A Sustainable Green Ammonia Synthesis by Renewable Route: A Condensed Research with Design Aspects

H.M.Bilal[1], A. Ahmad[1], Abdulaziz A. M. Abahussain[2], M.H.Nazir[3], S.Z.J. Zaidi[1,4]*

[1]Institute of Chemical Engineering and Technology, University of the Punjab, Pakistan.
[2] Department of Chemical Engineering, King Saud University, Riyadh 11451, Saudi Arabia.
[3] Faculty of Computing Engineering and Sciences, University of South Wales, United Kingdom.
[4] Laboratory for Energy Water and Healthcare Technologies, University of the Punjab, Pakistan.

Corresponding Author Email: zohaib.icet@pu.edu.pk

ABSTRACT

The study aims to develop a process design and integration of a tri-generation system for simultaneous production of electricity using renewable resources, hydrogen (H_2) and green ammonia (NH_3). Ammonia being a vital raw material, is gaining recognition as a sustainable fuel, particularly for heavy transport and as a significant hydrogen energy carrier. The proposed integrated plant contains an alkaline water electrolysis system for hydrogen production, which is then consumed in the Haber-Bosch process for ammonia synthesis. The electricity required for electrolysis process is generated through renewable resources, specifically wind and solar energy. The energy is stored in form of molten salt through thermal energy storage technology. The process design includes detailed material and energy balances for water electrolysis and ammonia production units. Results obtained by rigorous design of equipment such a hydrogen and oxygen separators, heat exchanger, electrolyzer for hydrogen production and ammonia synthesis reactor highlight optimized operational and design parameters. The economic feasibility assessment of the process was made through cost estimation of key components, such as separators, heat exchanger, electrolyzer, compressor and tubular reactor. The findings obtained by this study highlight the potential of this tri-generation system in providing the sustainable solution for energy and climate change crisis, specifically in countries like Pakistan where renewable energy resources are present in abundance.

NOMENCLATURE

MMCFD	million cubic feet per day
BtA	biomass-to-ammonia
PtA	power-to-ammonia
TES	thermal energy storage
LMTD	Log Mean Temperature Difference
AEC	Alkaline water electrolysis

1. INTRODUCTION

Ammonia is gaining recognition as a sustainable fuel with significant potential for global use in the future. Development of ammonia-based applications for heavy transport, power generation, and distributed energy storage is ongoing. If produced on a large scale, ammonia could potentially replace a significant portion of liquid fuel consumption today [1].

Due to the sporadic nature of renewable energy sources, it is mandatory to use an energy storage system with them. In such a scenario, liquified energy storage is a promising technology as to reduce bulk transportation and pipeline costs. For this reason, H_2 and NH_3 have been getting enormous attention as their storage and transportation in liquid form are developed subjects. Due to the complexities involved in the storage and transportation of H_2, it is recommended that it should be converted into NH_3. This ammonia will then be used

to get H_2 as well as a feedstock chemical for fertilizer and other chemical process industries. Having a reasonable calorific value, NH_3 can also be used as fuel when burned directly in the engine. Apart from that, blends of NH_3 can also be made for fuel purposes [2-4].

Due to the increasing number of humans, the demand for energy and other available resources is increasing exponentially. This led to a sharp depletion of natural energy sources such as petroleum and natural gas. Carbon, the basic element in organic compounds, leads to emissions such as CO_2 and CH_4. These gases are thought to be a threat in the 21st century as the world has been facing their severe effects in terms of acute weather conditions, changing weather profiles, diseases, and natural disasters such as floods and an increase in sea level etc. for the last decade [3,4].

There is a dire need to balance the supply and demand of power; however, it needs demand-side solutions and inclines

to surge the costs of grid integration intensely. Different approaches such as; hydrogen, hydropower, and batteries can be utilized to store the energy in different forms. Cost, time and amount of energy storage are the main criteria to choose optimal energy storage method [5]. Being a versatile chemical, NH_3 exhibits exceptional properties such as its high energy density marks it an energy storage medium. Another advantage in this context is that the conversion of NH_3 into energy is carbon free. H_2 is also stored in the form of NH_3 to effective storage and transportation. The maturation of NH_3 production technologies is also a factor that it is getting prior attention in the era of renewable technology while meeting the agenda of net-zero emissions by 2050 [6].

