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Title

Modulization of hydrogen storage in ammonia's form via photovoltaic system

Presentedby: **supervised by:**

Ouadah TsabetRaounak   Supervisor:PrKhellaf Abdellah

Niri Maya   Co-supervisor: Pr Naceur Wahib

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Abstract

Nowadays researchers are tending to use ammonia produced from renewable energy as a way to transport and store clean hydrogen, due to its advantages such as high density of hydrogen by weight and safety. In this work, we have used a system that consists of Haber-Bosch to produce ammonia and a proton exchange membrane electrolysis for hydrogen production in addition to a photovoltaic system for energy supply. and we have used MATLAB Simulink for modulization to compute the amount of hydrogen and nitrogen and the energy needed for the system, and CHEMCAD to compare the obtainedamount of hydrogen and nitrogen to that obtained from MATLAB Simulink. The results of this study indicate that for 1000(ton/h) of ammonia we obtained 411.31(ton/h) of nitrogen and 177.56(ton/h) of hydrogen and the amount of water that the proton exchange membrane electrolysis needs is 1.9531e+06(ton/h) in addition to the energy required by it 7.8915e+06(Gwh) and total energy output from the photovoltaic field 8.6261e+06 (Gwh) furthermore, the efficiency of electrolysis, when it increases, does effect the energy of electrolysis and total energy output from the photovoltaic field by decreasing it.

we found out that Adrar is the best location for installing photovoltaic panels due to its smallest peak power peak power= 1135013.16 KW_p.

keywords: ammonia, hydrogen, photovoltaic system, renewable energy, electrolysis, Haber-Bosch process

Résumé

De nos jours, les chercheurs ont tendance à utiliser l'ammoniac produit à partir d'énergies renouvelables comme moyen de transporter et de stocker de l'hydrogène propre, en raison de ses avantages tels que la densité élevée d'hydrogène en poids et la sécurité. Dans ce travail, nous avons utilisé un système composé de Haber-Bosch pour produire de l'ammoniac et une électrolyse à membrane échangeuse de protons pour la production d'hydrogène en plus d'un système photovoltaïque pour l'approvisionnement en énergie et nous avons utilisé pour la modulation MATLAB Simulink pour calculer la quantité d'hydrogène et d'azote et l'énergie nécessaire au système, et à CHEMCAD pour comparer la quantité d'hydrogène et d'azote que nous avons obtenue à partir de celui-ci et de MATLAB Simulink. Les résultats de cette étude indiquent que pour 1000 tonnes d'ammoniac, nous avons obtenu 411,31 tonnes d'azote et 177,56 tonnes d'hydrogène et la quantité d'eau dont l'électrolyse à membrane échangeuse de protons a besoin est de

1,9531e + 06 (tonne / h) en plus de l'énergie requise par celle-ci 7,8915e + 06 (Gwh) et de la production totale d'énergie du champ photovoltaïque 8,6261e + 06 (Gwh) de plus, l'efficacité de l'électrolyse lorsqu'elle augmente affecte l'énergie de l'électrolyse et la production totale d'énergie du champ photovoltaïque en la diminuant.

Nous avons découvert qu'Adrar est le meilleur endroit pour installer des panneaux photovoltaïques en raison de sa plus petite puissance de crête = 1135013,16 KWp.

Mots-clés : ammoniac, hydrogène, système photovoltaïque, énergie renouvelable, électrolyse, procédé Haber-Bosch.

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الملخص

يتجه الباحثون في الوقت الحاضر إلى إستخدام الأمونيا المنتجة من الطاقات المتجددة كوسيلة لنقل وتخزين الهيدروجين النظيف،نظرا لمزاياها مثل الكثافة العالية للهيدروجين من حيث الوزن والأمان. وقدإستخدمنافي هذا العمل نظاما يتكون من هابر-بوش لإنتاج الأمونيا وغشاء التبادل البروتوني للتحلل الكهربائي لإنتاج الهيدروجين بالإضافة إلى نظام كهروضوئي لإمداد الطاقة،وإستخدمنا في التعديل نظام ماتلابسيمولينكلحساب كمية الهيدروجين والنتروجين والطاقة اللازمة للنظام، كما إستخدمنا نظام كامكاد للمقارنة بين كمية الهيدروجين والنيتروجين التي حصلنا عليها منه ومن نظام ماتلابسيمولينك. تشير نتائج هذه الدراسة إلى إنه مقابل 1000(طن /ساعة) من الأمونيا حصلنا على 411.31(طن/ساعة) من النيتروجين و177.56 (طن /ساعة) من الهيدروجين وكمية الماء التي يحتاجها التحليل الكهربائي لغشاء التبادل البروتوني هي $1.9531*10^6$(طن /ساعة) بالإضافة إلى$8.915*10^6$(جيغا واط ساعة) من الطاقة التي يحتاجها وإجمالي الطاقة الناتجة من الحقل الكهروضوئي هي $8.6261*10^6$ (جيغا واط ساعة) علاوة على ذلك، فإن كفاءة التحليل الكهربائي عندما تزداد تؤثر على طاقة التحليل الكهربائي وإجمالي الطاقة الناتجة من الحقل الكهروضوئي بتناقصها.

لقد وجدنا أدرار هي أفضل موقع لتركيب الألواح الكهروضوئية نظرا لقلة ذروة الطاقة القصوى والتي تقدر ب $1.135013*10^{16}$ (كيلو واط /ساعة).

الكلمات الرئيسية:الأمونيا،الهيدروجين، النظام الكهروضوئي، الطاقة المتجددة، المحلل الكهربائي،نظام هابر-بوش.

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Nomenclatures

ATR:auto-thermal reforming

EEL: energy of electrolysis

Eg: energy of gas separation

Ehb: energy of Haber-Bosh

Er: energy of reaction

Es: energy of storage

ETPV: total energy output of photovoltaic system

FLH: full load hour

PPT: peak power

PV: photovoltaic system

SMR: steam methane reforming

General introduction

Hydrogen has been known for over 200 years. In the early sixteenth century, Paracelsus from Switzerland observed the formation of gas during the reaction between sulfuric acid and iron. [1] Later, in 1761, Robert Boyle successfully produced hydrogen by reacting iron filings with dilute acids.[2] In 1766, Henry Cavendish identified hydrogen as a flammable gas [3]. He demonstrated that burning hydrogen produces water, which led to the name hydrogen, derived from "hydro-gen," meaning "water-former"[4]

In the realm of sustainable energy, the quest for efficient energy storage solutions has taken center stage. Hydrogen has gained recognition for its potential to store energy effectively and contribute significantly to decarbonization efforts. However, challenges such as its low energy density by volume (9 MJ/L), high flammability, and susceptibility to leakage over, have catalyzed a shift towards exploring alternatives that not only mitigate these drawbacks but also offer enhanced efficiency and safety. Ammonia has emerged as a compelling alternative due to its higher energy density, along with easier handling and transportation characteristics.

Ammonia offers more than just its superior energy density which significantly reduces storage volume requirements compared to hydrogen, but also in its lower flammability and reduced leakage risks over time. These advantages position ammonia as a compelling contender for energy storage, especially in scenarios where space and safety considerations are paramount.

This thesis delves into the viability of utilizing ammonia for a hydrogen storage, we have worked on a system that consist of Haber-Bosh for ammonia's production and Proton Exchange Membrane electrolysis for hydrogen production furthermore a photovoltaic system for energy supply of our system.

By MATLAB Simulink, we have calculated the amount of hydrogen and nitrogen needs by fixing ammonia's generation rate, and for the electrolysis we have calculated the water needs, furthermore, we determined all the energies that our system needs such as energy of electrolysis (EEL), energy of photovoltaic system (ETPV) and energy of total peak power (PPT). And by CHEMCAD, we have computed the amount of ammonia for different amount of hydrogen and nitrogen than we compared it with results of MATLAB Simulink

The objective of our study is to make ammonia as an alternative for green hydrogen storage.

This work has been organized in three chapters for bibliography, then method and techniques, results and discussions, and finally a conclusion.

The first chapter talks about ammonia production proprieties, different types of ammonia and different processes to produce it.

The second chapter is a state of- the art about hydrogen production by PEM electrolysis via PV system.

The third chapter is about different methods of hydrogen storage and transportation.

Methods and technique we have shown the definition of equipment and software that we used to achieve our objective.

Finally result and discussion we have made different graphs for different parameters and we discussed them.

We have finished by a general conclusion that consist only of therelevantresults.

CHAPTER I

AMMONIA PRODUCTION

1.1. Introduction:

Ammonia, an odoriferous, colorless alkaline compound [5] and because of its distinctive odor, ammonia leaks can be easily detected. It consists of one nitrogen atom and three hydrogen atoms. Its production can be accomplished through traditional or renewable means, rendering it a versatile medium for storing and transporting hydrogen. Notably, when liquefied, ammonia contains approximately 48% more hydrogen by volume than hydrogen itself, making its transportation significantly safer. Moreover, its utilization results in zero carbon dioxide emissions, making it entirely carbon-free. Its range of applications is vast, serving as a fuel, refrigerant, hydrogen carrier, fertilizer, feedstock, cleaning agent, and more. Furthermore, it emerges as a promising fuel source for engines, gas turbines power generators, and burners [6]. Recently, numerous options for obtaining green ammonia have emerged, including the utilization of solar energy. Moreover, methods such as green Haber-Bosch and electrochemical processes offer alternative means of production.

1.2. Ammonia proprieties:

1.2.1. Molecular properties of ammonia:

The nitrogen atom has seven shell electrons corresponding to its nuclear charge number. One electron pair resides in the ground state 1s (K shell), and the remaining five electrons are spread across four orbitals within the principal quantum number 2 (L shell). Among these, one electron pair occupies the 2s level, and the three unpaired electrons each occupy one of the remaining three orbitals: 2px, 2py, 2pz. These unpaired electrons can form electron-pair bonds with the 1s electron of three hydrogen atoms. As a result, the three half-occupied orbitals of the L shell are nearly fully occupied, leading to the formation of an octet reminiscent of neon, consistent with the octet theory proposed by Lewis and Langmuir.[7]

$$:\overset{.}{\underset{.}{N}}\cdot \; + \; 3 \; H\cdot \; \longrightarrow \; \overset{\overset{..}{H}}{\underset{\underset{..}{H}}{:N:H}}$$

1.2.2 Physical properties:

Ammonia (NH_3) exhibits several distinct physical properties. It is a colorless gas with a pungent odor, highly soluble in water to form an alkaline solution. Ammonia has a relatively low boiling point (-33.34°C) and freezes into a crystalline solid at -77.7°C. It is

less dense than air, with a density of approximately 0.73 kg/m^3 at standard conditions.

Table 1. Detailed physical characteristics of ammonia [34,35].

| Properties	Unit	Value
Molar mass	g/mol	17.031
Density at STP	kg/m^3	0.769
Melting point	°C	−77.73
Boiling point at 100 kPa	°C	−33.4
Vapor pressure at 20 °C	kPa	858
Heat of evaporation	MJ/kg	1.371
Auto ignition temperature	°C	650
Critical temperature	°C	132.4
Critical pressure	MPa	11.28
Viscosity at 25 °C	µPa·s	10.07
Heat capacity at constant pressure (101.325 kPa, 15 °C)	kJ/mol·°C	0.037
Heat capacity at constant volume (101.325 kPa, 15 °C)	kJ/mol·°C	0.028
Heat of combustion	MJ/L	11.2
Thermal conductivity	mW/m·°C	22.19
Critical density	g/mL	0.24
Condensation pressure at 25 °C	MPa	0.99
Flammability limit (equivalence ratio)	–	0.63–1.4
Adiabatic flame temperature	°C	1800
Max. laminar burning velocity	m/s	0.07

Figure 1.1: Physical properties of ammonia. [8]

1.3. Why green ammonia:

Ammonia is also being considered an energy storage media and a source of hydrogen as the hydrogen content in liquid ammonia is 17.6 wt% compared with 12.5 wt% in methanol [9,10-12]. compared to compressed hydrogen (5.0 MJ/L at 70.0 MPa and 25∘C) and liquid hydrogen (8.49 MJ/L), liquid ammonia has a higher volumetric energy density (10.5 MJ/L) [74] ·Ammonia also has a higher heat of combustion (11.2 MJ/L) than liquid H_2(8.58 MJ/L) .Gaseous NH_3 can dissipate in the atmosphere relate Techno-economic analyses have shown that ammonia is more promising than traditional fuels, including gasoline, natural gas, liquefied petroleum gas (LPG), methanol, and H_2, owing to the lack of CO_2emissions.ReleaseNH_3 also has a lower risk of fire than that of H_2 because its auto-ignition temperature is higher (650 and 535 ∘C, respectively) [13].

1.4. Classification of ammonia:

There are three classifications for CO_2 emissions established based on the process of ammonia production. There are no limitations on the exact amount of carbon dioxide released in this method [14] " for instance, in producing grey ammonia through hydrocarbons as well, it is a major application. Blue ammonia follows to produce ammonium via a similar route as that used by grey ammonia; however, it reduces CO_2 emissions by using carbon capture and storage (CCS) technologies. Finally, green ammonia uses renewable energy sources to produce hydrogen through water electrolysis." [15]. This is ammonia's reaction down below:

$$3H_2+ N_2 \rightarrow 2\, NH_3$$
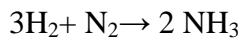
1.4.1. Grey ammonia:

In this process, it has been reported that the energy consumed is very huge about 8 MWh t The majority of energy usage during this process is for the creation of hydrogen gas by steam reforming of methane, and it`s responsible for 90% of the carbon emissions. In ammonia production. reforming other fossil fuels such as coal with steam led us to release a higher amount of carbon dioxide than that of natural gas.[16]
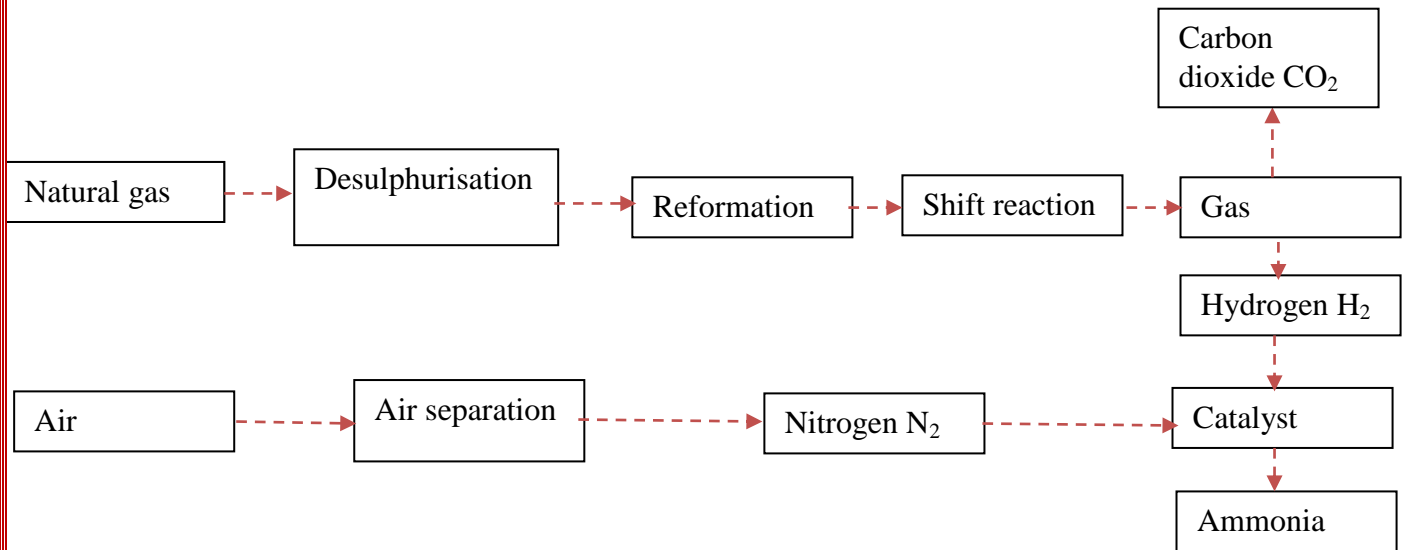
Figure 1.2: Grey ammonia production

