Exploring the Potential of Renewable Resources for Ammonia Production: A Pathway to Sustainable Energy in Pakistan

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Summary: Employing alternative and renewable energy sources can help lessen Pakistan's current energy crisis. Pakistan has an abundance of renewable energy resources, which can be harnessed to store intermittent renewable energy for later use. This makes it essential for Pakistan, as well as other developing economies, to produce ammonia from renewable resources. Consequently, initiating a Pakistan Ammonia Economy depends on adding ammonia to the energy supply chain. To this end, Pakistan must incorporate ammonia into its energy roadmap by utilizing its renewable energy resources, as many nations are already doing. This study estimates the potential for various renewable resources—mostly solar, wind, and biomass—that are readily available in Pakistan. An estimate is made for producing ammonia from each of these renewable sources using different proven and emerging technologies, including electrochemical synthesis and plasma-assisted methods. Although several studies have examined energy resources in Pakistan, their use for ammonia production is still lacking. According to the findings, biomass energy is estimated to generate about 50,000 tonnes of ammonia per year, while solar energy could produce approximately 65,000 tonnes annually**.** The paper also includes a case study on a prototype development for green ammonia production, utilizing solar energy. The case study demonstrates a sustainable approach to ammonia synthesis, providing practical insights for implementation. The policy implications suggest the need to integrate green ammonia into Pakistan's energy strategy**,** offering a pathway to reduce fossil fuel dependency and enhance energy security. However, detailed policy formulation and roadmap development are beyond the scope of this study.

Keywords: Renewable Energy**,** Green Ammonia Production**,** Energy Crisis**,** and Sustainable Development.

Introduction

Ammonia (NH_3) is a critical chemical used primarily in fertilizers. Commercially ammonia is produced via Haber-Bosch (HB) process by reacting the Nitrogen(N_2) gas from air with Hydrogen (H_2) gas under the high pressure, high temperature and reaction catalyst [1]. Carbon dioxide (CO_2) emissions are caused by the hydrogen, which is typically obtained from natural gas or other fossil fuels. In contrast, green ammonia is created through sustainable techniques and renewable energy sources, making it eco-friendly. Unlike traditional ammonia production, which relies on carbon fuel and results the huge amount of CO_2 emissions, green ammonia is produced from renewable energy resources *e.g*. solar, wind, hydropower [2]. This approach eliminates CO_2 emissions, making the entire process carbon-neutral. The term "green" refers to the sustainable and eco-friendly nature of this production method, contributing to the reduction of greenhouse gas emissions and promoting a cleaner environment.

Need Assessment of Green Ammonia

The traditional HB process uses fossil fuels which is a significant source of carbon dioxide emissions. With global ammonia production accounting for about 1-2% of total CO_2 emissions [3], transitioning to green ammonia can substantially decrease the carbon footprint of the agricultural and chemical industries [4, 5]. As the world increasingly shifts towards renewable energy, the challenge of efficient energy storage and transportation emerges. Green ammonia offers a solution as an energy carrier [6], storing renewable energy in a stable and transportable form. It can be used as a carbon-free fuel for power generation and transportation [7], particularly in the industries which are tough to electrify *e.g*. shipping, heavy industry etc [8].

Ammonia is predominantly used in fertilizers for agriculture, with additional applications in the chemical industry, energy storage, and steel

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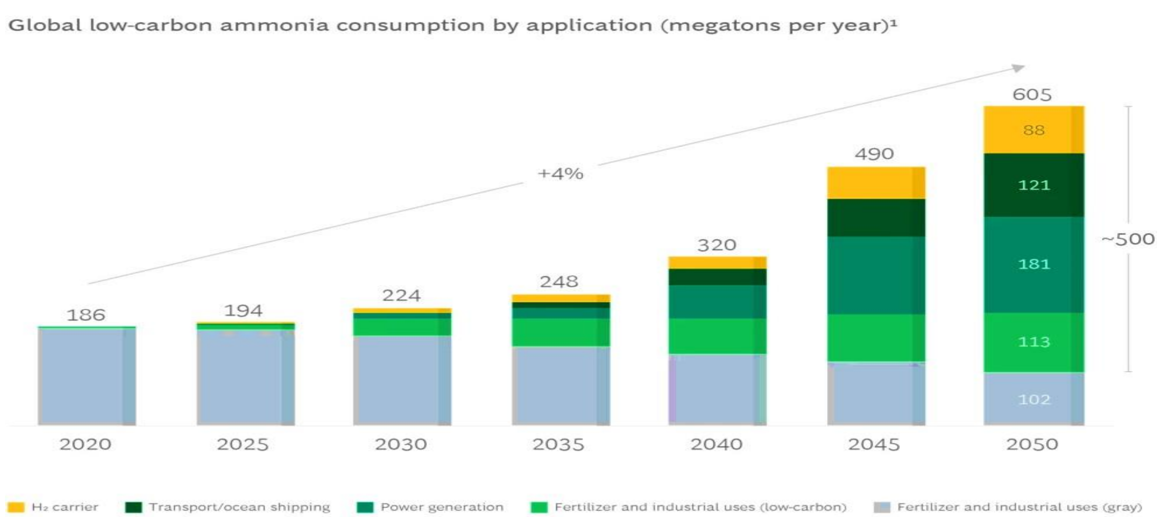
production. The potential of ammonia as a cleaner fuel is crucial for achieving net- zero emissions goals. Currently, ammonia production heavily depends on fossil fuels, resulting in significant carbon emissions. Transitioning to "green" ammonia, which is produced with minimal environmental impact, is essential for moving toward a cleaner energy future [9]. The global energy consumption stands at approximately 20 TW, with CO_2 levels around 400 ppm. With about two-thirds of the global population living below the poverty line, access to sustainable energy is critical for poverty reduction [9]. To meet global energy needs sustainably, an additional 10 TW of energy is required without increasing CO_2 emissions [10]. Most existing energy resources, such as coal, oil, and natural gas, are depleting and exacerbating global warming [11].

To the best of our knowledge, Pakistan currently lacks any plan or policy to introduce green ammonia into its energy reserves. There is limited literature addressing this issue, likely due to the absence of information on producing green ammonia from renewable energy sources. While other countries have made significant advancements in green ammonia technology, recognizing its environmental and economic benefits, Pakistan has yet to make substantial efforts in this domain. The lack of a strategic framework results in missed opportunities for integrating this sustainable energy source into the national energy mix. As a result, Pakistan remains heavily dependent on fossil fuels, contributing to environmental pollution and energy insecurity.

Energy derived from renewable sources, excluding large hydroelectric projects, constitutes less than 1% of the current energy supply in Pakistan [15, 16]. However, the country has ample renewable resources that could be harnessed to produce green ammonia through various conversion processes previously discussed. Additionally, Pakistan has diverse feedstocks and potential technologies suitable for optimizing ammonia production.

The current study aims to evaluate the total renewable energy resources available in Pakistan and explore how surplus electricity could be utilized for green ammonia production as an intermittent energy carrier. This approach allows ammonia to serve as an energy source during peak demand periods. Renewable energy from remote areas, such as solar and wind, could be converted into green ammonia and utilized in urban areas where land availability for energy production is limited. Furthermore, this green ammonia could meet the demands of agriculture and other industrial processes.

As part of this study, a lab-scale model was developed to demonstrate the conversion of solar energy into green ammonia using an energy-efficient process, accompanied by suitable calculations as a case study. This technical analysis is intended to encourage policymakers to recognize green ammonia as a valuable opportunity for energy storage and environmental protection. However, detailed policy formulation and the proposal of a comprehensive roadmap are beyond the scope of this research.