Green ammonia, as obvious from the name is produced from green resources. The main raw materials in the production of ammonia are H_2 and N_2. The source of N_2 for this reaction is air while there are multiple sources that exist for H_2 production. Fossil fuels are the main source of commercial production of H_2. To tackle the issues of minimizing the use of fossil fuels and greenhouse gases, a shift towards renewable resources is on the peak. So far in this context, renewable alternatives evolved for NH_3 production are biomass gasification and water electrolysis from renewable grid bases. These alternative processes are also called biomass-to-ammonia (BtA) and power-to-ammonia (PtA) [7,8].
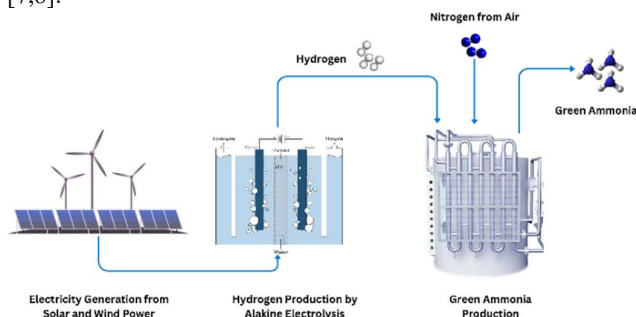

Figure 1. A tri-generation system for simultaneous production of electricity, hydrogen and green ammonia

The third technology which is called green ammonia production is a modern process to produce ammonia. In this process we replace the H_2 production route as accomplished in MtA and BtA with water splitting. Three types of technologies are prevailing in this context, namely Alkaline water electrolysis (AEC), Proton exchange membrane (PEM), and Solid oxide membrane (SOEC). In this study, we are focused only on alkaline water electrolysis (AEC). The reason is that this technology is developed as the materials used in this technology is developed and operational stability is high. In case of PEM electrolyzer, the technology is not fully developed to be utilized on large scale because the material used are scarce elements e.g., iridium and platinum. Solid oxide membrane (SOEC) is the most efficient technology but use of noble metals such as yttrium may cause a limitation when scales up [9].

Pakistan a country in the South Asia is a developing country. Currently it has been facing both the issues of energy crises and climate change. Primarily, major contributor of energy mix of Pakistan has been imported fuels for decades. Gas is the major energy source of country, it is being utilized in almost all industries, including feed stock for fertilizer production and fuel in power generation. Due to increase in use of fertilizer in agriculture sector, the demand of natural gas as a feed stock is also increasing. An increase in gas demand from 3,563 MMCFD in 2020 to 4,237 MMCFD is projected. The reduction in net supply to 2,102 MMCFD by 2025 and to 1,627 MMCFD by 2030 is also estimated. Besides of all the challenges with traditional fossil fuel-based energy resources, Pakistan is blessed with abundant renewable energy resources [10].

According to a survey conducted by National Renewable Energy Laboratory (NREL), USA in collaboration with USAID Pakistan has a potential of 2.9 MMW of solar energy. Pakistan also has a huge potential of wind energy, which can be utilized for power generation. In year 2007, there was a study conducted by National Renewable Energy Laboratories (NREL), USA under USAID sponsorship program for estimation of Pakistan wind energy potential. Giving to this study, the total potential of wind energy in Pakistan is about 346,000 MW out of which 120,000 MW is feasible.

2. PROCESS DESCRIPTION

For the sake of understanding and striking focus on the current energy scenarios we developed an integrated plant which in turn involved the production of following products; Green ammonia, Hydrogen and Electricity. The reason for developing an integrated plant is the need of the hour. An integrated plant evolves minimum energy and material loss and impinges less carbon footprints [11]. A tri-generation system is a set of multiple sub-systems that impart their respective contribution in the production of designated outputs. The combination of such technologies is a complex procedure as it requires the integration of inter and intra sub-system components. This tri-generation system will be developed as a modular design. Modular design magnifies the nature of process in such a way to split the process in an understandable way [12]. This approach usually encounters many benefits such as flexibility in plant sitting, minute safety issues during construction and imparting a space for future modification. The tri-generation system in our consideration, for instance, is divided into several modules, e.g., H_2 production section, NH_3 section and electricity generation unit. To make the study simpler a module can also be further divided into sub-modules.

2.1 Water Electrolysis Unit

In this unit the general reaction for the splitting of water into H_2 and O_2 occurs. In an electrochemical reaction, electricity is utilized to perform the conversion of raw material into the desired product. The main reaction for water electrolysis is given as,

