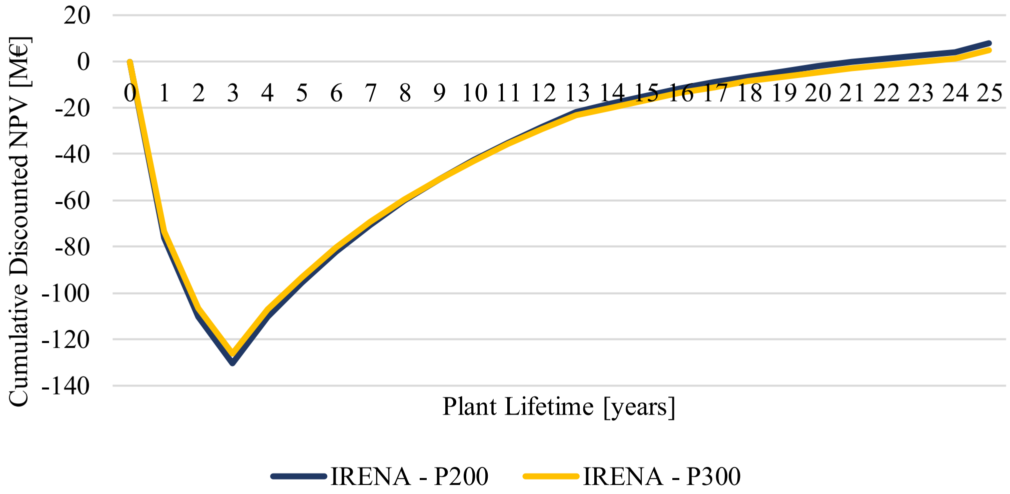


Figure 4.9 *NPV representation for the IRENA scenario of 200 bar and 300 bar configurations.*

The results obtained for the represented ammonia selling prices show a discounted pay-back-period (DPPB), i.e. the time required for the return of the initial investment (FCI minus the cost of land) after plant start-up, of about 6 years, a good value but slightly larger compared to commonly assumed best-practice of 4 years. *Table 4.18* reports both the return on investment (ROI) and the interest rate criterion (IRR), two economic parameters that measure, respectively, the efficiency of the investment and the highest interest rate (after-tax) the project can sustain (NPV equal zero). In the presented scenarios and configurations, ROI is about 15% in all cases at 15 years of plant lifetime, while IRR is slightly above 11%, meaning that the present projects can sustain slight increases in the cost of debt or equity while maintaining a positive NPV.

Table 4.18 *Economic Parameters of the selected scenarios (EC-LQ22 and IRENA) with arbitrarily fixed ammonia selling prices (6.80 €/kg and 2.30 €/kg, respectively).*

Economical Parameter	Scenario: *EC-LQ22*		Scenario: *IRENA*	
	P=200 bar	P=300 bar	P=200 bar	P=300 bar
Simple Discounted Pay-Back Period [years]	6.08	6.26	6.17	6.29
Net Present Value (NPV) @ 25 years [M€]	9.19	4.49	7.81	4.78
Interest Rate Criterion (IRR) @ 25 years [%]	11.92	11.47	11.78	11.50
Return on Investment (ROI) @ 15 years [%]	15.40	14.62	15.12	14.63
Return on Investment (ROI) @ 25 years [%]	19.36	18.51	19.00	18.47

4.3.2 Nitrogen Stream Integration Effect

The integration of the cold nitrogen stream produced in the ASU has been addressed and modelled in *Chapter §2.3.2.3*. In contrast, in this section, the economic effect of its integration has been addressed by estimating the potential savings produced by the heat integration of this cold stream and the impact on TCoP. Savings have been estimated as the difference in capital costs and refrigeration between the two configurations involving the interested units (i.e. *REFRIG* and *NITRO-INT* in *Figure 2.18*). As the heat-integration of the cold stream is performed to reduce the refrigeration duty, it is expected that higher savings are associated to scenarios with higher electricity costs. This assumption is evident in the results reported in *Figure 4.10*, where it can be noted the effect of electricity prices on refrigeration costs (also described in the appendix, *§A.1.2*).

A particular case in the IRENA scenario shows higher costs (4 k€/year) compared to the initial configuration (i.e., without heat-integration of nitrogen) in the 300 bar proposal. In comparison, 1 k€/year of savings are obtained in the 200 bar case: it can be concluded that for electricity prices close to 0.080 €/kWh, the effect of such integration becomes negligible or counter-effective.

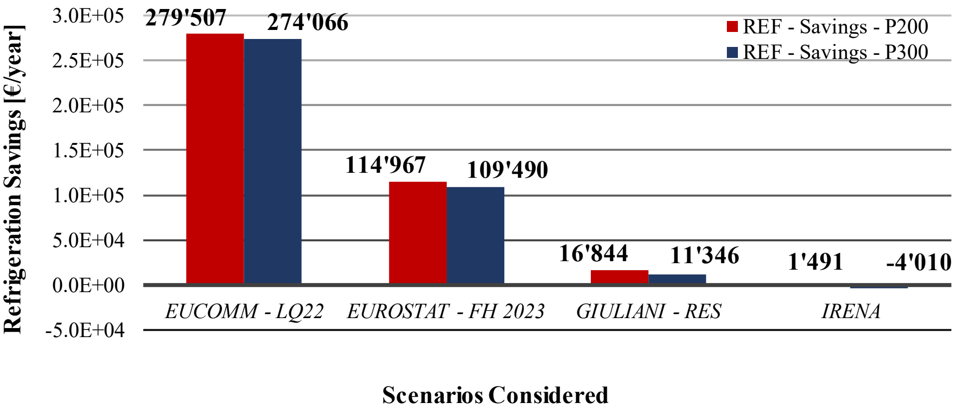


Figure 4.10 *Yearly savings of the refrigeration step achieved via cold-nitrogen heat-integration.*

Performing the economic analysis between the compared plant configurations (i.e. with and without nitrogen integration), the variation in the total cost of production compared to the base case has been assessed: generally, about 1 c€/kgNH_3 are saved in each scenario, except for *IRENA* at 300 bar, where negligible increases compared to the base case are obtained (about +0.01%). It must be noted that the addition of the nitrogen heat-integrator unit (*NITRO-INT*) does not impact the labor cost.

Conclusions

Climate goals fixed by the Paris Agreements and Net-Zero 2050 demand developing and implementing technologies capable of significantly reducing CO_2 emissions. This dissertation has discussed the case of ammonia. This chemical substantially contributes to the chemical sector's emissions, and its sustainable production may produce effects on other sectors (e.g., agriculture) and chemicals (e.g., urea).

After introducing the environmental background and the need to produce ammonia via processes with low-carbon emissions, this thesis frameworks the available production processes for ammonia synthesis, emphasising the electrified alternative that may significantly improve the environmental impact of ammonia production plants. Additionally, the conversion according to the Haber-Bosch process based on an electrified option (i.e., electrolysis and air separation) has been presented to retrieve crucial aspects helpful in developing the alternative route.

ASPEN® Plus has been used to simulate the proposed process in two configurations, i.e. operated at 200 and 300 bar. In both cases, a plant capacity of about 100 ton/day has been considered a representative scale for innovative ammonia plants. The sequence of unit operations has been selected according to the safety performance assessed through the application of hazard investigation techniques (*What If* and HAZOP analysis).

During both design and safety assessment, particular interest was given to the process storages, characterized by severe hazards mainly due to the holdup and the inherent characteristics of stored materials. Safety implications, associated with concepts related to plant operability, allowed for limiting the storage of intermediates and feedstocks while ensuring a safer and simpler design.

According to conceptual-design common practices, a study-estimation has been conducted. However, it should be noted that the adopted method may lack accuracy due to the lack of up-to-date data about equipment capital cost. The economic assessment of different alternatives was based on a sensitivity analysis of the electricity prices provided the core step based on the electrolysis. In particular, the considered scenarios involved data about the present electricity market situation (with two prices based on estimations of the European Commission and Eurostat about the last quarter of 2022 and the first half of 2023, respectively) and future scenarios based on the low-carbon production of electricity in Italy. Four scenarios were finally considered, and the two extremes were compared to assess plant performances in extreme situations.

The results obtained in the profitability analysis have been based on ammonia selling prices defined apriori (based on the total cost of production evaluated considering ammonia sold at the actual market price) to guarantee a positive discounted-net-present-value at the end of process lifetime, i.e., 25 years. The final configuration cannot produce market-competitive ammonia in the short period. In fact, the selling prices calculated in the two extreme scenarios (characterized by the highest and lowest electricity prices), i.e., 6.80 and 2.30 €/kg$_{NH3}$, are far from the actual market value (0.47 €/kgNH_3). The comparison made at fixed ammonia selling prices between the two configurations highlighted comparable process performances regarding the discounted pay-back period (about 6 years for both scenarios) and return on investment (18-19.5%). Nevertheless, the low-pressure configuration generally performed better, with slightly lower discounted-pay-back-period and higher ROI and IRR.

From a safety and economic perspective, the present work discussed an innovative route to produce ammonia based on an electrified process. The configuration operated at 200 bar showed better performances on both sides.

From a future perspective, it can be useful to increase the accuracy of results by adopting more sophisticated safety and economic assessment while approaching a decrease in the total costs of the process by exploiting alternative designs for the reactive section. Another critical point is the heat integration applied to the electrolysis and the reactor. Moreover, a detailed comparative safety assessment concerning the traditional route will benefit the framework's actual pros and cons in operating a fully electrified ammonia production process. Emerging risk scenarios coming with electrified configurations can be structurally embedded in evaluating the safety performance of innovative schemes.

Bibliography

[1] M. Erans, E.S. Sanz-Pérez, D.P. Hanak, Z. Clulow, D.M. Reiner, G.A. Mutch, Direct air capture: process technology, techno-economic and socio-political challenges, Energy Environ Sci 15 (2022) 1360–1405. https://doi.org/10.1039/d1ee03523a.

[2] R. Gholami, A. Raza, S. Iglauer, Leakage risk assessment of a CO2 storage site: A review, Earth Sci Rev 223 (2021). https://doi.org/10.1016/j.earscirev.2021.103849.

[3] United Nations, Paris Agreement, (n.d.). https://unfccc.int/process-and-meetings/the-paris-agreement (accessed November 30, 2023).

[4] J. Samadi, Development of a systemic risk management approach for CO2 capture, transport and storage projects, PhD Thesis, Ecole Nationale Supérieure des Mines de Paris, 2012. https://pastel.hal.science/pastel-00870894.