H_2 Carrier Transport /Shipping Power Generation Fertilizer and Industrial uses (Low Carbon) Fertilizer and industrial Uses (Grey)

Fig. 1: Projected demand of green ammonia [10].

We gathered data from reliable sources and appropriately cited them, providing an estimate of the potential annual production of green ammonia from various renewable energy sources, including solar, wind, and biomass. By adopting green ammonia and other sustainable practices, Pakistan can progress towards a cleaner and more sustainable future. This study seeks to identify and quantify the renewable resources in Pakistan that can be effectively utilized for green ammonia production. It also provides an overview of these resources, estimates potential output, and lays the groundwork for selecting the most appropriate technologies to advance a green ammonia economy. Given Pakistan's geographic and geological advantages, the country possesses vast renewable energy resources with significant potential for green ammonia production.

Production of Green Ammonia

In the production of green ammonia, renewable energy sources such as solar and wind power replace fossil fuels to produce hydrogen and drive the synthesis process, as shown in Fig. 2. The primary steps involve the electrolysis of water and the HB process. During electrolysis, renewable electricity from wind, solar, or hydropower splits water into hydrogen gas (H_2) and oxygen gas (O_2) [17]. This method is clean and sustainable, generating no CO_2 emissions. The resulting green hydrogen is then combined with nitrogen (N_2) extracted from the air via the HB process [18, 19] to produce green ammonia. This entire chain, powered by renewable energy, ensures carbon neutrality, significantly reducing the environmental footprint compared to traditional ammonia production methods.

Traditionally, Traditionally, ammonia synthesis relies heavily on the HB process, which demands high temperatures and pressures, consuming substantial amounts of fossil fuels. However, the shift towards renewable energy sources has led to the development of alternative methods for ammonia production. These include electrochemical synthesis [20], photocatalytic and photo-electrochemical synthesis [21, 22], biological production[23], and plasma-assisted synthesis[24]. In electrochemical synthesis, renewable electricity from wind or solar is utilized to drive nitrogen reduction reactions within an electrolyzer, making this method potentially carbon-neutral [25]. Photocatalytic and photo-electrochemical methods harness sunlight directly to split water for hydrogen production and reduce nitrogen, using specialized photocatalysts or photoelectrodes to enhance reaction efficiency. The biological production method is an innovative approach that employs genetically engineered microorganisms or enzymes, enabling ammonia synthesis under ambient conditions. Plasma-assisted synthesis involves generating plasma through renewable electricity, allowing nitrogen and hydrogen to react at lower temperatures and pressures compared to the traditional HB process. These emerging methodologies offer promising, sustainable alternatives to fossil fuel-based production, contributing to a more diversified and eco-friendly approach for green ammonia synthesis.

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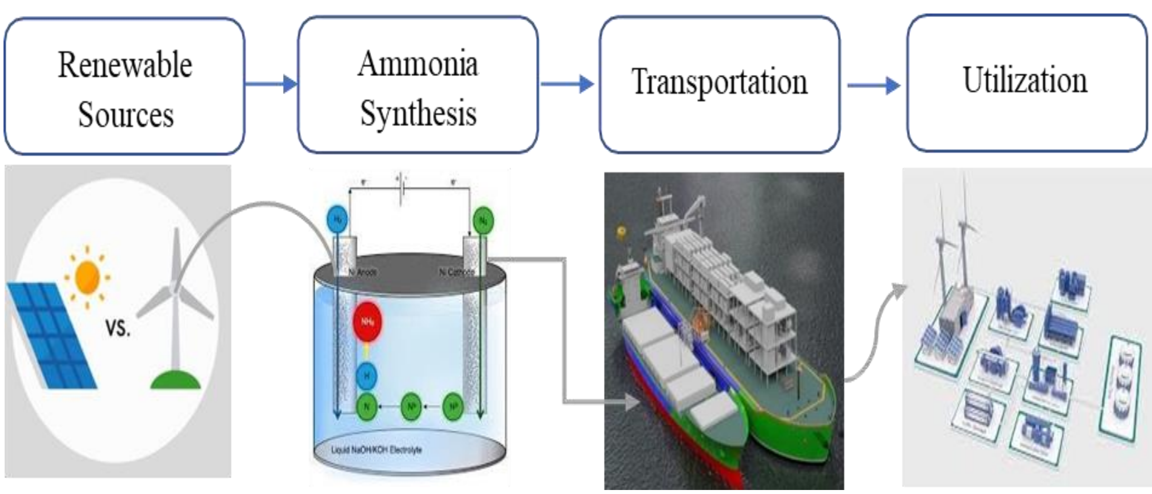

Fig. 2: Production of green ammonia, transportation and utilization process.

Energy Resources of Pakistan

Solar Resource

Pakistan is one of those countries where the sun heats the surface all year, indicating a high potential for solar power generation. In Pakistan, solar radiation intensity shows considerable variation across different regions and times of the year. The minimum intensity of 76.49 W/m² is recorded in Cherat in December, while the maximum intensity of 339.25 W/m² occurs in Gilgit. On a monthly basis, the national average ranges from 136.05 to 287.36 W/m². Notably, solar radiation exceeding 200 W/m² is common from start of February to end of October in Sindh province, from start of March to end of October in Balochistan province, from start of April to end of September in KPK, Northeran areas and Azad Kashmir and from start of March to end of October in Punjab. It is approx. 10 hours daily, the average intensity of solar radiation per unit area per day is 1500 W to 2750 W, especially in southern areas of Punjab, Sindh, and Baluchistan. In these regions, an area of 100 m² can produce between 45 to 83 MW power monthly [26]. The clear sky insolation incident on the horizontal surface, expressed in kilowatt-hours per square day (Kwh/m^2/Day).

Over the span from 2012 to 2022, the monthly averaged clear sky insolation incident on a horizontal surface exhibits a consistent pattern with seasonal variations. Generally, higher insolation values are observed from April to August, peaking around May and June, indicating the most significant solar energy availability during these months. The values tend to be lower in the winter months, particularly from November to January. Annual averages show slight fluctuations but remain relatively stable, reflecting consistent solar energy potential year-round as indicated by Table-1.

In Pakistan, the alternative energy development authority has reported that 28 solar power projects are going to be established in the country with the capacity of the 956.8 MW [28]. Raja and Twidell [29] were the first who developed the energy potential maps (month wise and year wise) for Pakistan by analyzing the 30 years of surface measured data of global level solar insolation with sunshine duration. The annual average daily solar irradiation in most parts of the country was found in the range from 4.4 to 6.0 kWh/m^2/day, with an average value of 5.3 kWh/m^2 [30]. While an estimated 30% of Pakistan has an insolation value higher than 6 kWh/m^2/day, the country's 10-year averaged data shows that the average insolation ranges from 5 to 7 kWh/m^2/day [31].

Solar Power Projects

Several solar power projects have been successfully completed across various regions in Pakistan. At Quaid-e- Azam Solar Park in Bahawalpur, four major projects were developed under the China-Pakistan Economic Corridor(CPEC) initiative [32]. QA Solar Pvt. Ltd., Appolo Solar Pakistan Ltd., Crest Energy Pakistan Ltd., and Best Green Energy Pakistan Ltd., each with a capacity of 100 MW. Additionally, Harappa Solar Pvt. Ltd. developed an 18 MW project in Sahiwal, while AJ Power Pvt. Ltd. commissioned a 12 MW project in Pind Dadan Khan. Furthermore, Zhenfa Pakistan New Energy Company (Pvt.) Ltd. completed a 100 MW solar project in Layyah, Punjab. Collectively, these solar projects contribute a total capacity of 530 MW to Pakistan's renewable energy sector.