$$H_2O \rightarrow H_2 + 0.5O_2$$
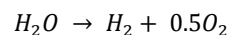
To establish this reaction an external source of electrical energy is introduced and the movement of charges from external source breaks the water molecule and hence causes the H_2 and O_2 to form. As the water electrolysis reaction involves the formation of charged species called ions, e.g., H^+, OH^-. Therefore, to produce such ions alkalis such as KOH and NaOH are used [13,14].
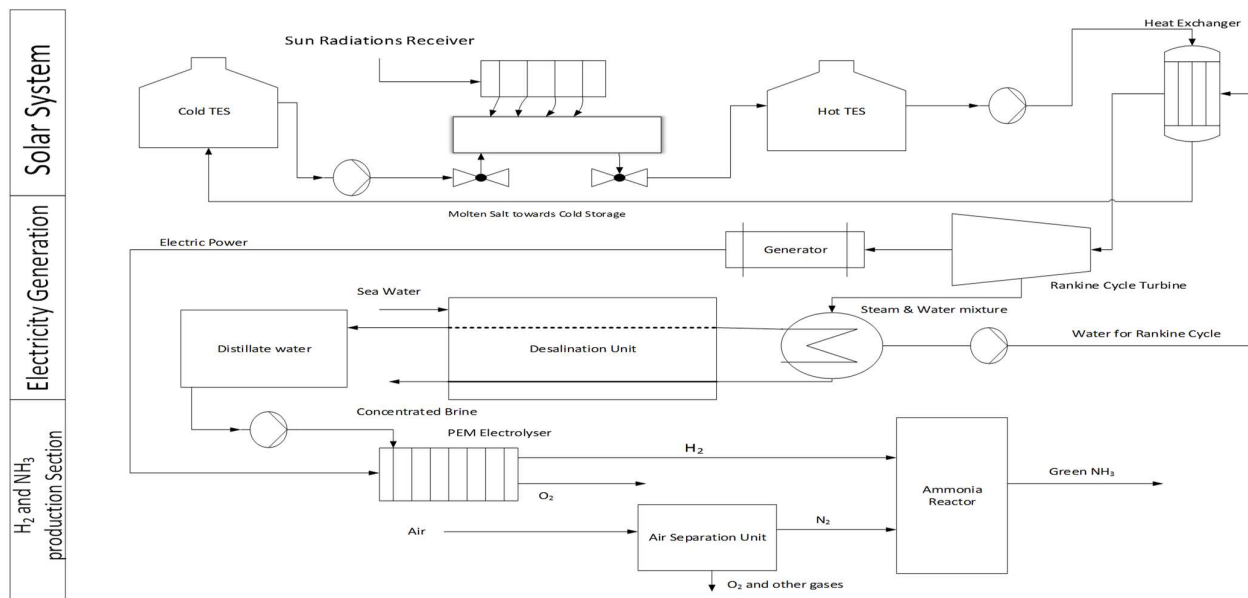
Figure 2. A process flow diagram of modern tri-generation system

Table 1. A general mass balance sheet for ammonia production

Species	Coefficient	Molecular weight	Molar balance by Hydrogen	Mass (kg)			
N_2	-1	28	0.5				
H_2	-3	2	1.5	3	**Ammonia Capacity Required**	1	kg
NH_3	2	17	1	17	**Hydrogen required**	0.176471	kg
H_2O	-1	18	1	18	**Water Required**	1.588235	kg
H_2	1	2	1	2	**Hydrogen Capacity Required**	0.176471	kg
O_2	0.5	32	0.5				

2.2 Ammonia Production

Compartments of the NH_3 molecule are nitrogen(N) and hydrogen(H_2). Haber-Bosch process was utilized to transform the presence of N and H into NH_3. Source of nitrogen was air for this process as air contains 79 mol% of nitrogen (N_2) in it. H_2 was produced and taken from the process of water electrolysis. In Haber-Bosch process the ammonia is produced under high temperature and pressure conditions. Optimum value of these parameters lie in the range of 15-25 MPa and 400-450 °C. Being a slow reaction, it requires the use of catalyst such as iron based catalytic bed. Also, a gas recycle system is mandatory because of the lower value of single pass conversion which is almost 15% [15]. A general mass balance sheet is shown on the table:

2.3 Electricity production

The main concern of this section was to provide the main supply of energy to drive the basic units of the tri-generation system. Here the source of energy were renewables such as wind and solar energy. As both of these resources are intermittent in nature, hence we must have to develop an energy storage system which has the potential of scale up at the commercial level and can store energy in an efficient manner (both cost effective and easy to operate) [16]. There are various options available to store the energy. On the priority basis batteries are thought to be an energy storage device but at commercial level batteries cannot be used because of their high capital cost, short service life and have

increased net energy consumption. Other technology which is under developing stages is called thermal energy storage (TES). This technology is promising because of its sustainability and economical concerns. Thermal energy storage technology is the combination of, Thermo-chemical energy, Sensible heat, and Latent heat storage phenomena [17]. In case of latent energy storage, the heat is stored in the material during the phase changing process. At commercial level this heat storage process occurs between solid and liquid phases. Melting or crystallization are the prevailed phenomenon during such phase transition processes [18].

$$Q_{TES}|_{T_L}^{T_H} = \int_{T_L}^{T_M} mC_p \, \Delta T + ma_m \Delta h_m + \int_{T_M}^{T_H} mC_p \, \Delta T$$

We utilized the thermal energy storage by molten salts. The eutectic mixtures of inorganic salts, for example $MgCl_2$, KCl and NaCl mixture, are show exceptional thermal and transport properties. So, in modern process, they can be used as thermal energy storage medium as well as heat transfer fluid. Currently, at commercial level mixture of nitrate and lithium-based salts are deployed because of their low temperature range and sustainability. But as these salts are expensive thereby diverted our attention to relatively cheaper options such as chloride salts [19].

