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ATMOSPHERIC NITROGEN FIXATION TO VARIOUS FORMS, DEVELOPMENT OF GREEN AMMONIA, SUSTAINABILITY AND ITS PERSPECTIVES

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ABSTRACT :

There is a large amount of nitrogen gas in the atmosphere ,but plants are unable to utilize due to its stable and unreactive nature . In nature, most nitrogen is harvested from the atmosphere by microorganisms to form ammonia, nitrites, and nitrates that can be used by plants. Nitrogen fixation is essential to life because fixed inorganic nitrogen compounds are required for the biosynthesis of all nitrogen-containing organic compounds, such as amino acids and proteins, nucleoside triphosphates and nucleic acids. As part of the nitrogen cycle, it is essential for agriculture and the manufacture of fertilizer. **Ammonia has the highest nitrogen content of any commercial fertilizer ,making it a popular source of nitrogen**

despite the potential hazards it poses . Intensive research efforts culminated in the development of several commercial nitrogen-fixation processes. The most-productive approach is the direct combination of nitrogen with hydrogen.There is considerable research interest into finding transition metal catalysed systems which will absorb dinitrogen and produce ammonia for fertilizers cheaply and without the necessity for high temperature and pressure.The formation of this stable dinitrogen complex led to studies with other metals .The fundamental requirement for fixed forms of nitrogen for life on earth both

at present and at the past had led to broad and significant interest in origin and evolution of biological and industrial nitrogen fixation methods .

Key words : Nitrogen fixation ,fertilizers,combination ,manufacture ,ammonia ,dinitrogen etc.

INTRODUCTION

Nitrogen fixation is a chemical process by which molecular nitrogen with a strong triple covalent bond, in the air is converted into ammonia (NH3) or related nitrogenous compounds, typically in soil or aquatic systems biologically and also now commercially [2] . About 10 percent of natural nitrogen fixation takes place by physicochemical methods and 90 percent by biological methods [9].Biological nitrogen fixation or diazotrophy is an important microbially mediated process that converts dinitrogen (N2) gas to ammonia (NH3) using the nitrogenase protein complex**..In nature Nitrogen is fixed, or combined, in nature as nitric oxide by lightning and ultraviolet rays, but more significant amounts of nitrogen are fixed as ammonia, nitrites, and nitrates by soil microorganisms.** More than 90 percent of all nitrogen fixation is effected by them. Two kinds of nitrogen-fixing microorganisms are recognized: free-living (nonsymbiotic) bacteria, including the cyanobacteria (or blue-green algae) *Anabaena* and *Nostoc* and genera such as *Azotobacter*, *Beijerinckia*, and *Clostridium*; and mutualistic (symbiotic) bacteria such as *Rhizobium*, associated with leguminous plants, and various *Azospirillum* species, associated with cereal grasses.The symbiotic nitrogen-fixing bacteria invade the root hairs of host plants, where they multiply and stimulate the formation of root nodules, enlargements of plant cells and bacteria in intimate association. Within the nodules, the bacteria convert free nitrogen to ammonia, which the host plant utilizes for its development. To ensure sufficient nodule formation and optimum growth of legumes (e.g., alfalfa, beans, clovers, peas, and soybeans), seeds are usually inoculated with commercial cultures of appropriate *Rhizobium* species, especially in soils poor or lacking in the required bacterium .

Nitrogenous materials have long been used in agriculture as fertilizers, and in the course of the 19th century the importance of fixed nitrogen to growing plants was increasingly understood. Accordingly, ammonia released in making coke from coal was recovered and utilized as a fertilizer, as were deposits of sodium nitrate (saltpetre) from Chile. Wherever intensive agriculture was practiced, there arose a demand for nitrogen compounds to supplement the natural supply in the soil.[9] At the same time, the increasing quantity of Chile saltpetre used to make gunpowder led to a worldwide search for natural deposits of this nitrogen compound. By the end of the 19th century it was clear that recoveries from the coal-carbonizing industry and the importation of Chilean nitrates could not meet future demands. Moreover, it was realized that, in the event of a major war, a nation cut off from the Chilean supply would soon be unable to manufacture munitions in adequate .amounts.[17] .In industrial processes the three most-productive approaches were the direct combination of nitrogen with oxygen, the reaction of nitrogen with calcium carbide, and the direct combination of nitrogen with hydrogen. The possibility that atmospheric nitrogen