There is one large scale PV solar power plant in Pakistan named Quaid-i-Azam solar park having the planned capacity of 1000 MW, in which 400 MW is already installed and operational [33]. Its successful operation deliberately represents the usefulness, cost effectiveness and working conditions feasibility of large -scale power production from the solar energy in Pakistan. This economical and abundant solar energy can be used directly or indirectly for the production of the hydrogen as explained in Section 2.4. The projects vary in capacity and location, with notable installations at the Quaid-e-Azam Solar Park in Bahawalpur, Sahiwal, Pind Dadan Khan, and Layyah in Punjab. Collectively, these projects have added a total of 530 MW to Pakistan's solar power capacity [34].

Table-1. Monthly averaged insolation incident on horizontal surface [27].

Parameter	YEAR	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	ANN
Monthly Averaged Clear Sky Insolation Incident on Horizontal Surface (Kwh/m^2 /Day)	2012	4.1	5.32	6.32	7.35	8.01	7.88	7.31	6.85	6.28	5.47	4.44	3.93	6.11
	2013	4.26	5.13	6.47	7.36	8.22	7.89	7.14	6.77	6.37	5.27	4.27	3.88	6.09
	2014	4.1	5.12	6.36	7.45	7.1	7.99	7.18	6.96	6.36	5.3	4.45	3.9	6.08
	2015	4.15	5	6.23	7.45	8.06	7.61	7.21	7.01	6.4	5.42	4.39	3.92	6.08
	2016	4.22	5.31	6.2	7.51	8.06	7.67	7.26	6.95	6.35	5.51	4.38	3.84	6.1
	2017	4.13	5.27	6.36	7.58	7.9	7.63	7.14	6.83	6.46	5.39	4.14	4.01	6.07
	2018	4.15	5.02	6.38	7.34	7.93	7.68	7.06	6.69	6.18	5.3	4.45	3.96	6.01
	2019	4.12	5.23	6.37	7.35	8.13	8.12	7.3	7.06	6.23	5.22	4.34	3.95	6.12
	2020	4.13	5.09	6.23	7.49	8.14	8.09	7.51	7.07	6.6	5.65	4.4	3.96	6.2
	2021	4.33	5.15	6.35	7.54	7.76	7.76	7.19	6.96	6.06	5.44	4.4	3.85	6.07
	2022	4.12	5.15	6.39	7.49	7.9	7.97	7.11	6.98	6.38	5.37	4.31	3.85	6.09

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Wind Resource

The approximated potential of wind energy in Pakistan is about 50000 MW [35]. A certain study report reveals that Pakistan possesses an excellent wind corridor in the Islamabad, Karachi, and Thatta regions. Wind turbines require a minimum wind speed of 3 to 4 kilometers per second to function effectively. In Pakistan, the wind speeds in this corridor range from 6 to 7.5 meters per second, which is ideal for turbine operation. The potential of wind energy in Pakistan is categorized as moderate. Wind class is a technical term which is used to represents the wind potential of a specific region with the availability of air for wind power. The capacity of different areas of Pakistan in this regard are mentioned in the Fig.3. The available data indicates that approximately 20% of Pakistani areas having the category of fair to excellent. In general wind class 3+ category is considered suitable for power generation.

The worst-case scenario for the GOP of Pakistan is marked by the highest greenhouse gas (GHG) emissions from the energy sector, approximately 48.62 million tons, along with the consumption of nearly 14.19 million tons of oil equivalent (Mtoe) of fossil fuels [33, 36]. With the recent published data by Intergovernmental Panel on Climate Change (IPCC), 90 % of the carbon emissions are increased in South Asia due to human activities [37, 38].

Wind Power Projects

The 36 wind power projects have a total capacity of nearly 1900 MW and are currently operational, providing electricity to the National Grid. These projects, ranging in capacity from approximately 30 to 60 MW each, collectively contribute significantly to the generation of renewable energy in Pakistan. Jhimpir in Sindh serves as the focal point for wind power generation in the country, benefiting from its favorable wind conditions. The province of Sindh, known for its large industrial growth, has emerged as a center for wind energy projects, harnessing its natural resources to contribute to the national energy mix. The development of these wind power projects underscores Pakistan's commitment to increase the power capacity from the renewably energy resources and further to reduce the reliance on the fossil fuels, to contribute in the global goals of sustainable development and mitigating the climate change.

Several wind energy projects have been developed across the Jhampir and Gharo regions in the Thatta district of Pakistan. These projects, implemented by various local and international companies, contribute significantly to the country's renewable energy capacity, amounting to a total of 1845.475 MW. The details of these projects, including the names, capacities, and locations, are available at ref [32].

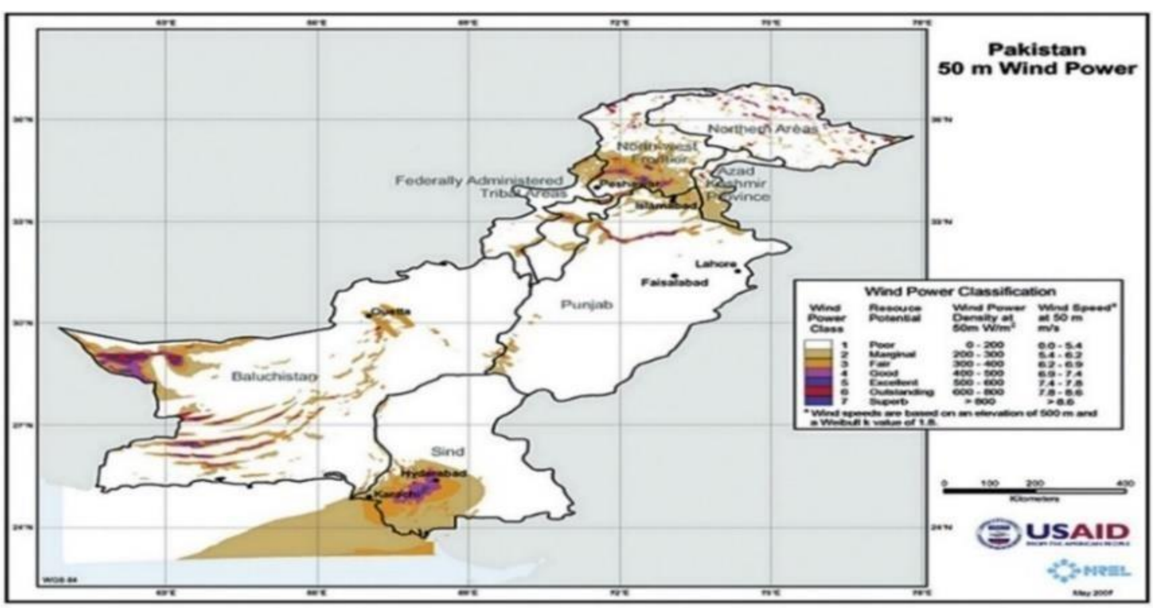


Fig 3. Wind map of Pakistan.

Biomass Resource

Biomass is a key renewable resource that has been used for centuries and currently providing the approximately 9 percent of the world primary need of energy [39]. In Pakistan, about 62 percent of population lives in the rural part of country with agriculture as primary source of income. Traditional biomass resources in Pakistan include wood and animal dung. In rural and low-income areas, people rely heavily on fuels like cow dung, firewood, and crop residues for their daily energy needs. However, Pakistan has very little forest cover, with only 5.3% of the land being forested [40], hence placing it among the nations with the fewest forest resources. Therefore, using wood as a biomass fuel is not advisable. In contrast, animal dung is a significant biomass source because of the large livestock population in Pakistan, estimated 62 million animals are present including buffaloes, cows, camels, horses, mules and donkeys. The livestock population is growing at a rate of 8%, according to the annual livestock report by the Ministry of Livestock, Government of Pakistan [41]. With these animals approximately 23.25 million cubic meter of biogas can be produced daily from these animals' dung. A significant additional source of biomass is agricultural waste from different crops. Table-2 enlists different crops that produce residues and the estimated amount of biomass that can be obtained from them.