1.4.2. Blue ammonia:

The emission of carbon dioxide gas from grey ammonia plants has had a very negative impact on the climate, causing scientists to consider storing and reusing it, this process produced us blue ammonia. Blue ammonia produces by different process like steam methane reforming (SMR) and auto-thermal reforming (ATR) in the SMR process "The two important medications are that (i) the process CO_2 is stored rather than vented and (ii) a post combustion CO_2 capture unit is fitted in the flue gas stream of the firing".[17]
The majority of research on blue ammonia has centered around the advancement of novel reforming techniques aimed at decreasing CO_2 emissions.
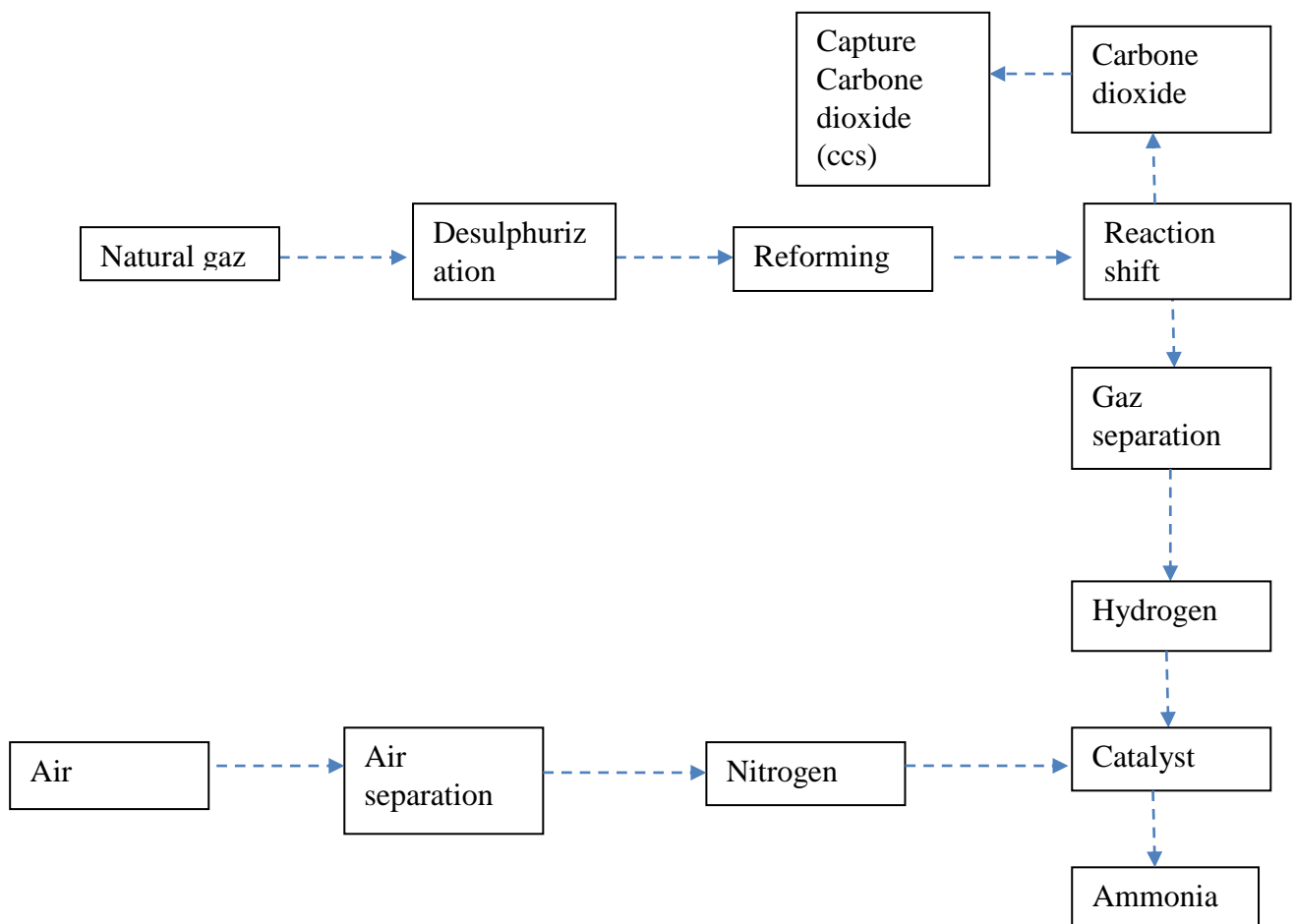
Figure1.3: Blue ammonia production

1.4.3. Green ammonia:

Green ammonia is created by using renewable electricity to split water into hydrogen and oxygen, and extracting nitrogen from the air. The hydrogen and nitrogen are then combined in a Haber-Bosch reactor, making the process environmentally friendly.

Figure 1.4: Green ammonia production

1.4.4. Green ammonia production process:

Recently, an increasing number of companies have been dedicating investments to green ammonia production. This trend aims to explore novel technologies, enhancing efficiency, and competitiveness compared to traditional p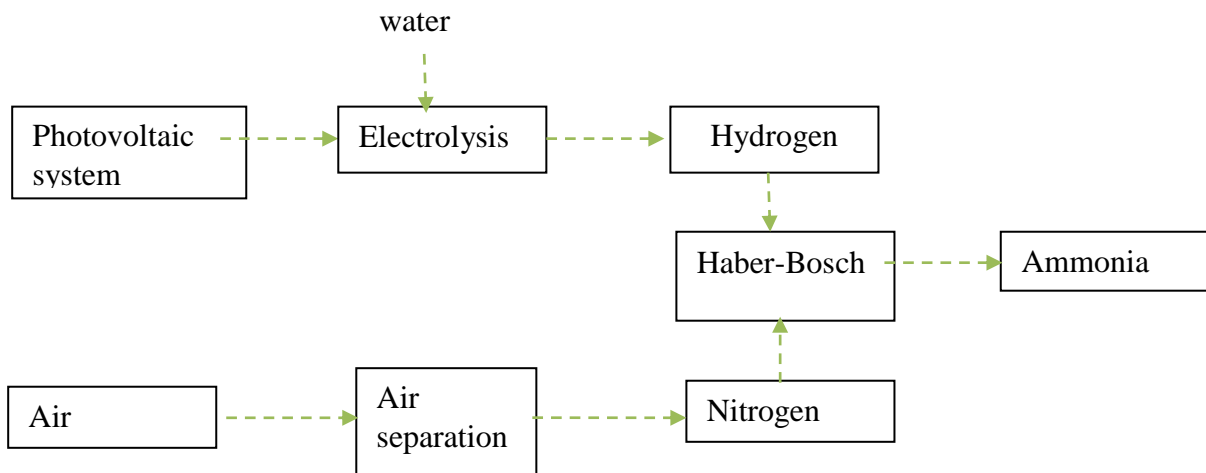roduction methods. As the landscape of energy evolves, green ammonia emerges as a pivotal player in this transition. Its role extends to facilitating the integration of renewable energy into the grid and curbing the carbon footprint associated with transportation and industrial processes.[18]

1.4.4.a. Green Haber-Bosch process:

The most prevalent method of ammonia production currently is the large-scale Haber-Bosch process, which operates under intense reaction conditions. The process typically involves the ammonia converter functioning at temperatures ranging from 400 to 500°C and pressures exceeding 150-200 ATM [7]. Due to its energy-intensive nature, this process consumes approximately 2% of the world's total energy production [5]. Green ammonia production seeks to revolutionize this process by exclusively utilizing renewable electricity from sources like solar, wind, and hydro power. The production of green ammonia typically involves two main phases. Firstly, hydrogen production via photovoltaic-electrolysis yields pure hydrogen. Subsequently, in the second phase, the obtained hydrogen and nitrogen from ambient air are injected into the Haber-Bosch reactor. However, Haber–Bosch process plants have some constraints imposed due to design [19,20] and operation limitations,[21] which originate from requirements of autothermic operation of the reactor system, catalyst type, feed content and composition. Additionally, due to the relatively low conversion rates (ranging from 25 to 35%), unreacted reactants must undergo separation through condensation and subsequent recycling. Recycling is crucial for maximizing the effective utilization of the feed gas. Consequently, the flow rate of recycled reactants, also known as the recycle load, is several times higher than that of the feed flow rate. This recycling process typically results in overall conversions ranging from 97% to 99%. [22,23]
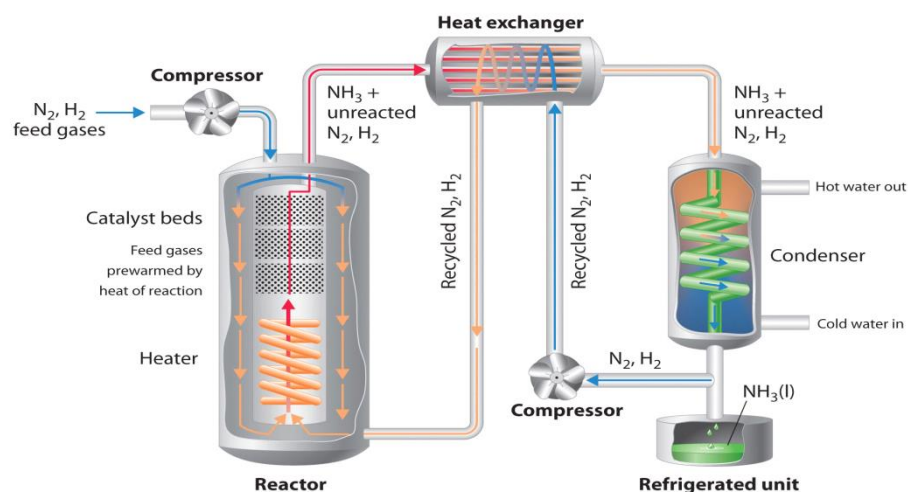
Figure 1.5: Haber-Bosh process [24]

1.4: Electrochemical ammonia synthesis:

Electrochemical synthesis of ammonia holds promise as a more sustainable and energy-efficient alternative to traditional Haber-Bosch synthesis this process can be applied at ambient conditions (temperature, pressure)[25-27], particularly when powered by renewable energy sources, to reduce carbon dioxide emissions[28]. "In the electrochemical cell nitrogen is fed to the cathode where the nitrogen reduction reaction takes place while water is fed to anode and oxidized to oxygen" [26,27]. The electrolyte that currently used is Liquid electrolytes because it can operate under atmospheric temperature and pressure [29] However, further research and development are needed to overcome technical challenges and make this technology at large scale. The reaction at cathode and anode are basically reversible.

Reduction: $N_2 + 6\,H^+ + 6\,e^- \rightleftharpoons 2\,NH_3$

Oxidation: $3\,H_2 \rightleftharpoons 6\,H^+ + 6\,e^-$
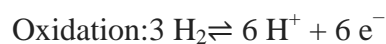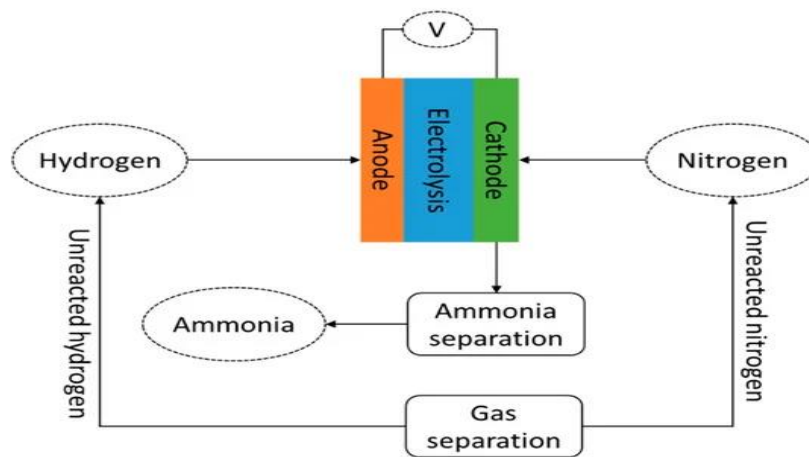
Figure1.6: Schematic diagram of electrochemical ammonia synthesis.[30]

1.5. State-of-the-Art:

Ammonia possesses several favorable traits that makes it a potential candidate for hydrogen storage more than hydrogen itself. And there are three types of ammonia one ofitis green ammonia which is considered as an energy carrier and a good alternative for fossil fuels. it's produced by utilizing renewable energy sources for water electrolysis and air separation unit for H_2 and N_2 production combining them in Haber-Bosch, to avoid the CO_2 emissions.

Firstly, scientists conducted numerous studies to produce green ammonia, and from these studies we have a study from Chile [31] they have done research about the production of green ammonia and its export to Japan objective of this study is to conduct a technical and economic evaluation of producing ammonia through electrolysis using renewable energy sources such as solar, wind, and hydraulic power. A sensitivity analysis was conducted on key parameters including plant operating hours, the size of the ammonia synthesis plant (correlated with the capacity of the electrolysis plant in MW), electricity price, electrolysis cost, Haber-Bosch cycle cost, and ammonia sales price. This study focuses on producing green ammonia using hydrogen generated by a Siemens electrolysis powered by solar energy. The electrolysis consumes 15 liters of untreated water to produce 2,687 kg of hydrogen and 21,582 kg of oxygen per hour, both at 35 bar pressure and high purities. Additionally, it generates surplus thermal energy of 60 MWh, which exits the unit as water at 65°C. The hydrogen is then combined with nitrogen from a cryogenic system in the Haber-Bosch process, requiring 5 MWh of electricity for compression and air separation. The unit utilizes 2,687 kg of hydrogen per hour to produce 15,000 kg of liquid ammonia at 18 bar pressure and high purity. Finally, the produced ammonia is stored in a Lapesa brand

stainless-steel tank at the generation pressure of 18 bar, with a capacity of 30,000 tons, allowing for approximately 2,000 hours of full system operation. The result was obtained by this study is by an optimization procedure was carried out to minimize the Net Present Value (NPV) and determine the most suitable electrolysis stack size for a green ammonia production facility. The NPV for the base scenario amounted to $77,414,525, with a payback period of 7.62 years. Sensitivity analysis highlighted that the primary influencers on NPV were the ammonia synthesis plant size and electricity pricing. Moreover, a triangular probability distribution of specific variables indicated a 95% confidence level, with a 76.1% likelihood of positive NPV occurrence. Through optimization, a stack dimension of 164.21 MW was identified as the most favorable, considering its impact on operational expenditure (OPEX), capital expenditure (CAPEX), and investment risk.