reacts with certain chemicals was first observed by Desfosses in 1828. He observed that mixtures of alkali metal oxides and carbon react at high temperatures with nitrogen. With the use of barium carbonate as starting material, the first commercial process became available in the 1860s, developed by Margueritte and Sourdeval.[16] The resulting barium cyanide reacts with steam, yielding ammonia. A method for nitrogen fixation was first described by Henry Cavendish in 1784 using electric arcs reacting nitrogen and oxygen in air. This method was implemented in the **Birkeland–Eyde process**.[8] The fixation of nitrogen by lightning is very similar natural occurring process.Frank-Caro process Caro developed a way to fix nitrogen in the form of calcium cyanamide. The Frank-Caro and Ostwald processes dominated industrial fixation until the discovery of the Haber process. During the first decade of the 20th century air or any other uncombined mixture of oxygen and nitrogen is heated to a very high temperature, and a small portion of the mixture reacts to form the gas nitric oxide. [10]The nitric oxide is then chemically converted to nitrates for use as fertilizers. One such method used the reaction of nitrogen with calcium carbide at high temperatures to form calcium cyanamide, which hydrolyzes to ammonia and urea. **The cyanamide process** was utilized on a large scale by several countries before and during World War I, but it too was energy-intensive, and by 1918 the Haber-Bosch process had rendered it obsolete. The most common ammonia production method is the Haber process. [14][15]]The Haber-Bosch nitrogen reduction process for industrial fertilizer production revolutionized modern day technology.[12] Fertilizer production is now the largest source of human-produced fixed nitrogen in the terrestrial ecosystem. Ammonia is a required precursor to fertilizers, explosives, and other products. The Haber process requires high pressures (around 200 atm) and high temperatures (at least 400 °C), which are routine conditions for industrial catalysis.

This process uses natural gas as a hydrogen source and air as a nitrogen source. The ammonia byproduct has resulted in an intensification of nitrogen fertilizer globally. In industry, ammonia is synthesized from atmospheric nitrogen and hydrogen by the Haber-Bosch method, a process that Fritz Haber developed about 1909 and which soon after was adapted for large-scale production by Carl Bosch.[7] Commercially produced ammonia is used to make a wide variety of nitrogen compounds, including fertilizer and explosives.

The Haber-Bosch process directly synthesizes ammonia from nitrogen and hydrogen and is the most economical nitrogen-fixation process known. About 1909 the German chemist Fritz Haber ascertained that nitrogen from the air could be combined with hydrogen under extremely high pressures and moderately high temperatures in the presence of an active catalyst to yield an extremely high proportion of ammonia, which is the starting point for the production of a wide range of nitrogen compounds.[16] This process, made commercially feasible by Carl Bosch, came to be called the Haber-Bosch process or the synthetic ammonia process. **The Haber-Bosch method is now one of the largest and most-basic processes of the chemical industry throughout the world. This currently accounts for the majority of the reduced nitrogen that is used agriculturally with the world's increasing dependence on agriculture to feed its population.** .Nitrogen fixation, along with photosynthesis is the basis of all life on earth. Current understanding suggests that no plant fixes its own nitrogen. Some plants (mainly legumes) fix nitrogen via symbiotic anaerobic microorganisms (mainly rhizobia). The nature of biological nitrogen fixation is that the dinitrogenase catalyzes the reaction-splitting triple-bond inert atmospheric nitrogen (N(2)) into organic ammonia molecule (NH(3)). All known nitrogenases are found to be prokaryotic, multi-complex and normally oxygen liable.

Biological nitrogen fixation is insufficient to meet global demands , so in recent years world production of ammonia on industrial scale has risen from one million tonnes per year in 1950 to 110 million tones in 1992.[16]About 75 percent of ammonia produced is used as fertilizer.