[5] A. Sodiq, Y. Abdullatif, B. Aissa, A. Ostovar, N. Nassar, M. El-Naas, A. Amhamed, A review on progress made in direct air capture of CO2, Environ Technol Innov 29 (2023). https://doi.org/10.1016/j.eti.2022.102991.

[6] Our World In Data, CO2 emissions by sector, (n.d.). https://ourworldindata.org/ghg-emissions-by-sector (accessed November 30, 2023).

[7] OECD, Primary Energy Supply, (n.d.). https://data.oecd.org/energy/primary-energy-supply.htm#:~:text=Primary%20energy%20supply%20is%20defined,plus%20or%20minus%20stock%20changes. (accessed November 30, 2023).

[8] Statista, Italian Primary Energy Supply by Source, (n.d.). https://www.statista.com/statistics/873552/energy-mix-in-italy/ (accessed November 30, 2023).

[9] World Economic Forum, Nature Positive: Role of the Chemical Sector, n.d.

[10] O. Roelofsen, K. Somers, E. Speelman, M. Witteveen, Energy Insights Practice - Plugging in: What electrification can do for industry, 2020.

[11] P. Sorknæs, R.M. Johannsen, A.D. Korberg, T.B. Nielsen, U.R. Petersen, B. V. Mathiesen, Electrification of the industrial sector in 100% renewable energy scenarios, Energy 254 (2022). https://doi.org/10.1016/j.energy.2022.124339.

[12] Royal Society, Ammonia : zero-carbon fertiliser, fuel and energy store., (n.d.). royalsociety.org/green-ammonia (accessed July 12, 2023).

[13] International Energy Agency - IEA, Ammonia Technology Roadmap: Towards more sustainable nitrogen fertiliser production, n.d. www.iea.org/t&c/.

[14] K. Kolmetz, J. Aprilia, Air Separation Units - Engineering Design Guidelines, 2013. www.klmtechgroup.com.

[15] B. V. Piguave, S.D. Salas, D. De Cecchis, J.A. Romagnoli, Modular Framework for Simulation-Based Multi-objective Optimization of a Cryogenic Air Separation Unit, ACS Omega 7 (2022) 11696–11709. https://doi.org/10.1021/acsomega.1c06669.

[16] C.A. Mora, A. Orjuela, Modeling, validation and exergy evaluation of a thermally-integrated industrial cryogenic air separation plant in Colombia, Chemical Engineering Research and Design 185 (2022) 73–86. https://doi.org/10.1016/j.cherd.2022.07.005.

[17] Downie, Industrial Gases, 1997.

[18] Cryogenic Technologies, Ullmann's Encyclopedia of Industrial Chemistry C (n.d.). https://doi.org/10.1002/14356007.a04.

[19] A.W.K. Quarshie, C.L.E. Swartz, P.B. Madabhushi, Y. Cao, Y. Wang, J. Flores-Cerrillo, Modeling, simulation, and optimization of multiproduct cryogenic air separation unit startup, AIChE Journal 69 (2023). https://doi.org/10.1002/aic.17953.

[20] CASALE - Private Comunication, (2023).

[21] N. Ade, A. Alsuhaibani, M.M. El-Halwagi, H. Goyette, B. Wilhite, Integrating safety and economics in designing a steam methane reforming process, Int J Hydrogen Energy 47 (2022) 6404–6414. https://doi.org/10.1016/j.ijhydene.2021.11.240.

[22] NACFE - North American Council for Freight Affairs, Hydrogen Executive Summary, n.d.

[23] B.C. Tashie-Lewis, S.G. Nnabuife, Hydrogen Production, Distribution, Storage and Power Conversion in a Hydrogen Economy - A Technology Review, Chemical Engineering Journal Advances 8 (2021). https://doi.org/10.1016/j.ceja.2021.100172.

[24] A. Buttler, H. Spliethoff, Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-to-gas and power-to-liquids: A review, Renewable and Sustainable Energy Reviews 82 (2018) 2440–2454. https://doi.org/10.1016/j.rser.2017.09.003.

[25] F. Bezzo, E. Barbera, Process technologies for carbon-neutral fuels - Università degli Studi di Padova, (2022). www.dii.unipd.it.

[26] M.R. Rahimpour, M.A. Makarem, M. Meshksar, Advances in Synthesis Gas Methods, Technologies and Applications, Volume 1, Syngas Production and Preparation, 2022nd ed., Elsevier, n.d.

[27] K. Chau, A. Djire, F. Khan, Review and analysis of the hydrogen production technologies from a safety perspective, Int J Hydrogen Energy 47 (2022) 13990–14007. https://doi.org/10.1016/j.ijhydene.2022.02.127.

[28] S. Shiva Kumar, V. Himabindu, Hydrogen production by PEM water electrolysis – A review, Mater Sci Energy Technol 2 (2019) 442–454. https://doi.org/10.1016/j.mset.2019.03.002.

[29] R. Dominguez, E. Calderón, J. Bustos, Process Safety in electrolytic green hydrogen production, in: Production Management and Process Control, AHFE International, 2022. https://doi.org/10.54941/ahfe1001634.

[30] M. Cipolletta, V.C. Moreno, V. Cozzani, Green Hydrogen Production Routes: a Inherent Safety Assessment, Chem Eng Trans 90 (2022) 55–60. https://doi.org/10.3303/CET2290010.

[31] Lin Ye, Richard Nayak-Luke, Rene Ban˜ares-Alca´ntara, Edman Tsang, Reaction: “Green” Ammonia Production, Chem 3 (2017) 712–714. https://doi.org/10.1016/j.chempr.2017.10.016.

[32] I. Rafiqul, C. Weber, B. Lehmann, A. Voss, Energy efficiency improvements in ammonia production - Perspectives and uncertainties, Energy 30 (2005) 2487–2504. https://doi.org/10.1016/j.energy.2004.12.004.

[33] Pattabathula Venkat, Richardson Jim, Introduction to Ammonia Production, Aiche September (2016).

[34] M.R. Rahimpour, M.A. Makarem, M. Meshksar, Advances in Synthesis Gas Methods, Technologies and Applications, Volume 3, Syngas Products and Usages, 2022nd ed., Elsevier, n.d. https://doi.org/https://doi.org/10.1016/B978-0-323-91878-7.00016-2.

[35] J.A. Moulijn, M. Makkee, A.E. Van Diepen, Chemical Process Technology, Second Edition, 2013.

[36] A. Dechany, K. Van Geem, J. Proost, Process implications of electrifying ammonia production, Curr Opin Chem Eng 40 (2023). https://doi.org/10.1016/j.coche.2023.100915.

[37] H. Zhang, L. Wang, J. Van herle, F. Maréchal, U. Desideri, Techno-economic comparison of green ammonia production processes, Appl Energy 259 (2020). https://doi.org/10.1016/j.apenergy.2019.114135.

[38] Ammonia & Ammonium Nitrate, Ullmann's Encyclopedia of Industrial Chemistry A (n.d.). https://doi.org/10.1002/14356007.

[39] S.M. Ghoreishian, K. Shariati, Y.S. Huh, J. Lauterbach, Recent advances in ammonia synthesis over ruthenium single-atom-embedded catalysts: A focused review, Chemical Engineering Journal 467 (2023). https://doi.org/10.1016/j.cej.2023.143533.

[40] R. Eggers, Industrial High Pressure Applications: Processes, Equipment and Safety, n.d.

[41] A.A. Moghaddam, U. Krewer, Poisoning of ammonia synthesis catalyst considering off-design feed compositions, Catalysts 10 (2020) 1–16. https://doi.org/10.3390/catal10111225.

[42] M. Yoshida, T. Ogawa, Y. Imamura, K.N. Ishihara, Economies of scale in ammonia synthesis loops embedded with iron- and ruthenium-based catalysts, Int J Hydrogen Energy 46 (2021) 28840–28854. https://doi.org/10.1016/j.ijhydene.2020.12.081.

[43] Ammonia: principles and industrial practice, Wiley-VCH, 1999.

[44] J. Barrera Gajardo, Technical-economic analysis of the electrosynthesis of ammonia, Politecnico di Torino, 2021.

[45] M. Alfian, W.W. Purwanto, Multi-objective optimization of green urea production, Energy Sci Eng 7 (2019) 292–304. https://doi.org/10.1002/ese3.281.

[46] International Energy Agency, Italian Energy Generation by Source, (2023). 19/07/2023https://www.iea.org/countries/italy (accessed July 19, 2023).

[47] D. Maporti, F. Galli, P. Mocellin, G. Pauletto, Flexible ethylene production: Electrified ethane cracking coupled with oxidative dehydrogenation, Energy Convers Manag 298 (2023). https://doi.org/10.1016/j.enconman.2023.117761.

[48] Eurostat, Eurostat - Electricity Prices for non-household Consumers, (n.d.). https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Electricity_price_statistics#Electricity_prices_for_non-household_consumers (accessed December 12, 2023).

[49] Redazione Rivista Energia, Qual è il mix elettrico più economico per un'Italia CO2 free?, (2022). https://www.rivistaenergia.it/2022/06/qual-e-il-mix-elettrico-piu-economico-per-unitalia-co2-free/ (accessed December 12, 2023).

[50] M. Borasio, S. Moret, Deep decarbonisation of regional energy systems: A novel modelling approach and its application to the Italian energy transition, Renewable and Sustainable Energy Reviews 153 (2022). https://doi.org/10.1016/j.rser.2021.111730.

[51] European electricity markets - Volume 15, 2023.

[52] A. Darde, R. Prabhakar, J.P. Tranier, N. Perrin, Air separation and flue gas compression and purification units for oxy-coal combustion systems, in: Energy Procedia, 2009: pp. 527–534. https://doi.org/10.1016/j.egypro.2009.01.070.

[53] D.P. Hanak, D. Powell, V. Manovic, Techno-economic analysis of oxy-combustion coal-fired power plant with cryogenic oxygen storage, Appl Energy 191 (2017) 193–203. https://doi.org/10.1016/j.apenergy.2017.01.049.

[54] AirLiquide - Private Comunication, (2023).

[55] D.R. Woods, Rules of thumb in engineering practice, Wiley-VCH, 2007.

[56] Aspentech, Aspen Plus® Ammonia Model, 2008. http://www.aspentech.com.

[57] G. Froment, K. Bischoff, J. De Wilde, Chemical Reactor Analysis and Design, 3rd Edition, John Wiley & Sons, Inc., n.d.