3. MATERIAL AND ENERGY BALANCE

3.1 Mass balance for water electrolysis

In this unit, the water splits into H_2 and O_2. The mass

balance is done according to guidelines given in. In main process, the water after pre-treatment enters the electrolyzer where it gets ionized by the addition of KOH and then the addition of electricity entails the production of H_2 and O_2. For

1 stack the water flow rate required is given as 20 kg/s. This requirement of water is very large because only 1 % of conversion is possible in this case of water electrolysis.
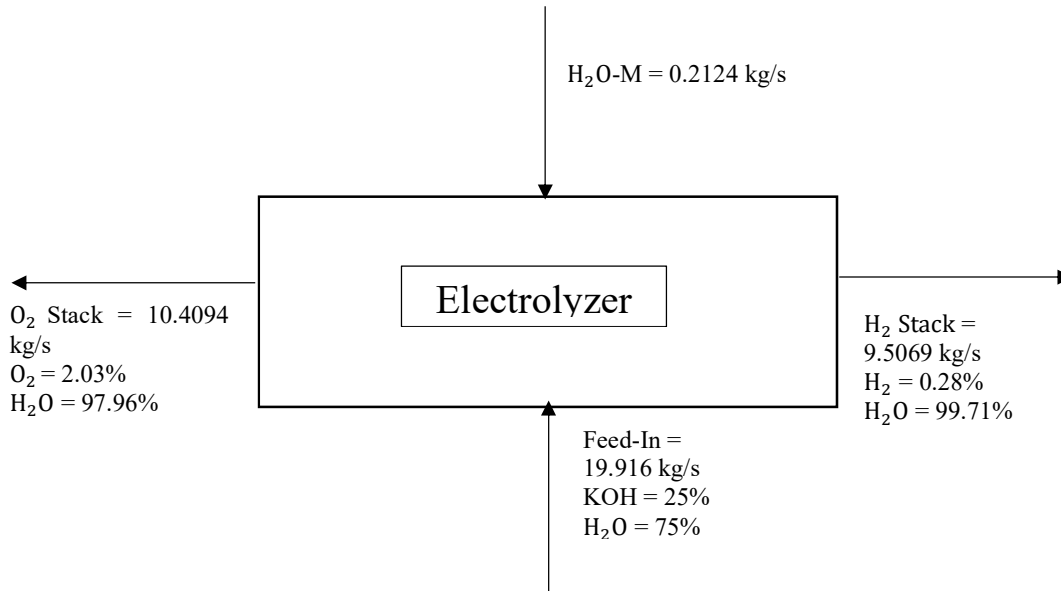

Figure 3. Mass Balance around Electrolyzer

Table 2. Inlet streams to Electrolyzer

Inlet Stream	Components	Mass flowrate kg/s	Mass fraction	Percentage %
Feed-In	H_2O	14.937525	0.75	75
	KOH	4.979175	0.25	25
H2O-M	H_2O	0.2124	1	100

Table 3. Outlet streams to Electrolyzer

Outlet Streams	Components	Mass flowrate kg/s	Mass fraction	Percentage %
H_2-Stack	H_2	0.0268	0.002819005	0.281900514
	H_2O	9.4801	0.997180995	99.71809949
O_2-Stack	O_2	0.212	0.020366207	2.036620747
	H_2O	10.1974	0.979633793	97.96337925

3.2 Energy balance for water electrolysis

The source of energy to the electrolyzer are in the form of lye entering to the water electrolyzer and electricity. The electricity required for the water splitting will be calculated as utility requirement.

The energy from the electrolyzer is taken by the gases produced and the water or lye which is bounded to those gases. Also, energy would also be lost to the environment by the mechanisms of heat transfer.
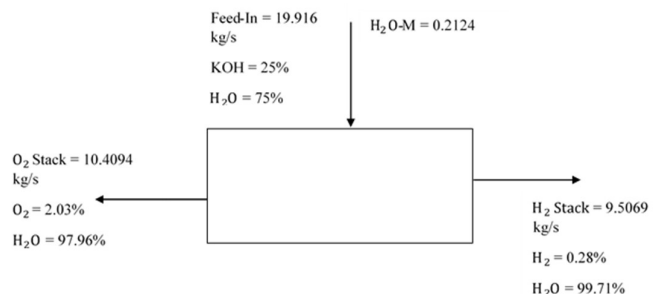

Figure 4. Energy Balance around Electrolyzer

Table 4: Inlet streams to Electrolyzer

Inlet Stream	Components	Mass flowrate kg/s	Molecular Weight (kg/kmol)	Molar flowrate kmol/s	Cp kJ/kgK	Hin kJ/s (kW)
Feed-In	H_2O	14.937525	18	0.8298625	3.168367	2839.653295
	KOH	4.979175	56	0.088913839		
H_2O-M	H_2O	0.2124	18	0.0118	4.171643	39.87256652

Total heat input = 2.879 MW

Table 5: Outlet streams to Electrolyzer

Outlet Stream	Components	Mass flowrate kg/s	Molecular Weight (kg/kmol)	Molar flowrate kmol/s	Cp kJ/kgK	Hout kJ/s (kW)
H_2-Stack	H_2	0.0268	2	0.0134	14.5	17.487
	H_2O	9.4801	18	0.52667	4.1716	1779.6417
O_2-Stack	O_2	0.212	32	0.00662	0.9218	8.7946875
	H_2O	10.1974	18	0.56652	4.1716	1914.2961

