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SUSTAINABLE NITROGEN FIXATION

Agrochemical research in food production adapted to planetary limits

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Today's global food production depends on the fixation of atmospheric nitrogen by using the Haber–Bosch process. The application of this catalytic system laid the foundations for the development of industrial agriculture and led to an unprecedented acceleration in the growth of human societies during the so-called *Green Revolution*. However, it appears that this production model will not be able to adapt to the current challenges of energy sustainability and climate crisis response. The Haber–Bosch cycle has a major impact on energy consumption and carbon dioxide emissions. In order to rethink this agri-food model, this present article examines chemical and technological development strategies to move towards an energy and environmentally sustainable model.

Keywords: **nitrogen fixation**, **ammonia synthesis**, **Haber–Bosch process**, **sustainability**, **fertilisers**.

Living organisms mostly comprise a select group of elements from the periodic table: carbon, hydrogen, oxygen, nitrogen, phosphorus, and sulphur. A diet rich in these elements is therefore essential for any species. Nitrogen, in particular, is widely available in atmospheric air; it is, in fact, its main constituent (≈78 %). In nature, it is incorporated into the soil by a process known as *nitrogen fixation*, in which bacteria convert gaseous nitrogen (N_2) into ammonia (NH_3), ammonium ions (NH_4^+), and other derivatives through an enzymatic reaction. These molecules are then used as essential nutrients in the synthesis of complex biomolecules such as proteins or nucleic acids.

> **«The availability of abundant nitrogen and other essential element salts in agricultural soils is vital for food production»**

From a chemical point of view, this transformation is not trivial. Although from a thermodynamic point of view the conversion of nitrogen gas to ammonia occurs spontaneously under normal ambient conditions, this reaction requires a very high activation energy because the triple bond between the two nitrogen atoms must be broken. This energy barrier means that although it is a thermodynamically spontaneous reaction, if no more energy is added to the system, the conversion will not take place for an almost infinite amount of time. However, nature has adapted and manages to set this process in motion thanks to highly specialised bacteria such as cyanobacteria. The latter are traditionally known as *blue-green algae*, although they are not related to the plant kingdom. Through the action of nitrogenase enzymes, these bacteria negate the energy barrier required for the dissociation of gaseous nitrogen. In chemical terms, nitrogenase enzymes act as excellent catalysts for the fixation of environmental nitrogen – i.e., they facilitate a chemical reaction by significantly reducing the activation energy, thereby accelerating the rate of the reaction and promoting its repetition until the reactants decompose.

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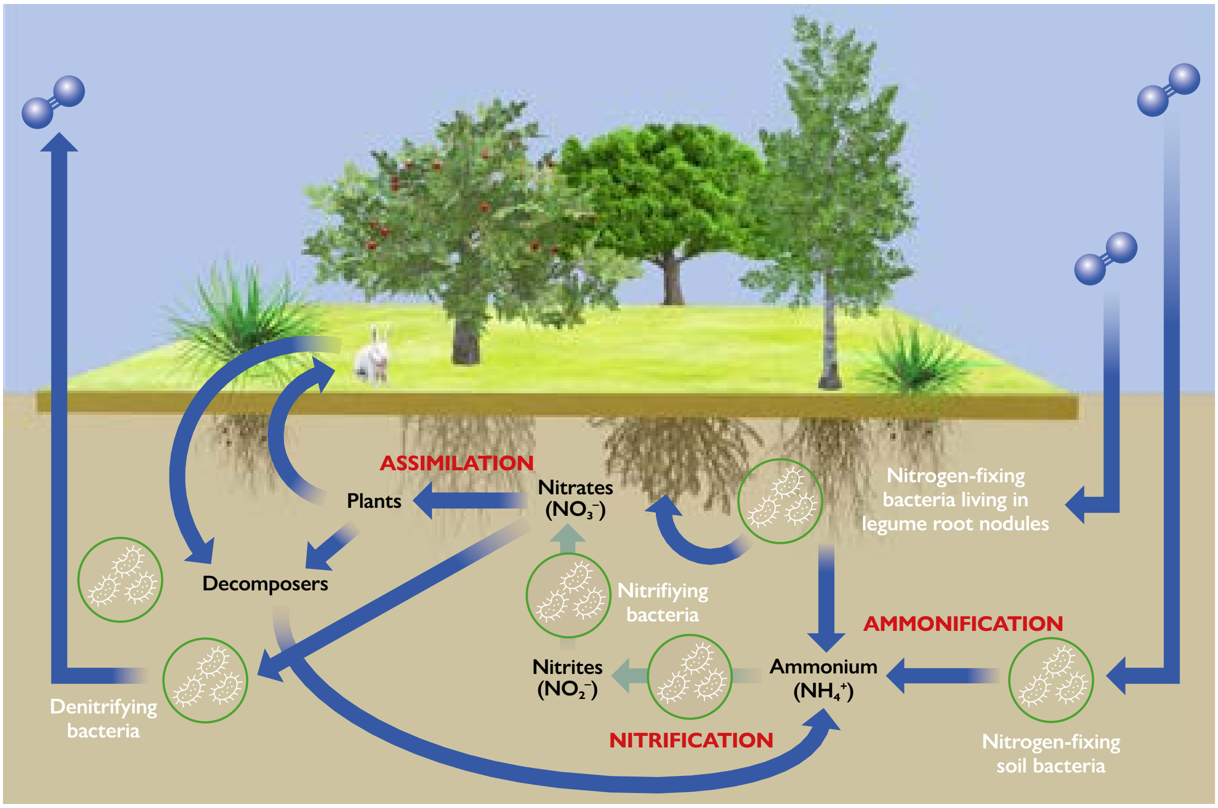

Diagram of the biological nitrogen cycle. The decomposition of organic matter allows bacterial activity to fix nitrogen in the soil in the form of ammonium ions and other nitrogen species. After oxidative nitrification, nitrogen becomes available as an essential nutrient for the growth of plant species.