BACKGROUND

Nitrogen is a critical limiting element for plant growth and production. Even though it is one of the most abundant elements (predominately in the form of nitrogen gas (N2) in the Earth's atmosphere), plants can only utilize reduced forms of this element. Nitrogen fixation is the process by which atmospheric nitrogen is converted by either a natural or an industrial means to a form of nitrogen such as ammonia, nitrates ,nitrites, urea etc.. Plants acquire these forms of "combined" nitrogen by: 1) the addition of ammonia and/or nitrate fertilizer (from the Haber-Bosch process) or manure to soil, 2) the release of these compounds during organic matter decomposition, 3) the conversion of atmospheric nitrogen into the compounds by natural processes, such as lightning, and 4) biological nitrogen fixation . **The reduction of atmospheric nitrogen is a complex process that requires a large input of energy to proceed .**The nitrogen molecule is composed of two nitrogen atoms joined by a triple covalent bond, thus making the molecule highly inert and nonreactive. Nitrogenase catalyzes the breaking of this bond and the addition of three hydrogen atoms to each nitrogen atom. Microorganisms that fix nitrogen require 16 moles of adenosine triphosphate (ATP) to reduce each mole of nitrogen (Hubbell & Kidder, 2009). These organisms obtain this energy by oxidizing organic molecules. Biological nitrogen fixation (BNF) occurs when atmospheric nitrogen is converted to ammoniaa nitrogenase enzyme.

The overall reaction for BNF is:

$$N2+16\ ATP +8e\text{-}+ 8H^{+} \rightarrow 2NH3 +H2 +16\ ATP +16\ Pi$$

The process is coupled to the hydrolysis of 16 equivalents of ATP and is accompanied by the co-formation of one equivalent of Hydrogen. The conversion of N into ammonia occurs at a metal cluster called FeMoco, iron- molybdenum cofactor. The mechanism proceeds via a series of protonation and reduction steps wherein the FeMoco active site hydrogenates the Nitrogen substrate. [1] .Until the early 19th century, the available fixed nitrogen, stockpiled by natural processes over .millions of years, was enough to sustain the earth's population. **But with rapidly increasing populations and the dramatic growth of large cities in industralized nations, the demand for increased supplies led to the beginnings of the nitrogenous fertilizer industry. [4].These fertilizer forms were further supplemented by the ammoniacal by-products from coal gas production.**

Further increasing demand led to the invention of several processes, some of which were commercially successful. Calcium cyanamide is the inorganic compound with the formula CaCN2. It is the calcium salt of the cyanamide 2 (CN^{2-}) anion. This chemical is used as fertilizer. and is commercially known as nitrolime. It was first synthesized in 1898 by Adolph Frank and Nikodem Caro (Frank–Caro process).Frank and Caro discovered the ability of alkaline earth carbides to adsorb atmospheric nitrogen at high temperatures. Frank and Caro also noted the formation of ammonia from calcium cyanamide.[19]

CaCN2 + 3 H2O → 2 NH3 + CaCO3

The first process, implemented in 1905, was the Birkeland-Eyde .The Birkeland–Eyde process was one of the competing industrial processes in the beginning of nitrogen based fertilizer production. [8] .It is a multi-step nitrogen fixation reaction that uses electrical arcs to react atmospheric nitrogen (N2) with oxygen (O2), ultimately producing nitric acid (HNO3) with water.[1] The resultant nitric acid was then used as a source of nitrate ($NO3^{-}$) in the reaction

$$\mathbf{HNO3+H2O \rightarrow H3O^{+} + NO^{3-}}$$

which may take place in the presence of water or another proton acceptor.

It was developed by Norwegian industrialist and scientist Kristian Birkeland along with his business partner Sam Eyde in 1903,[8]based on a method used by Henry Cavendish in 1784.