[58] A. Araújo, S. Skogestad, Control structure design for the ammonia synthesis process, Comput Chem Eng 32 (2008) 2920–2932. https://doi.org/10.1016/j.compchemeng.2008.03.001.

[59] J.C. Morud, S. Skogestad, Analysis of Instability in an Industrial Ammonia Reactor, n.d.

[60] B. V. Babu, R. Angira, Optimal design of an auto-thermal ammonia synthesis reactor, Comput Chem Eng 29 (2005) 1041–1045. https://doi.org/10.1016/j.compchemeng.2004.11.010.

[61] B. Lin, T. Wiesner, M. Malmali, Performance of a Small-Scale Haber Process: A Techno-Economic Analysis, ACS Sustain Chem Eng 8 (2020) 15517–15531. https://doi.org/10.1021/acssuschemeng.0c04313.

[62] NIST, Nitrogen - Antoine Equation Parameters, (n.d.). https://webbook.nist.gov/cgi/cbook.cgi?ID=C7727379&Mask=4&Type=ANTOINE&Plot=on#ANTOINE (accessed January 27, 2024).

[63] W. Seider, D. Lewin, J.D. Deader, S. Widagdo, R. Gani, Ka Ming NG, Product and Process Design Principles - Synthesis, Design and Evaluation, Fourth, Wiley, 2017.

[64] P.K. Roy, A. Bhatt, B. Kumar, S. Kaur, C. Rajagopal, Consequence and risk assessment: Case study of an ammonia storage facility, 2011.

[65] E. De Rademaeker, B. Fabiano, S.S. Buratti, L. Storti, D. Buccoliero, C. Paesani, A Risk Based Approach on Selection of Refrigerated Ammonia Storage, in: 2013. www.aidic.it/cet.

[66] GUIDANCE FOR INSPECTION OF ATMOSPHERIC, REFRIGERATED AMMONIA STORAGE TANKS, 2008.

[67] R.M. Nayak-Luke, C. Forbes, Z. Cesaro, R. Bãnares-Alcántara, Techno-Economic Aspects of Production, Storage and Distribution of Ammonia, in: Techno-Economic Challenges of Green Ammonia as an Energy Vector, Elsevier, 2020: pp. 191–207. https://doi.org/10.1016/B978-0-12-820560-0.00008-4.

[68] Oxygen Generation and Storage: Vacuum-Insulated Evaporator System, 2021.

[69] CRYOLOR ASIA PACIFIC, Vertical Cryogenic Storage Tank (Standard Pressure), n.d. www.cryolor.com,.

[70] Gazzetta Ufficiale - DECRETO 7 luglio 2023, (n.d.). https://www.gazzettaufficiale.it/eli/id/2023/07/21/23A04081/sg (accessed February 9, 2024).

[71] R. Moradi, K.M. Groth, Hydrogen storage and delivery: Review of the state of the art technologies and risk and reliability analysis, Int J Hydrogen Energy 44 (2019) 12254–12269. https://doi.org/10.1016/j.ijhydene.2019.03.041.

[72] H. Barthélémy, Hydrogen storage - Industrial prospectives, Int J Hydrogen Energy 37 (2012) 17364–17372. https://doi.org/10.1016/j.ijhydene.2012.04.121.

[73] Hydrogen, Ullmann's Encyclopedia of Industrial Chemistry H (n.d.). https://doi.org/10.1002/14356007.a12.

[74] M. Bogar, Hydrogen Storage Methods, (n.d.).

[75] D.C. Hendershot, An overview of inherently safer design, Process Safety Progress 25 (2006) 98–107. https://doi.org/10.1002/prs.10121.

[76] F. Eljack, M.K. Kazi, V. Kazantzi, Inherently safer design tool (i-SDT): A property-based risk quantification metric for inherently safer design during the early stage of process synthesis, J Loss Prev Process Ind 57 (2019) 280–290. https://doi.org/10.1016/j.jlp.2018.12.004.

[77] C.T. Leong, A.M. Shariff, Inherent safety index module (ISIM) to assess inherent safety level during preliminary design stage, Process Safety and Environmental Protection 86 (2008) 113–119. https://doi.org/10.1016/j.psep.2007.10.016.

[78] Inherent safety in design, ABB Consulting (n.d.). www.abb.com/consulting.

[79] D.C. Hendershot, Inherently Safer Design An Overview of Key Elements, 2011. www.asse.org.

[80] P. Mocellin, Industrial process safety and risk analysis - Università degli Studi di Padova, (2021).

[81] Robert H. Perry, Don W. Green, Perry's Chemical Engineers' Handbook, 8th Edition, 2008.

[82] T. Kletz, What you don't have can't leak, 1978.

[83] M. Athar, A.M. Shariff, A. Buang, S. Nazir, H. Hermansyah, T.L. See, Process equipment common attributes for inherently safer process design at preliminary design stage, Process Safety and Environmental Protection 128 (2019) 14–29. https://doi.org/10.1016/j.psep.2019.05.033.

[84] A. Castillo-Landero, J. Aburto, J. Sadhukhan, E. Martinez-Hernandez, A process modularity approach for chemical process intensification and inherently safer design, Process Safety and Environmental Protection 168 (2022) 54–66. https://doi.org/10.1016/j.psep.2022.09.054.

[85] F.I. Khan, P.R. Amyotte, How to make inherent safety practice a reality, Canadian Journal of Chemical Engineering 81 (2003) 2–16. https://doi.org/10.1002/cjce.5450810101.

[86] A. Lorenzetti, Processi Chimici Innovativi - Università degli Studi di Padova, (2021).

[87] T.A. Kletz, Inherently Safer Design: The Growth of an Idea, n.d.

[88] X. Gao, A.A. Abdul Raman, H.F. Hizaddin, M.M. Bello, Systematic review on the implementation methodologies of inherent safety in chemical process, J Loss Prev Process Ind 65 (2020). https://doi.org/10.1016/j.jlp.2020.104092.

[89] Airgas - Air Liquide, Nitrogen - Safety Datasheet, (n.d.).

[90] Airgas - Air Liquide, Nitrogen - Liquid - Safety Datasheet, (n.d.).

[91] Airgas - Air Liquide, Oxygen - Safety Datasheet, (n.d.).

[92] Airgas - Air Liquide, Oxygen - Liquid - Safety Datasheet, (n.d.).

[93] Airgas - Air Liquide, Hydrogen - Safety Datasheet, (n.d.).

[94] O.A. Rosyid, B. Besar, T. Energi -Bppt, Risk analysis for the infrastructure of a hydrogen economy, 2006.

[95] INC. MATHESON TRI-GAS, Ammonia - Safety Datasheet, (n.d.).

[96] CAMEO Chemicals, Anhydrous Ammonia - CAMEO Chemicals, (n.d.). https://cameochemicals.noaa.gov/chemical/4860 (accessed July 17, 2023).

[97] CAMEO Chemicals, Ammonia Solutions - CAMEO Chemicals, (n.d.). https://cameochemicals.noaa.gov/chemical/24008 (accessed July 19, 2023).

[98] Air Liquide, Ammonia Anhydrous - Safety Datasheet, (n.d.).

[99] Carl Roth, Ammonia Solution - Safety Datasheet, (n.d.).

[100] S.Y. Jeong, D. Jang, M.C. Lee, Property-based quantitative risk assessment of hydrogen, ammonia, methane, and propane considering explosion, combustion, toxicity, and environmental impacts, J Energy Storage 54 (2022). https://doi.org/10.1016/j.est.2022.105344.

[101] CDC - IDHL for Ammonia, (n.d.). https://www.cdc.gov/niosh/npg/npgd0028.html (accessed July 17, 2023).

[102] W. Blom, H. Sønberg Fanø, R. McTaggart, G. Solvi, M. Tsypkin, L. Ruhlmann, B. Smit, S. Montel, L. Phillips, S. David Toxvaerd, J. Cockerill Marc Gascuel, C. Donis, M. Loic Joly, A. Serpollier, P. Lian Xiaofei, C. Tianshan, P. Power Jasper Hollander, G. Rexwinkel, J. Zonneveld, T.-N. Hubertus Rosenow, G. Damann, M. Dommers, Safety Aspects of Green Hydrogen Production on Industrial Scale, n.d.

[103] W.H. Al-Dahhan, E. Yousif, F.H. Hussein, Chemical Risk Assessment for Urea-Ammonia Production Plant, International Journal of Public Health & Safety Research Article 6 (2021) 2021. https://www.airgas.com/msds/001026.pdf,.

[104] M.R. Murphy, S.K. Singh, Chemical interaction matrices, Process Safety Progress 34 (2015) 368–372. https://doi.org/10.1002/prs.11783.

[105] CRW4 - CCPS Software for Interaction Matrixes , (n.d.). https://www.aiche.org/ccps/resources/crw-overview (accessed November 11, 2023).

[106] CAMEO Chemicals - Interaction Charts, (n.d.). https://cameochemicals.noaa.gov/reactivity (accessed November 11, 2023).

[107] Brandoni, Compatibilità chimica dei materiali rispetto alle sostanze chimiche, (n.d.). www.brandoni.it.

[108] ASCO, Materiali dei prodotti e compatibilità, (n.d.). http://www.asconumatics.eu/.

[109] Sodium Hydroxide - Market Price January 2024, (n.d.). https://businessanalytiq.com/procurementanalytics/index/sodium-hydroxide-price-index/ (accessed January 25, 2024).

[110] Potassium Hydroxide - Market Price January 2024, (n.d.). https://businessanalytiq.com/procurementanalytics/index/potassium-hydroxide-price-index/ (accessed January 25, 2024).

[111] AirGas - AirLiquide, Argon - Safety Datasheet, (n.d.).

[112] Sigma Aldrich, Magnetite - SafetyDatasheet, (n.d.).

[113] Martin & Robson, Magnetite - SafetyDatasheet, (n.d.).

[114] Powder Technology Inc., Magnetite - SafetyDatasheet, (n.d.). http://www.powdertechnologyinc.com.

[115] Stainless-Steels in ammonia production - Designer's Handbook, American Iron and Steel Institute, 2020. www.nickelinstitute.org.

[116] H.J. Pasman, Risk analysis and control for industrial processes - gas, oil and chemicals : a system perspective for assessing and avoiding low-probability, high-consequence events, n.d.

[117] S.B. Harrison, Managing enterprise risk Cryogenic safety in air separation units, n.d. www.mem.gov.cn/gk/tzgg/.