Biomass resources are not used much for producing useful energy. In rural areas, people usually use biomass for cooking on open fires or simple stoves, which are very inefficient, transferring only 5–15% of the fuel's energy to the food [43]. Biomass may be converted into energy and hydrogen in a variety of methods. The two main methods are directly converting biomass into hydrogen or indirectly converting biomass into electricity, which can then be used to produce hydrogen. However, using electricity to produce hydrogen is not very efficient.

Ammonia Production from Renewable Resources-An Estimation

The possibility for producing ammonia from renewable energy sources is largely dependent on the availability of land. In Pakistan, land is a scarce resource, and its availability is restricted because of the country's dense urban population. Thus, granting land for the purpose of producing solar electricity is linked to several social and political limitations. All five provinces of Pakistan have vast areas of land that might be used to build solar power facilities but are unsuitable for farming. In order to address this issue, the government of Pakistan has offered incentives and allocated 6,500 acres of land in the Cholistan desert near Bahawalpur for the construction of solar power facilities (1000 MW) [44]. The Sindh Land Scrutiny Committee has also granted permission to build 21 solar and wind power facilities totaling 1880 MW on 15,089 acres of government land [45].

Solar Ammonia Generation

Because of its strong relationship to per capita energy use, the phrase "solar electric footprint" differs for various affluent regions. When the USA and other countries' per capita energy use is compared, a significant discrepancy is seen. As to the World Bank data presented in Fig.4, per capita energy consumption in Pakistan is 482 kgoe, but in the USA it is 703 kgoe.

Table-2: Annual availability of crops and their residue in Pakistan [42].

Crop	Annual output (Thousand MT)	Residue type	Residue/kg	Available residue (Thousand MT)
Sugarcane	49,500	Bagasse,	0.33	16,500
		Top and leaves	0.05	2800
		Pod		
Wheat	24,000	Stalks	0.3	7200
		Husks	1.5	36,000
Rice	6900	Stalks	0.2	1400
		Straw	1.5	10,400
		Boll Shell	1.5	10,400
Cotton	3000	Husk	1.1	3300
		Stalks	1.1	3300
		Cobs	3.8	11,900
Bajra	500	Husks	0.33	152
		Stalks	0.3	142
		Cobs	2	950
Maize	300	Stalks	0.3	90
		Cobs	2	600
Dry Chilly	190	Stalks	1.5	285
Barley	85	Stalks	1.3	110

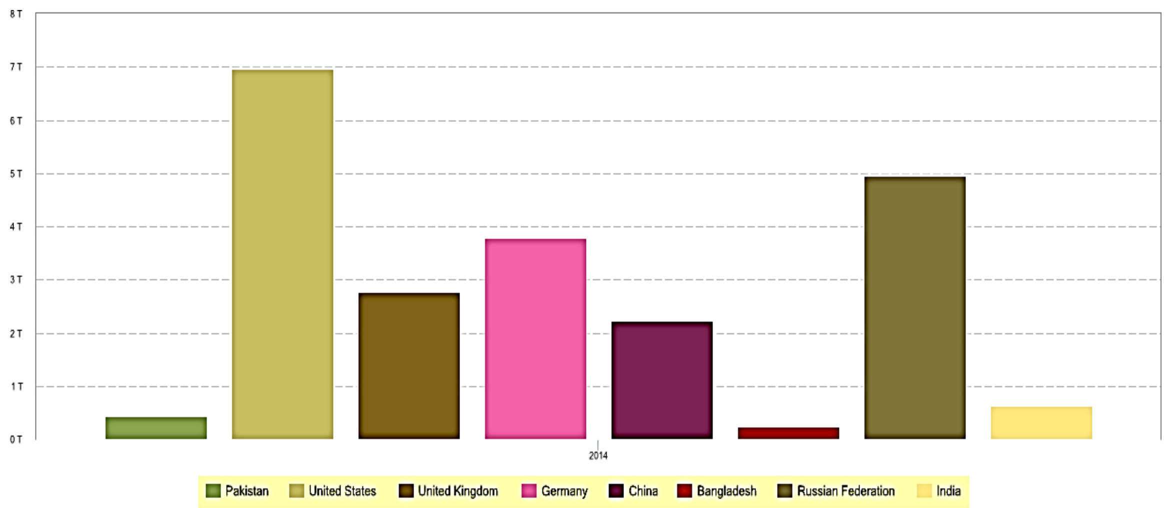


Fig 4: Energy use per capita in kg of oil equivalent (kgoe) [44].

A considerable land area is necessary due to the extensive footprint of solar energy. By utilizing solar power, Pakistan can generate the required electricity and additionally produce substantial amounts of hydrogen. This hydrogen can then be converted into ammonia, illustrating the feasibility and benefits of solar-based ammonia production. This approach not only addresses the electricity needs but also opens up opportunities for sustainable ammonia production, which is crucial for various industrial applications. This approach could be particularly advantageous for producing solar ammonia in remote regions of Punjab, Sindh, and Balochistan. In these areas, ammonia could serve as a practical solution for energy storage and transportation, enabling the intermittent delivery of energy to urban centers where direct utilization of solar power is often limited due to space constraints. Furthermore, the synthesized green ammonia has versatile applications beyond energy, such as serving as a critical input for the agricultural sector (*e.g*., fertilizers) and various processing industries, thereby enhancing its overall value as a sustainable and multifaceted energy carrier. The integration of solar energy into the production process emphasizes the importance of renewable energy sources in achieving energy and chemical production sustainability. The analysis provided in Table-3 highlights Pakistan's significant potential for green hydrogen and ammonia production using solar energy, where land area availability becomes a pivotal factor. Based on current data, Pakistan's electricity demand in 2022 was approximately 31,000 MW as shown in Table-3 [46]. The solar electric footprint is 6.5 acres per 1,000 kWh, which demonstrates the land efficiency required for solar power generation. To meet this energy demand, a total of 201,500 acres of land would be necessary for solar installations. The potential for hydrogen production is also significant, with the capacity to produce 4,105 thousand tonnes, assuming 53.5 kWh of electricity per kilogram of hydrogen. And the ammonia production potential is estimated at 50 thousand tonnes, indicating the capacity for using hydrogen in ammonia synthesis. These values emphasize the substantial role that solar energy can play in sustainable energy production and industrial applications in Pakistan. The solar-based ammonia synthesis process begins with surplus renewable energy, splitting water to produce hydrogen. This hydrogen, along with vaporized nitrogen, undergoes high-pressure synthesis in a magnetite-catalyzed reactor, achieving efficient ammonia production. This model emphasizes renewable integration in large-scale chemical production, boosting sustainability while addressing energy independence.

Table-3: Solar Ammonia production potential in Pakistan [44].

Electric Power demand in 2022	**31,000 MW**
Solar electric foot print	**6.5 acres/1000 KWh**
Total land required	**201500 acres**
Electric Power potential	**31,000 MW**
H_2 production potential (@53.5 KWh/kg)	**4,105 (1000 tonnes)**
Ammonia Production Potential	**50 1000 tonnes)**

Synthesis Process

Green ammonia production involves several key processes that uses renewable energy to convert it in useful product. The potential for solar ammonia production in Pakistan is provided in Table-3 and the process is illustrated in Fig. 5.