So lately, to avoid damaging the non-flexible Haber Bosch (HB) catalytic reactor there is challenge that face green ammonia production which is the energy intermittency and unpredictability of renewable energy sources while ensuring a steady state in this r research ,[32] in this research , they have selected the technologies for the system which is Photovoltaic (PV), Wind Turbine (WT) and Concentrated Solar Power (CSP) for RE sources; Lithium-ion batteries and Molten salt for energy storage; Proton Exchange Membrane (PEM) for Electrolysis; Pressure Swing Adsorption (PSA) for Air Separation Unit (ASU) are injected into storage tanks and ready to be processed in the HB reactor and the conventional HB technology for the ammonia synthesis reactor. furthermore, using Energy Storage System (ESS) for H-B to ensure its steady state production mode since it's the only non-flexible process in the system the authors selected the site based on the solar and wind resource map in Morocco. The System Advisor Model (SAM) software was selected to model the system, offering both graphical and C++ script interfaces for designing, modeling, and simulating the entire green ammonia plant in addition studies have identified two main Key Performance Indicators (KPIs): HB Load Factor (LF) and Levelized Cost of Ammonia (LCOA), this work was done considering 3 different scenarios: PV/Battery, PV/Wind/Battery and PV/CSP to determine the optimal configuration of the installation. the RE sources were oversized by a multiplier factor 2.2 During the early morning and night periods, the surplus energy generated can sufficiently charge the Energy Storage System (ESS), enabling it to power the HB process. The findings from the simulation demonstrate that the PV/Battery scenario emerged as the most optimal renewable energy setup for powering the 4t/d Green Ammonia plant, achieving the highest calculated capacity factor (97.9%). Andit indicates that the electrolysis is

responsible for the majority of electricity consumption in the plant, accounting for as much as 83% in large-scale facilities, whereas the ASU and HB collectively contribute only 17% to the overall power usage. The selected electrolysis for this work was the PEM technology due to its high flexibility and low response time, it is very energy intensive and has the highest SEC value (6.6 kWh/Nm3H2).to assess the economic performance of the plant, the LCOA metric was used, the findings reveal that the most advantageous investment is in the PV/Battery scenario, boasting the lowest (LCOA) at $774 per ton. when HB LF (%) is high which lead to yield increase therefore the most efficient configuration identified involves a 6 MW photovoltaic (PV) system coupled with 11 MWh of lithium-ion battery storage. with a LCOA of 774 $/tNH3 we can control the LCOA by reducing the CAPEX of the battery the authors say that reducing 50% of this parameter can decrease the cost under the 500 $/t threshold.

To improve the velocity of ammonia reaction Extensive research has been conducted over the past century to develop effective catalysts for this process [33]. to reduce operating temperature and pressure while improving reactant conversion to ammonia and they have emphasized the importance of catalysts, because they have played a vital role in the Haber-Bosch process, driving efficient ammonia production. These alternative catalysts such as including electrode, hydride, amide, perovskite oxide hydride/oxynitride hydride, nitride, and oxide promoted metals such as Fe, Co, offer potential advantages over conventional ones, particularly in terms of efficiency and sustainability.

In conclusion, green ammonia has many distinctive properties that make it the most important energy carrier in these years these studies show that we can produce ammonia with renewable energies like solar and wind by Haber –Bosch process with zero CO_2gas emissions but we have many challenges such as the expensive cost for production compared with conventional fossil fuel-based process and the complex conditions such as higher pressure 200bar and temperature 450°C.

CHAPTRE Ⅱ

HYDROGEN PRODUCTION VIA PHOTOVOLTAIC SYSTEM

2.1. State of the art:

Decarbonizing the planet stands as a paramount objective for countries worldwide by 2050, aimed at mitigating the impacts of climate change. The process involves various methods of hydrogen production, categorized into gray, blue, and green hydrogen [34]. Gray hydrogen is derived from coal or natural gas through chemical reactions [35], while blue hydrogen utilizes Carbon Capture and Storage (CCS) to trap greenhouse gases during natural gas conversion [36]. On the other hand, green hydrogen, produced via water electrolysis, emerges as a pivotal solution for global decarbonization. Hydrogen, an abundant element in the universe, serves as a promising environmentally friendly renewable energy carrier. It finds utility as a feedstock in chemical and petrochemical industries, facilitating the production of ammonia and synthetic fuels. Consequently, there's a growing interest in green hydrogen production through electrolysis, especially for large-scale implementation in renewable energy-based power plants, industrial, and transportation applications. Various electrolysis methods exist, with alkaline, PEM, and solid oxide (SOEC) being common. PEM electrolysis offers advantages like high current density, efficiency, proton conductivity (0.1 ± 0.02 S cm^1), lower thickness (R20–300 mm), and suitability for high-pressure operations, making it a preferred choice.[37]

2.1.2. Photovoltaic system:

Solar energy, which is clean, renewable, and abundant, can be harnessed to supply power to off-grid homes and businesses. A promising approach to obtaining clean hydrogen involves combining a photovoltaic system with an electrolysis, utilizing excess electrical energy to produce hydrogen.

In their study [38] on the performance analysis and optimization of standalone solar PV systems for green hydrogen production, aimed to evaluate system performance and develop optimization techniques to minimize global annual loss (GAL) while maximizing green hydrogen production. The hybrid power system under investigation comprised an inverter, a load from a manufacturing application, solar modules, and batteries for short- and long-term storage (PV/BT/PEMWE). Primarily, energy generation was attributed to the PV module, supplemented by battery backup, with surplus energy being converted into green hydrogen via the PEM electrolysis. The findings indicated that optimal system performance, achieving a minimum global annual loss (GAL) and a hydrogen production

rate (HPR) of 10.97% and 40,864.70 m3, respectively, was attained with a combination of 647 solar photovoltaic cells (NPV), 120 batteries (NBT), and a parallel-series electrolysis cell configuration of 12/15 (Np/Ns). These parameters facilitated the most efficient and desirable operational conditions.

In this research [39] have discussed about the best module for hydrogen production via solar energy in Saudi Arabia, they have done experiments comparing proton exchange membrane (PEM) electrolysis powered by either concentrated (750 sun) InGaP/GaAs/Ge-based or non-concentrated (1 sun) Si-based photovoltaic (PV) modules they have found that ultra-high concentrated (UHC) photovoltaic (PV) module connected in series stands out as the best module for hydrogen production. This module is highlighted as being more beneficial compared to silicon (Si)-based PV modules when it comes to obtaining higher production and solar-to-hydrogen STH efficiency per unit area. the researcherssuggest that using the UHC PV module in conjunction with electrolysis systems leads to higher hydrogen production rates and greater efficiency (~28–30% efficiency). in converting solar energy into hydrogen gas.

2.1.3. Hydrogen production by PEM electrolysis:

Several authors have previously investigated and explained the production of green hydrogen from PEM water electrolysis.

conducted a study on the potential for green hydrogen production in Jordan [40], focusing on Aqaba in the south of the country. The research employed two types of electrolysis, namely alkaline (ALK) and proton exchange membrane (PEM), integrated with PV systems to fulfill the energy requirements of these electrolyzes and the compressor. Two models were developed using MATLAB for each electrolysis type to assess the required PV solar system capacity and investment costs from 2022 to 2025, factoring in the technological learning curves. Furthermore, a techno-economic model was established to evaluate the feasibility of utilizing this technology, comparing the utilization of PV systems and grid electricity for hydrogen production. The decision variable for this model, derived from the MATLAB code, was the area of the PV system required to generate 1000 moles/s of hydrogen. In 2022, the ALK electrolyzes system consumed 16.381 MW, decreasing to 14.218 MW by 2025, while the PEM electrolyzes consumed 15.505 MW in 2022, decreasing to 14.002 MW by 2025. The PEM electrolyzes demonstrated a notably higher production rate compared to ALK, reaching a maximum of 1783 kg/s on the same day (N = 261). The levelized cost of hydrogen (LCOH) was calculated to be 4.42 USD/kg

and 3.13 USD/kg when utilizing electricity from the grid and PV systems, respectively. The payback period for covering the capital cost of the PV system was estimated at 11 years within the project's lifespan, with a net present value (NPV) of USD 441.95 million. Additionally, the adoption of PV systems led to a reduction of 3042 tons/year in CO_2 emissions compared to grid electricity generated from fossil fuels, resulting in annual savings of USD 120,135 based on an assumed value of 39 USD/ton of CO_2.

In a similar vein,[41] investigated the potential for producing solar hydrogen using renewable resources in the Oran region (Latitude: 35°42'N, Longitude: 0°38'W) in Algeria. Their study utilized a precise monthly solar radiation mathematical model, and they opted for the PEM electrolysis due to its efficiency, longevity, and strong performance. The findings indicate that annual hydrogen production ranges from 1.94×105 to 5.50×105 kg per 1 km2 surface area. Moreover, the cost of hydrogen production from solar resources in Oran proves to be competitive, with the price of 1 kg of hydrogen estimated at \$3.53.

In [42] explored the potential of low-temperature electrolysis using polymer electrolyte membranes (PEM) in facilitating the transition to hydrogen energy. Their work focused on evaluating the performance of a proton exchange membrane in the water electrolysis process under room temperature and atmospheric pressure conditions. The catalyst-coated membrane (CCM) utilized for the electrolysis tests was a commercial Nafion™ 117-based proton exchange membrane sourced from Quintech. This membrane featured 1 mg cm^{-2} of platinum (Pt) on the cathode side and 2 mg cm^{-2} of iridium (Ir) with carbon on the anode side, denoted as Ir-Pt-CCM of Nafion™ 117.

For the cathode side, two different electrodes were employed: the titanium electrode (Titanium-E) with an Ohmic resistance of 0.2 Ohm, and the carbon electrode (Carbon-E) with an Ohmic resistance of 1.4 Ohm. The electrolysis cell, provided by DeltaES.r.l., was compact with dimensions of $87 \times 87 \times 15$ mm and weighed approximately 200 g. The effective area of the Ir-Pt-Nafion™ 117 CCM was 36 cm^2, in contact with two porous titanium electrodes serving as the anode and cathode, respectively.

The study demonstrated that the 36 cm^2 active area of Ir-Pt-Nafion™ 117 CCM yielded a hydrogen production rate of 0.024 g min^{-1} at the highest current density of 1.1 A cm^{-2}, achieving an energy efficiency of 20%. The maximum energy efficiency of 75% was attained at the lowest current density of 0.03 A cm^{-2}, while the Faradaic efficiency

rangedfrom 88% to 98%. The peak hydrogen production reached approximately 0.02 g min^{-1} at a current density of 1.1 A cm^{-2} and a power of around 280 W.

Furthermore,[43] they have done research to analyze the techno-economic potential of waste heat recovery from multi-MW scale green hydrogen production. Specifically, the researchers conducted a study on a 10 MW proton exchange membrane electrolysis process integrated with a heat recovery system utilizing an organic Rankine cycle (ORC) to facilitate hydrogen compression. Their investigation focused on the technical outcomes, indicating that the electrolysis's first-law efficiency surged from 71.4% to a remarkable 98% when waste heat recovery was combined with the ORC. This configuration enabled the ORC to generate sufficient power for compressing hydrogen from the electrolysis's outlet pressure to higher levels essential for storage or transportation. Additionally, an economic evaluation was undertaken to assess the feasibility of implementing waste heat recovery coupled with ORC. The analysis revealed a 0.43£/MWh increase in the levelized cost of hydrogen (LCOH) due to the additional CAPEX and OPEX costs, emphasizing the impact of electricity prices on LCOH. revealing how electricity prices influence the LCOH. The research took into account the additional capital expenditure and operating expenditures related to the ORC to determine whether the savings from not purchasing electricity for hydrogen compression would outweigh these additional costs.

In the similar context [44] they have chosen the proton exchange membrane water electrolysis PEMEW Capable of adapting to the non-uniformity and intermittency of renewable energy, this fast dynamic operation offers the advantage of producing hydrogen with higher purity to achieve carbon peaking in 2030 and carbon neutrality in 2060 in China. This article identified the cost of hydrogen production through PEMEW from 2020 to 2040 is crucial for its viability as an alternative energy source. by Using a bottom-up approach, scenario analysis, learning curve method and H2A model. Current Scenario: Hydrogen production cost is 7.26$/kg, with capital cost at 4450$/kg. Capital and electricity costs account for 47.6% and 34.7% of the total cost, respectively Future Scenario: Improved electrolysis technology reduces capital cost to 812 $/kg and hydrogen production cost to 2.60 $/kg. Electricity cost becomes the predominant factor at 56.4%.t in the scenario of 2040–2060.

Finally, we infer that we can produce hydrogen by renewable energies via PV system but there are lot of challenges such us the intermittency of solar energy, and the levelized cost of electrolysis and electricity however, the researchers are working on it.

HYDROGEN STORAGE AND TRANSPORTATION

3.1. Introduction:

Hydrogen storage plays a pivotal role in the advancement of hydrogen energy technologies, offering a means to efficiently store and transport hydrogen for various applications, it involves methods such as compression, liquefaction, and adsorption, each with its own set of advantages and challenges.

3.2. Modes of hydrogen storage:

3.2.1. Physical:

3.2.1.a Compressed hydrogen:

The predominant approach to hydrogen storage involves compressing hydrogen at high pressures [45,46]. This method facilitates rapid filling and release rates of hydrogen [45]. However, the compression process consumes approximately 13–18% of the lower heating value of hydrogen [47,48]. Storage typically utilizes cylindrical vessels due to challenges in accommodating spherical vessels onboard. Thus, there is a demand for lightweight, cost-effective vessel materials capable of withstanding high pressures [49].

3.2.1.b. Liquefied hydrogen:

Liquid hydrogen (LH_2) is non-corrosive [50] and possesses significantly higher density, resulting in a substantial increase in volumetric energy density. With a density of approximately 71 g/L [51], liquid hydrogen is obtained by cooling it below its critical temperature of -240°C, as hydrogen cannot be liquefied above this point. the normal boiling temperature of hydrogen is -253°C [52] The storage of hydrogen as a liquid is a well-established technology [53], Utilizing liquid hydrogen allows for a reduction in tank size, as its density is nearly 1.5-2 times greater than that of hydrogen compressed at high pressure. Consequently, storage can be achieved at low pressures, enabling the utilization of thin and cost-effective storage tanks.