[118] How to Improve Reliability and Safety of Air Separation Units, n.d.

[119] NASA, Safety standards for oxygen and oxygen systems - Guidelines for Oxygen System Design, Materials Selection, Operations, Storage, and Transportation, n.d.

[120] P.E. Starr Tze, K. Grant, E. Sherwin, Addressing the process safety concerns of hydrogen in a net zero economy, (2022). https://beta.elsevier.com/connect/addressing-the-process-safety-concerns-of-hydrogen-in-a-net-zero-economy?trial=true (accessed July 21, 2023).

[121] J. Casal, Evaluation of the Effects and Consequences of Major Accidents in Industrial Plants, Elsevier, 2008.

[122] S.I. Sandler, Chemical, Biochemical and Engineering Thermodynamics, Fifth Edition, Wiley, n.d.

[123] Crowl, Louvar, Chemical Process Safety, Fundamentals with Applications, Fourth Edition, Pearson, 2020.

[124] R. Turton, J.A. Shaeiwitz, D. Bhattacharyya, W. Whiting, Analysis, Synthesis, and Design of Chemical Processes, Fifth Edition, Prentice Hall, 2018.

[125] G. Towler, R. Sinnott, Chemical Engineering Design - Principles, Practice and Economics of Plant and Process Design, 2008. http://elsevier.com.

[126] F. Bezzo, Process Design - Università degli Studi di Padova, (2022).

[127] Chemical Engineering Plant Cost Index, CEPCI - May, 2023 - Towering Skills., (n.d.). https://toweringskills.com/financial-analysis/cost-indices/ (accessed February 21, 2024).

[128] Ammonia - Market Price November 2023, (n.d.). https://businessanalytiq.com/procurementanalytics/index/ammonia-price-index/ (accessed November 20, 2023).

[129] Il Sole 24 Ore, Fisco, in tasse il 59% dei profitti delle imprese, (n.d.). https://www.ilsole24ore.com/art/fisco-tasse-59percento-profitti-imprese-AC0L5U1 (accessed February 22, 2024).

[130] Aspentech, Aspen Plus® User Guide, 1981. http://www.aspentech.com.

[131] W.L. Luyben, Estimating refrigeration costs at cryogenic temperatures, Comput Chem Eng 103 (2017) 144–150. https://doi.org/10.1016/j.compchemeng.2017.03.013.

[132] G. Maschio, Impiantistica di Processo - Università degli Studi di Padova, (n.d.).

[133] Sigma-Aldrich, Nafion - Safety Datasheet, (2023).

[134] Chemours, Nafion^{TM} N117 - Safety Datasheet, (2017).

[135] ThermoFisher, Zeolite - Safety Datasheet, (n.d.).

[136] Zeolite Products, Zeolite - Safety Datasheet, (n.d.).

Appendix

The last chapter of the work, the appendix, contains a variety of information used in the work and included here for completeness, lightening of the dissertation text and ease of reference.

A.1 Process Modelling in *ASPEN® Plus*

A.1.1 Thermodynamic Models

In the case of ammonia, the species are handled in hydrogen-rich environment at high pressure and temperature, therefore Soave-Redlich-Kwong (SRK) equation of state (EoS) is the best equation available, especially with the Boston-Mathias α-function that corrects the temperature dependance term of the SRK; Peng-Robinson EoS, is a suitable alternative [130].

A.1.2 Process Utilities

Information about the utilities considered in this work has been reported in *Table A.1.*
As reported in [55], cooling-water maximum outlet temperature has been fixed: Tmax=50°C.

Table A.1 *Utilities available for the process modelled with costs and operative conditions.*

Utility	Operative Conditions / Scenario		Costs	Ref.
Tower Water	T_{in}=35°C & T_{out}=45°C		2.5×10^{-5} €/kg	[126]
Cooling Water	T_{in}=25°C & T_{out}=30°C – T_{max}=50°C [55]		5×10^{-5} €/kg	
Refrigerated Water	T_{in}=5°C & T_{out}=10°C		3.13×10^{-4} €/kg	
Refrigeration at -20/-15°C	Ammonia single-stage refrigeration train		-	-
Electricity	European Commission Last-Quarter 2022		0.4962 €/kWh	[51]
	Eurostat First-Half 2023		0.25 €/kWh	[48]
	Giuliani	100% RES	0.103 €/kWh	[49]
		100% RES + H_2 Storage	0.132 €/kWh	
		RES + 60 GW NUKE	0.085 €/kWh	
		RES + 60 GW NUKE + H_2 Storage	0.108 €/kWh	
		RES + 40 GW NUKE	0.089 €/kWh	
		RES + 40 GW NUKE + H_2 Storage	0.106 €/kWh	
	Borasio		0.096 €/kWh	[50]
	IRENA		0.080 €/kWh	[47]

Refrigeration Costs

Refrigeration costs have been estimated rigorously [124,126] and the result has been compared with the result of the correlation provided in [131]. Comparable refrigeration costs are obtained for similar electricity prices, but being of interest of this elaborate the comparison of different electricity-prices scenarios, the rigorous correlation reported in *Equation A.1* has been implemented. It must be noted that it has been considered a refrigeration cycle driven by ammonia at -30°C (ensuring in both configurations the minimum approach temperature of 15°C). The resulting costs of refrigeration are reported in the following *Figure A.1*.

$$C_{ref}\left(\frac{€}{GJ}\right) = C_{elec}\left(\frac{€}{kWh}\right) \cdot \frac{453'553{,}33\, kJ/h}{3600\, kJ/kWh} + 1{,}4535533\ GJ/h * 0{,}8\left(\frac{€}{GJ}\right) \tag{A.1}$$

The estimation has been performed considering: a cooling-duty of 1 GJ, cost of cooling-water at 0.8 €/GJ; the other two values in *Equation A.1* are the compression power demanded by the compressor and the total condenser duty.

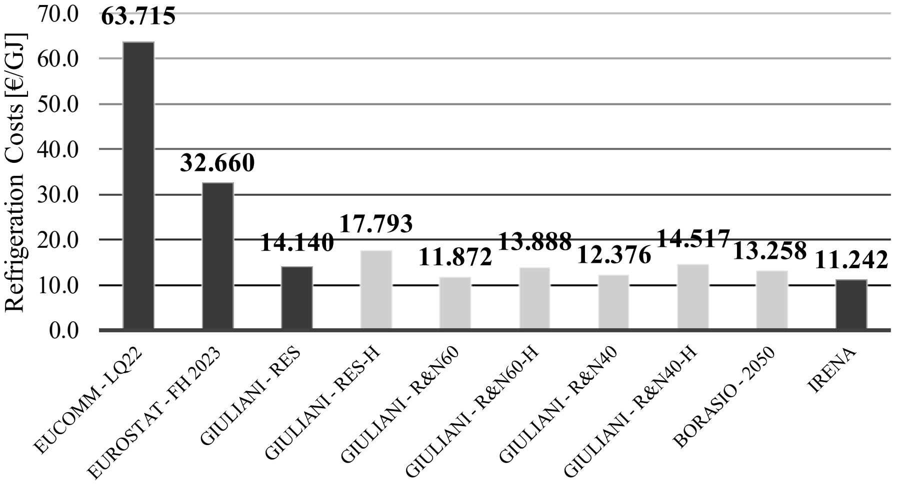


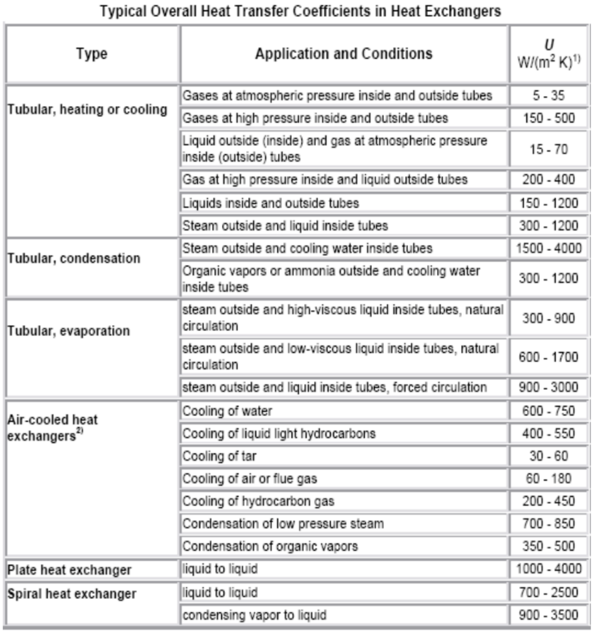
Figure A.1 *Cost of refrigeration in the different scenarios considered as function of electricity price.*

Heat-Exchanger Modelling

In the present work it has been fixed at 15°C the minimum-approach-temperature (ΔT_{min}) in heat-exchangers, being a common industrial practice [20].

Heat-exchangers global heat-transfer coefficient has been fixed for the whole process depending on the two fluids in heat-contact. Considering the values reported in *Figure A.2* below, 300 W/m^2K and 150 W/m^2K have been applied in considered process heat-exchangers.

Figure A.2 *Table reporting global-heat-transfer coefficient ranges for different heat-exchange configurations* [132].



Typical Overall Heat Transfer Coefficients in Heat Exchangers

Type	Application and Conditions	U W/(m^2 K)$^{1)}$
Tubular, heating or cooling	Gases at atmospheric pressure inside and outside tubes	5 - 35
	Gases at high pressure inside and outside tubes	150 - 500
	Liquid outside (inside) and gas at atmospheric pressure inside (outside) tubes	15 - 70
	Gas at high pressure inside and liquid outside tubes	200 - 400
	Liquids inside and outside tubes	150 - 1200
	Steam outside and liquid inside tubes	300 - 1200
Tubular, condensation	Steam outside and cooling water inside tubes	1500 - 4000
	Organic vapors or ammonia outside and cooling water inside tubes	300 - 1200
Tubular, evaporation	steam outside and high-viscous liquid inside tubes, natural circulation	300 - 900
	steam outside and low-viscous liquid inside tubes, natural circulation	600 - 1700
	steam outside and liquid inside tubes, forced circulation	900 - 3000
Air-cooled heat exchangers$^{2)}$	Cooling of water	600 - 750
	Cooling of liquid light hydrocarbons	400 - 550
	Cooling of tar	30 - 60
	Cooling of air or flue gas	60 - 180
	Cooling of hydrocarbon gas	200 - 450
	Condensation of low pressure steam	700 - 850
	Condensation of organic vapors	350 - 500
Plate heat exchanger	liquid to liquid	1000 - 4000
Spiral heat exchanger	liquid to liquid	700 - 2500
	condensing vapor to liquid	900 - 3500

A.1.3 Economic Results

A.1.3.1 Economic Potential

During the development of the conceptual design and the modelling of the process, the engineer must consider, in addition to the technical feasibility of the process, also the economical one. This preliminary estimation of the economic profitability is performed contextually to the design and it is called "economic-potential" (EP), a metric divided into different "levels", based on different stages of process design and plant sections.