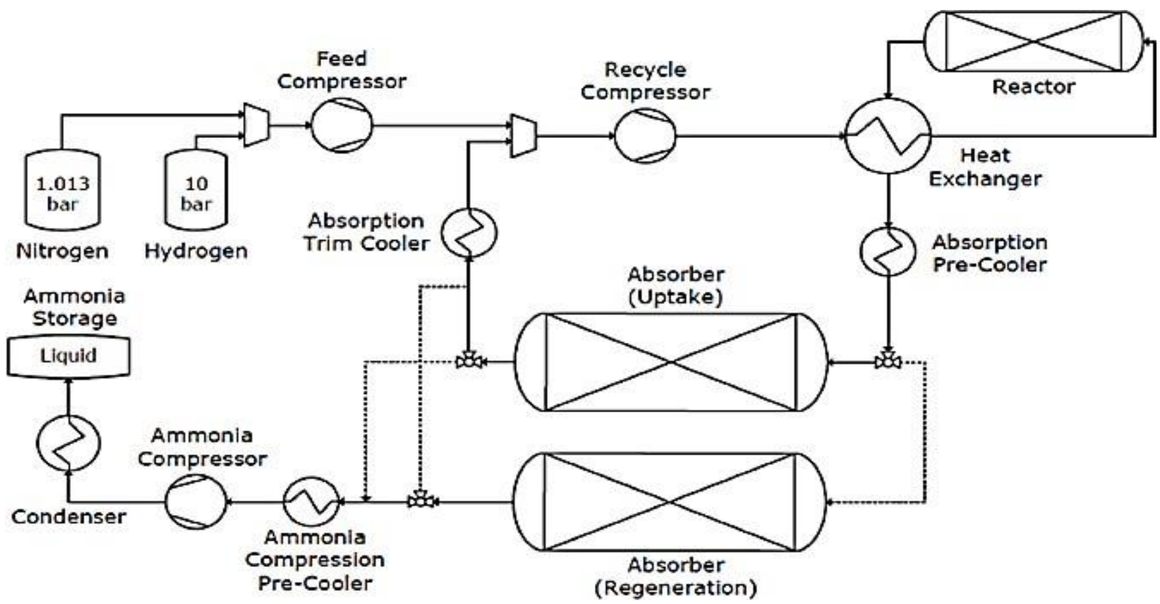


Fig. 5: Process diagram for production of green ammonia [47].

Green ammonia production starts with an electrolyzer that utilizes surplus electricity from renewable energy resources *e.g*. wind turbines or solar power to split water into hydrogen H_2 and oxygen O_2 gases. At the same time, liquid nitrogen is vaporized into gaseous nitrogen, readying it for integration into the ammonia synthesis process. The hydrogen and nitrogen mixture is then compressed to 20 bar, increasing its reactivity for an efficient conversion into ammonia [48]. The reactor is composed of inner and outer vessels, with the inner vessel housing a heater and magnetite beds. The pressure and temperature are monitored on the outer cylinder, while the heater elevates the temperature of the gases to 200 degrees Celsius, creating optimal conditions for ammonia synthesis. Magnetite beds serve as catalysts, enhancing the conversion of reactants into ammonia. The absorber unit captures gaseous ammonia from the reactor, and to drive the reaction towards completion, the absorbed ammonia is heated in the presence of a catalyst. This step separates the absorbed ammonia from the absorbent, ensuring the reaction proceeds irreversibly towards ammonia formation. The combined operation of the reactor and absorber units facilitates green ammonia production, with the reactor providing the necessary synthesis conditions and the absorber ensuring the reaction's irreversibility. The efficiency and effectiveness of this process heavily rely on the role of magnetite beds and the heating within the absorber [49].

Direct Solar-to-Hydrogen (DSTH)

Direct Solar-to-Hydrogen (DSTH) technology represents an advanced and promising approach to sustainable hydrogen production, bypassing traditional intermediate steps such as electrolysis. In DSTH systems, solar energy is directly converted into hydrogen through photo electrochemical (PEC) cells, which use sunlight to split water H_2O molecules into hydrogen H_2 gas and oxygen O_2 gas. This process involves semiconductor materials that absorb the energy form sunlight and produce the charge carrier and then drive the splitting of water reaction. The DSTH technology offers significant efficiency improvements by eliminating the need for electrical energy conversion, thereby reducing energy losses associated with traditional photovoltaic-electrolyzer systems. Recent advancements in DSTH technology focus on enhancing the efficiency and stability of PEC cells through the development of novel semiconductor materials, surface coatings to prevent corrosion, and innovative cell designs that maximize light absorption and charge separation [50, 51]. These improvements are crucial in making of DSTH more viable and competitive option for hydrogen H_2 production on industrial scale, with the contribution of shifting the global trends to clean, affordable and sustainable energy resources.

DSTH technology, while promising for sustainable hydrogen production, is still in the experimental and pilot stages, facing significant challenges in achieving commercial readiness. Key hurdles include the high cost of materials, relatively low conversion efficiencies, and technical complexities of large-scale implementation.

Although proof-of-concept projects demonstrate feasibility, substantial advancements in material science, cost reduction, and scalability are required before DSTH technology can be commercially viable. Continued research and supportive policies are essential to accelerate its transition to widespread use.

Wind Ammonia Generation

Global wind data indicates that about 20% of Pakistan area has the category of `Fair to Excellent` as wind resources [52]. The Wind class category 3+ is generally considered as suitable for generation of power from wind resources. Theoretical total capacity calculations are provided in Table-4, from which potential green hydrogen and green ammonia calculations are derived.

Table-4: Wind Resource and Capacity [44].

Green Ammonia Potential from Wind Energy in Pakistan	
Electric power demand in 2022	19,000 MW
Capacity factor on-land	25-50%
Electric power potential	9,500 MW @ 50%
H_2 production potential (53.5 KWh/kg)	179,245.4 (1000 tonnes)
Ammonia Production Potential	1.775 (1000 tonnes)

These calculations provide insights into the potential for green hydrogen and green ammonia production based on the theoretical total capacity of wind power generation in different regions of Pakistan. The renewable resources of wind and solar in Pakistan are mostly located in those areas which are lacking in the infrastructure and electrical power supply infrastructure. These regions population density is comparatively low, with only one person per square kilometer, and lack access to an electrical transmission network. In the result, the electrical devices are not much to use in these areas, resulting in low consumption of electrical power. The surplus power generated from wind and solar resources can be efficiently converted into hydrogen through electrolysis. These wind and solar resource areas in Pakistan serve as natural initiators for the hydrogen economy. Due to the absence of an electrical transmission network, there is a need to convert the available power into an alternative energy source, with hydrogen being the most favorable option. However, while green hydrogen is a feasible solution, its transport can be challenging. As a result, green ammonia emerges as the ultimate solution for the energy transmission problem.

Biomass Ammonia Generation

The innovative process of converting biomass into ammonia through sustainable and environmentally friendly methods is gaining attention. This approach leverages biomass, an abundant and renewable resource, to produce green ammonia, a crucial chemical for fertilizers and various industrial applications. By utilizing advanced technologies such as gasification and pyrolysis, biomass can be efficiently transformed into hydrogen, which is then synthesized into ammonia [53]. This approach provides a workable alternative for renewable energy and environmentally friendly farming methods by minimizing carbon emissions and decreasing dependency on fossil fuels [54, 55]. Table- 5 shows the potential hydrogen and ammonia production from various crop residues in Pakistan, highlighting the quantities of available residue and the corresponding potential yields.

