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Application of water electrolysis for green ammonia production: a plant simulation study

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Abstract- Renewable energy has received a significant global attention. Green hydrogen is undoubtedly a viable energy source due to its efficiency and environmental friendliness. Thus, this study was proposed to provide insights about the design and feasibility of switching from natural gas to green hyrogen for the production of ammonia. The aim of this study is to design a green ammonia plant with a capacity of 140000 tons per year using green hydrogen and raw nitrogen. The inclusive study involved process simulation using ASPEN HYSYS v11.0, Equipment design, equipment spacing, plant layout, and finally evaluation of profitability. The plant design was made for all the units including heat exchangers, separators, reactors, etc., and is completed based on the data calculated by material and energy balance. Results revealed that, approximately, 189920 tons/year of water and a 2 MW electrolyzer are required to achieve the desired production. The overall process is highly exothermic effluent temperature from the electrolyzer and ammonia reactor increased by 160% and 68%, respectively. The economic investigation showed that the fixed capital investment required is approximate 22.4 million USD. The production cost of green ammonia was $1350/ton which is comparable to the global price of $1400/ton.

Keywords- green ammonia, electrolyzer, green hydrogen, renewable energy.

1. INTRODUCTION

Ammonia (NH_3) had a global production of 235 million tons in 2019. Making it, after sulfuric acid (H_2SO_4), the second most manufactured chemical worldwide. Like hydrogen, ammonia can be produced from various main sources of energy, including nuclear, solar, wind, geothermal, hydro, biomass, coal, and natural gas sources. Ammonia can be produced via many conversion technologies: thermochemical, electrochemical, photochemical, and plasma. However, this is generally hindered by technological viability, total energy efficiency, and environmental aspects. Crop fertilization uses up to 80% or more of the ammonia produced, in the form of aqua ammonia (an aqueous solution of ammonia), ammonium sulfate $(NH_4)_2SO_4$, ammonium phosphate $(NH_4)_3PO_4$, ammonium nitrate NH_4NO_3, and urea $(NH_2)_2CO$. The greatest application of ammonia is as an energy carrier. Ammonia is also used to produce nitric acid (HNO_3), nylon, and other polyamides, Refrigerants within homes, commercial and industrial refrigeration systems, dyes, cleaning agents, and explosives[1,2].

2. LITERATURE REVIEW

The Haber-Bosch process is a widely used technique for producing ammonia developed in 1909 by Fritz Haber and Carl Bosch, which has a negative effect due to excessive emissions of greenhouse gases. In addition, its high energy consumption is a result of its high operating temperature and pressure. For sustainable ammonia production, the technology that was most used is water electrolysis along with renewable technologies such as solar and wind energy to produce the green hydrogen used instead of H_2 from methane in the Haber-Bosch process [3].

A. AMMONIA SYNTHESIS TECHNOLOGIES

In general, the prospective ammonia synthesis technologies can be classified into methane-based Haber-Bosch and electrolysis-driven Haber Bosch, where the H_2 is produced from renewable energy.

Figure 1 illustrate the two different technologies used. The pros and cons of each technology is explained in Table 1.

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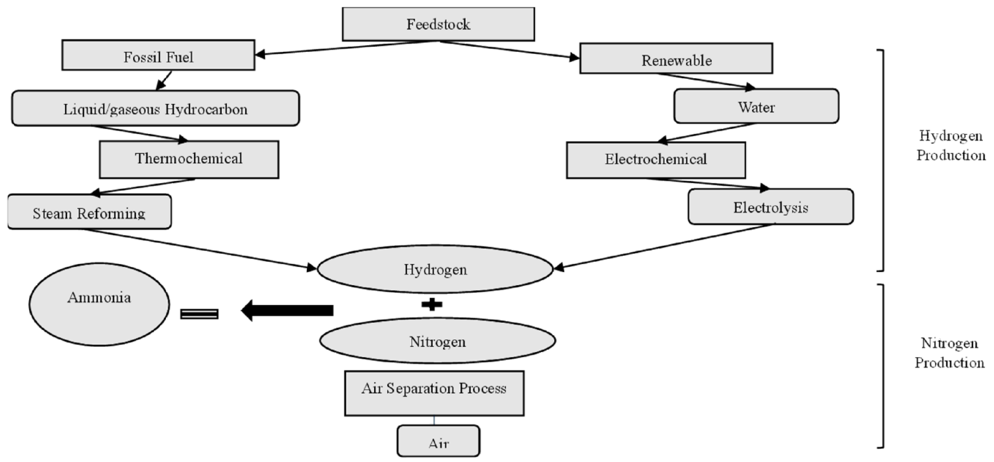

Figure 1 illustrates the different technologies used for ammonia production [4].