Total heat output = 3.72 MW

3.3 Mass balance on ammonia reactor

The mass balance is significant for finding the change in conversion of the reactants with respect to the length of bed of reactor. To solve the mass balance, it was necessary to have a known value for the area. However, since at this stage of the design the reactors have not been sized, it was challenging to take an assumption of an accurate area value. Therefore, an iteration method was employed. Random area values were inputted into the equations until the calculated numbers yielded meaningful results. This iterative process allowed for finding a suitable area value.
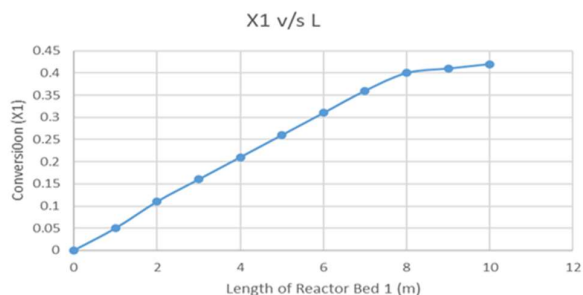

Figure 6. Conversion across the length of the reactor 2

Figure 5. Conversion across the length of the reactor 1

It is clear from plots that 11% conversion was achieved in reactor 1 and the bed length along this conversion is 2m. This length is the length of catalyst bed only; it does not represent the whole reactor length. After the completion of reaction in reactor 1, the product and unconverted reactants are fed to reactor 2 as feed where the same reaction occurs again. For the reactor 2, the conversion was 10% and the catalyst bed length is 2.5m. In case of reactor 3, to achieve conversion of 7.5% the catalyst bed length should be 2.7 meters.
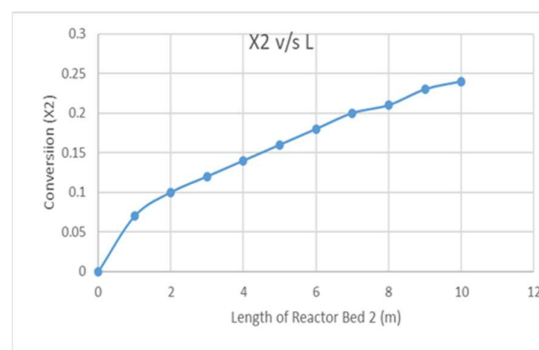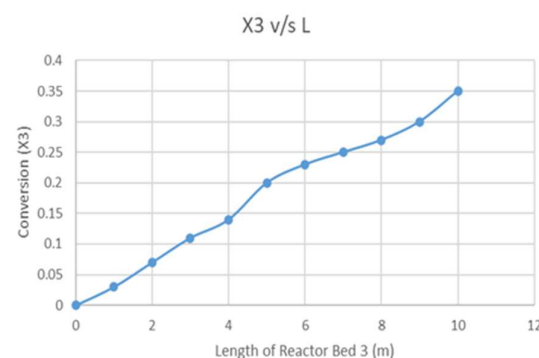

Figure 7. Conversion across the length of the reactor 3

This study was performed to determine the required length of catalyst for each reactor for a given conversion. An increase in catalyst bed length from 2m to 2.5m and then to 2.7m can be seen as the reactants progress through each reactor. This increment in bed length is due to the decrease in reaction rate as time passes. Now, let's apply Mass Balance around Ammonia Reactor,

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$
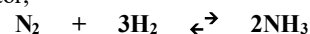
Limiting Reactant = H_2. Demand production of NH_3 = 1200 tones/day = 2941 $kmolNH_3$/hour
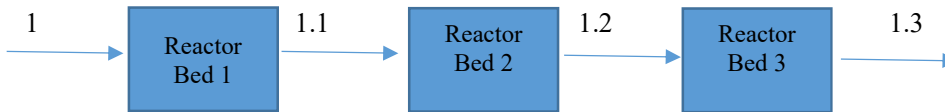
Figure 8. Temperature distribution across the length of reactor 1

Table 6: Mass balance on ammonia reactor

Compo-nents	1 (kmol/hr)	1.1 (kmol/hr)	1.2 (kmol/hr)	1.3 (kmol/hr)
N_2	1471.6	1323	1191	1101
H_2	4411.8	3970	3357	3305
Inerts	0.12	0.12	0.12	0.12
NH_3	2204	2498	2762	2941
Total feed	8087.52	7991.12	726.12	7347.12

3.4 Energy balance on ammonia reactor

The relationship between reactor bed length and temperature can be determined by the energy balance analysis. Using this relationship, the appropriate length of the reactor bed is determined based on the desired temperature profile. The selected bed length is then validated by comparing it with the conversion versus bed length relationship. Now, the temperature profile can be obtained by using the desired bed length for each reactor from this equation.