The first estimation of the economic potential considers the simple "input-output structure" of the process and aims to evaluate if a positive income may be achieved for the productivity of interest; EP-2 (economic-potential of level two) is the first level of analysis and it is evaluated as reported in *Equation A.2*.

$$EP_2 = revenues - \begin{pmatrix} cost\ of \\ feedstock \end{pmatrix} - \begin{pmatrix} cost\ of\ feed \\ equipment \end{pmatrix} - \begin{pmatrix} cost\ of\ feed \\ utilities \end{pmatrix} - \begin{pmatrix} cost\ of \\ waste\ treat. \end{pmatrix} \tag{A.2}$$

EP-2 is used to make the following estimations, that adds additional costs to the previous estimation to account for the additional equipment and utilities requirements:

$$EP_3 = EP_2 - \begin{pmatrix} cost\ of\ reaction \\ equipment \end{pmatrix} - \begin{pmatrix} cost\ of\ reaction \\ utilities \end{pmatrix} \tag{A.3}$$

$$EP_4 = EP_3 - \begin{pmatrix} cost\ of\ separation \\ equipment \end{pmatrix} - \begin{pmatrix} cost\ of\ separation \\ utilities \end{pmatrix} \tag{A.4}$$

The degree of analysis considered allows to avoid the estimation of costs associated to pumps for pressures lower than 10 bar and process vessels having low impact on the total CAPEX.
In the present work the estimation of equipment capital cost is performed by applying the method developed by *Guthrie* and presented in the following paragraph. Additionally, since EP is a yearly-basis estimation of process profitability, in addition to product, feedstock and utilities contributions, the purchase of process equipment must be added and this is performed commonly assuming that yearly equipment cost weights 1/3 of its CAPEX.

A.1.3.2 Profitability Analysis

Table A.2 *Productivity and demands of the two plant configurations.*

Economical Parameter	Scenario: *ES-FH2023*		Scenario: *G-RES*	
	P=200 bar	P=300 bar	P=200 bar	P=300 bar
Discounted Pay-Back Period [years]	6.28	6.43	6.17	6.28
Net Present Value (NPV) [M€]	4.80	1.027	8.09	4.95
Interest Rate Criterion (IRR) [%]	11.48	11.13	11.81	11.52
Return on Investment (ROI) @ 15 years [%]	14.62	14.02	15.17	14.66
Return on Investment (ROI) @ 25 years [%]	18.48	17.83	19.06	18.51

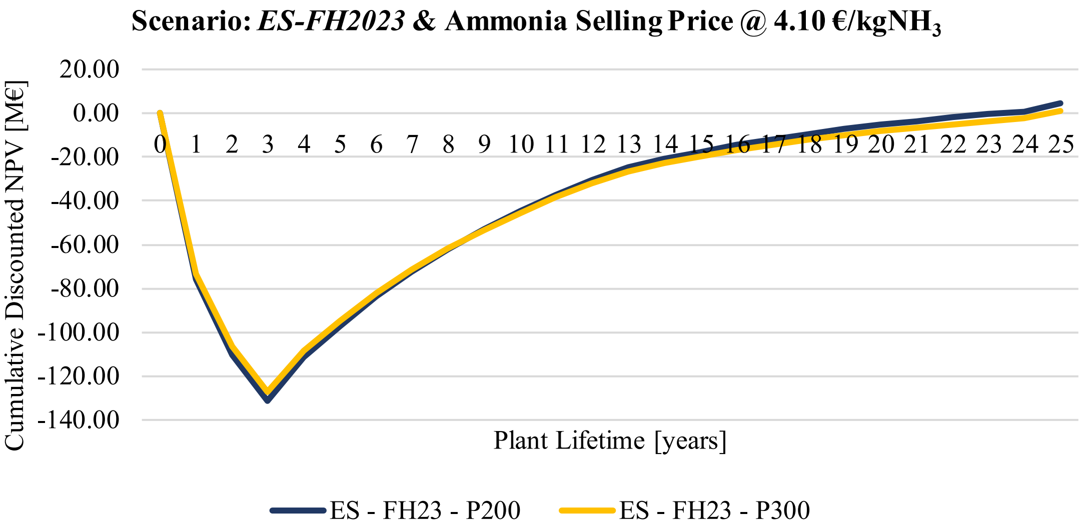


Figure A.3 *NPV representation for the ES-FH2023 scenario and both configurations considered.*

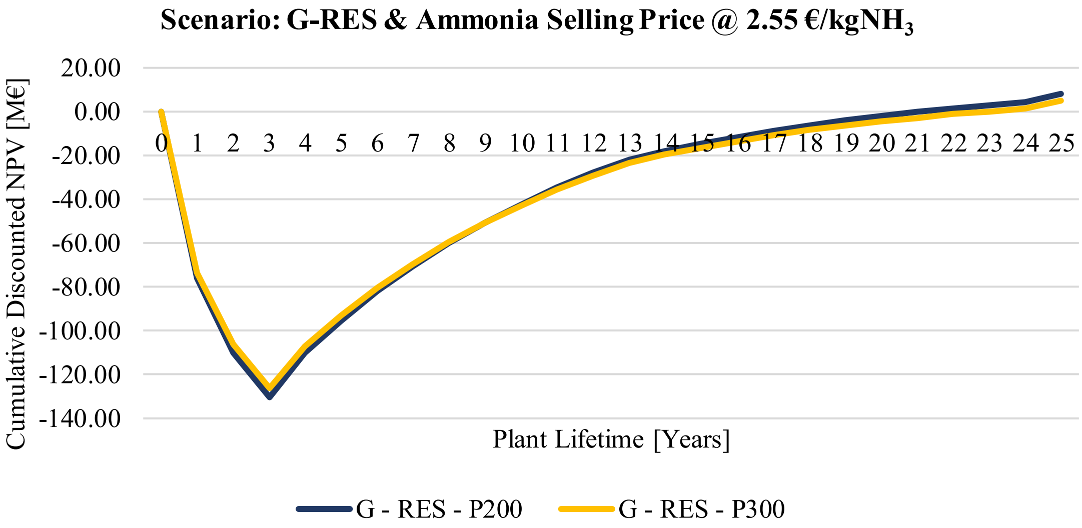


Figure A.4 *NPV representation for the G-RES scenario and both configurations considered.*

A.2 Safety Information

A.2.1 Compatibility Matrix – Report

The following tables collects, per each pairs of chemical included in the interaction matrixes discussed in *Chapter §3*, information about the compatibility issues that may arise because of their interaction. Information here contained comes from different sources: [105–108,111–114,133–136].

A.2.1.1 Electrolysis

Table A.3 *Interaction Matrix additional information about electrolysis unit.*

Binary Interaction		**Hazards**
Demineralized Water	*Hydrogen*	No evidence of reactions.
	Oxygen	Reacts with species dissolved into water, creating corrosive and toxic species and releasing gases. Being demineralized, such hazards are not expected.
	NaOH	When mixed heat is released (heat of dissolution), fumes may be created.
	KOH	When mixed heat is released (heat of dissolution), fumes may be created
	Nafion®	
	S-S AISI 304	Class "*A*" compatibility
	S-S AISI 316	Class "*A*" compatibility
Hydrogen	*Oxygen*	Flammable and explosive mixture. Exothermic reaction, may increase the pressure in confined environments due to gas release. Reaction may be violent, intense and explosive. Mixture unstable when heated.
	NaOH	No known hazardous reaction
	KOH	No known hazardous reaction
	Nafion®	No known hazardous reaction
	S-S AISI 304	Class "*A*" compatibility
	S-S AISI 316	Class "*A*" compatibility
Oxygen	*NaOH*	Exothermic reaction at ambient conditions with release of gaseous products. Intense or violent reaction with products that may be toxic or corrosive.
	KOH	Exothermic reaction at ambient conditions with release of gaseous products. Intense or violent reaction with products that may be toxic or corrosive.
	Nafion®	Nafion® is not compatible with strong oxidizing agents
	S-S AISI 304	Class "*A*" compatibility
	S-S AISI 316	Class "*A*" compatibility
NaOH	*S-S AISI 304*	Class "*A*" compatibility
	S-S AISI 316	Class "B" compatibility, light attack to the material
KOH	*S-S AISI 304*	Class "*B*" compatibility, light attack to the material
	S-S AISI 316	Class "*B*" compatibility, light attack to the material
Nafion®	*S-S AISI 304*	
	S-S AISI 316	

A.2.1.2 Air Separation Unit

Table A.4 *Interaction Matrix additional information about ASU.*

Binary Interaction		**Hazards**
Water	*Nitrogen*	No known hazardous reaction
	Oxygen	Reacts with species dissolved into water, creating corrosive and toxic species and releasing gases.
	Argon	No known hazardous reaction
	Carbon Dioxide	No known hazardous reaction
	Zeolite	No known hazardous reaction
	S-S AISI 304	Excellent compatibility
	S-S AISI 316	Excellent compatibility
Nitrogen	*Oxygen*	No known hazardous reaction
	Argon	No known hazardous reaction
	Carbon Dioxide	No known hazardous reaction
	Zeolite	No known hazardous reaction
	S-S AISI 304	Excellent compatibility
	S-S AISI 316	Excellent compatibility
Oxygen	*Argon*	No known hazardous reaction
	Carbon Dioxide	No known hazardous reaction
	Zeolite	No known hazardous reaction
	S-S AISI 304	Acceptable compatibility under cryogenic conditions, excellent at normal one
	S-S AISI 316	Acceptable compatibility under cryogenic conditions, excellent at normal one
Argon	*Carbon Dioxide*	No known hazardous reaction
	Zeolite	No known hazardous reaction
	S-S AISI 304	Excellent compatibility
	S-S AISI 316	Excellent compatibility
Carbon Dioxide	*Zeolite*	No known hazardous reaction
	S-S AISI 304	Excellent compatibility
	S-S AISI 316	Excellent compatibility
Zeolite	*S-S AISI 304*	
	S-S AISI 316	