I. Methane-based Haber-Bosch.

Ammonia is generally produced in high capacity plants (1,000 to 1,500 t/d) utilizing the Haber-Bosch process. Over 90% of ammonia produced worldwide comes from fossil fuels [5]. Approximately 96% of the hydrogen (H_2) needed for the manufacturing of ammonia through the Haber-Bosch process comes from fossil fuels, while the remaining 4% is produced by electrolysis. A typical Steam Methane Reforming (SMR) process produces nearly 9–10 tons of carbon dioxide (CO_2) comparable to each ton of hydrogen produced. Worldwide, 72% of the hydrogen generated for ammonia production is through the SMR process [4]. This process is complex to decarbonize due to the direct release of CO_2 as an SMR side reaction. Figure 2 illustrates a block flow diagram of the Haber-Bosch process.

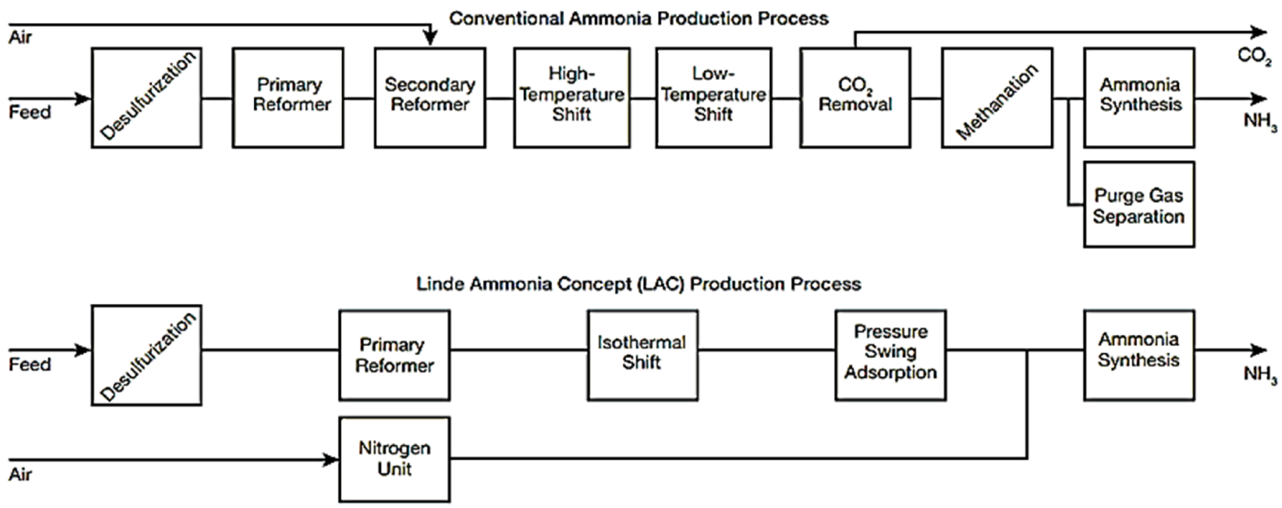

Figure 2 A block flow diagram of the Haber-Bosch process [6].

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II. ELECTROLYSIS-DRIVEN HABER BOSCH (GREEN AMMONIA)

Green ammonia can be manufactured from renewable energy. Carbon-free hydrogen is produced using renewable electricity by water electrolysis, so-called power-to-hydrogen (PtH) as shown in Figure 3. Therefore, the coupling of PtH and the Haber-Bosch process avoids the use of fossil fuels [8].

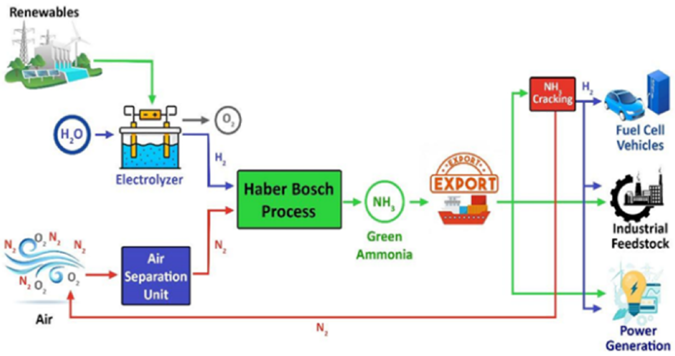

Figure 3 illustrates the power of the hydrogen process for ammonia production.

Table 1 Pros and cons of electrolysis-driven ammonia synthesis method and the common Haber-Bosch method [4,5,7].