Table-5: Green hydrogen & ammonia estimation from crop residue [42, 44].

Crop	Residue type	Available residue 1000 MT	Potential H_2 availability ($\times 10^3$ tonnes)	Potential NH_3 availability ($\times 10^3$ tonnes)
Wheat	Stalks	7200	554	2.7438
	Husks	36,000	2769	13.7143
Rice	Stalks	1400	108	0.5349
	Straw	10,400	800	3.9622
	Boll Shell	10,400	800	3.9622
Cotton	Husk	3300	254	1.2580
	Stalks	3300	254	1.2580
	Cobs	11,900	915	4.5318
Bajra	Husks	152	12	0.0594
	Stalks	142	11	0.0544
	Cobs	950	73	0.3615
Maize	Stalks	90	7	0.0346
	Cobs	600	46	0.2278
Dry Chilly	Stalks	285	22	0.1089
Barley	Stalks	110	8	0.0396
Total		86,229	6633	65.7041

The low moisture contents are highly desirable to get the higher efficiency in energy conversion. Regardless of the moisture content, supercritical water gasification (SWG) maintains constant conversion efficiency. However, to get the higher efficiencies it is required to reduce the moisture content of feedstock, which demands the additional energy input. This additional energy to lower the moisture content, reduces the overall process efficiency. Pyrolysis offers a comparable and efficient process as compare to the thermal gasification.

Types of Direct Methods for Converting Biomass to Hydrogen

Thermochemical Methods

In thermochemical methods, various processes convert biomass into hydrogen, including pyrolysis mode gasification, steam mode gasification, steam reforming of biomass-oil and supercritical water gasification. Pyrolysis heats biomass without oxygen, producing gases, bio-oil, and char, with hydrogen in the gas [56, 57]. Gasification partially oxidizes biomass at high temperatures, creating hydrogen-rich syngas. Steam gasification uses steam instead of air to produce hydrogen-rich syngas. Steam reforming of bio-oils involves reacting biomass-oil with high pressure steam as catalytic reaction to generate to generate the hydrogen gas H_2 [58]. Supercritical water gasification uses supercritical water to gasify biomass, efficiently converting it into hydrogen and other gases.

Biological Methods

In biological methods, hydrogen can be produced using green algae and cyanobacteria to split water, photo- fermentation, dark-fermentation, and hybrid reactor systems. Green algae and cyanobacteria utilize sunlight to split water molecules, releasing hydrogen. Photo-fermentation involves microorganisms converting organic substrates into hydrogen using light. Dark-fermentation uses anaerobic bacteria to break down organic matter and produce hydrogen in the absence of light. Hybrid reactor systems combine different biological processes to optimize hydrogen production efficiency [59].

This flowchart shown in Fig.6 categorizes different pathways for converting biomass into various products. Biomass sources include agricultural residue, food waste, forest residue, biochar, and sewage sludge. These sources undergo various conversion processes, categorized broadly into thermochemical, electric, transesterification, and biological methods. The end products of these processes include biofuels like biodiesel and ethanol, biogas, glycerol, and gases such as carbon dioxide (CO_2) and hydrogen (H_2). These conversion processes involve steps like pyrolysis, gasification, microbial electrolysis, and others, with the water gas shift (WGS) reaction playing a role in generating CO_2 and H_2.

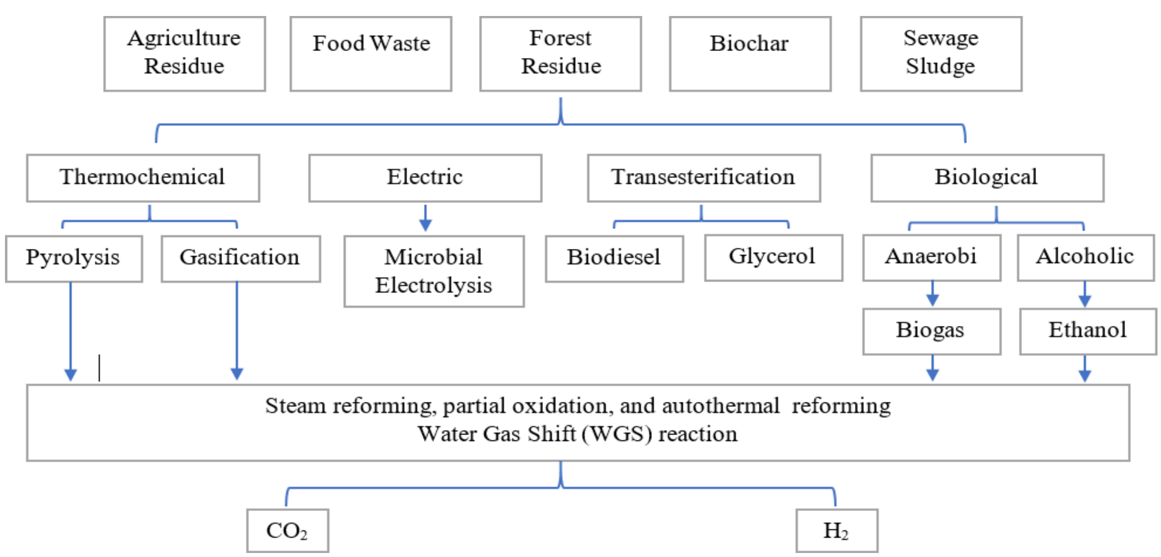


Fig. 6: Hydrogen H_2 gas generation by biomass [60].

Gasification and pyrolysis

Gasification and pyrolysis are advanced methods for converting biomass into valuable gases and liquids. Gasification involves using heat and gasifying agents such as air, steam, or oxygen to produce syngas, which is rich in hydrogen and carbon monoxide [61]. There are various methods of gasification, including air gasification, steam gasification, oxygen gasification, and supercritical water gasification. Each method has distinct processes, reactor conditions, advantages, disadvantages, and product yields. Firstly, air gasification utilizes air as a gasifying agent in a fluidized bed reactor at temperatures between 700-900°C, often mixed with steam. This method can achieve maximum conversion but faces challenges in tar removal from the product. It produces high yields of hydrogen and gas at high temperatures [62]. Secondly, steam gasification employs steam along with air in a fluidized bed gasifier at 770°C with a specific steam-to-biomass ratio. It yields a high hydrogen-to-carbon monoxide ratio, making it suitable for large-scaleindustrial production. However, it also results in high tar content and CO_2 emissions. The hydrogen yield ranges from 19.4% to 42.6% [63]. In contrast, oxygen gasification involves supplying pure oxygen into a circulating fluidized bed gasifier, producing syngas with low tar content. However, the purification of oxygen is an energy-intensive process. In addition, gasification with supercritical water uses supercritical steam as the gasification agent in a tubular batch reactor at 650°C with a heating rate of 30°C/min. This method achieves high conversions and hydrogen contents without tar and coke formation, but requires a high energy input to [64] pump the feedstock and works under strict conditions. The hydrogen yield is between 30% and 40% [65]. Finally, fast pyrolysis takes place at moderate temperatures in the absence of oxygen with a high heat transfer rate to the biomass particles in a fluidized bed reactor at atmospheric pressure. This method can produce gas with a high hydrogen content, but has a low hydrogen yield and high energy consumption. The product yield includes 12% gases (2-3 wt% hydrogen to biomass), 72% bio-oil and 16% charcoal [66].

Although Supercritical water gasification (SWG) demonstrates the good efficiency at the laboratory level production, its industrial level feasibility has yet to be not verified. Therefore, biomass gasification is assumed to be the most feasible process of converting the biomass to hydrogen H_2 gas. From the estimation, about 13 kg of dried bone-biomass is required for the production of 1 kg hydrogen gas [64]. The hydrogen production potential through biomass gasification is estimated at 6633 thousand tonnes. Additionally, the potential for ammonia production is estimated at 65.7041 thousand tonnes as illustrated in Table-6.