A.2.1.3 Ammonia Synthesis

Table A.5 *Interaction Matrix additional information about ammonia synthesis loop.*

Binary Interaction		**Hazards**
Hydrogen	*Nitrogen*	No known hazardous reaction
	Ammonia	No known hazardous reaction
	Argon	No known hazardous reaction
	Oxygen	Flammable and explosive mixture. Exothermic reaction, may increase the pressure in confined environments due to gas release. Reaction may be violent, intense and explosive. Mixture unstable when heated.
	Magnetite	No known hazardous reaction
	S-S AISI 304	Excellent compatibility
	S-S AISI 316	Excellent compatibility
Nitrogen	*Ammonia*	No known hazardous reaction
	Argon	No known hazardous reaction
	Oxygen	No known hazardous reaction
	Magnetite	No known hazardous reaction
	S-S AISI 304	Excellent compatibility
	S-S AISI 316	Excellent compatibility
Ammonia	*Argon*	No known hazardous reaction
	Oxygen	Violent, intense or explosive reaction may occur, generating gases and causing pressurization
	Magnetite	No known hazardous reaction
	S-S AISI 304	Excellent compatibility
	S-S AISI 316	Excellent compatibility
Argon	*Oxygen*	No known hazardous reaction
	Magnetite	No known hazardous reaction
	S-S AISI 304	Excellent compatibility
	S-S AISI 316	Excellent compatibility
Oxygen	*Magnetite*	Strongly exothermic reaction that may cause gases release and pressurization. Reaction products may be toxic.
	S-S AISI 304	Excellent compatibility
	S-S AISI 316	Excellent compatibility
Magnetite	*S-S AISI 304*	
	S-S AISI 316	

A.2.2 HAZID Preliminary Analysis – What if Analysis

In the following paragraph is reported the "*What if*?" analysis performed on the developed process design.

Table A.6 *Complete "What if?" analysis.*

What if	Consequences	Recommendation
Reactor Unit		
reactor leaks (no catastrophic failure)	Release of the material contained at high pressure and temperature: made of flammable species, it may be ignited readily; the contained materials have toxicological concern	- Frequent maintenance operations for control of external reactor integrity - Implement sensors for detection of hydrogen releases and loss of pressure - Alert workers and plant emergency shut-down operations should begin when the scenario occurs
reactor collapse	Same as above Mechanical collapse	- Check the material of construction degradation degree during maintenance (reactor and support elements / reactor internals), cover it with protective paintings - Maintain a suitable distance between process units to avoid chain effects
reactor cooling capacity decreases	Temperature inside the reactor increases (runaway reaction), affecting reactor material integrity: catastrophic rupture of the reactor may occur if the condition is protracted over time	- Strict reactor temperature control and alarm for threshold overcome - Safety measures (e.g. stop the feed and discharge)
	Temperature inside the reactor beds increases (runaway reaction), increasing sintering phenomena, with a variation in reactor performances due to loss in catalytic efficiency	Same as above - Reactor performance changes after strong sintering, performance evaluation may be necessary
	Temperature inside the reactor increases, overcoming the auto-ignition temperature of hydrogen (500-570°C), dangerous situations in case there are unintended air intakes	- Same as first scenario - Correct process insulation to avoid air intake
bed support breaks	Bed collapses inside the reactor, creating a chain-effect with potential catastrophic failure of the unit and release of the entrained materials (flammability and toxicological concerns)	- Adequate choice of construction material and sizing are necessary - To avoid a failure associated to improper operative conditions (material degradation) a suitable control of reactor temperature is necessary - During catalyst substitution a revision of material degradation is advised, eventually a substitution of support elements is suggested

(continued on next page)

(Table A.6, continued from previous page)

coolant leaks in reactor beds	Due to the operative temperature in the reactor part of the coolant (tower water) vaporizes, increasing the pressure in the unit	- Safety relief valve opens to avoid catastrophic failure of the reactor, discharging a mixture of steam, syngas and ammonia, with flammable and toxicological concern
	Using water as coolant it attacks the catalyst, causing sintering and poisoning it, causing a loss in performance and requiring (if the leak is large or protracted in time) the substitution of the catalyst beds	- Control of plant performances over the time can help understanding if there are losses in catalytic performances - Cooling stream Flow/Pressure control can be implemented - During catalyst substitution a check of reactor internals state of degradation (heat-exchangers) is suggested
accidents in reactor's nearby units occurs	Chain effects involving the reactor may occur, e.g. units that inadvertently hit the reactor creating a leak, cold streams released from cold units may affect safe operation of valves, pipes blockage (inlet/outlet/utility)	- Emergency shut-down operations should begin when reactor integrity is questioned or at risk - If possible reactor feed should be stopped and the contained materials discharged
reactor pressure increases	Extreme reactor pressure can cause the catastrophic rupture of the vessel and release of the contained materials (fire and toxicological concerns)	- Pressure control on reactor feed is advised and a relief valve opening in such situations is necessary
	Higher reactor pressure changes the reaction behavior, increasing the rate (higher temperatures in the reactor are found)	Same as above - Temperature control with action on the cooling stream is advised
reactor pressure decreases	Smaller reactor pressure changes the reaction behavior, decreasing the rate (reactor temperature decreases at constant cooling-rate)	- Temperature control with action on the cooling-stream flowrate is advised
reactor controls do not operate properly	Deviation from the defined behavior occurs, leading to uncontrollable process operations	- Redundance of control systems
reactor outlet is blocked	Reaction proceeds inside the unit reaching equilibrium conditions, with increasing beds temperature; due to poor fluid movement cooling provided by heat-exchangers is not enough. Temperature increase can overcome the auto-ignition temperature of hydrogen and also cause sintering of catalyst.	- By-pass that can deviate the flux avoiding the plugged section - Flow meter to control the flowrate along the pipe and block the fed stream to the reactor if the situation is prolonged in time to avoid repercussions on the compression train (outlet stream excessive temperature)
composition of the reactor feed changes	Reaction kinetic behavior changes depending on reactants ratio, with a variation in reactor temperature profile and behavior	- Composition analyzer/inferential controller is required - A proper control of reactor temperature is necessary

(continued on next page)

(Table A.6, continued from previous page)

Separation Section		
a black out occurs	Loss of coolant flows is observed, with variation of the separation efficiency and smaller process flowrate due to loss in up-flow compression	- Valves that isolates the different separation units (especially flash vessels) may be considered and NRVs may be installed - Emergency purge of flash vessel content may be considered being mainly occupied by syngas under pressure
coolant leaks occurs	Contamination of the product stream with consequences on the downstream units depending on both process and utility temperatures (e.g. if loss in CW-HX1 occurs, in REFRIG cooling water freezes)	- Maintenance increased frequency - Flow and pressure sensors
	Poisoning of the reactor catalyst if the leaks involves cooling-water	Same as above - Emergency valves that close the recycle stream and reactor feed when the leak is detected to avoid catalyst poisoning
recycle compressor breaks	Make-up is mixed with recycled stream at lower pressures, decreasing reactor operative pressure and efficiency (with low dynamic the process occurs recursively due to the closed recycle loop)	- By-pass of the broken unit and back-up compressor is necessary - Increased maintenance frequency is suggested
flash vessel leaks (no catastrophic failure)	Release of the material contained at high pressure and low temperatures (-4°C or -10°C): made of flammable species, it may be ignited readily; the contained materials have toxicological concern; the released flashing stream may affect nearby workers	- Frequent maintenance operations for control of external vessel integrity - Implement sensors for detection of releases and loss of pressure - Alert workers and plant emergency operations should begin when the scenario occurs - A back-up vessel can be considered for emergency operations
accidents in flash vessels' nearby units occurs	Chain effects involving the flash may occur, e.g. units that inadvertently hit the vessel creating a leak of a cold stream that may affect safe operation of nearby process units (chain effect propagation)	- Emergency shut-down operations should begin when reactor integrity is questioned or at risk - If possible reactor feed should be stopped and the contained materials discharged

(continued on next page)

(Table A.6, continued from previous page)

Compression Section		
a black out occurs	Loss in compression power is obtained and backflows may be observed from the reactor section towards storage units or electrolysis/ASU units	- NRVs must be installed between process units and valves with automatic closing when loss in power occurs must be installed between different sections
leak of coolant occur	Contamination of the make-up stream with water and consequent poisoning of the reactor catalyst	- Flow and pressure sensors to control the adequate operation of cooling-units with emergency valves to avoid catalyst poisoning - Increased maintenance frequency is suggested
compressor unit breaks	Unit is not capable of increasing stream pressure (reactor feed pressure decreases, with repercussions on reaction kinetic behavior)	- By-pass of the broken unit and back-up compressor is necessary, increased maintenance frequency is suggested
	Unit output flow is blocked (increase in output temperature of previous compressors due to blocked stream that may damage the unit integrity)	Same as above - Temperature control for each compressor to avoid integrity damages
Electrolysis Unit		
a black out occurs	In case of AEL, being necessary a minimum load to avoid cross permeation, a loss in the energy supply determines the stop of unit operations and an increased cross-permeation with formation of an easily-ignitable mixture of pure H_2 and O_2	- Unit operations must be stopped and the contained species purged
unit or pipelines leak	O_2/H_2 releases, with flammability concern (oxidant or easily ignited substance)	- Frequent maintenance and control of gaskets is suggested
overpressure in the unit	Pressure increases both cross-permeation (hazards due to mixture properties) and failure of unit seals/flanges if not designed to support this scenario	- Pressure safety sensors and relief valve must be installed
membrane degrades	O_2/H_2 permeate through the membrane and mix, creating an easily ignitable mixture	- Frequent maintenance and substitution of the membrane when degradation signs are present on its surface - Control of the quality of the outlet streams to detect early possible degradation and proceed with preventive maintenance operations

(continued on next page)

(Table A.6, continued from previous page)