Process name	Advantages	Disadvantages
Methane-based Haber-Bosch	1. It is the most efficient way. 2. It has a high overall yield, making it a commercially viable method for large-scale ammonia production. 3. The method is scalable. 4. It is well-established. 5. It is recommended for continuous ammonia production.	1. its high-energy consumption. 2. There were environmental problems related to the process, especially due to the large quantities of greenhouse gases emission 3. Safety concerns while operating in high pressure and high-temperature environments.
Electrolysis-driven Haber Bosch (Green Ammonia)	1. No direct carbon dioxide emissions. 2. Use of green ammonia in agriculture as a fertilizer provides a sustainable alternative, contributing to improved soil health. 3. It offers flexibility in scale, allowing for both large-scale centralized and smaller-scale decentralized facilities. 4. Reduction of fossil fuel consumption and greenhouse gas emissions, 5. It can be used as a vector to transport hydrogen. 6. It has better energy density	1. Still under development. 2. There were challenges in terms of efficiency, cost-effectiveness, and scalability that must be dealt with. 3. It is pricey compared to traditional processes because of the present expenses related to renewable energy technologies

B. GREEN AMMONIA PLANT PROCESS

The plant for green ammonia synthesis is preferably located in areas with abundant sources of water and high solar irradiance [9,10]. In this study, solar energy (photovoltaic PV) was selected because the electrical energy provided is the main driving force for water electrolysis [11,12]. The solar cells' efficiency persists as the main drawback of the photovoltaic systems. a maximum efficiency of 25% was reported yet, extensive research and development is required to maintain high efficiencies in industrial applications [13].
In light of the need to reduce emissions and save energy, green hydrogen must gradually replace gray hydrogen in ammonia production. Photovoltaic water electrolysis is a promising process for hydrogen production [8]. Hydrogen gas has numerous industrial applications, especially in the oil and gas sector, fuel cells, petrochemical industry, fertilizer industry, and petroleum and metal refining industry [7]. Generally, hydrogen and oxygen were co-generated from water a moderate operating conditions water electrolysis technologies [9]. After comparing all types of water electrolysis, alkaline technology was the best choice for this research.
The key distinction was that renewable ammonia production technologies rely on renewable energy sources, such as electricity from solar or wind, to power the ammonia synthesis process. Renewable ammonia production technologies aim to reduce greenhouse gas emissions and dependence on fossil fuels by utilizing sustainable energy sources.

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A previous study examined a design that utilized hydroelectric power and achieved a peak efficiency of over 60% by obtaining hydrogen through alkaline electrolysis at 80 °C. However, this approach was abandoned because it couldn't compete with the emergence of abundant and inexpensive natural gas. Recently, there has been renewed interest in electrically driven ammonia synthesis due to changes in the energy landscape and growing environmental pressures to transition away from fossil fuels [10].

The electric HB with alkaline electrolysis was the best choice for this research because it has Low operating and capital costs with high efficiency, and it was suitable for large-scale processes.

Based on the literature review the air separation unit for nitrogen production, the alkaline technology for hydrogen production, and the electric HB with alkaline electrolysis for ammonia production were the most suitable processes for green ammonia production.

C. METHODOLOGY

After assessing the significance of green ammonia in its role in the green energy transition and applications, a methodological plan was made for designing the most optimum, feasible, and recent method to produce green ammonia. Several software programs were used as a means of providing figures and data, including Aspen HYSYS V11, Aspen Process Economic Analyzer V11, Microsoft Excel 365, and Microsoft Visio 2013. Figure illustrate the flow chart of process identification.

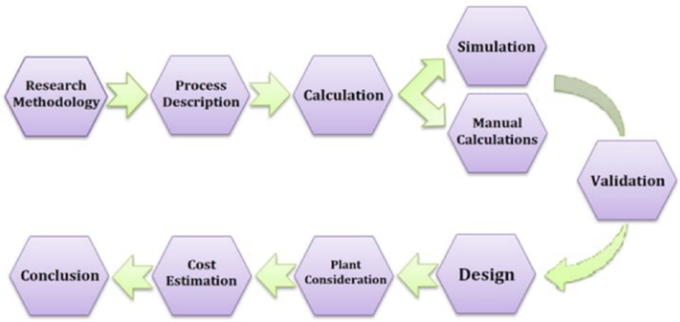

Figure 4 The flowchart of the process identification.

4. PROCESS FLOW DIAGRAM FOR GREEN AMMONIA

Figure illustrates the process flow diagram for the green ammonia plant. The PFD was drawn using Microsoft Visio Professional 2016. In this research, the whole process consists of two main parts: water electrolysis and ammonia synthesis, for ASU unit, was replaced by taking N_2 feed directly from the nitrogen production plant. The first one was hydrogen production by using the alkaline electrolysis with KOH. In Electrolyzer, water molecules were separated into hydrogen and oxygen by 5% conversion, due to the absence of the required Electrolyzer in Aspen HYSYS V11, it was assumed that hydrogen production would be through a conversion reactor. So Feed, consisting of H_2O and KOH, was heated before entering the reactor to reach 65 °C, and entered the reactor at 25860 kmole/h and 26.7 bar. The Electrolyzer bottom product was sent to a separator to separate O_2 from H_2O and KOH, then liquids were recycled back to the feed while O_2 was ready for selling with high purity. The Electrolyzer top product was sent to a splitter to purify H_2 for the ammonia synthesis process. The last step was ammonia manufacture. The common Haber-Bosch synloop is used for ammonia production. In the ammonia synthesis part: the H_2 and N_2 then were mixed, compressed then heated to enter the Haber Bosch reactor the stream conditions were 450 °C, 144 bar with a molar flow of 4725 kmole/h. The reactor was designed for the conversion of 40%. The ammonia product stream was cold and sent to a separator that separated the ammonia away from the surplus of reactant. Ammonia was produced by a molar flow of 920.6 kmole/h. The entire process was designed for the annual production rate of 150k tons from green ammonia.