Total Ammonia Production Potential

The discussion on Pakistan's renewable energy resources also covers the technologies available for producing ammonia from these sources. The potential of ammonia NH_3 production from the renewable energy source is considered adequate and feasible based on technology and practicality. Table 6 illustrates the potential ammonia production from each renewable energy resource.

Table-6: Annual NH_3 production potential from Renewable energy resources.

Renewable Energy Resource	**Annual Production ($\times 10^3$ tonnes)**
Solar	**50**
Wind	**1.775**
Biomass	**65.70**

According to this biomass emerges as having the greatest potential for ammonia production. This aligns with Pakistan's agricultural based economy, where a significant amount of residue from crops is produced on the whole year. Fig.9 shows that lower ammonia production cost using biomass as feedstock compared to other renewable energy.

Fossil fuel reforming is the cheapest method for producing hydrogen, costing less than $2 per kilogram. Coal gasification is slightly more expensive, also under $2 per kilogram. Hybrid thermochemical cycles cost a bit more, just over $2 per kilogram. Electrolysis and biomass gasification are in the mid-range, costing around $3 to $4 per kilogram. PV electrolysis is more expensive, costing over $6 per kilogram. Photo-catalysis and photo-electrolysis have higher costs, while the photo-electrochemical method is the most expensive, costing nearly $10 per kilogram. This shows the wide variation in costs for different hydrogen production methods (and so for green ammonia production as well).

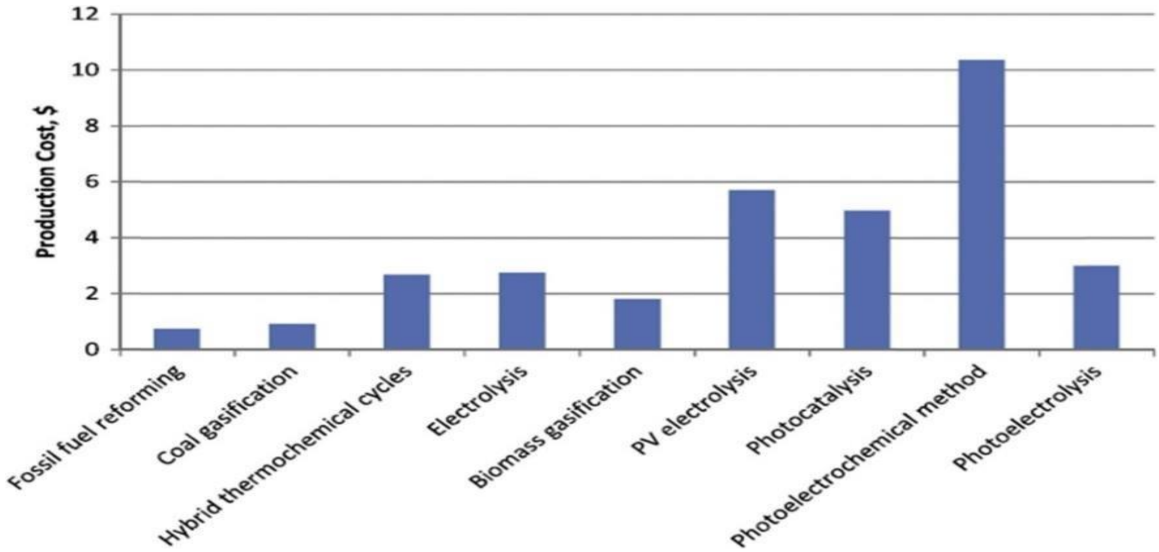


Fig. 7: Hydrogen H_2 gas production costs (per kg) for selected methods of production [67].

Case Study (Solar Ammonia Production)

In recent years, the urgency of transitioning to sustainable industrial practices has intensified globally, with particular emphasis on reducing greenhouse gas emissions and dependency on fossil fuels. Ammonia production, a critical process for the agricultural industry, currently relies heavily on energy-intensive methods that contribute significantly to carbon emissions. For countries like Pakistan, where agriculture forms a substantial part of the economy, adopting greener production methods is essential not only for environmental benefits but also for enhancing energy security. This project aligns with both national and international sustainability goals, such as the United Nations Sustainable Development Goals (SDGs), by demonstrating a practical approach to renewable-based ammonia production. By harnessing Pakistan's abundant solar resources, our prototype paves the way for more resilient agricultural practices and offers a cleaner, sustainable energy carrier, potentially benefiting multiple industrial sectors.

This case study details our journey from concept to prototype, providing valuable insights for scaling and advancing green ammonia technology. In the current scenario, mostly the ammonia is produced through HB process. But it is energy-intensive, operating under high temperatures & pressures, heavily reliant on fossil fuels and leading to significant CO_2 emissions. In countries i.e., Pakistan which are already facing the energy crises and CO_2 emission issues i.e. Smog etc., the ammonia production from the HB process can be a costly process and hazard to the environment. Recent advancements aim to incorporate renewable-driven hydrogen production to reduce its carbon footprint, but challenges remain due to the high energy demand and low single-pass conversion rates that necessitate recycling.

Alternatively, the reaction-absorption cycle offers a promising, energy-efficient approach, using lower temperatures and moderate pressures. However, the stability of absorbent materials, typically metal halides, poses a barrier to large-scale adoption. While it holds potential for reducing emissions, improvements in material durability and scalability are needed for widespread implementation [68]. Table-7 highlights brief comparison of the HB and reaction-absorption processes.

Table-7: Comparison Table: HB vs. Reaction-Absorption Cycle [68].

Parameter	HB (H-B) Process	Reaction-Absorption Cycle
Operating Temperature	**400-450°C**	**180-300°C**
Operating Pressure	**15-25 MPa**	**2 MPa**
Energy Source	**Primarily fossil fuels, renewable options emerging**	**Compatible with renewable energy sources**
CO_2 Emissions	**High (1.8% of global emissions)**	**Lower potential emissions**
Conversion Rate	**~15-20% per pass, requires recycling**	**Higher conversion rates due to absorption**

In the light of the above comparison provided in Table-7, reaction-absorption process is used as novelty in this research work, of prototype model development to produce the green-ammonia.

Our project aimed to address the growing need for sustainable industrial practices by developing a prototype for green ammonia production. Recognizing Pakistan's potential in renewable energy, we focused on utilizing solar energy to produce ammonia, which is essential for fertilizers and can serve as an energy carrier. Traditional ammonia production methods are highly energy-intensive and dependent on fossil fuels, contributing significantly to greenhouse gas emissions. In contrast, our green ammonia production process leverages renewable resources, offering a cleaner and more sustainable alternative. This case study outlines the steps we took to develop, construct, and test our prototype, highlighting its efficiency and potential impact on sustainable agriculture and energy storage in Pakistan.

Prototype Development

The prototype was constructed with the following components with a brief description of their functions.