3.2.1.c. Cryo-compression:

This method of hydrogen storage was first introduced by Aceves et al. [54], Cryo-compressed hydrogen, a cryogenic gas in a supercritical state, undergoes compression rather than liquefaction, resulting in gaseous hydrogen being compressed at temperatures around -233∘C and pressures ranging from 100 to 450 bar. Compared to cryogenic storage and liquefied hydrogen, cryo-compressed storage offers a higher storage density of

approximately 80 g/L, surpassing the former by approximately 10 g/L [55-58].

3.2.1.d. Adsorption:

Activated carbons are widely used in various gas sorption applications due to their favorable surface properties [59]. Materials suitable for hydrogen storage via physical adsorption encompass microporous carbon structures, metal-organic frameworks, and zeolites. These adsorbents are extensively researched and boast high surface areas, a crucial factor in adsorption processes due to its surface-dependent nature.[49] according to Zhou et al. [60] Activated carbons have been found to contain approximately 5 wt %(H_2) at a temperature of 77 (K) and pressure ranging between 30 to 60 bar. In a recent study by Zhao and al [61,62], the hydrogen capacity within single-walled carbon nanotubes (SWCNTs) was reported to be 1.73 wt% at the same temperature of 77 K but at a higher pressure of 100 bar.

3.2.2. Chemical:

3.2.2.a. Metal hydride:

Metal hydrides constitute a category of hydrogen carrier materials utilized for storing and transporting hydrogen gas. Initially, hydrogen undergoes amalgamation with metal hydride-forming alloys at the production site, triggering an exothermic reaction [63]. This reaction facilitates the absorption and storage of hydrogen within the metal hydride material. Subsequently, the hydrogen-saturated metal hydride material is transported to its designated destination via conventional transportation means such as trucks, trains, or ships. Upon arrival, the stored hydrogen is released by heating the metal hydride material [64]. The now-exhausted metal hydride material can be conveniently transported back to the production site for re-hydrogenation, thus enabling a closed-loop transportation system.

Light metal borohydrides, including lithium (Li), sodium (Na), calcium (Ca), and magnesium (Mg), boast exceptionally large volumetric and gravimetric hydrogen capacities, rendering them extensively studied as hydrogen carriers [65–68]. This approach offers several advantages, including high hydrogen storage density in volume, elimination of the need for high-pressure containers, attainment of high-purity hydrogen, and enhanced safety and flexibility. However, it also presents some drawbacks such as low mass storage density, high cost, temperature requirements for hydrogen adsorption and release, and poor cyclic stability in some materials.

3.2.2.b. Liquid organic:

Liquid Organic Hydrogen Carriers (LOHCs) are chemical compounds utilized for hydrogen storage and transport. LOHCs possess the capability to reversibly bond with hydrogen molecules via chemical reactions, allowing for the storage of hydrogen under manageable conditions. These compounds consist of two components: a hydrogen-lean organic compound (LOHC−) and a hydrogen-rich organic compound (LOHC+) [69]. The process of hydrogen storage using LOHCs, as elucidated by Modisha et al. [68], involves converting LOHC− into LOHC+ through a catalytic hydrogenation reaction to store hydrogen. Subsequently, the release of hydrogen is achieved by converting LOHC+ back into LOHC− through a catalytic dehydrogenation reaction [70]. This approach offers several advantages, including high hydrogen storage density, convenience in storage, transportation, and maintenance with high safety standards, and the ability for repeated use.

3.2.2.c. Ammonia:

Ammonia exhibits a higher auto-ignition temperature of 650°C compared to hydrogen (520°C), methane (630°C), and propane (450°C), making it inherently safer [8]. Liquid ammonia is transported globally via various means such as ships, pipelines, trains, and trucks [71-73] To maintain ammonia in a liquid state, which closely resembles that of propane, two primary methods are employed. The first method involves increasing its pressure while keeping the temperature at ambient levels, typically around 0.99 MPa at 25 ∘C. The second method entails reducing the temperature while maintaining the pressure at atmospheric levels; in this scenario, ammonia is cooled to approximately −33.4 ∘C at atmospheric pressure [74]. These mild conditions are advantageous, as they allow for the use of lightweight and cost-effective tanks while preserving volumetric density, upon reaching its destination, ammonia can be converted back into hydrogen through a catalytic process, providing a dependable source of hydrogen for various applications, especially within the chemical processing industry.[75] Hence, the economic viability of ammonia storage is considered well established, along with established regulations governing its operations and storage.

3.3. Hydrogen transportation:

3.3.1. Gaseous transport:

Gaseous hydrogen transportation involves distributing hydrogen gas in its gaseous state. This process necessitates compressing hydrogen at high pressures and transporting it in specialized containers to ensure safety and compliance with regulations. The primary methods for gas compression include mechanical techniques such as piston and diaphragm compressors, as well as centrifugal compression. Advanced methods also exist, including ionic liquid piston compression [and electrochemical compression based on PEM electrolysis principles. This approach offers several advantages, including rapid hydrogen refueling, well-established technology, operation at room temperature, and relatively low cost. However, it also presents some drawbacks, including low energy density, energy consumption during high-pressure hydrogen compression, larger storage volume compared to fuels like gasoline, and increased requirements for storage containers due to safety considerations [76].

3.3.2. Liquid transport:

Liquid hydrogen transport involves conveying hydrogen in its liquid state, typically achieved at extremely low temperatures (-253 °C). Liquid hydrogen provides an efficient means of transporting large volumes of hydrogen over extended distances compared to the gaseous method. In this process, hydrogen gas is cooled through liquefaction technologies such as the Linde-Hampson cycle, Claude cycle, Brayton cycle, magnetic refrigeration, thermoacoustic, and two-stage mixed refrigerant cycles. While each of these technologies has its operational principles, complexity, cost, scalability, and benefits as outlined by Zhang et al. [76,77], they collectively enable greater hydrogen density, enhancing the efficiency of hydrogen transportation in liquid form.

From storage tanks, liquid hydrogen is loaded into specialized containers or insulated cryogenic tanks designed to handle the low-temperature environment, minimizing heat transfer and maintaining hydrogen in its liquid state. These tankers are typically equipped with pressure relief systems to maintain low temperatures and pressures during transit. Primarily, liquid hydrogen transportation to end-users or storage facilities occurs via road, although alternative modes like rail or ship may be considered based on infrastructure availability. Upon arrival, the cryogenic tanker connects to the hydrogen system of the end-user or storage facility, facilitating the transfer of liquid hydrogen to suitable storage tanks or processing units. For most applications, liquid hydrogen is vaporized and warmed to ambient temperature before use.

Transporting hydrogen as a liquid offers several advantages. Liquid hydrogen possesses a higher energy density compared to its gaseous counterpart, enabling more hydrogen to be efficiently transported in terms of volume and weight. This makes it well-suited for long-distance transportation, facilitating the movement of larger quantities of hydrogen in a compact form. Similar to gaseous hydrogen, liquid hydrogen transportation plays a vital role in advancing the energy sector and chemical industry, particularly as it is frequently utilized as a propellant in rocket engines, necessitating transport to launch sites. Liquid hydrogen also offers flexibility in transportation modes, including road, rail, and ship. Moreover, it minimizes hydrogen loss due to diffusion or leakage thanks to its cryogenic storage.[75]

Method and Technique

Methodology:

4.1Haber-Bosch process:

To produce ammonia, we have chosen Haber-Bosch process because it's the most common method it is an exothermic reaction which means it does release energy and reversible This means that ammonia (NH_3) can decompose back into nitrogen (N_2) and hydrogen (H_2) under certain conditions. and it works on high pressure and temperature we have selected respectively (200bar, 400°C) [8] To maximize ammonia production, the process is typically run at high pressures and moderate temperatures, balancing the kinetics and thermodynamics to achieve the best yield. We have suggested multiple quantities of ammonia to calculate the amount of hydrogen and nitrogen that we needed to combine in the reactor with an iron-based catalyst that helps increasing the reaction rate.

The reaction is:

$$3H_2 + N_2 \rightarrow 2\ NH_3$$
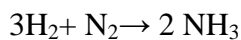
To calculate hydrogen, we use the equation bellow:

$mH_2 = 3*MH_2*MNH_3 1(i)/(2*MNH_3)$ …………………………………………………… (1)

mH_2: hydrogen need rate (ton/h)

MH_2: the molar mass of hydrogen(g/mol)

MNH_3: the molar mass of ammonia (g/mol)

And for nitrogen using the following equation:

$mN_2 = MN_2*MNH_3 1(i)/(2*MNH_3)$ …………………………………………………… (2)

mN_2: nitrogen need rate (ton/h)

MN_2: the molar mass of nitrogen (g/mol)

MNH_3: the molar mass of ammonia (g/mol)

4.2. Electrolysis:

For hydrogen production we have used PEM electrolysis it does operates under lower temperatures (20–80∘ C). During the PEM water electrolysis process, water is electrochemically split into hydrogen and oxygen. In this process, initially at the anode side water molecule is decomposed to generate oxygen (O_2) and protons (H+), and electrons (e−). The generated oxygen eliminated from the anodic surface and the remaining protons are traveled through the proton-conducting membrane to the cathode side and the

electrons are traveled through the external circuit to the cathode side. At the cathode side, the external circuit to the cathode side[78].

Figure 4.1: Principle of PEM electrolysis.[78]

Then we have calculated the energy supply and the amount of water for different quantities of hydrogen production by using the equations bellow.

For energy consumption by electrolysis, we use:

el = 1000*MH$_2$1(i)*120/ (3.6*0.75) …………………………………………………. (3)

el : energy consumption by electrolysis (GWh)

And for the water quantities we use:

Water = 1000*MWH*MH21(i)………………………………………………… (4)

Water: water need rate (kg/h)

MWH:mass of water for produce 1kg of H$_2$ (g/mol)

4.3. Nitrogenseparation:

4.3.1Pressure swing adsorption:

In the PSA process compressed air first passes through a series of filters to remove entrained oil and water. The purified air is then directed to one of two adsorption vessels filled with carbon molecular sieves (CMS). Remaining impurities, such as carbon dioxide and residual moisture, are adsorbed by the CMS at the entrance of the adsorbent bed.

Under high pressure, the CMS selectively adsorbs oxygen, allowing nitrogen to pass through at the desired purity level. While one vessel is producing nitrogen, the second vessel is depressurized to release the adsorbed oxygen, which is then vented to the atmosphere. The automatic cycling of adsorption and desorption between the two beds enables continuous nitrogen production. A wide range of flow and purity combinations can be achieved by adjusting the size of the air compressor and the adsorption vessels containing the CMS. PSAs can economically produce nitrogen gas at flow rates from less than 5,000 scfh to more than 60,000 scfh, and at purities ranging from 95% to 99.9995%.the energy of separation use in Matlab is Esg=100kwh/ton of nitrogen[79].
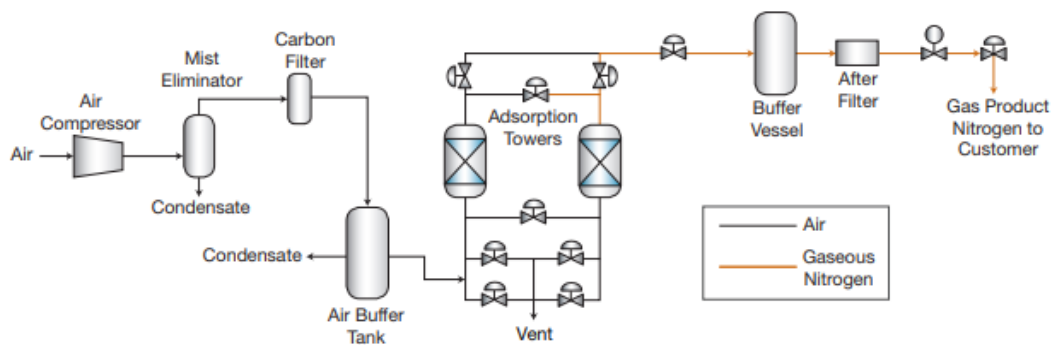
▲ Figure 1. PSA systems can provide a reliable, low-cost nitrogen supply to meet a wide variety of process requirements.

Figure 4.2: PSA systems can provide a reliable, Low –cost nitrogen supply to meet a wide variety of process requirements[79].

4.4.Photovoltaic system:

The PV system converts directly the electromagnetic energy of the solar radiation into electrics the photons of the electromagnetic solar radiation incident on the PV Celle "free" electrons generating then a DC. courant many models, theoretical as well semi-empirical exist for the determination of the generated electrical energy [80,81].

The most used model is the one-diode methods model [82] in this model the PV cell is considered as a DC current generator in parallel with a diode.

The current generator represents the solar radiation flux incident on the cell and the diode to take into account the polarization phenomena at the PV cells. electrical resistances, Serie resistance and shunt resistance, are included in the model to take into account H^+ the electrical losses a schematic representation of this model represented in the figure
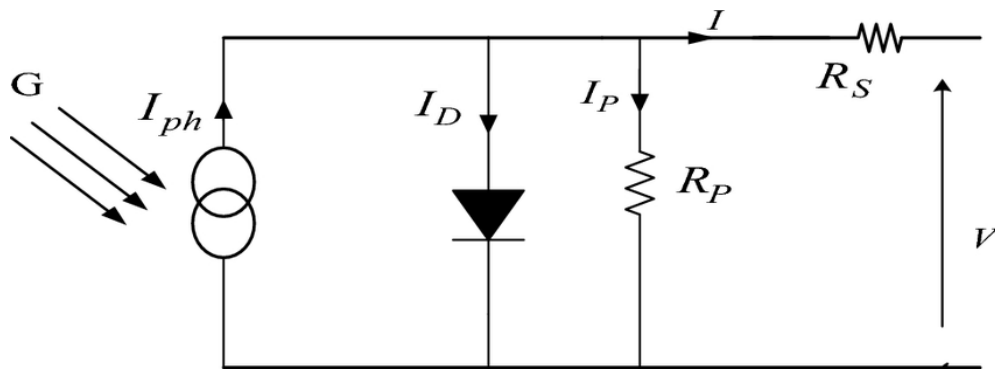
Figure 4.3: one-diode model of PV cell[83].

Among other modeled the thermal model and the two-diode model which are more elaborated model than the one-diode model.

The semi-empiric models relate the maximum power delivered par the PV systems well as the effects of the manufacturing technology and the environment conditions on this maximum power

The relation is given by [84]:

P_{pr}: $P_N f$ (Tm, T_n, G_N, T_{Noct}, Vw, G_0)

Where f (Tm, T_n, G_N, T_{Noct}, Vw, G_0) is a function that depends on the meteorological as well as the radiological conditions as well as on the technology.