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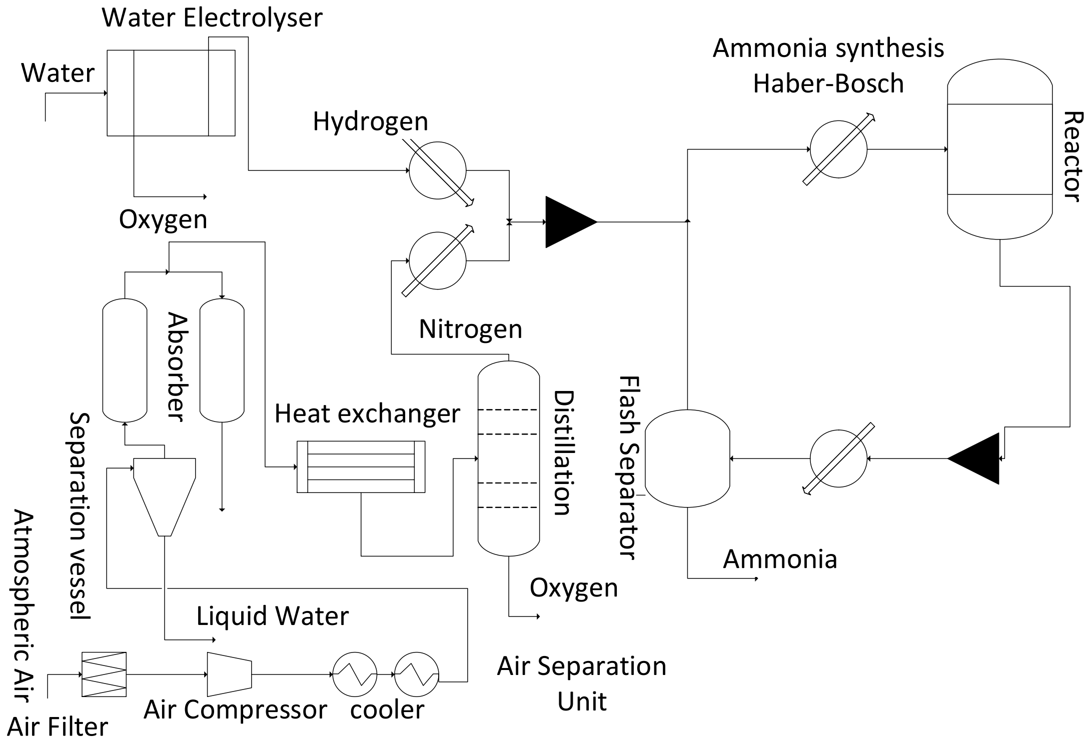

Figure 5 Illustrate the flow diagram of the green ammonia synthesis process.

5. SIMULATION

The process was simulated using Aspen HYSYS. Figure demonstrates the whole flow sheet of the process that was simulated by using Aspen HYSYS respectively.

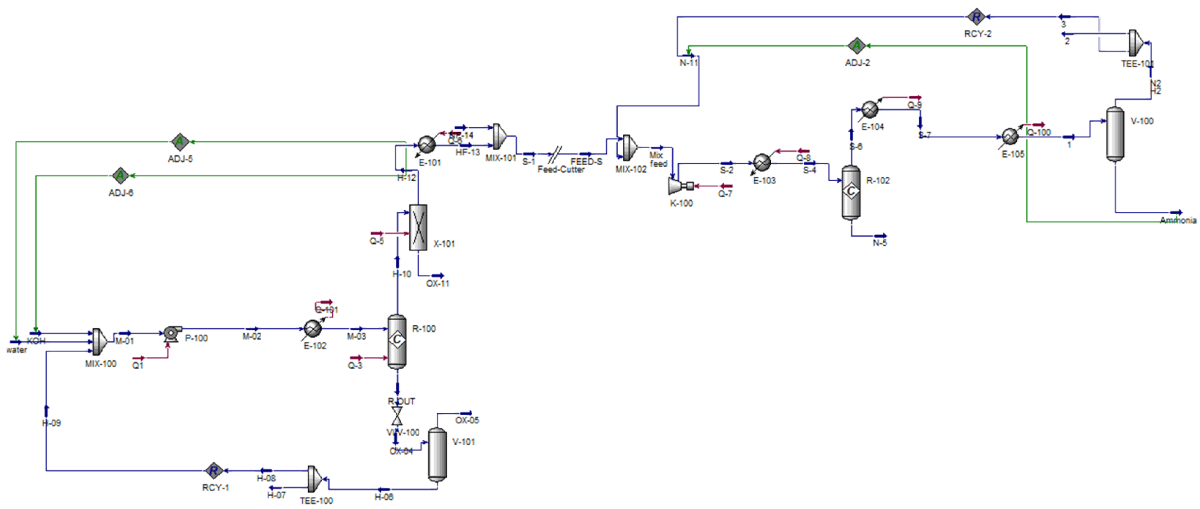

Figure 6 HYSYS process flow sheet.