Birkeland–Eyde process is relatively inefficient in terms of energy consumption. Therefore, in the 1910s and 1920s, it was gradually replaced in Norway by a combination of the Haber process and the Ostwald process.[8] The Haber process produces ammonia (NH3) from molecular nitrogen (N2) and hydrogen (H2), the latter usually but not necessarily produced by steam reforming methane (CH4) gas in current practice. The ammonia from the Haber process is then converted into nitric acid (HNO3) in the Ostwald process.[The Haber

process,[14] also called the Haber–Bosch process, is an artificial nitrogen fixation process and is the main industrial procedure for the production of ammonia today.[14][15] It is named after its inventors,the German chemists Fritz Haber and Carl Bosch, who developed it in the first decade of the 20th century. .[16]. The process converts atmospheric nitrogen (N2) to ammonia (NH3) by a reaction
with hydrogen (H2) using a metal catalyst under high temperatures and pressures. Before the development of the Haber process, ammonia had been difficult to produce on an industrial scale,with early methods such as the **Birkeland–Eyde** process and Frank –Caro process all being highly inefficient
When first invented, the Haber process competed against another industrial process, the cyanamide process. However, the cyanamide process consumed large amounts of electrical power and was more labor-intensive than the Haber process. As of 2018, the Haber process produces 230 million tonnes of anhydrous ammonia per year.[9]The ammonia is used mainly as a nitrogen fertilizer as ammonia itself, in the form of ammonium nitrate, and as urea. The Haber process consumes 3–5% of the world's natural-gas production (around 1–2% of the world's energy supply).In combination with advances in breeding, herbicides and pesticides, these fertilizers have helped to increase the productivity of agricultural land: The energy-intensivity of the process contributes to climate change and other environmental problems:leaching of nitrates into ground water, rivers, ponds and lakes; expanding dead zones in coastal ocean waters, resulting from recurrent eutrophication; atmospheric deposition of nitrates and ammonia affecting natural ecosystems; higher emissions of nitrous oxide (N2O), now the third most important greenhouse gas following CO2 and CH4.. The Haber–Bosch process is one of the largest contributors to a buildup of reactive nitrogen in the biosphere, causing an anthropogenic disruption to the nitrogen cycle.

Since nitrogen use efficiency is typically less than 50%, farm runoff from heavy use of fixed industrial nitrogen disrupts biological habitats. Nearly most of the nitrogen found in human tissues originated from the Haber–Bosch process.[9] **While synthetic nitrogen fuels modern agriculture, its production is energy-intensive, and its application leads to aquatic pollution and greenhouse gas emissions.**
Sustainable intensification of agriculture to provide both food for humans and feedstocks for bio-based fuels and materials requires alternative options for nitrogen management.[17] For nearly fifty years, nitrogen fixation in cereal crops has been pursued to address this challenge. Efforts to engineer plants for nitrogen fixation have made strides through eukaryotic nitrogenase expression and a deepened understanding of root nodulation pathways, but deployment of transgenic nitrogen fixing cereals may be outpaced by population growth .[13].In recent years use of inorganic fertilizer risen at the expense of biological nitrogen fixation .Alternative technologies are currently under development such as electrochemical synthesis ,photochemical synthesis ,homogeneous catalysis etc.

ANALYTICAL DISCUSSION

The nitrogen cycle is one of the most important biogeochemical cycles on Earth because nitrogen is an essential nutrient for all life .Nitrogen must be converted to its usable form like ammonia which can be used by plants and other organisms. All organisms use ammonia to form aminoacids ,protein and other nitrogenous compounds .Biological Nitrogen fixation BNF is a process which converts nitrogen to ammonia which can be utilized by plants .**Anually ,approximately 2.5 × 10^{11} kg ammonia are fixed from the atmosphere by biological nitrogen fixation (by legumes and cyanobacteria) and approximately 8 × 10^{10} kg NH_3 are manufactured by ammonia industry .Currently ,approximately 2 tons of industrially fixed nitrogen are needed as fertilizer for crop rotation to equal the effects of 1 ton of nitrogen biologically fixed by legume crops [20].Therefore ,biologically –fixed nitrogen influences the global nitrogen cycle substantially less than industrially fixed nitrogen .On the other hand ,world population has now been increasingly relying on nitrogen fertilizers in order to keep up with the demands of food and economic growth rates .[20] More than 83 % of NH_3 synthesized is used in making fertilizers** . The requirement of nitrogen fertilizer is increasing day by day as it is a essential element for the growth and development of plants .Nitrogen deficiency is a widespread problem in many soils used for production of staple cereal crops To supplement natural nitrogen fixation, farmers add large amounts of nitrogen-containing fertilizer to their soils such that nitrogen never becomes a limiting nutrient for plant growth. The produced fertilizers have increased crop yield by 400 % and still using under 15% of the global total land area .It has been estimated that nearly 80% of the N_2 located in human tissues stem from the Haber- Bosch process .However, of the nitrogen added to fields most of which is in the form of NH_3 and NO_3^- only 30−50% is taken up by plants, while the remainder