By technological parameters, it is meant the parameters related to the nature of the PV cells as well as manufacturing.

- Nature of material: silicon or other materials
- Structure of the material:
- Monocrystal
- Polycrystal
- Thin film
- Amorphous

Another way of the expressing this relation is to use the concept of efficient.

In this case, we have the following relation $\eta = \eta_0 f$ (Tm, T_n, G_N, T_{Noct}, V_W, G_0)

Where η_0 is the efficiency of the PV system at normal conditions. many forms of this function are represented in the literature.

In the case when where the PV cells are manufactured from silicon, this function takes the form:[85]

$$F(T_m, T_a, G_i, T_{Noct}, V_w, G_0) = (1+\alpha_i(T_m-T_0))[1+C_1\ln(Gi/G_0)+C_2(\ln(Gi/G_0))^2+\beta_r(T_m-T_0)]$$

Where:

T_m = PV model temperature

T_G = Ambient temperature

$T_0 = 25\ ^0C$

$G_0 = 1\ kw/m^2$

G_i = irradiance incident on the PV module

The factors αi, βr, C1, C_2 parameters determined experimentally: [86]

$\alpha i = 1.20*10^{-3} /\ ^0C$

$\beta r = -4.60*10^{-3} /\ ^0C$

$C_1 = 0.033$

$C_2 = - 0.0092$

The PV module temperature T_m is determined from the ambient temperature T_a, the nominal operation temperature T_{Noct} and the irradiance incident on the PV module G_i [85]

$$T_m = (T_{Noct}- 20)\ (G_i/800)\ +T_a$$

$T_{Noct} = 48\ ^0C$

In the present work, semi-empirical relation as well as meteorological and radiometric data and the PV module characteristics are used for the relation of the energy produced by the PV module.

4.5. Simulation:

We have worked with MATLAB Simulink to calculate quantities of hydrogen and nitrogen and water and the energies of different processes in the system that are the energy of gas separation(eg), energy of Haber –Bosch process(eh), energy of hydrogen storage(es), energy of reaction(er), energy of PV system(et).

For calculate these energies we using thefollowing equations:

For energy of gas separation, we use the equation bellow:

$$eg = esg*MN21(i) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (5)$$

eg: energy of air separation (KWh/ton of NH_3).

esg: energy of nitrogen separation (KWh/ton of N_2).

For Haber –Bosch reactor using the following equation:

$$eh = ehb*MNH31(i)*1000 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (6)$$

eh: energy consumption by Haber-Bosh reactor for different mass of ammonia (MWh).

ehb: energy consumption by Haber-Bosh reactor (MWh/ton of NH_3).

To calculate the energy of hydrogen and nitrogen storage we use the equation bellow:

$$es = est*MH_21(i)*1000 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (7).$$

es: energy of hydrogen storage for different mass of ammonia (KWh).

est: energy of hydrogen storage (KWh /kg of H_2).

The heat of ammonia reaction is determined by the above equation:

$$er = dh*1000*MNH_3*MNH_31(i)/3600 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (8).$$

er: heat of reaction for different mass of ammonia (kj).

dh: heat of reaction (kj/mole of NH_3).

Finally total energy of pv system is calculate by the equation bellow:

$$et = el(i)+eh+es+eg-er\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(9).$$

et: total energy of photovoltaic system (GWh).

Table 1: The constants values using in MATLABSimulink:

Constant	Value	Unit
Molar mass of H_2	2.016	g/mol
Molar mass of N_2	14.01	g/mol
Molar mass of NH_3	17.031	g/mol
Water mass need to produce 1kg of hydrogen	11	kg H2O /kg H2
Efficiency	0.75	%
The lower heating value	120	Mj/kg
Energy of air separation	200	Kwh /ton of N2
Energy of Haber-Bosh reactor	50	Mj /ton of NH3
Energy of hydrogen storage	2	Kwh /kg of H2
Heat of reaction	46	Kj/mole of NH3
Full load hour	600	

4.6. Table 2: CHEMCAD Simulation:

EQUIPMENT	The conditions entering the equipment
Compressor	Pressure out :200 atm
Kinetic reactor	Number of reaction:1
	Reactor pressure :200atm
	Specific reactor type: PFR
	Conversion :0.65 for hydrogen
	Frequency factor :17900
Heat exchanger	Temperature of steam 7: -35.52°C

RESULT AND DISCUSSION

Result and discussion:

5.1 Introduction:

By MATLAB Simulink we have calculated parameters of our system like the hydrogen and nitrogen needs rates and the energies of our process in system such us energy output from PV system and we plot them in graphs and column chart.

5.2 Mass balances:

Table 3: nitrogen and hydrogen needrate.

mNH_3 (ton/h)	200	400	600	800	1000
mH_2 (ton/h)	35.512	71.023	106.54	142.05	177.56
mN_2 (ton/h)	82.262	164.52	246.79	329.05	411.31
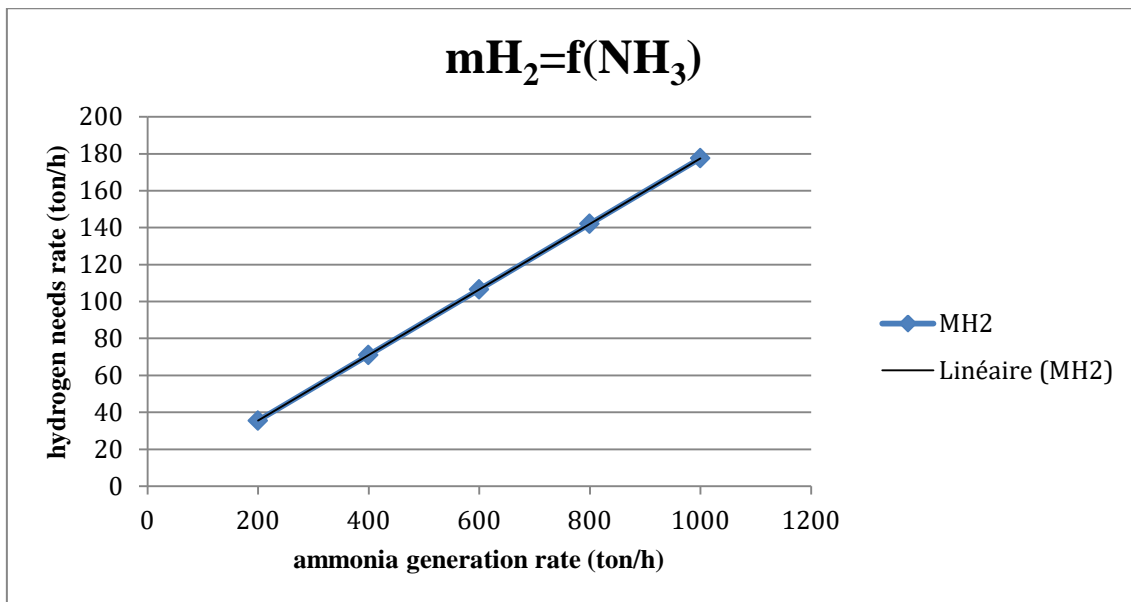
Figure 5.1: Relationship between hydrogen needs rate and ammonia generation rate.
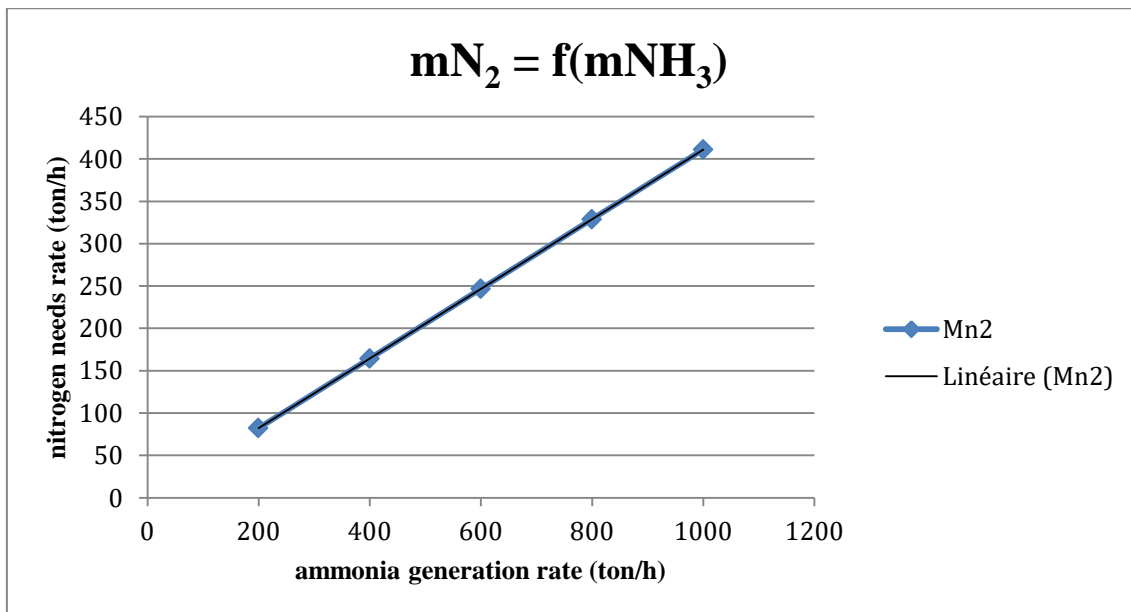
Figure5.2: Relationship between nitrogen needs rate and ammonia generation rate.

Discussion:

Figure (5.1) and figure (5.2) represents a linear graph of hydrogen and nitrogen needs rate (tons/h) versus the ammonia generation rate (tons/h) we notice that the hydrogen and nitrogen need rate increase directly with the ammonia generation rate according to these equations respectively is

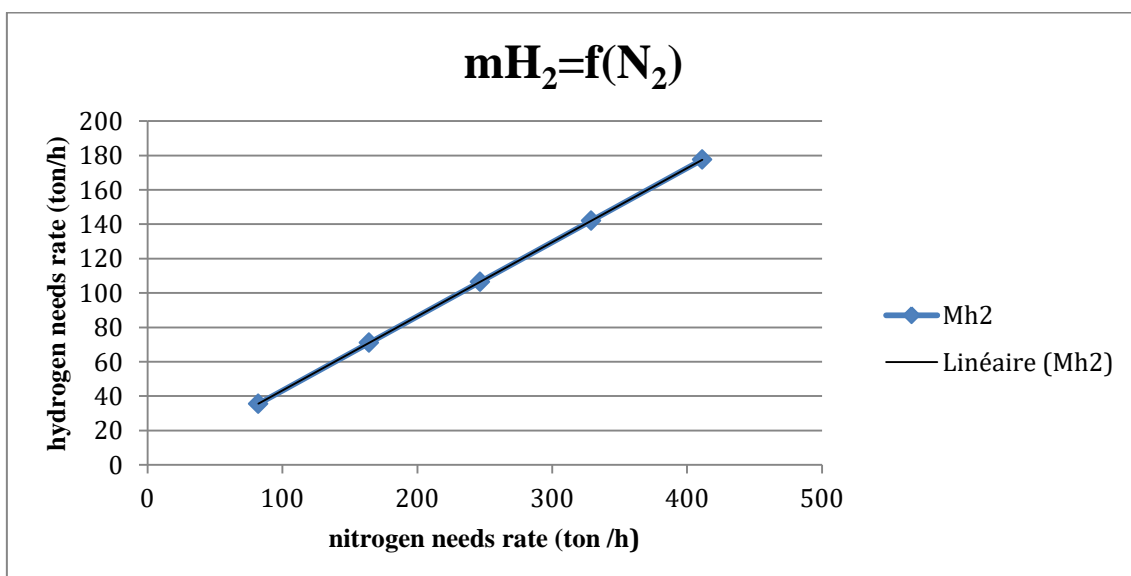Y = 0.1776X+0.0001 and Y = 0.4113X+0.00014.

Figure5.3: Relationship between hydrogen needs rate and nitrogen needs rate.

Discussion:

According to the graph in figure (5.3) it is noted that the hydrogen rate increases with the increase of nitrogen rate according to the linear equation (1) below:

$y = 0,431x + 0,000$ ……………………………………………… (1)

the amount of nitrogen is much greater than the amount of hydrogen due to the stoichiometric proportions dictated by the chemical equation of the reaction and In terms of mass, molecular nitrogen (N_2) has a molar mass of 28 g/mol (since each nitrogen atom has a mass of about 14 g/mol), whereas dihydrogen (H_2) has a molar mass of 2 g/mol (each hydrogen atom having a mass of about 1 g/mol). Thus, for every 28 grams of N2, 6 grams of H_2 are needed.
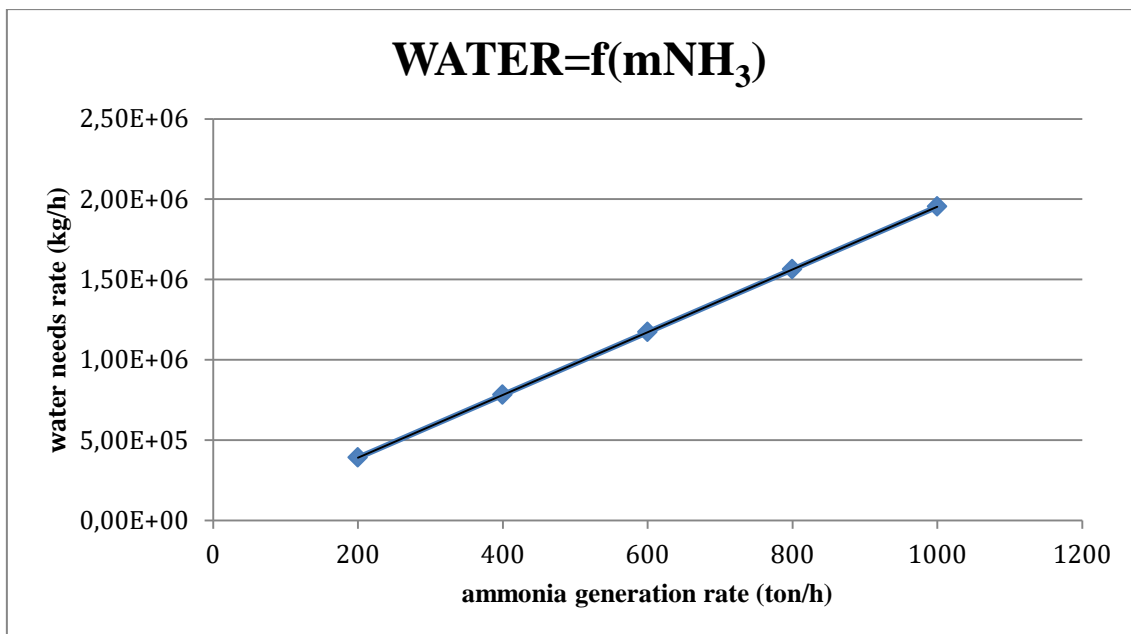

Figure5.4: Relationship between water needs rate and ammonia generation rate.