6. Material balance

Material balance for this study has been carried out using Microsoft Excel 365 to calculate the amount of Hydrogen and Nitrogen needed per hour to produce Ammonia with a goal quantity of 170741 tons per year (920.6 Kmol/hr).

The process data and assumption are as follows: the conversion of the electrolyzer was 5%, The conversion of the ammonia reactor was 40%, the Final product had a purity of 99%, The recycle ratio for water and KOH was 0.5, The recycle ratio for mixer (MIX-102) was 0.99, Ammonia has 0.80 recovery.

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performing material balance on MIX-100, where the water feed was 15860 kmol/hr, So total (Out) = 15860 + 10000 = 25860kmol/hr.

For electrolyzer, mass balance, the conversion water to H_2 in electrolyzer was 5%, In = 25860 kmol/hr of water, $\mathbf{n_{H2}}$ = 25860 x 0.05 = 1293 kmol/hr Oxygen recovery from Hysys = 94%, $\mathbf{2H_2O \rightarrow 2H_2 + O_2}$ From the stoichiometry H_2 = ½O_2, $\mathbf{n_{O2}}$ = 1293 x 0.5 x 0.94 = 607.7 kmol/hr, Water recovery (from Hysys) to Separator (V-101) = 97%, $\mathbf{n_{H2O}}$ = 25860 x 0.97 x (1-0.05) = 23830 kmol/hr.

For v-101: In = 23830 kmol/hr, Water recovery (from Hysys) = 88.3%, $\mathbf{n_{H2O}}$ = 23830 x 0.883 = 21042 kmol/hr, return to be recycled with the catalyst in ratio = 0.5

MIX-102 mass balance is summarized as follows: **In + recycle = Out**
For H_2: 1383 + 2069 = 3452 kmol/hr, N_2: 694 + 348.5 = 1042.5 kmol/hr, NH_3: recycle = Out = 230.15 kmol/hr.

The result of the ammonia reactor mass balance is $\mathbf{N_2 + 3H_2 \rightarrow 2NH_3}$. The conversion of ammonia in the reactor was 40%, $\mathbf{n_{H2}}$ = 3452 x (1-0.4) = 2071 kmol/hr. from stoichiometry N_2 = 1/3 H_2 , $\mathbf{n_{N2}}$ = 1042.5 – ((3452-2071)/3) = 582 kmol/hr. from stoichiometry NH_3 = 2/3 H_2 , $\mathbf{n_{NH3}}$ = 3452 x 0.4 x (2/3) + 230 = 1151 kmol/hr.
Separator (V-100) mass balance results are: Hydrogen recovery from Hysys = 99.9%, $\mathbf{n_{H2}}$ = 2071 x 0.999 = 2069 kmol/hr, return to be recycled. Nitrogen recovery from Hysys = 99%, $\mathbf{n_{N2}}$ = 582 x 0.99 = 576 kmol/hr, return to be recycled. Ammonia recovery from Hysys = 80%, $\mathbf{n_{NH3}}$ = 1151 x 0.8 = 921 kmol/hr.

7. Energy balance

The energy balance for the manufacture of green ammonia was developed step by step to determine the stream temperature and needed heating or cooling duties for the electrolyzer and ammonia reactor. The mathematics and calculations of energy balance were carried out using Microsoft Excel 365.

A. Energy balance on electrolyzer

$$Q = \xi \Delta \hat{H}_r + \sum n_{out} \hat{H}_{out} - \sum n_{in} \hat{H}_{in}$$

The heat of reaction is calculated by:

$$\Delta \hat{H}_r = \sum \nu_i \Delta H^o{}_{fi} + \int_{Tstd}^{T} C_p \, dt$$

Where ν_i is the stochiomtertic coefficnet, $\Delta H^o{}_{fi}$ is the standard enthalpy of formation, and C_p is the specific heat capacity.

Table 2 Heat capacity calculation for R-100.

Electrolyzer			
□ $\mathbf{H_i \, n_i}$	7.80E+07 kJ/h	$\mathbf{\Sigma H_o \, n_o}$	2.74E+08 kJ/h

Table 3 Energy balance required data for R-100.