$$dT/dL = R_{NH_3} \Delta H_R \eta / (F_{total}) (C_{p,mix})$$

After solving the equation for each reactor, it is obtained that the feed enters at its auto-ignition temperature (673K) in first bed. Afterwards, the temperature will reach to 702K for the bed length of 2m, which requires quenching as it is too high to enter in reactor 2. if the bed length is 2m then the temperature reached will be 702 K. The temperature is reduced to 688K from 702K after quenching. This quenching is performed by using cold unconverted syngas fresh feed. In reactor 3, the inlet stream temperature is 710 K, as it receives the outlet stream from reactor 2 after cooling. After undergoing the reaction in the 2.7-meter-long bed of reactor 3, the temperature reaches 748 K.
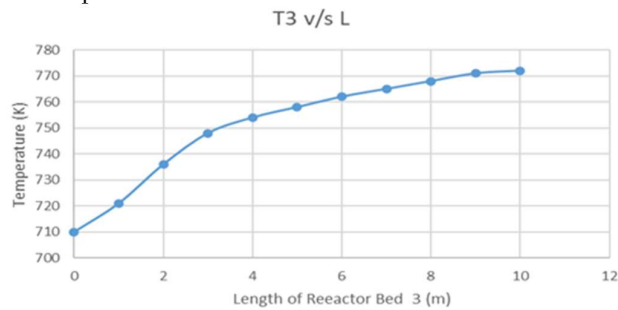

Figure 10. Temperature distribution across the length of reactor 3.

Table 7: Energy balance on ammonia reactor

Heat generated by reaction	Q_{rxn} (J /mol)	-270588235.3
Heat of reactants	H_r (J / mol)	13757901295
Heat of Products	H_p (J / mol)	17524144873
Heat generated by products	Q_p (J / mol)	4036831813

Figure 9. Temperature distribution across the length of reactor 2.

4. EQUIPMENT DESIGN

4.1 Design of a horizontal separator for H_2 side

In this unit, all the water which is not converted into H_2 will be separated from the gas stream. The lye droplets can be carried over by the high flow rate stream of H_2. To get the purified form of H_2 gas a separator is required which is simply a horizontal vessel having demister pads in it. After a certain surge time, the water molecules will be coalescence and due to prominent effects of gravity they can be collected at the

bottom of the separator. The calculated design parameters are given below in specification sheet [20].

Table 8: Specification sheet of a horizontal separator for H_2 side

Design Parameter	Value	Unit
Mass Flow Rate (Liquid)	10.4098	kg/s
Mass Flow Rate (Gas)	0.0268	kg/s
Separator Cells per Unit	10	cells
Density (Liquid)	1280	kg/m³
Density (Gas)	1.15	kg/m³
Separation Factor (F_LV)	2.454674	-
K Value (K_V)	0.005684	-
K Value for Horizontal Separator (K_h)	0.007105183	-
Maximum Vapor Velocity (u_max)	0.07223743	m/s
Area of the Separator (A)	3.226076519	m²
Minimum Diameter (D_min)	4.531869481	m
Volume Flow Rate (Liquid)	0.081326563	m³/s
Surge Time (t_s)	300	s
Volume of Liquid (V_L)	24.39796875	m³
Volume of Vessel	30.49746094	m³
Length of Vessel (L)	9.453421442	m

4.2 Design of a horizontal separator for O_2 side

As we know that, during electrolysis of water, not only H_2 is produced instead we get another valuable gas O_2. At the anode side of the electrolyzer we are get O_2 at a sufficient rate which is higher than the subsequent flow rate of H_2. This produced oxygen gas also carries some amount of unconverted water and KOH mixture with it. To purify the produced O_2 gas we need a device which serves the appreciable residence time to the stream of flowing gas. For this purpose, separator is

utilized. The calculated design parameters are given below in specification sheet [20].

Table 9: Specification sheet of a horizontal separator for O_2 side

Design Parameter	Value	Unit
Mass Flow Rate (Liquid)	9.4801	kg/s
Mass Flow Rate (Gas)	0.212	kg/s
Separator Cells per Unit	10	cells
Density (Liquid)	1280	kg/m³
Density (Gas)	18.3	kg/m³
Separation Factor (F_LV)	1.676506721	-
K Value (K_V)	0.020959553	-
K Value for Horizontal 'Separator (K_h)	0.026199441	-
Maximum Vapor Velocity (u_max)	0.026199441	m/s
Area of the Separator (A)	1.746682927	m²
Minimum Diameter (D_min)	3.334625747	m
Volume Flow Rate (Liquid)	0.074063281	m³/s
Surge Time (t_s)	300	s
Volume of Liquid (V_L)	22.21898438	m³
Volume of Vessel	27.77373047	m³
Length of Vessel (L)	15.9008427	m

4.3 Heat exchanger design for H_2 side

The heat exchanger design requires the conditions of both the fluids involved in the heat transfer operation. As we know that lye from the outlet of the horizontal phase separator is at about 80°C and we will have to cool it down to the prevailed conditions of the electrolyzer i.e., 70°C. We shall start the calculations by defining the physical properties of the fluids involved. The cooling water will be utilized for the cooling purpose because it is cheap, readily available and non-toxic in nature. To accomplish the design of heat exchanger we have used Delaware method as given by [21,22].