Discussion:

The graph in figure (5. 4)represents the increase of water needs rate with the increase of ammonia generation rate according to the linear equation (2) bellow:

$y = 1953x + 24$ ……………………………………………… (2)

We observed that the amount of water is very large for the amount of ammonia produced that's why we have to provide a permanent and substantial source of water consumption for this project.

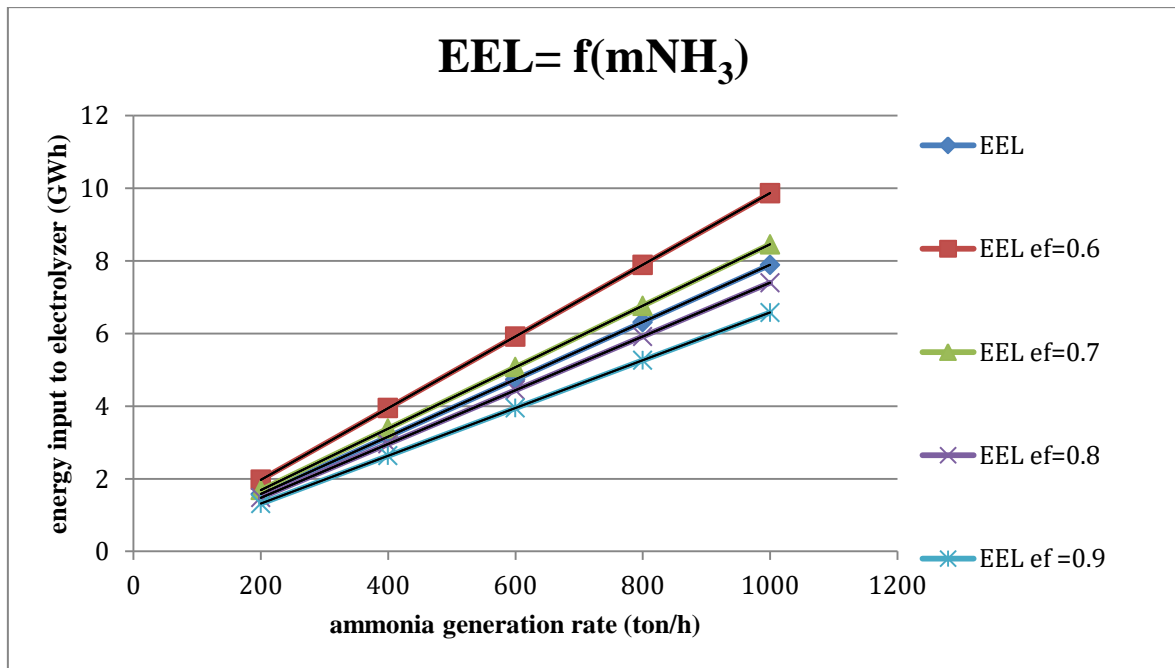## 5.3. Energy balance at the electrolysis:

Figure5.5: Relationship between the energy input to electrolyzes and the ammonia generation rate with a variable efficiency.

Discussion:

Figure (5.5) represents a linear graph of the energy input to electrolyzes versus ammonia generation rate with variable efficiency we notice that for 400tons of ammonia and ef=0.6 and 0.9the difference is33.33% and for 800tons of ammonia it is the same that means the lines increase at the same rate when the energy needs decrease with the increase of efficiency when we double production rate.

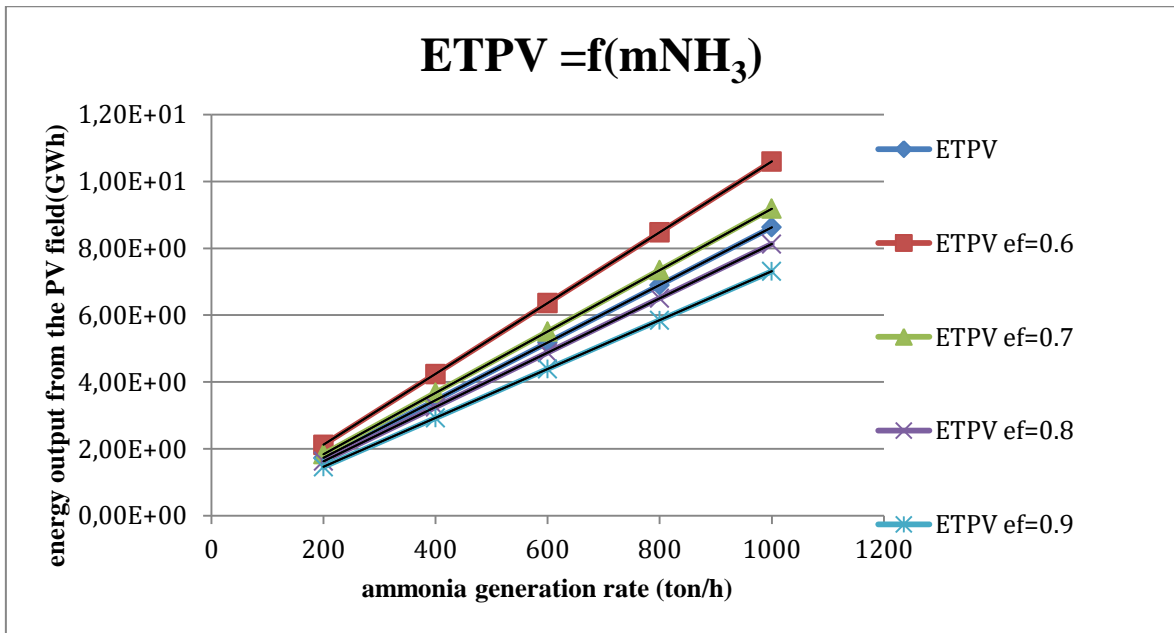## 5.4. Energy balance at the PV system:

Figure5.6: Relationship between the energy output from the PV field and the ammonia generation rate with variable efficiency.

Discussion:

figure 6 represents a linear graph of energy output from the PV field versus ammonia generation rate with variable efficiency we notice that for 400tons of ammonia and ef=0.6 and 0.9 the difference is31.13% and for 800ton of ammonia is 31.01% the energy output decrease with increase of efficiency when we double the production rate.
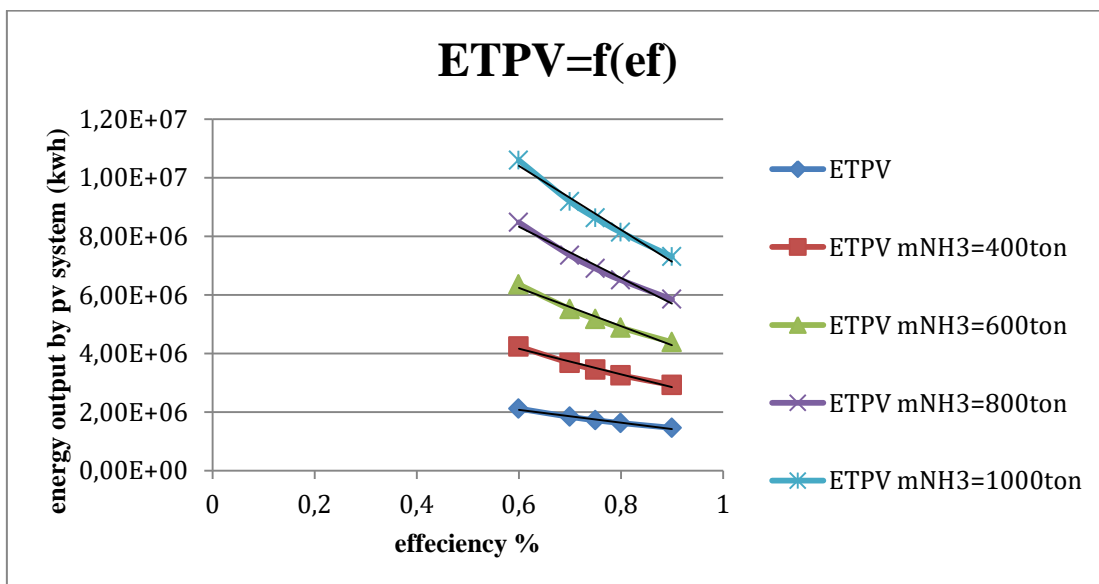

Figure5.7: The variation of energy output by PV versus the efficiency of electrolysis with various amount of ammonia**.**

Discussion:

There are drops in the energy required by the PV system, with an increase in electrolysis efficiency this drop depends on the production rate of ammonia because the less you produce ammonia the less energy you need and more electrolysis efficiency improves less energy is wasted and more of input energy contributes directly to the desired reaction.

5.5. Required peak power:

Table 4: The difference between peak power (eta=100%) and peak power (eta=65%)

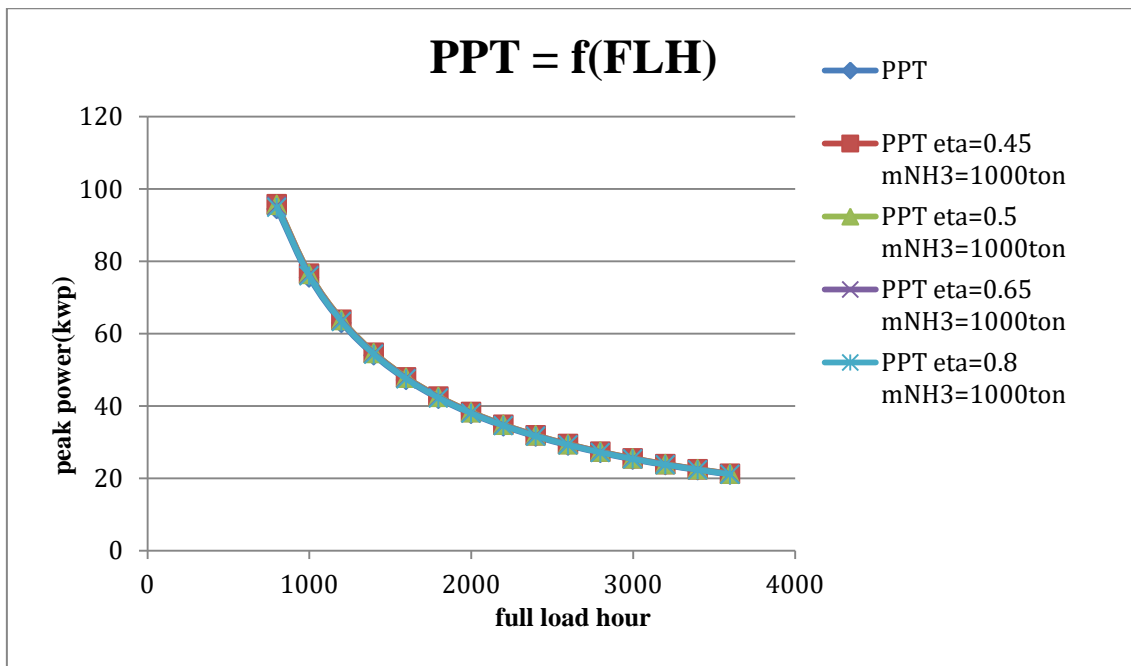| Full load hour	Peak power (eta=100%)	Peak power (eta=65%)	ΔPPT (%)
800	94.456	95.29	0.88
1000	75.565	76.232	0.88
1200	62.971	63.527	0.88
1400	53.975	54.451	0.88
1600	47.228	47.645	0.88
1800	41.98	42.351	0.88
2000	37.782	38.116	0.88
2200	34.348	34.651	0.88
2400	31.485	31.763	0.88
2600	29.063	29.32	0.88
2800	26.987	27.226	0.88
3000	25.188	25.411	0.88
3200	23.614	23.823	0.88
3400	22.225	22.421	0.88
3600	20.99	21.176	0.88

Figure5.8: Relationship between the peak power as and full load hour for various heat recovery (eta).

Discussion:

According to the graph in figure (5.9)and the table in figure(5.8)the peak power is decrease with the increase of the full load hour with an exponential function, the drop rate is around 5 and the difference between Ppt(eta=100%) and Ppt(eta=65%) is too small ΔPpt=0.88% in different values of FLH which means   the recuperation of heat will not play an important role for the case of ammonia production rate of 1000 ton/hours   because the heat of reaction is to small then other energies of the system .
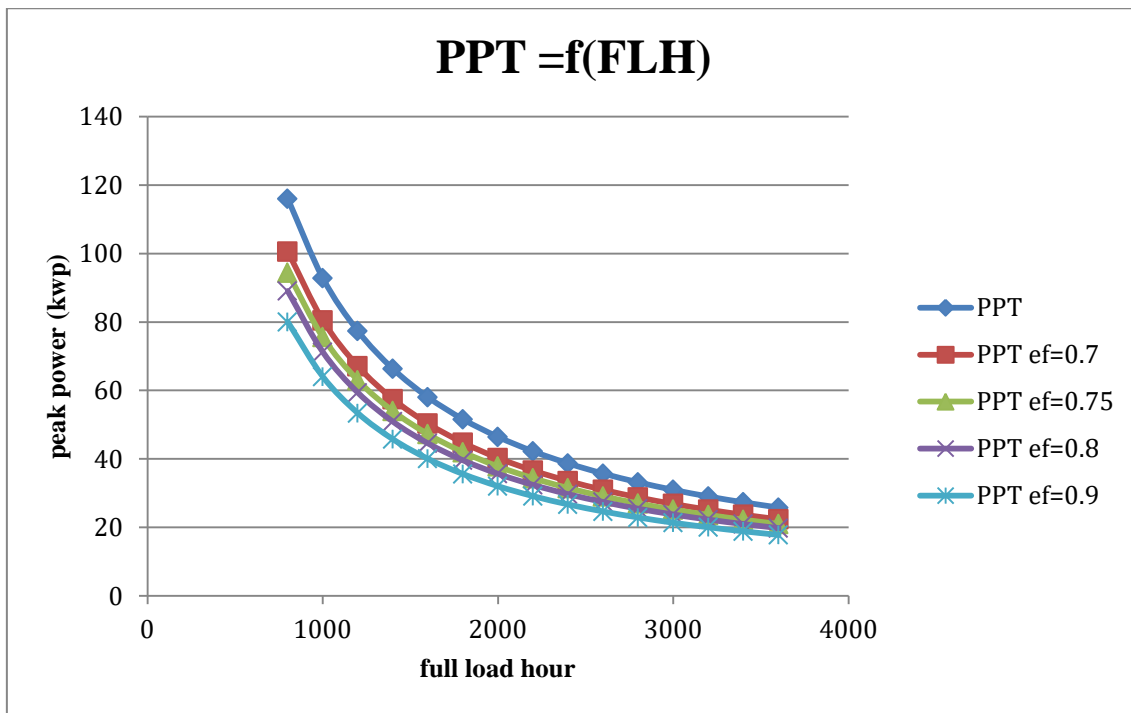
Figure5.9: Relationshipbetween the peak power and full load hour for a various efficiency.