is metabolized by soil microorganisms in processes with detrimental environmental impacts. The first of these processes, that is, nitrification, refers to the biological oxidation of NH_3 to NO_2^- and NO_3^-, which have low retention in soil and pollute waterways, leading to downstream eutrophication and ultimately 'dead zones' (low oxygen zones) in coastal waters, for example, the Gulf of Mexico.[9] In a second process, namely, denitrification, NO_3^- and NO_2^- undergo stepwise reduction to N_2O and N_2. Substantial amounts of the N_2O produced in this process escape into the atmosphere, contributing to climate change and ozone destruction. Recent results suggest that nitrification also affords N_2O. The conversion of atmospheric nitrogen into valuable substances such as fertilisers and fine chemicals is essential for agriculture and many other processes that sustain life on the planet. Ammoniacal fertilizers contain the nutrient nitrogen in the form of ammonium or ammonia .Ammoniacal fertilizers are readily soluble in water and therefore readily available to crops.Except rice, all crops absorb nitrogen in nitrate form. These fertilizers are resistant to leaching loss, as the ammonium ions get readily absorbed on the colloidal complex of the soil. Ammonia (NH_3) is the foundation for the nitrogen (N) fertilizer industry. It can be directly applied to soil as a plant nutrient or converted into a variety of common N fertilizers, but this requires special safety and management precautions.Almost 80 percent of Earth's atmosphere is composed of nitrogen gas (N_2), but in a chemically and biologically unusable form. In the early 1900s, the processor combining N_2 and hydrogen (H_2) under conditions of high temperature and pressure was developed.This reaction is known as the Haber-Bosch process: [$3H_2$ + N_2 $2NH_3$]. **The classical production method ,the Haber-Bosch process ,relies basically on natural gas . whereas ammonia has also the capability of being produced from renewable energy sources ex . solar ,wind etc.A variety of fossil-fuel materials function as a source of H_2, but natural gas (methane) is most common. Therefore, most NH_3 production occurs in locations with a ready supply of natural gas. Ammonia has the highest N content of any commercial fertilizer, making it a popular source of N**

despite the potential hazard it poses and the safety practices required to use it. For example, when NH_3 fertilizer is applied directly to soil, it's in a pressurized liquid that will immediately become vapor if

exposed to air after leaving the tank. Although the Haber–Bosch process is the most important method of nitrogen fixation, the process is associated with major environmental concerns because it is very energy intensive and requires non-renewable feedstock to generate hydrogen. Hence, alternative ways of nitrogen fixation are being studied, from plasma synthesis and biological processes to metallocomplex catalysis, while existing methods are being improved using novel catalysts. Considering energy efficiency, the Haber–Bosch process and non-thermal plasma nitrogen fixation are promising methods for green industrial nitrogen fixation. Although metallocomplex nitrogen fixation takes place at ambient pressures, energy estimations show that this method does not provide higher energy efficiency than biological nitrogen fixation or the Haber–Bosch process.[5] Biological nitrogen fixation on the other hand, has energy