T_1 (°C)	T_2 (°C)	T_{ref} (°C)	ΔH_r (kJ)	ξ (kmol/h)
65	??	25	285000	1293

The exit temperature was determined by trial and error, $\mathbf{T_2}$ **(°C) =** 168.533

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B. Energy balance on ammonia reactor

The reaction is adiabatic, so
$$Q = 0 = \xi \Delta \hat{H}_r^{\circ} + \sum n_{out} \hat{H}_{out} - \sum n_{in} \hat{H}_{in}$$
This equation was used to calculate the heat in the equipment using Excel by using data in Table 4 and Table 5.

Table 4 Heat capacity calculation for R-101.

Ammonia reactor			
$\Sigma H_i n_i$	6.95E+07	**$\Sigma H_o n_o$**	1.12E+08

Table 5 Energy balance required data for R-101.

T_1 (°C)	**T_2 (°C)**	**T_{ref} (°C)**	**ΔH_r**	**ξ**
450	??	25	-92400	460.325

The exit temperature was determined by trial and , **T_2 (°C) =** 756.5121116

8. SIMULATION RESULTS VS MANUAL CALCULATIONS

The validation of the manual calculation by comparing them with HYSYS computational results for the production rate is shown in **Tabke 6**. There was a slight difference between the manually calculated values and that was calculated by HYSYS.

Table 6 Comparison between manual calculation and HYSYS for green ammonia production rate.

Property	**HYSYS**	**Manual Calculations**
Production rate Kmole/hr.	910 kmol/h	920 kmol/h
$Error = \frac{calculated\ value - HYSYS\ value}{calculated\ value} \times 100$	1.08%	

9. EQUIPMENT DESIGN

In this section, the design of electrolyzer R-100, Ammonia reactor R-101, heat exchanger E-102, and Separator V-100 and V-101 was shown.

A. ELECTROLYZER DESIGN

The Electrolyzer design was based on the produced hydrogen volumetric flow rate. The hydrogen production rate was calculated using material balance and it was 2586 kg/hr. The electrolysis reaction occured at 65°C and 2700 Kpa. By using the ideal gas law and the individual gas constant for hydrogen the volume of the electrolyzer is calculated and it is equal to 1335.12 Nm^3/hr [11]. This amount of hydrogen requires a 2MW electrolyzer [12]. Alkaline technology estimated an average cost of 700 to 1100 USD per KW [13]. Taking the minimum price. Cost of R-100 = 700 USD x 2000 KW= 1400000 USD.

B. AMMONIA REACTOR DESIGN

In the ammonia production part, the widely used Haber-Bosch reactor is chosen for ammonia manufacture. The calculation steps can be found elsewhere. The design calculation results are shown as parameters in **Table 7** [14-17].

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Table 7 Reactor design parameters summary.

Design of the reactor body (shell)	
Parameter	value
$D_{reactor}$ (m)	4.34
$L_{reactor}$ (m)	10
V_r (m^3)	98
Wall thickness (mm)	42.5
Design of Catalyst bed Tubes	
$N_{(tube)}$	480 tubes
$L_{(tube)}$ (m)	6
$d_{(tube)}$ (m)	0.12

C. HEAT EXCHANGER DESIGN

The heat exchanger is illustrated in Figure . The hydrogen feed was headed to the shell side and heating steam was headed to the tube side as it is the fluid with a higher tendency to foul or corrode. Steam was available at 330°C and was allowed to cool down to 329.5 °C.

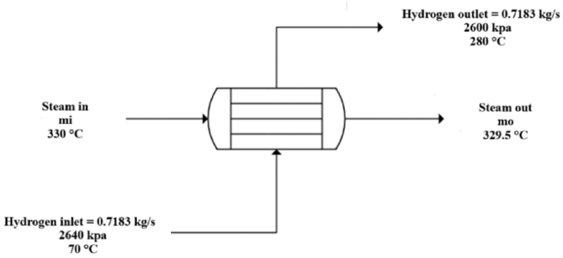

Figure 7 illustrates the heat exchanger inlet and outlet streams.

Assume that the characteristics of the fluids will be considered as a constant average amount throughout the design and only the heat transfer in the lateral direction in the tubes will be considered (the other two dimensions of heat transfer were neglected). The design calculation of the heat exchanger will follow Kern's method and the calculation steps can be found elsewhere[18-20]. The design results are shown in **Table** .

Table 8 Summary of design parameters calculations.

Design parameter	
Number of tubes	212
Shell diameter	590.55 mm
Tube diameter	16 mm 20 mm
Tube length	4.88 m
Tube pitch	25 mm
Baffle spacing	590.55 mm
Material of construction	Stainless steel
Number of passes	4
Heat transfer coeff. for shell side	843.589 $W/m^2.°C$
Heat transfer coefficient. for tube side	952.209 $W/m^2.°C$
Pressure drop for tube side	35 Kpa
Pressure drop for shell side	62.627Kpa

D. SEPARATOR VESSEL DESIGN

There were two separator vessels in the plant. The design of the two was calculated using Aspen Hysys and it was shown in Table 9.