Process Issues		
relief valve opens inadvertently / is not sealed properly when closed	Release of toxic and flammable materials contained in the unit	- Frequent maintenance operations on valve mechanics - Proper sensors to detect unwanted releases or leakages
a black out occurs	Process control is lost	- An emergency generator or accumulation system (in the worst case scenario a fuel cell that uses either the ammonia produced or part of the hydrogen stored) is necessary to satisfy the minimum plant demand to bring operations in a safer condition - Emergency shut-down operations are required - Valves that avoid backflows and that are closed when black-out occurs are necessary (especially between process sections, e.g. electrolysis, storage and compression sections)
pipe leakage occurs	Released stream of gas (at either high or low temperatures) or liquid (at low temperatures) that may affect nearby workers (e.g. frostbite and toxicological concerns), it can lead to fires (easily ignited) and chain effects on nearby unit	- Flow and pressure sensors must be installed to monitor process operations - Maintenance frequency should be increased to avoid such concerns and protective measures (e.g. protective coating paintings) can be considered
seals loose insulation capacity	Release of process streams occurs, with toxicological and flammability concerns; chain-effects on nearby units may occur depending on the release conditions	- More frequent maintenance is suggested - Seals substitutions may be considered after defined operative hours as precaution - Correct seals materials must be chosen depending on the operative conditions
incident involving pipelines occurs	Flammable and toxicological concerns regards the spills from process pipelines since are involved gaseous H_2, N_2 and NH_3 in different purities. If the incidents involves the product stream (liquid ammonia) the release will create a boiling pool and a flashed stream of toxic species.	- An adequate piping location must be chosen to minimize incidents due to chain-effects from other unit failure - Protective elements should be placed near pipelines at height where those may be hit by machinery (e.g. forklift) - Process sensors capable of detecting leakages (e.g. pressure losses or flow decrements) may be installed with emergency operations for isolate a section of the plant and if possible bypass the leak

A.2.3 HAZID Analysis – HAZOP

Table A.7 *Complete HAZOP analysis.*

ID-Number	**Guide-Word**	**Element**	**Deviation**	**Possible Causes**	**Consequences**	**Safeguards**	**Comments**	**Action Required**
Electrolyser – Node Zero								
Design Intent: Production of H_2 and O_2 from water electrolysis								
Operative Conditions: P=20 bar, T=70°C								
0.1	More	Flow	More Flow	- Faulty instrumentation and controls - Faulty valves (excessive opening) -Wrong operation of the electrolysers stacks	- Wrong reactants ratio, variation in rate of reaction and reactor residence times (may damage the catalyst) - Compressor-train capacity varies - Higher hydrogen content in the downstream mixture enhances safety risks in case of loss of containment	- Flow meters	- Redundancy of the control systems and valves - By-pass of most important valves in case of failure - Control and manage downstream compressors to operate the plant properly	- Control redundancy of flow-meters - Safety interlock to avoid reactor irreversible damages (current density) - Maintenance

0.2	Less	Flow	Less Flow	- Faulty instrumentation and controls - Faulty valves (excessive closing) -Failure/Wrong operation of the electrolysers stacks	- Wrong reactants ratio, variation in rate of reaction and residence times in the reactor unit (may damage the catalyst) - Compressor-train capacity varies	- Flow meters	As Deviation *0.1*	As Deviation *0.1*
0.3	No	Flow	No Flow	As Deviation *0.2*	- Wrong reactants ratio for downstream reaction - Compressor-train capacity varies, it may damage compressor units	- Flow meters	As Deviation *0.1*	As Deviation *0.1* - Emergency operation to counter effects of the loss of one fed-stream
0.4	More	Temperature	More Temperature	- Wrong operation of electrolysers units	- Variation of temperature of the downstream flowrate, it may cause compressors damages if not countered properly	- Temperature meters	- Inadequate electrolyser operation may increase temperature of the produced hydrogen stream with consequences on compressor-train operations (considered the operative range of AEL cells)	- Control redundancy

0.5	Less	Temperature	Less Temperature	As Deviation *0.4*	- Variation of temperature of the downstream flowrate, it may cause reaction efficiency variation if not countered properly	- Temperature meters	- Excessive cooling may be performed, reducing temperature in the reactor and causing effects on the kinetic-behavior of the process (consequences on the whole synthesis loop)	As Deviation *0.4*
0.6	More	Temperature	More Temperature	As Deviation *0.4*	- Increase in temperature outside standard boundaries enhances safety hazards due to hydrogen-oxygen handling	- Temperature meters	- Safety hazards associated to hydrogen/oxygen at high temperature interactions with construction materials, seals, etc.	- Temperature control redundancy - Alarm for process variable deviation - Safety interlock to avoid compressors irreversible damages - Maintenance
0.7	More	Pressure	More Pressure	As Deviation *0.4*	- Pressure variation cause excessive compression performed by compression units	- Pressure meters	- Higher pressure changes reaction kinetic behavior - Overpressure may damage process units	As Deviation *0.4* - Process variable deviation alarm

							- Pressure increase may cause damages to installed compressors	- Safety interlock to avoid compressors or heat-exchangers irreversible damages
0.8	Less	Pressure	Less Pressure	As Deviation *0.4*	- Compression provided by the train may not be sufficient, backflow may occur	- Pressure meters	- To respect compressors design limits (temperature and compression ratio) eventually a by-pass towards early compressors may be considered	As Deviation *0.7*
0.9	More	Pressure	More Pressure	As Deviation *0.4*	- Increase in pressure outside standard boundaries enhances safety hazards due to hydrogen-oxygen handling and cross-permeation	- Pressure meters	- Safety hazards associated to hydrogen/oxygen cross-permeation and mixing cannot be neglected: readily ignitable explosive and flammable mixture is obtained	- Pressure control redundancy - Alarm for process variable deviation - Safety interlock to avoid compressors or heat-exchangers

								irreversible damages
0.10	More	Concentration	More Concentration (Oxygen)	- Hydrogen purification section fails	- Increased oxygen content in the hydrogen stream will poison the ammonia catalyst (>5ppm), causing sintering and loss in efficiency	- Inferential Controller	- Additionally to safety concerns related to the hydrogen/oxygen mixture, the presence of oxygen changes the efficiency of the overall plant, decreasing it over time	- Emergency shut-down to avoid catalyst poisoning - Alarm for process variable deviation - Safety interlock to avoid catalysts poisoning
Syngas Mixer – Node One *Design Intent: Mixing of Pure Hydrogen and Nitrogen streams* *Operative Conditions: P=20 bar, T_{max}=150°C*								
1.1	More	Temperature	More Temperature	- Wrong operation of electrolysis/ASU units or of compressors from storage section - Wrong operation of inter-cooling units	As Deviation *0.4*	- Temperature meters	- Inadequate upstream operations that cause increase in temperature may have consequences on compressor-train integrity and operation	- Control redundancy in the syngas section units - Alarm for process variable deviation - Safety interlock to

								avoid compressors irreversible damages - Maintenance
1.2	Less	Temperature	Less Temperature	As Deviation *1.1*	As Deviation *0.5*	- Temperature meters	As Deviation *0.5*	As Deviation *1.1*
1.3	More	Pressure	More Pressure	As Deviation *1.1* - Wrong operation of compression units	As Deviation *0.7*	- Pressure meters	As Deviation *0.7*	As Deviation *1.1*
1.4	Less	Pressure	Less Pressure	As Deviation *1.3*	As Deviation *0.8*	- Pressure meters	- The design pressure fixed may not be achieved by the number of unit used in the process, affecting downstream processes	As Deviation *1.1*
1.5	Reverse	Flow	Reverse Flow	- Faulty valves	- Backflow may affect the upstream sections (ASU, Electrolysis, Storages)	- NRVs	- Proper maintenance	- Install flow control systems and NRVs - Maintenance
1.6	More	Flow	More Flow	As Deviation *0.1* -Wrong operation of the ASU	- Wrong reactants ratio, variation in rate of reaction and residence times in the reactor unit	- Flow meters	- Redundancy of the control systems (inferential controller) and valves	- Install flow control systems - Alarm for process variable deviation

					(may damage the catalyst) - Compressor-train capacity varies		- By-pass of most important valves in case of failure - Control and manage compressors power to operate the plant properly	- Safety interlock to avoid reactor irreversible damages - Maintenance
1.7	Less	Flow	Less Flow	As Deviation *0.2* -Wrong operation of the ASU	As Deviation *1.6*	- Flow meters	As Deviation *1.6*	As Deviation *1.6*
1.8	No	Flow	No Flow	As Deviation *1.7*	- Missing feeds cause irreversible damages to compressors	- Flow meters	As Deviation *1.6* - Emergency closing of non-return valves from the reaction and storage/syngas sections and shut-down of the compressor-train to avoid damages	As Deviation *1.6* - Alarm for process variable deviation - Safety interlock to avoid compressors irreversible damages
1.9	More	Power	More Power	- Compressor unit failure or internals damages - Control-loop failure	As Deviation *0.7*	- Pressure meters	- Additional unit for back-up is advised in case of rupture of the main one	- Maintenance - By-pass of damaged unit

1.10	Less	Power	Less Power	As Deviation *1.9*	As Deviation *1.4*	- Pressure meters	As Deviation *1.9*	As Deviation *1.9*
1.11	No	Power	No Power	As Deviation *1.9* - Damages to the electricity grid or blackout	- Syngas cannot be sent to the reaction section, backflow may occur - If involves only one unit downstream damages to unit may be caused	- Pressure meters - Correct valve positioning and NRVs	- Once power is not provided to compressors, downstream units may end in cavitation; backflows may occur too	- By-pass of broken units - Shut-down operations in case of black-out are necessary

Recycle Mixer – Node Two

Design Intent: Mixing of compressed syngas with recycled syngas from the separation section

Operative Conditions: P=35 bar, T_{max}=45°C

2.1	More	Temperature	More Temperature	As Deviation *1.1* - Variation in separation operative temperature	As Deviation *0.4*	- Temperature meters	As Deviation *1.1*	As Deviation *1.1* - Separation performance control and regulation
2.2	Less	Temperature	Less Temperature	As Deviation *2.1*	As Deviation *0.5*	- Temperature meters	As Deviation *1.2*	As Deviation *2.1*
2.3	More	Pressure	More Pressure	As Deviation *1.3* - Variation in separation section operative pressure	As Deviation *0.7*	- Pressure meters	As Deviation *1.3*	As Deviation *2.1*