Table 10: Physical properties of the fluids

Properties	Lye	Water	Units
Temperature Inlet	152	100	°F
Temperature Outlet	137	120	°F
Heat Capacity	0.996397	0.756764458	Btu/(lbm·°F)
Density	79.9104	62.43	lbm/ft³
Thermal Conductivity	0.364250869	0.082047726	lbm/(ft·h)
Flow Rate	1470960	-	lbm/h
Viscosity	2.201748836	1.525102176	lbm/(ft·h)

Table 11: Specification sheet of a heat exchanger for H_2 side

Parameters	Value	Unit
Type	AES	
Material of Construction	Plain Carbon Steel	
Tube Pitch	Square	
Heat Exchanger Duty (Q)	16697553.71	Btu/hr
Cooling Water Flow Rate (m)	837896.6279	lbm/hr

Log Mean Temperature Difference (ΔT_lm)	34.43952874	°F
LMTD Correction Factor (R)	1.333333333	
LMTD Correction Factor (P)	0.288461538	
LMTD Correction Factor (α)	0.864864865	
LMTD Correction Factor (S)	0.288461538	
LMTD Correction Factor (F)	0.95627075	
Heat Transfer Coefficient (U_guess)	300-500	Btu/(h·ft²·°F)
Design Overall Heat Transfer Coefficient (U_D)	185.1932921	Btu/(h·ft²·°F)
Over Design (%)	25	

4.4 Green Ammonia Reactor Design

The green Ammonia reactor type is Fixed Bed Reactor, the catalyst in the form of tubes embedded inside the reactor. For this design practice, a multi-tubular reactor assembly is selected as the preferred way of catalyst dispersion in the fixed bed. This choice is based on the large amount of catalyst calculated in the previous section. The reactor structure consists of several cylindrical tubes that hold the catalyst particles in a vertical position inside a vertical vessel. The process involves the entrance of syngas feed to the reactor from the head section of reactor and passing down through these tubes packed with catalyst particles. The product then exits from the bottom of the bed. This is a three reactor system, detail of designing parameters is given below [23,24,25]

4.5 Electrolyzer design

A device in which electrochemical reaction takes place is called electrolyzer. We used alkaline electrolyzer system, the DC power generated from a combined system of renewable solar and wind energy is supplied to the electrolyzer cell stack. Within the stack, the water-splitting reaction takes place using anode and cathode electrodes immersed in an electrolyte solution consisting of 20%–30% potassium hydroxide (KOH). This reaction converts the water into hydrogen and oxygen gases [26,27].

Table 12: Design parameters of Green Ammonia Reactor

Parameters	Reactor 1	Reactor 2	Reactor 3
RNH_3 (mol/m³.hr)	399.1026	300	180.9186
Length of Catalyst Bed (m)	2	2.5	2.7
Diameter of Catalyst Bed (m)	1	1.2434	1.3116
Number of Catalyst Tubes (n)	31	37	41
Length of Reactor (m)	3.3	4	4.2046
Diameter of Shell (m)	1.3	1.45	1.5046
Reactor Volume (m³)	4.4	6.31	7.2
Cylindrical Shell Thickness (mm)	531	593	616
Hemispherical Head Thickness (mm)	190	212	220
Pressure Drop across Reactor (Pa)	2440	3040	3290
Quench Stream Temperature (K)	612.44	-	655.26

Table 13: Design parameters of alkaline electrolyzer system

Parameter	Value	Unit
Faradic Efficiency	0.86	-
Effective Area	2.66	m²
Number of Electron Transfer (z)	2	-
Current Density (i-cell)	0.316971	A/cm²
Number of Cells Required (E-cells)	326	-
Faraday's Constant (F)	96485	C/mol
Total Stacks	100	-
Total Moles of H_2 Required	1225.55	mol/s
Total H_2 Required	4412 Kmol/hr	-
Moles of H_2 for 1 Stack	12.25	mol/s
Current Density for 1 Stack	0.316971	A/cm²
Voltage Required for 1 mol of H_2O	1.2762	V
Total Voltage Required for 1225.55 mol/s	1564.046	V

5. COST ESTIMATION (PLEASE VERIFY THE NUMEROTATION)

5.1 O₂ Separator cost estimation

The cost estimation for this unit is done according to the procedure given in [28]. The formula for calculating the total cost is given by the following equation.

$$C_P = F_M C_V + C_{PL}$$

Table 13a: O₂ Separator cost estimation

Parameter	Value	Unit
Weight of the Separator (W)	68600	lb
Thickness of Separator (t_s)	20	mm
Inner Diameter of Separator (D_i)	11	feet
Length of Separator (L)	16	meters
Purchase Cost for Empty Horizontal Vessel (C_V)	$96,453.43	USD
Added Cost for Platforms and Ladders (C_PL)	$37,229	USD
Total Purchase Cost (C_P)	$133,682	USD