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Table 9 Design parameters for V-100 and V-101 separator.

Parameter	**V-100**	**V-101**
Volume (m^3)	4.982	533.9
Liquid volume (m^3)	4.62	57.2
Diameter (m)	1.219	5.791
Height (m)	4.267	20.27
Material type	Carbon steel	Carbon steel
Chemical Eng. Index	252.5	252.5
Mass density (kg/m^3)	7861	7861
Allowable stress (Kpa)	$9.446x10^4$	$9.446x10^4$
Shell thickness (mm)	101.6	6.350
Corrosion allowance (mm)	3.175	3.175

10. GENERAL PLANT CONSIDERATIONS

The design of a plant involves various critical considerations to ensure its efficient and safe operation. One key factor was selecting an appropriate site location, taking into account geological stability, accessibility to transportation networks and resources, and conducting environmental impact assessments to minimize harm to local ecosystems and communities. The plant layout was also crucial, including equipment spacing for maintenance access and potential expansions, as well as optimizing material flow for efficient operations. Safety zones and areas for emergency response and fire protection should be designated within the layout. Additionally, assessing wind direction and weather patterns was important to position equipment and emissions stacks effectively to minimize pollutant dispersion and enhance safety, particularly in regions prone to extreme weather conditions. Ensuring safety and security measures, such as fire prevention and suppression systems and access control, was paramount for protecting critical infrastructure. Looking ahead, plant designs should incorporate scalability and future expansion possibilities to accommodate increasing energy demands or technological advancements. Aesthetic considerations should not be overlooked, as the visual impact on the local community can influence public perception. Furthermore, operational efficiency should be a priority in planning, focusing on process integration and maintenance accessibility to optimize energy efficiency and reduce operational costs. By addressing these multifaceted considerations, plants can be designed to meet energy needs while minimizing environmental impacts and ensuring long-term sustainability.

A. EQUIPMENT SPACING

Equipment spacing was essential to provide safe locations of the utilized equipment across the plant. For example, if an explosion happens and equipment spacing is not considered, it may affect other equipment and cause other severe problems. The required tables for equipment spacing were obtained [21]. The spacing is demonstrated in Figure .

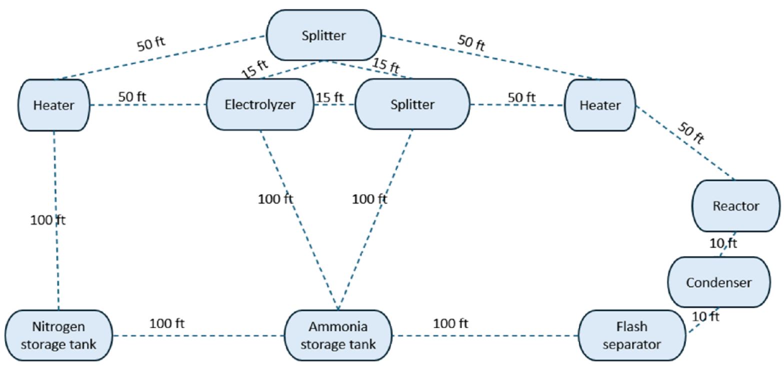

Figure 8 Equipment spacing of green ammonia plant.

B. PLANT LAYOUT

In the overall plant layout, careful consideration should be given to equipment spacing, the administrative area, and the identification of potential areas for future expansion. Additionally, it was crucial to consider the wind direction and intensity when determining the orientation of the plant. Figure illustrates the importance of this aspect. To gather information about the wind patterns in Damietta, it would be advisable to analyze the wind atlas or wind rose specifically for that region. This analysis will provide valuable insights for positioning equipment and structures strategically, ensuring optimal safety measures, and minimizing the dispersion of pollutants [22,23]. Figure Illustrate the plant layout at Damietta port.

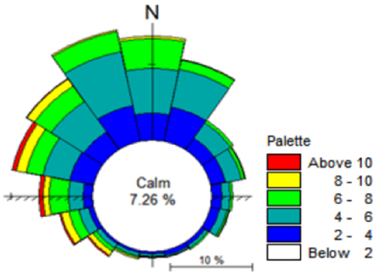

Figure 9 wind rose of Damietta [4].