Electrolysis Unit

The first stage of the prototype involved the construction of an electrolysis unit. We used a proton exchange membrane (PEM) electrolyzer to produce hydrogen from water. PEM electrolyzers are preferred for their compact size, high efficiency, and suitability for intermittent power sources like solar and wind energy. Their operational flexibility complements renewable energy sources [69]. This process involved splitting water molecules into hydrogen gas and oxygen gas using electrical power from renewable sources *e.g.* solar, wind etc. The chemical reaction for this process proceeds in accordance with following chemical equation (eq.1).

$$2H_2O\ (l) \rightarrow 2H_2\ (g) + O_2\ (g) \qquad (1)$$

Ammonia Synthesis Reactor

The final stage of the prototype involved the synthesis of ammonia. We used a modified HB process with a ruthenium-based catalyst. Ruthenium catalysts work effectively at lower temperatures and pressures, making the process more energy-efficient and viable for distributed production [70]. The traditional HB process operates at very high temperatures and pressures, making it unsuitable for small-scale or distributed production. By using a ruthenium-based catalyst, we were able to conduct the reaction at lower temperatures and pressures, making the process more energy- efficient and suitable for smaller-scale operations. The chemical reaction for ammonia synthesis is given by following chemical formula (eq. 2).

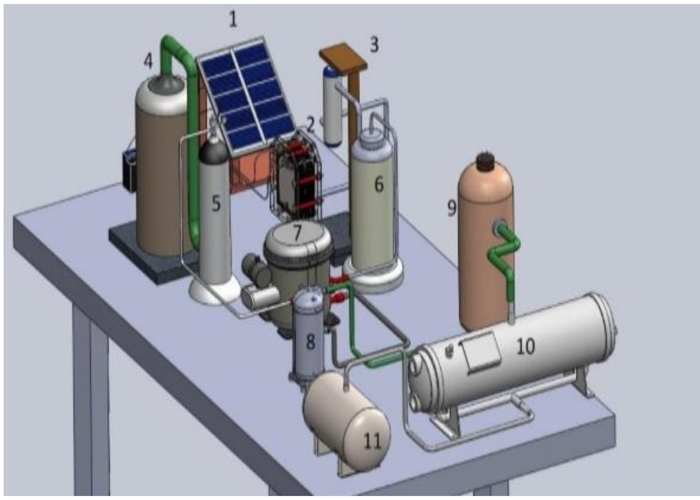
$$3H_2\ (g) + N_2\ (g) \rightarrow 2NH_3\ (g) \qquad (2)$$

Absorber Unit

In our green ammonia production project, the absorber unit was essential for making ammonia efficiently and ensuring it stayed pure. It worked by absorbing ammonia gas and stopping it from turning back into hydrogen and nitrogen. This helped us produce more ammonia and keep our system running smoothly. The absorber unit was crucial for maintaining the quality needed for ammonia used in fertilizers, which are vital for agriculture.

Final Prototype

The final prototype for our green ammonia production system integrates all the key components, ensuring efficient and reliable operation and the CAD model is illustrated in the Fig.9. The PEM electrolyzer, powered by sustainable energy sources *e.g.* solar and wind, produced hydrogen by splitting water molecules. The hydrogen was then combined with nitrogen, in the modified HB reactor, which used a ruthenium-based catalyst to synthesize ammonia at lower temperatures and pressures. The produced ammonia was directed to the absorber unit, which ensured its purity by preventing decomposition back into hydrogen and nitrogen. Advanced control and monitoring systems regulated the flow of gases and maintained optimal operating conditions. This integrated system demonstrated the feasibility of using renewable energy for sustainable ammonia production, providing valuable insights for future developments and scaling up of green ammonia technologies. Fig.8 shows the final setting of prototype.



1. PV Panel and Battery
2. Electrolyzer
3. Hydrogen Backfire Arrestor Vessel
4. Liquid Nitrogen Vessel
5. Gaseous Nitrogen Vessel
6. Hydrogen Vessel
7. Compressor
8. Reaction Chamber
9. Ammonia Absorption Unit
10. Ammonia Regeneration Vessel
11. Ammonia Gas Storage

Fig. 8: Green ammonia production plant (Prototype) Efficiency Analysis.

Energy Consumption

Energy consumption measurement in the green ammonia production project was carried out to evaluate efficiency at each stage. Digital power meters were used to monitor the energy consumption of the electrolysis unit, absorber unit, and ammonia synthesis reactor. These meters recorded the voltage (V) and current (I) supplied to each unit, and instantaneous power (P) was calculated using following formula (eq. 3).

$$P = V \times I \quad (3)$$

To determine total energy consumption over time (t), power usage was integrated using following formula (eq. 4).

$$E = P \times t \quad (4)$$

By summing the energy consumptions from each unit, the total energy consumption of the system was estimated. The efficiency of ammonia production was calculated by dividing the total amount of ammonia produced by the total energy consumed, yielding an overall efficiency metric. This thorough measurement process provided a clear understanding of the energy efficiency and sustainability of the green ammonia production prototype.

Ammonia Production Efficiency Calculation

To determine the efficiency of our ammonia production process, we compared the amount of ammonia produced to the total energy consumed. This calculation provides a clear indication of how effectively the energy used in the process is converted into ammonia.

The efficiency was calculated using the following the following equation (eq. 5).

$$Efficiency = \frac{Amount\ of\ ammonia\ produced\ (kg)}{Total\ Energy\ Consumed\ (kWh)} \quad (5)$$

This formula expresses efficiency as the ratio of ammonia output to energy input, indicating how much ammonia is produced per unit of energy consumed. We divided the total quantity of ammonia produced by the total energy consumed to obtain the efficiency ratio. For instance, if the total ammonia produced was 1.5 kg and the total energy consumed was 10 kWh.

$$Efficiency = \frac{0.2\ kg}{1\ kWh} \quad (6)$$

The theoretical efficiency of the absorption process is higher compared to the HB process for ammonia production. Specifically, the absorption process requires 5–20 MJ of energy per kilogram of ammonia, with a theoretical efficiency of 15–20%, whereas the HB process consumes 28–35 MJ of energy per kilogram of ammonia, with a theoretical efficiency of approximately 11–11.3% [71].

The given lab-scale model has produced 0.2 kg of ammonia per kWh, which is equivalent to 3.6 MJ of energy for 0.2 kg of ammonia. In comparison, producing the same amount of ammonia through the HB process would require approximately 4.6–7 MJ, which is higher than the energy consumption of the absorption process. Due to lower energy requirements, milder operating conditions, and reduced CO_2 emissions, the absorption process is more energy-efficient and environmentally friendly.

Conclusions

Pakistan must utilize and develop all available energy sources to address the energy crisis and ensure economic sustainability. Progress in industrial and transport infrastructure requires substantial energy resources. As green ammonia and ammonia-based applications advance globally, Pakistan needs to create a roadmap for transitioning to an ammonia economy. Utilizing renewable energy resources for ammonia production is essential and feasible given Pakistan's abundant renewable resources. Among these, biomass should be prioritized to develop the ammonia supply chain, integrated with solar energy and waste of feedstocks. The technologies of converting the biomass to ammonia are feasible and established, further can be tailored to gross root level feedstock with expertise. Countries worldwide are investing in ammonia production and ammonia cracking as sources for hydrogen, recognizing ammonia as a viable medium for the easy transportation of renewable energy. This trend highlights the importance of ammonia in the global energy landscape and underscores the need for Pakistan to join this movement. The government plays a critical role in promoting the ammonia economy. Financial incentives and support should be considered for the technology providers and users to promote and adopt the new technologies. Economic considerations must be integrated into the development of renewable energy projects to establish an ammonia supply chain. The findings of this study can inform the creation of an ammonia energy roadmap for Pakistan.

The case study discussed shows that how renewable energy can be utilize to produce clean and green energy in Pakistan. It also provides a practical foundation for reducing carbon emissions and supporting sustainable agricultural practices in the country. By utilizing renewable energy resources, we can significantly decrease dependence on fossil fuels, promote energy independence, and improve economic growth through sustainable technologies. This approach will not only contribute in the development of the eco-friendly environment but also to ensure the a more reliable and sustained energy future of Pakistan.

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