efficiency comparable to that of the Haber–Bosch process. Industries use the Haber-Bosch process to reduce nitrogen essentially in the same way. As Conventional agriculture has depended upon this process to produce the commercial fertilizer needed to grow most of the world's hybrid crops. But this approach comes with many consequences, including using fossil fuels for the energy needed to produce this fertilizer, the resulting carbon dioxide emissions and pollution from burning these fuels, and adverse affects on human health .[5]**Overuse of these chemical fertilizers has led to an upset in the nitrogen cycle and consequently to surface water as well as groundwater pollution. Increased loads of nitrogen fertilizer to freshwater, as well as marine ecosystems, has caused eutrophication**, the process whereby these systems have a proliferation of microorganisms, especially algae. This "greening" of the water column has caused decreased levels of dissolved oxygen (DO) in bottom waters as planktonic algae die and fuel microbial respiration. These depleted DO levels result in massive mortality of aquatic organisms and create so-called dead zones. Significant advances in sustainable productivity must be achieved to prevent a massive expansion in land use and greenhouse gas emissions. One of the greatest challenges in agriculture is supplying sufficient plant-available nitrogen to cereal crops, which provide 45% of the world's dietary energy consumed directly by humans in addition to providing feed for animal agriculture and a feedstock for bio-based fuel production and manufacturing[4]. Chemical synthesis of nitrogen fertilizer through the Haber-Bosch process supported increases in agricultural productivity .Additionally, due to the instability of synthetic nitrogen fertilizers in soils, more than half of the nitrogen fertilizer applied globally is lost to leaching and evolution of nitrous oxide, a potent greenhouse gas

.Increasing global nitrogen use efficiency will therefore be a significant target in efforts to sustainably intensify agriculture. Because plants do not have the capability of "fixing" nitrogen, it must be provided externally for maximal productivity. However, only a very small proportion of the nitrogen on earth (less and 0.001%) is cycling at anyone time between its usable fixed form in terrestrial pools and its inert molecular form in its atmospheric pool. Nitrogen fixation controls the atmosphere-to-terrestrial (land or sea) flow, nitrification and denitrification convert ammonia to nitrate and then to nitrogen gas which is lost to the atmosphere, while leaching and erosion move fixed nitrogen between land and sea. **Though the total biological fixation of nitrogen to ammonia and other nitrogeneous products is estimated to be twice than total nitrogen fixation by non-biological processes The biological world apparently stays ahead of a nitrogen deficiency because the fixation rate is just above the denitrification rate. For crop productivity to reach commercially acceptable levels currently, extensive augmentation by commercially produced nitrogen fertilizer is necessary.** Such problems have encouraged present-day research into all areas of nitrogen fixation.[5][9] But there is an alternative Researches have been done to make fertilizers with green ammonia .

Green ammonia is crucial to tackle the existential challenges of producing enough food to feed a growing global population and generating CO2-free energy. Ammonia (NH3), a compound of nitrogen and oxygen, is mainly used to manufacture fertilizers. 80% of the annual global production of over 170 million metric tons is used in this way. And that should become even more in the next few years. ammonia is conventionally produced using natural gas as

a fuel. Unfortunately, this accounts for around 1.4% of global fossil-fuel consumption and CO2 emissions.. Technology has been developed that can produce green ammonia from just water, air and electricity generated from renewables. The process involved, alkaline water electrolysis (AWE), is based on the proven chlor-alkali electrode technology developed by thyssenkrupp Uhde Chlorine Engineers, whose expertise and experience in electrolysis technology and EPC execution are based on more than 500 projects with over 10 GW capacity installed worldwide .Green ammonia production is where the process of making ammonia is 100% renewable and carbon-free. ... Approximately 88 percent of ammonia made annually is consumed in the manufacture of fertilizer In recent years the use of fertiliser has risen at the expense of biological nitrogen fixation (BNF), mostly because of increased usage in the developing world.