Discussion:

We note that with the increase of full load hour there is a drop in the required peak power, the drop rate is around 5. despite the decrease of peak power, and the efficiency of electrolysis is high means that less electrical energy is needed to produce the same amount of hydrogen which means efficiency playan important role.

Figure5.10: Energy output from the PV field per full load hour versus full load hour with a constant efficiency 60%.

Figure5.11: Energy output from the PV field per full load hour versus full load hour with a constant efficiency 70%.
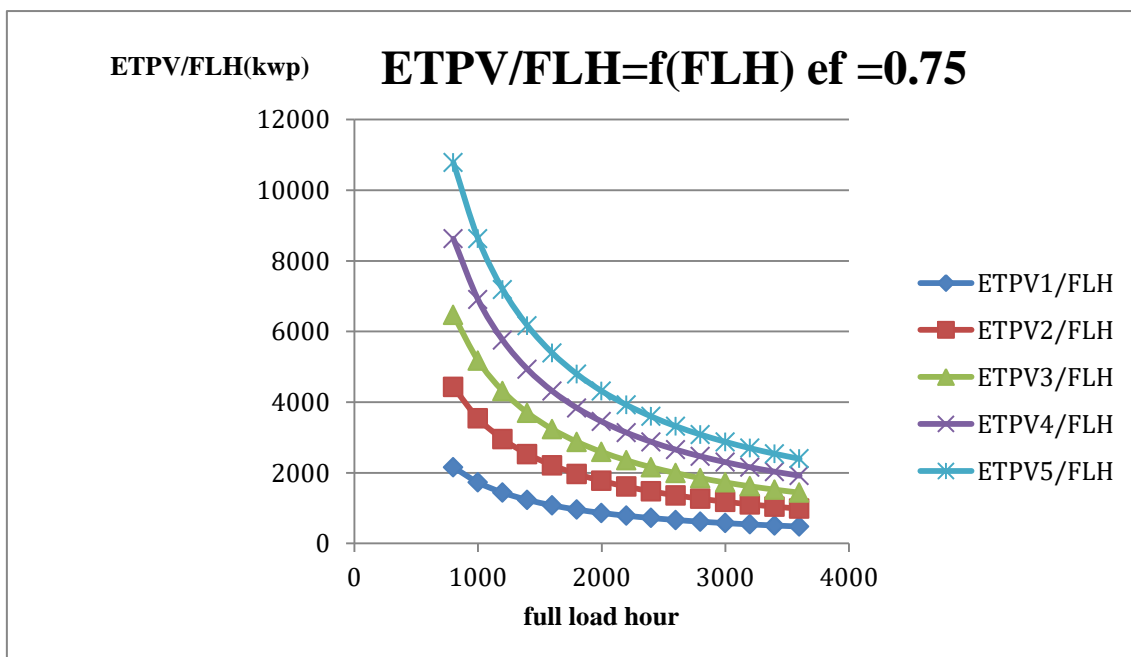
Figure5.12: Energy output from the PV field per full load hour versus full load hour with a constant efficiency 75%.
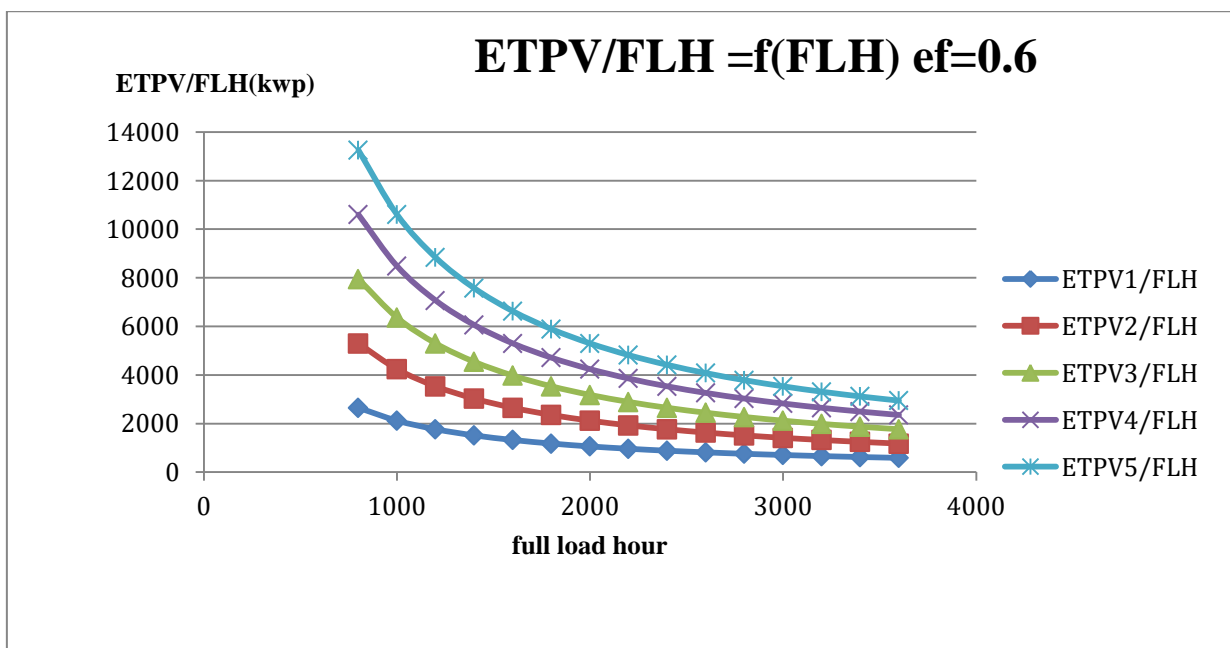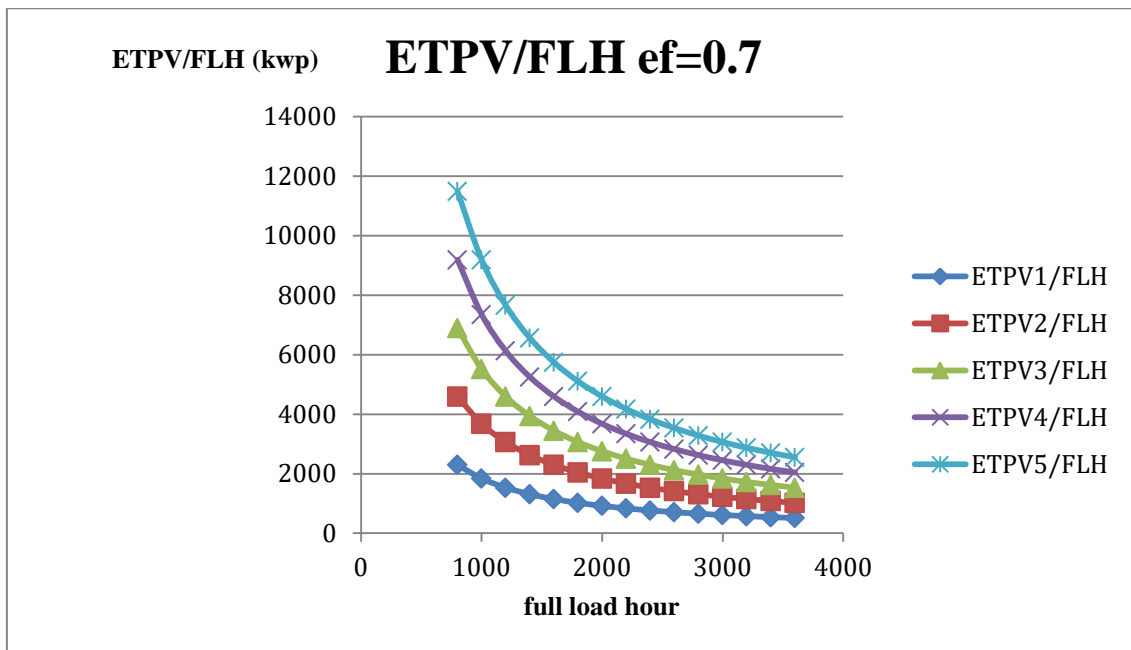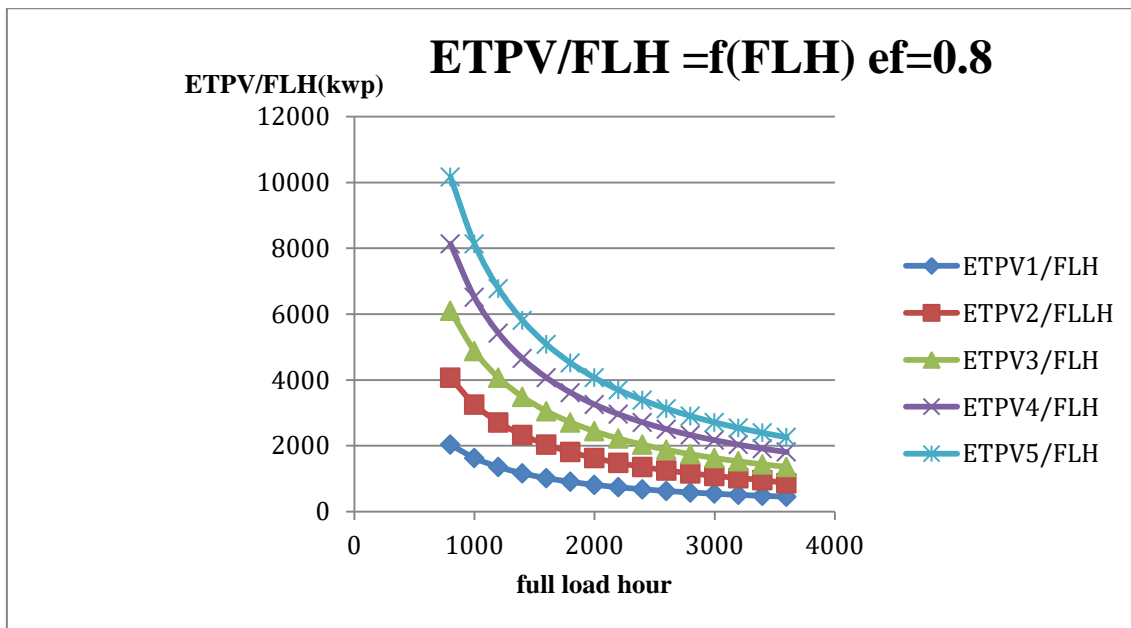
Figure5.13: energy output from the PV field per full load hour versus full load hour with a constant efficiency 80%

Figure5.14: energy output from the PV field per full load hour versus full load hour with a constant efficiency 90%.

Discussion:

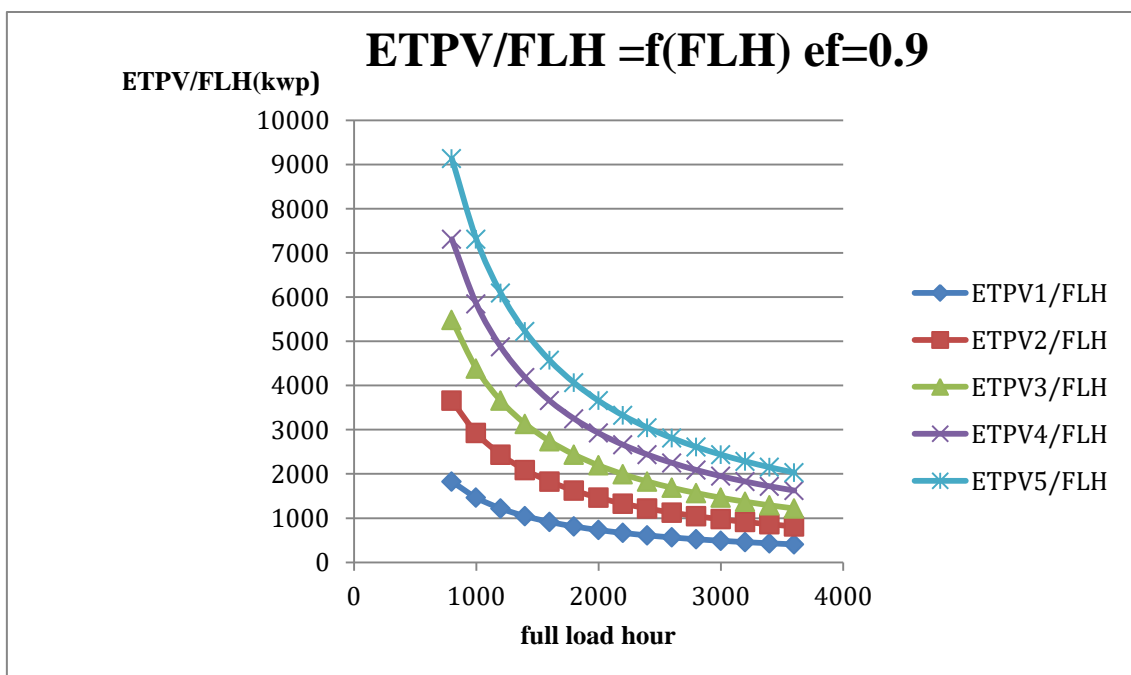For figure 8 and 10, 11, 12, 13, 14, We note that with the increase of full load hour there is a drop in the required peak power and ETPV/FLH, the drop rate is around 5. furthermore, the efficiency of electrolysis is increasing which means that less electrical energy is needed

to produce the same amount of hydrogen which means efficiency play an important role, that's why peak power decrease and ETPV/FLH as well owing to the fact that ETPV/FLH means how much energy the system actually generates when it operates at the maximum capacity and it used to assess the efficiency and performance of solar power systems.

5.6. Applications of peak power in different sites in Algeria:

We have chosenfour sites in Algeria (Algiers, Djelfa,Ghardaia and Adrar) and we have calculated the peak power of this sites and we plot them in two histograms the first is for incline plane and the two histograms for two axes.

For incline plane:

Table5: variation of peak power in (Algiers, Adrar, Ghardia,Djelfa) in incline plane.

Sites	Alger	Djelfa	Ghardia	Adrar
FLH	5.65	6.15	6.78	7.02
ETPV1/FLH	305345.133	280601.626	254528.024	245826.211
ETPV2/FLH	610690.265	561040.65	508908.555	491509.972
ETPV3/FLH	916053.097	841577.236	763377.581	737279.202
ETPV4/FLH	1221398.23	1122097.56	1017831.86	983034.188
ETPV5/FLH	1526743.36	1402617.89	1272286.14	1228789.17

For two axes:

Table6: variation of peak power in (Algiers, Adrar, Ghardia,Djelfa) in two axes.