2.4	Less	Pressure	Less Pressure	As Deviation *2.3*	As Deviation *0.8*	- Pressure meters	As Deviation *1.4*	As Deviation *2.1*
2.5	Reverse	Flow	Reverse Flow	- Faulty valves - More pressure in “Node Three, Reactor”	- Backflow may affect the separation section and causing over-pressurization As Deviation *1.5*	- NRVs	- Proper maintenance is advised	- Install flow control systems - Install NRVs - Maintenance
2.6	More	Flow	More Flow	- Variation in separation efficiency - Reaction efficiency variation and cascade effect on separation	- Variation in reactor residence times and conversion per-pass - Compressor-train capacity varies	- Flow meters	- Adequate control system to manage and minimize deviations from steady-state - Control and manage compressors power	- Flow control systems redundancy - Maintenance
2.7	Less	Flow	Less Flow	As Deviation *2.6*	As Deviation 2.*6*	- Flow meters	As Deviation *2.6*	As Deviation *2.6*
2.8	No	Flow	No Flow	- Blockage in the recycle stream - Too-low pressure in the recycle stream (backflow may occur)	- Missing feeds cause compression to over-perform (over-pressurize) - Backflow may occur in the recycle stream (see Deviation *2.5*)	- Flow meters - NRVs	As Deviation *2.6*	As Deviation *2.6* - Emergency closing of NRVs from reaction and separation sections - Alarm for process variable deviation

								- Safety interlock to avoid compressors irreversible damages
2.9	More	Power	More Power	As Deviation *1.9*	As Deviation *1.9*	- Pressure meters	As Deviation *1.9*	As Deviation *1.9*
2.10	Less	Power	Less Power	As Deviation *1.10*	As Deviation *1.10*	- Pressure meters	As Deviation *1.10*	As Deviation *1.10*
2.11	No	Power	No Power	As Deviation *1.11*	As Deviation *1.11*	- Pressure meters - Correct valve positioning - NRVs	As Deviation *1.11*	As Deviation *1.11*

Reaction Section – Node Three

Design Intent: Catalytic conversion of syngas into ammonia

Operative Conditions: $P=200$ *or* 300 *bar,* $T_{range}=70\text{-}490°C$

3.1	More	Temperature	More Temperature	- Lack of cooling-capacity upstream - Loss of control on cooling units	- Reaction kinetic is affected - Catalyst temperature threshold (490°C) may be surpassed and the catalyst damaged	- Temperature meters	- Temperature increase may have consequences on compression and reactor integrity	- Temperature control redundancy - Alarm for process variable deviation

								- Safety interlock to avoid reactor irreversible damages
3.2	Less	Temperature	Less Temperature	- Excessive cooling-capacity upstream - Loss of control on cooling units	- Catalyst activation temperature (400°C) may not be reached, affecting rection kinetic	- Temperature meters	As Deviation *0.5*	As Deviation *3.2*
3.3	More	Pressure	More Pressure	- Faulty instrumentation and controls of recycle compressors and upstream multi-stage compressors	- Ammonia productivity is increased, with faster kinetic, higher heat released and temperature increase (Deviation *3.1*)	- Pressure meters	- Higher pressure changes reaction kinetic behavior and separation performances - Overpressure may damage process units	- Pressure control redundancy - Alarm for process variable deviation - Safety interlock to avoid reactor irreversible damages - Maintenance
3.4	Less	Pressure	Less Pressure	As Deviation *3.3*	- Smaller pressure decreases reaction rates, with smaller heat released and	- Pressure meters	As Deviation *1.4*	As Deviation *3.3*

					temperature decrease (see Deviation *3.2*)			
3.5	Reverse	Flow	Reverse Flow	- Faulty Valves - Over-pressurization of the separation section or depressurization of the upstream section	- Species entrained in the reactor flows backwards; reaction continues because of catalyst presence	- Flow meters - NRVs	- Proper maintenance is advised	- Install flow control systems and NRVs - Maintenance
3.6	More	Flow	More Flow	- Variation in separation efficiency due to variation in operative conditions (Deviation *3.15-3.17*) - Wrong productivity of ASU/Electrolysers or excessive flowrate from storage units	- Decrease of per-pass conversion leads to increase in flowrates to be treated downstream - Conversion decrease reduces reactor temperature too (see Deviation *3.2*)	- Flow meters	- Adequate control system to manage and minimize deviations from steady-state - Control and manage compressors power - Maintenance to valves and pneumatic cables for valve control	- Flow control redundancy - Maintenance
3.7	Less	Flow	Less Flow	As Deviation *3.6*	- Per-pass conversion increases with residence time, leading to higher heat release ratios temperature increase (see Deviation *3.1*)	- Flow meters	As Deviation 3.*6*	As Deviation 3.*6*

					- Separation section deviates from steady-state, adjustments are necessary			
3.8	No	Flow	No Flow	As Deviation *3.6* - Blockage of pipelines due to accidents - Failure of valves (excessive closing) - Loss of power (loss of pumping capacity)	- Mixture is entrained in the reactor (assuming no backflow, otherwise see Deviation *3.5*), where the reaction still occurs because of the catalyst: equilibrium is reached - If released heat is not discharged effectively, catalyst sintering occurs	- Flow meters	As Deviation 3.*6*	As Deviation 3.*6* - Alarm for process variable deviation - Safety interlock to avoid reactor irreversible damages and discharge of the reactor content
3.9	More	Power	More Power	As Deviation *1.9*	As Deviation 1.9	- Pressure and flow meters	As Deviation *1.9*	As Deviation *1.9*
3.10	Less	Power	Less Power	As Deviation *1.10*	As Deviation *1.10*	- Pressure and flow meters	As Deviation *1.10*	As Deviation *1.10*
3.11	No	Power	No Power	As Deviation *1.11*	As Deviation *1.11*	- Pressure and flow meters	As Deviation *1.11*	As Deviation *1.11*

						- Correct valve positioning - NRVs		
3.12	Part of	Mixing	Part of Mixing	- Improper deposition during catalyst replacement - Catalyst movement due to external causes during shut-downs and maintenance	- Preferential-paths for the synthesis mixture: residence times are affected, localized effects (e.g. sintering) and overall losses in efficiency occurs (e.g. smaller residence times reduces per-pass conversion)	- Monitor of reactor performance	None	- Proper catalyst placement in the reactor during loading - Safe-zone around the reactor during maintenance operation nearby to avoid hitting the unit
3.13	More	Reaction	More Reaction	- Residence time variation caused by flowrate decrease (see Deviation *3.7*) - Pressure increase (see Deviation *3.3*)	- Increased reaction rate (so conversion) means more heat released; at constant cooling bed temperature increases (Deviation *3.1*)	- Temperature and flow meters	- Rapid controllers dynamics is suggested to avoid excessive temperature variation	As Deviation *3.7* - Suitable controller (dynamics) to minimize temperature effects
3.14	Less	Reaction	Less Reaction	- Residence time variation caused by	- Decrease in bed temperature due to	- Temperature	As Deviation *3.14*	As Deviation *3.6*

				flowrate increase (see Deviation *3.6*) - Pressure decrease (see Deviation *3.4*)	decrease in reaction rate (see Deviation *3.2*)	and flow meters		
3.15	More	Cooling	More Cooling	- Faulty control-loop and valves	- Excessive cooling in the reactor unit (see Deviation *3.2*) - Cold recycle stream (excessive cooling in the separation section) may cause a decrease in reactor temperature (Deviation *3.2*)	- Temperature and flow meters	- Damages to the control loops or valves	- Control-loop redundancy - Maintenance
3.16	Less	Cooling	Less Cooling	As Deviation *3.15*	- Insufficient cooling in reactor (Deviation *3.1*) - Hot recycle stream (less cooling in the separation section) may cause a decrease in reactor temperature (Deviation *3.1*)	- Temperature and flow meters	- Damages to the control loops or valves - Faulty pumps not capable of satisfy the cooling demand	As Deviation *3.15*
3.17	No	Cooling	No Cooling	As Deviation *3.15* - Blockage of pipelines of coolant - Coolant upstream damages/failure	As Deviation *3.16*	- Temperature and flow meters	None	- Emergency shut down of the plant procedures - Alarms for workers

3.18	More	Concentration	More (Ammonia) Concentration	- Variation in reaction rate (see Deviation *3.13*) - Variation in separation efficiency	- Decrease of single-pass conversion and of heat production (reactor temperature decrease) - Higer separation is required and heat-exchangers should handle such situation	- Flowrate and temperature meters	- Reactor temperature is controlled by internal heat-exchangers, therefore their action must handle the fluctuation in the feed composition - In case of separation inferential controllers should be considered to vary the heat duty and recover the liquid product	- Control redundancy - Maintenance
3.19	Less	Concentration	Less (Ammonia) Concentration	- Variation in reaction rate (see Deviation *3.14*) - Variation in separation efficiency	- Increase of single-pass conversion and heat production (temperature increase) - Smaller separation is required and heat-exchangers should handle such situation	- Flowrate and temperature meters	As Deviation *3.18*	- Control redundancy

Ammonia Purification – Node Four

Design Intent: Recovery of pure ammonia in liquid phase and recycle of unreacted syngas

Operative Conditions: P_{range} *=200 or 300-35 bar,* $T_{average}$*=-10 or -5°C*

4.1	Reverse	Flow	Reverse Flow	As Deviation *3.5*	As Deviation *3.5*	- Flow meters - NRVs	As Deviation *3.5*	As Deviation *3.5*

4.2	More	Temperature	More Temperature	- Lack of cooling-capacity in the separation section	- Separation is inefficient: ammonia purity is not on specification at the operative temperature (at constant pressure)	- Temperature and pressure meters	- A variation in temperature at constant pressure leads to a variation in flashing efficiency - Chain effect on temperature of the recycle must be considered (see Deviation *2.1*)	- Control redundancy - Maintenance
4.3	Less	Temperature	Less Temperature	- Excessive cooling in the separation section	- Inefficient separation: ammonia purity is above specification at the operative temperature	- Temperature and pressure meters	As Deviation *4.2* (reference: Deviation 2.*2*)	As Deviation *4.1*
4.4	More	Pressure	More Pressure	- Faulty lamination valve or control	- Ammonia purity decreases, has more syngas is entrained - Recycle pressure is high for the compressor unit	- Pressure meters	- Recycle stream is smaller	- Maintenance
4.5	Less	Pressure	Less Pressure	- Faulty lamination valve or control	- Ammonia purity increases - Recycle pressure is low for the compressor unit, (Deviation *2.4*)	- Pressure meters	- Recycle stream is larger, with more ammonia (see Deviation *3.18*)	- Maintenance

Process Issues – General Safety Concerns								
5.1	No	Control or Measure	No Control or Measure	- Faulty process server - Blackout - Breakage of data or pneumatic cables	- Loss of control of process operations	- Back-up generators - Valve emergency positioning	- Generators - Blackout: back-up generators to operate properly emergency shut-down operations - Correct choice of valves for safe operations in case of emergency - Emergency-situation handling capability and simulations	- Install emergency-generators - Operators emergency courses for handling of critical situations