Currently 2.4 billion people depend on synthetic fertiliser for protein (Smil 2001), but predictions of population growth in developing countries indicate that they will need an additional 15 million tonnes of protein nitrogen over the next 50 years. As a result the increasing use of intensive agricultural systems relying on inorganic N looks set to continue because its application gives a reliable boost to crop yield in a cost effective manner. It also increases productivity because land can be used to grow cereals continuously rather than requiring regular rotation with legumes to replace N as in the BNF model (Crews and Peoples 2004;Jenkinson 2001).Unfortunately the consequence of intensive agriculture on the environment can be significant. It has been shown that in infertile tropical soils, organic matter decreases rapidly resulting in erosion and desertification (Graham and Vance 2000). In addition, the cost of inorganic fertilizer is .However, the process of making ammonia is currently not a "green" process. It is most commonly made from methane, water and air, using steam methane reforming (SMR) (to produce the hydrogen) and the Haber process.[11][18] About 96 percent of the hydrogen required for the production of ammonia via bosch process is derived from fossil fuels (Parkinson et al 2018).The remaining 4 percent is generated from electricity which will include some indirect use of fossil fuels from coal or natural gas electrical generation .(Michael et .al 2015) Unlike conventional ammonia, which is typically produced using natural gas as feedstock, green ammonia is produced by using solar/wind/hydropower to produce electricity that then feeds an electrolyser to extract hydrogen from water, while nitrogen is separated from air using an air separation unit.There are no large-scale green ammonia plants today, but producers and technology companies are starting to pave the wayto a greener approach.

Green ammonia synthesis via the Haber–Bosch (HB) process has become a major field of research in the recent years for production of fertilizers and seasonal energy storage due to drastic drop in cost of renewable hydrogen. While the field of catalysis and engineering has worked on this subject for many years, the current process of ammonia synthesis remains essentially unaltered. As a result, current industrial developments on green ammonia are based on the Haber Bosch process, which can only be economical at exceptionally large scales. [18] To address this need, research and development is under way around the world to replace the century-old Haber-Bosch process for manufacturing ammonia from N2 and H2, powered by renewable electricity. This involves replacing H2 obtained from steam-reformed CH4 to H2 that is instead obtained from electrolyzed H2O. This transition will enable the changeover from the Haber-Bosch production of NH3 to electrochemical, plasma chemical, thermochemical, and photochemical generation of NH3. If ammonia can eventually be produced directly from N2 and H2O powered by just sunlight, at a

technologically significant scale, efficiency, and cost, in a "solar ammonia refinery," green ammonia can change the world! It is well known that the century-old Haber-Bosch process, $N_2 + 3H_2 \rightarrow 2NH_3$, is thermally powered by fossil energy, resulting in a greenhouse gas intensive process, which needs to be replaced by one driven instead by renewable energy.[17] To address this issue, we need to replace the energy-intensive synthesis process of ammonia from N2 and H2 by one powered instead by renewable electricity.

IMPLICATIONS AND CONCLUSIONS

The reduction of atmospheric nitrogen is a complex process that requires a large amount of energy

N2 fixation is a grand challenge because N2 molecule is thermodynamically stable with an extremely high triple-bond energy. In nature, only a small group of microorganisms could biologically fix N2 to NH3 with the enzyme nitrogenase . **Due to important role of ammonia as a fertilizer in the agricultural industry and its promising aspects as an energy carrier , and other industrial applications many studies have recently attempted to find the economically viable production process of ammonia synthesis** .The most commonly utilized ammonia production method is the haber – bosch process. The downside to this technology is high –greenhouse gas emissions and high amount of energy usage There are several significant environmental reasons to seek alternatives to chemically fixed nitrogen fertilizer: it affects the balance of the global nitrogen cycle, pollutes groundwater, increases the risk of chemical spills, and increases atmospheric nitrous oxide (N2O), a potent "greenhouse" gas. **The urgency of replacing fossil fuels and mitigating climate change motivates us to progress toward more sustainable methods for N2 reduction reaction based on clean energy.**. Commercially produced ammonia is used to make a wide variety of nitrogen compounds ,including fertizers .Ammonia is the foundation of the nitrogen fertilizer industry .It can be directly applied to soil as a plant nutrient or converted to a variety of common nitrogen fertilizers For sustainable ammonia production ,the most widely adopted technology is water electrolysis coupled with renewable technologies such as wind ,and solar energy to produce hydrogen .As hydrogen is the key component for ammonia synthesis our focus should be on the sustainable hydrogen production pathways. Green ammonia is intended to be used in the production of carbon neutral fertilizer products and can be essential to enable sustainable food production .

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