Table 13b: H₂ Separator cost estimation

Parameter	Value	Unit
Weight of the Separator (W)	64697	lb
Thickness of Separator (t_s)	20	mm
Inner Diameter of Separator (D_i)	14.85	feet
Length of Separator (L)	9.45	meters
Density of Separator Material (ρ)	0.284	lb/in³
Purchase Cost for Empty Horizontal Vessel (C_V)	$93,181	USD
Added Cost for Platforms and Ladders (C_PL)	$29,518	USD

Parameter	Value	Unit
Total Purchase Cost (C_P)	$122,699	USD

O₂ Separator cost estimation

The guidelines to calculate the cost of a shell and tube heat exchanger are given by [28]. The formula for the purchase cost of floating head shell and tube heat exchanger are given as,

$C_P = F_P F_M F_L C_B$

H₂ Separator cost estimation

The cost estimation guidelines for a horizontal separator are given in [28]. The reason why we horizontal separator is that when a small amount of a gas is associated with the liquid then usually horizontal separator is preferred. The formula for calculating the total cost is given by the following equation.

$$C_P = F_M C_V + C_{PL}$$

Table 14: O₂ Separator cost estimation

Equipment	Energy Input (kW)	Previous Cost ($)	Current Cost ($)
Feed Compressor	690	115,000	179,000
Quench Feed Compressor	140	17,500	27,200

5.2 Green Ammonia reactor cost estimation

The cost of reactor is estimated on the basis of method in which Pressure inside the reactor matters [29]. Hence, Estimated Cost = Ce = a + b P

The cost that we can get from the above equation is the previous year cost of the reactor. Hence, cost of the recent year can find by the following formula [30].

Current Estimated Cost = Ce,current = CICEcurrent / CICEprevious Ce,previous

Table 15: Green ammonia reactor cost estimation

Equipment	Previous Cost Index (CICE_Pprevious)	Current Cost Index (CICE_Pcurrent)	Previous Cost (Ce,2010) in $	Current Cost (Ce,2021) in $
Reactor 1	576.1	614.5	143,601.625	153,173.4049
Reactor 2	576.1	614.5	178,158.875	190,034.0717
Reactor 3	576.1	614.5	182,082.6	194,219.3329

5.3 Compressor cost estimation

The compressor is Rotary type compressor and cost of compressor can be find by getting to know its energy input. By using the energy input, we can find the cost of previous year compressor and thus for finding cost of recent year compressor, we used the formula of Cost Index.

Table 16: Compressor cost estimation

5.4 Electrolyzer cost estimation

To estimate the costs of electrolyzer plants at different capacities and predict future cost reductions until 2030, a modified power law approach has been developed. This approach incorporates a learning curve or technology development rate, building upon the cost estimation method introduced by Oi et al. By utilizing this method, the collected data can be effectively used for cost estimations and forecasting cost reductions in the future [31].

The resulting equation, giving the cost of an electrolyser plant in $/kW, is shown below:

$$C = \left(k0 + \frac{k}{Q} Q^{\wedge}a\right)\left(\frac{V}{V0}\right)^{\wedge}\beta$$

Thereby, the revised equation captures both cost reductions due to scale up of the best available technology for a given year, which at infinite scale would reduce to

$$C = (k0)\left(\frac{V}{V0}\right)^{\wedge}\beta$$

Here is a summary of the obtained projection parameters and the corresponding standard errors (SE) from performing non-linear least squares curve fitting of the cost equation to the collected cost data for the electrolyzer technologies [32].

Table 16: Summary of the obtained projection parameters

Parameter	AEL
A	0.649
B	−27.33
k_0	301.04
K	11,603
V_0	2020
SE	547

Table 17: Cost of electrolyzer of our requirement

Parameter	Value
Voltage requirements for 1 stack	15.55 V
Current requirements for 1 stack	9135 A
Power requirement for 1 Stack	142.11 kW
Power requirement for 100 stacks	142117 kW
Cost Estimated from Graph	$500/kW
Total Cost Estimated	$ 71,058,881.25

6. CONCLUSIONS

This study about tri-generation system for electricity, hydrogen and green ammonia production provides a sustainable solution for energy and climate crisis in order to achieve carbon neutrality. The detailed energy and material balance analysis for hydrogen and ammonia synthesis processes, conforms the efficiency and optimized utilization of resources for our system. The technical feasibility of our proposed system was attested by detailed equipment design, incorporating alkaline water electrolyzer, ammonia reactor, gas separators and heat exchanger.

The economic viability of tri-generation system was accessed by cost estimation analysis of key equipment. Despite of a significant initial investment, this study highlights the tri-generation technology as economical and scientifically sound solution. Specifically, in context of Pakistan's renewable energy landscape, our results and findings contribute to advancement of sustainable energy solutions.

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