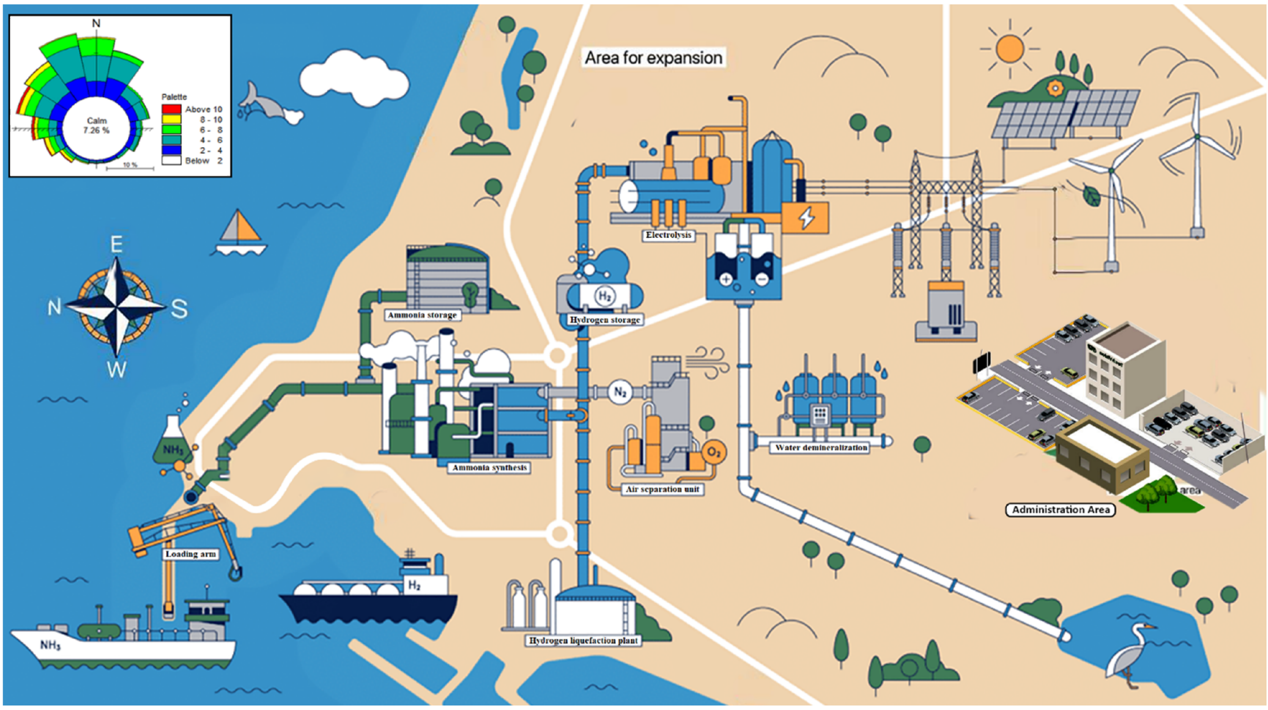

Figure 10 Plant layout for Green Ammonia production at Damietta Port.

C. SITE LOCATION

The following sites have been taken into consideration: Damietta Port, East Port-Said industrial zone, October industrial zone, 15 May industrial zone, Abo Rawash industrial zone, New Al Nubaria, or Fayoum industrial zone. The following reasons have been used as a basis for choosing the best area: location, according to the marketing area, raw material supply, transport facilities, availability of labor, availability of utilities: water, fuel, power, availability of suitable land, environmental impact, and effluent disposal, local community considerations, climate, and political and strategic considerations. As a result, one can assume that the Damietta port was the most optimum for a green ammonia production plant.

11. COST ESTIMATION

After the design of process equipment, the cost of each piece of equipment is now evaluated as a first step in estimating the cost required for plant erection. The cost of equipment by using Aspen Hysys for separator vessels, and pump. R-100 cost was calculated using data from [13]. R-101 cost was calculated from [24]. Heat exchanger cost was calculated using Aspen Hysys 11 and by using data from [25]. Compressor cost was calculated from [25]. Cost estimation consists of equipment cost [24,25], capital investment[26], fixed [27] and variable operating cost[28-30], and depreciation cost. The calculation steps can be found elsewhere. The calculation results are shown in Table 10.

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Table 10 The cost calculation summary.

Parameter	Cost (USD)
equipment cost	4670774
capital investment	22,401,031
Direct production cost	160310317
Annual production cost	192372380.4
Production cost per ton	1350/ton
depreciation cost	420369.66

12. CONCLUSION

In this paper literature review of green ammonia synthesis from green hydrogen produced by an alkaline electrolyzer, and ammonia synthesized using the Haber Bosch process. First, a full process description has been illustrated. Second, by using Aspen HYSYS V11 a simulation for the full process was made. Third, A manual calculation for material and energy balance was made by using Microsoft Excel 365. After that, a comparison between HYSYS and manual calculation for ammonia production rate was made and produced an error equal to 1.08%. Fourth, a design for an electrolyzer, ammonia reactor, heat exchanger, and two separators was assembled. Fifth, a plant consideration was assembled which includes equipment spacing, plant layout, and site location for the plant. The Damietta port was the optimum for a green ammonia production plant. Finally, cost estimation for the plant was calculated and as a result, the cost required for producing 1 ton of green ammonia was 1350 USD/ton. For future work, an optimization of the process should be made to reduce the cost per ton.

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