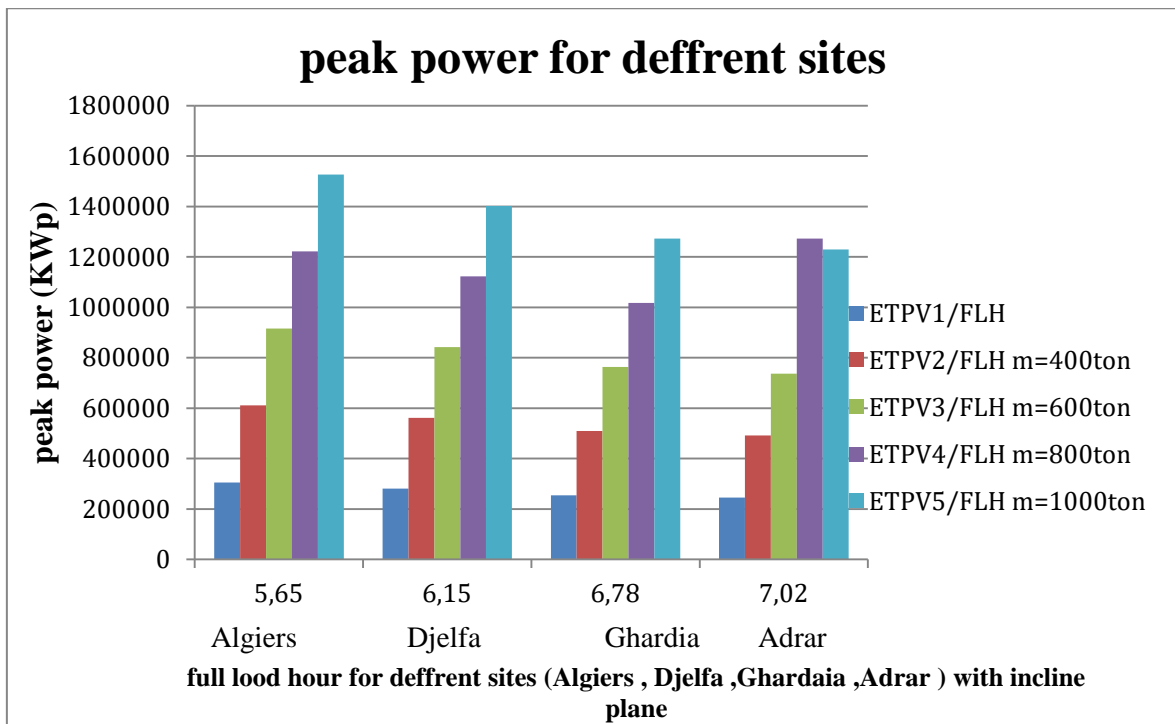| sites	Alger	Djelfa	Ghardia	Adrar
FLH	7.60	8.34	9.14	9.53
ETPV1/FLH	227000	206858.513	188752.735	181028.332
ETPV2/FLH	454000	413717.026	377505.47	362056.663
ETPV3/FLH	681013.158	620587.53	566269.147	543095.488
ETPV4/FLH	908013.158	827446.043	755021.882	724123.82
ETPV5/FLH	1135013.16	1034304.56	943774.617	905152.151

Figure5.15: The relationship between peak power and full load hour in different sites in incline plane.
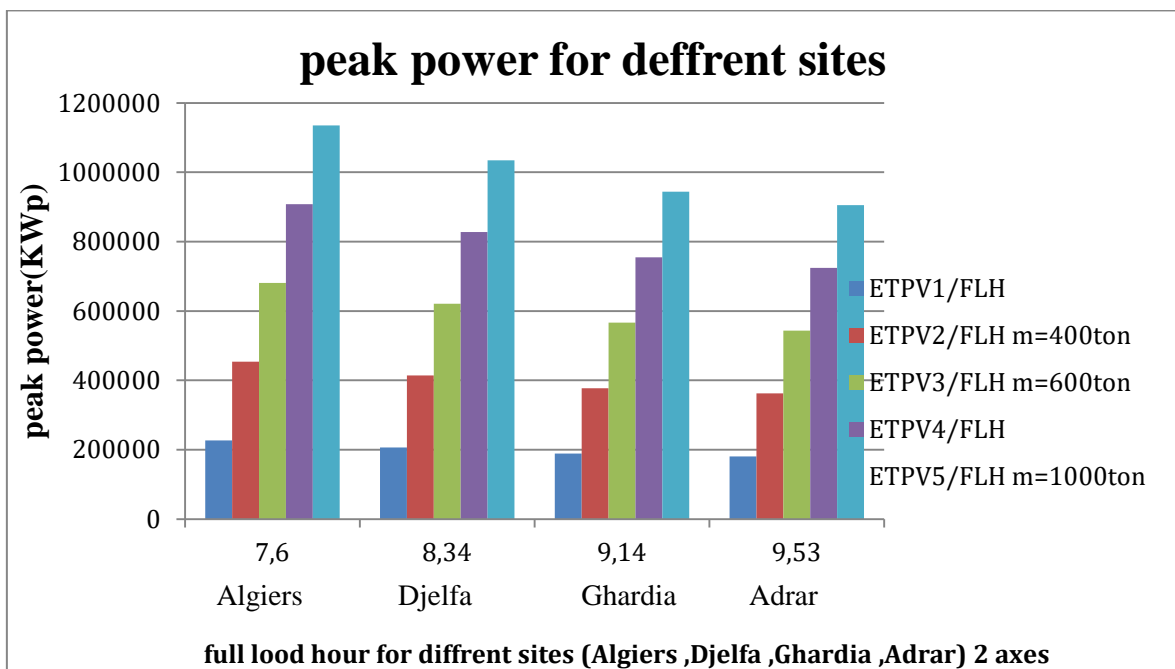

Figure5.16: The relationship between peak power and full load hour in different sites in tow axes**.**

Discussion:

The histograms in figure 16and 17 represent the relationship between peak power in different sites in Algeria (Alger , Djlfa , Ghardia and Adrar) and full load hour for incline and two axes   in this sites we noted that the surface of peak power in two histograms increase with increase of full load hour and with increase of ammonia generation rate in the figure 16   the big PV filed surface is in Algeria site with full load hour FLH =5.65 and the small PV field surface is in Adrar site with FLH=7.02 and the big value is from Algeria site with ammonia generation rate =1000ton /h Ppt=1526743.36 and for figure 17 the big surface is from Algeria site with FLH=7.6 and the small PV filed surface is in Adrar site with FLH=9.53 the big value is from Algeria sit with ammonia generation rate =1000ton/h Ppt= 1135013.16 Kwp   from these result we have chosenAdrar sit for our system because the PV filed surface in this sites is smaller than other sites and this lead us to less cost which means more economically competitive .

5.7. The results obtained by CHEMCAD:

The flowsheet:

We have done a simulation of ammonia synthesis at 290bar and 421 °C [87]and we used a kinetic reactor of PFR type and by adding the amounts of hydrogen and nitrogen we found out in the outputs of dynamic vessel that the amount of nitrogen is really small so we can't recycle it back that's why we have eliminated this step we suppose that it's the cause that we obtained a different amount between MATLAB and CHEMCAD.
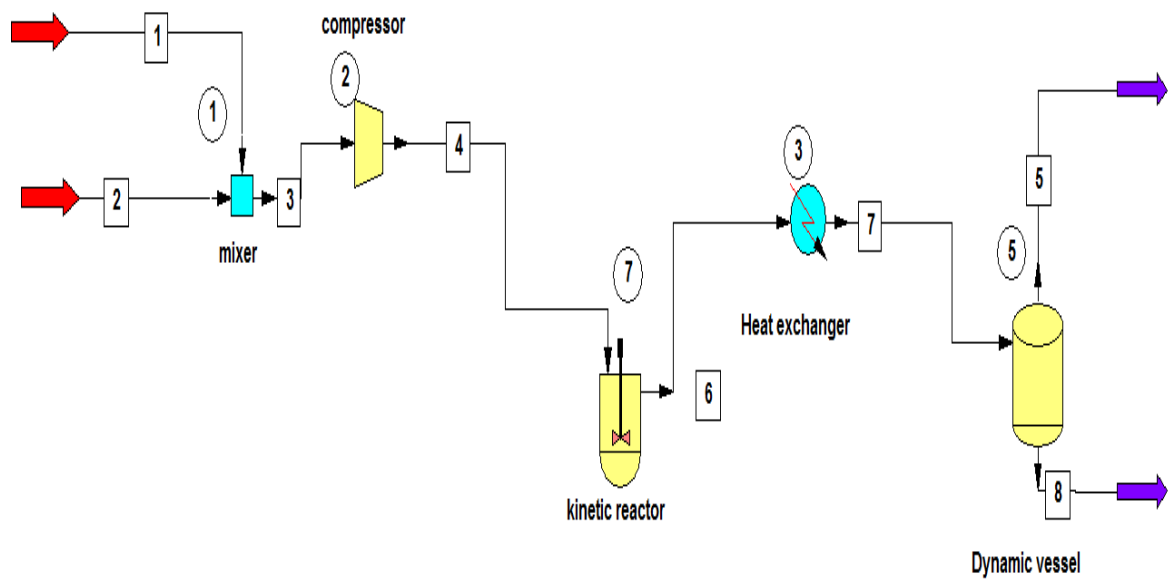
Figure 5.17: flowsheet of ammonia synthesis.

Table 7: ammonia production process stream information for different nitrogen and hydrogen rate:

Stream No.	3	8	5
Name			
- - Overall - -			
Molar flow kmol/h	20553.2873	5817.4484	8862.9176
Mass flow kg/h	117774.0044	98706.1081	19069.6593
Temp C	24.9854	-35.5201	-35.5201
Pres atm	1.0000	200.0000	200.0000
Vapor mole fraction	1.000	0.0000	1.000
Enth kJ/h	-10978.	-4.1631E+008	-1.7775E+007
Actual vol m3/h	502990.6169	146.0663	980.2470
Std liq m3/h	609.2093	160.1430	255.1653
Std vap 0 C m3/h	460674.1196	130390.2295	198650.3102
Flowrates in kg/h			
Hydrogen	35512.0018	49.7887	17704.2595
Nitrogen	82262.0026	0.0000	0.0000
Ammonia	0.0000	98656.3121	1365.4000

Stream No.	3	8	5
Name			
- - Overall - -			
Molar flow kmol/h	358204.3610	8727.5894	337731.2426
Mass flow kg/h	874750.0000	148083.1954	726671.0000
Temp C	24.9981	-35.5201	-35.5201
Pres atm	1.0000	200.0000	200.0000
Vapor mole fraction	1.000	0.0000	1.000
Enth kJ/h	1.1239E+005	-6.2457E+008	-6.7735E+008
Actual vol m3/h	8766817.7769	219.1350	37353.3965
Std liq m3/h	10351.3994	240.2535	9723.3547
Std vap 0 C m3/h	8028665.9998	195617.1087	7569789.0089
Flowrates in kg/h			
Hydrogen	710230.0001	74.6950	674640.2923
Nitrogen	164520.0000	0.0000	0.0000
Ammonia	0.0000	148008.4944	52030.2129

Stream No.	3	8	5
Name			
- - Overall - -			
Molar flow kmol/h	61662.0000	17452.6149	26590.3200
Mass flow kg/h	353330.0007	296123.0000	57212.3498
Temp C	24.9854	-35.5201	-35.5201
Pres atm	1.0000	200.0000	200.0000
Vapor mole fraction	1.000	0.0000	1.000
Enth kJ/h	-32933.	-1.2490E+009	-5.3329E+007
Actual vol m3/h	1509023.7838	438.2056	2940.9147
Std liq m3/h	1827.6900	480.4363	765.5410
Std vap 0 C m3/h	1382070.0726	391176.7626	595986.0294
Flowrates in kg/h			
Hydrogen	106540.0027	149.3685	53115.9110
Nitrogen	246790.0000	0.0000	0.0000
Ammonia	0.0000	295973.5006	4096.4410

Stream No.	3	8	5
Name			
- - Overall - -			
Molar flow kmol/h	82214.2124	23269.9388	35452.4784
Mass flow kg/h	471100.0149	394827.0000	76280.3737
Temp C	24.9854	-35.5201	-35.5201
Pres atm	1.0000	200.0000	200.0000
Vapor mole fraction	1.000	0.0000	1.000
Enth kJ/h	-43911.	-1.6653E+009	-7.1103E+007
Actual vol m3/h	2011988.2926	584.2687	3921.0776
Std liq m3/h	2436.8684	640.5759	1020.6843
Std vap 0 C m3/h	1842720.3777	521564.2029	794619.3637
Flowrates in kg/h			
Hydrogen	142050.0058	199.1562	70818.6538
Nitrogen	329050.0000	0.0000	0.0000
Ammonia	0.0000	394628.0000	5461.7243

Stream No.	3	8	5
Name			
- - Overall - -			
Molar flow kmol/h	102766.4402	29087.2486	44314.6563
Mass flow kg/h	588870.0008	493531.0000	95348.4472
Temp C	24.9854	-35.5201	-35.5201
Pres atm	1.0000	200.0000	200.0000
Vapor mole fraction	1.000	0.0000	1.000
Enth kJ/h	-54888.	-2.0816E+009	-8.8877E+007
Actual vol m3/h	2514952.8014	730.3316	4901.2431
Std liq m3/h	3046.0463	800.7151	1275.8284
Std vap 0 C m3/h	2303370.6828	651951.3318	993253.0378
Flowrates in kg/h			
Hydrogen	177560.0090	248.9438	88521.4356
Nitrogen	411310.0000	0.0000	0.0000
Ammonia	0.0000	493282.0000	6827.0108

General conclusion

The difficult properties of hydrogen in storage have prompted scientists to find a successful and easy ways to store hydrogen one of these ways is to store it on ammonia form. This thesis has explored the modeling of green hydrogen storage in the form of ammonia, using a photovoltaic system.

We have established a mathematical model in MATLAB Simulink to determine the required mass quantities of nitrogen and hydrogenas well as the amounts of water, for different ammonia flow rates and to evaluate the energy requirements for each process in our system.

The results obtained by this study shows that to produce 200ton/h and 1000ton /h of ammonia we need respectively 822662ton/h and 411310 ton/h of nitrogen and 53512ton /h 177560 ton/h of hydrogen and the energy required by electrolysis EEL= 1.352 Gwh (200ton/h) and EEL=6.5762 Gwh (1000ton/h) with 90% of efficiency and 1.46Gwh of energy output from the PV system for 200 ton/h of NH_3 and 7.31Gwh of this energy for 1000ton/h of NH_3.

Finally, to operate this system we studied four sites (Algiers, Djelfa, Ghardia and Adrar) and the most suitable sites for this project is the Adrar sit because it has the smallest peak power which led to a smaller pv field surface which means the lowest cost than the other sites.

In conclusion, this study has demonstrated that the combination of PV systems and ammonia-based hydrogen storage is promising solution for advancing renewable energy storage. By addressing both technical and economic challenges, this approach can contribute to a more sustainable and resilient energy future.

This study can be further completed by Future research and development could focus on optimizing the efficiency of the electrolysis and ammonia synthesis and further reducing cost and enhancing system performance. finally, you can study the validation of our system through pilot scale experiments.

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