SOURCE: Emanuela Accardo

The availability of abundant nitrogen and salts of other essential elements in agricultural soils is vital for food production. Historically, this contribution has been made by organic waste used to fertilise fields. However, since the work of the German researcher, Justus von Liebig, at the end of the 19th century, the targeted application of nitrogen compounds has been associated with a significant increase in crop yields. Thus, nitrogenous fertilisers – such as potassium nitrate from Chile (remembered for its famous advertisements) or sodium nitrate from India – became much sought-after products.

«Most industrially produced ammonia is considered grey, brown, or black in terms of its environmental impact»

These nitrogen compounds soon played an essential role in the subsequent changes in the agricultural production model during the so-called *Green Revolution*. During the first half of the 20th century, humanity witnessed a radical transformation of the agricultural production model based on the replacement of animal traction with mechanical traction, changes in the concentration and planning of cultivated land, standardisation of the most productive crop varieties with the introduction of hybrid seed packages, and the use of new products to increase yields – mainly fertilisers and pesticides. The resulting crops proved superior in terms of productivity, yield consistency, and resistance to external factors, leading to an unprecedented increase in food production (Wu & Butz, 2004). Furthermore, the addition of new chemicals – especially nitrogen derivatives – was key in this «revolution». Guano production and mineral nitrogen extraction would never have been sufficient to meet the needs of the abrupt increase in human populations seen at the time. However, chemical research was about to change the way the world was fed. In 1910, German chemists Fritz Haber and Carl Bosch achieved one of the greatest milestones in chemistry of all time: the fixation of atmospheric nitrogen to produce ammonia on an industrial scale, just as cyanobacteria do in nature.

In the Haber–Bosch thermocatalytic process, ammonia is formed by the reaction of hydrogen (H_2) and nitrogen in the presence of a catalyst and under conditions of high pressure and temperature. Typically, the gas mixture reacts in the presence of an iron composite supported on a promoter – such as aluminium oxide (Al_2O_3), potassium oxide (K_2O), or ruthenium on carbon – which acts as a catalyst, at pressures between 100 and 300 bar and temperatures in the range of 400 to 500 °C. It also requires highly purified reagents, and so a prior hydrogen and oxygen refinement step is required.

While nitrogen is purified from the air, hydrogen is mainly obtained from natural gas – methane (CH_4) – or carbon dioxide reforming, both of which produce toxic gases such as carbon monoxide (CO). Therefore, most industrially produced ammonia is considered grey, brown, or black in terms of its environmental impact. In addition, the large amount of energy required to maintain the reaction conditions and purify the reactants is not derived from renewable sources. Thus, the above should give us an idea of the environmental impact of the industry. The global production of ammonia using the Haber–Bosch process is 170 million tonnes per year and is estimated to account for 3–5 % of natural gas consumption and 1–2 % of the global energy demand. As a result, its production is thought to be responsible for up to 1.5 % of all greenhouse gas emissions (Wang et al., 2018). To get an idea of what this value represents, we have to consider that the energy consumption of this industrial process on a global scale is greater than the total energy demand of Spain per year.

In a sense, this great milestone of early 20th century chemical research succeeded in replicating the natural process by which nitrogen is incorporated into the life cycle. But the newly developed process was only possible because of the widespread availability of energy derived from carbon and fossil fuels. Therefore, in the current historical moment, marked by the climate emergency and the need to maintain a sustainable production system by decarbonising the economy, we must rethink the methods used to incorporate these nutrients into arable land. The current challenge is to overcome the energy dependence of the Haber–Bosch process and its

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In 1910, the German chemists Fritz Haber (left) and Carl Bosch (right) achieved one of the greatest milestones of chemistry of all time: fixing atmospheric nitrogen for the production of ammonia on an industrial scale, just as cyanobacteria do in nature.

associated carbon footprint. More than a century later, proposals from chemical research are once again key to this necessary change.

NEW CATALYTIC METHODS FOR SUSTAINABLE NITROGEN FIXATION

As explained above, catalysis make it possible to speed up chemical reactions, reducing the energy required to make products and thus, their environmental, energy, and economic impact. While at the beginning of the 20th century one of the main research objectives was to artificially synthesise nitrogen compounds from aerial nitrogen, the new philosopher's stone in the field of agrochemistry is to achieve the same thing using a sustainable process in terms of energy consumption. The fact that this phenomenon occurs naturally demonstrates that it is theoretically possible and has inspired researchers to think about new catalytic strategies to make it a reality. Some of the most important initiatives are discussed in more detail below.

Production of ammonia through electrical catalysis (electrocatalysis). This innovative way of producing ammonia requires the use of electricity in electrocatalytic processes. This consists of mixing nitrogen gas directly with hydrogen, or even directly with water, in the presence of a an *electrolyzer* (Marnellos & Stoukides, 1998). These devices consist of three elements that make up the electrochemical system: two electrodes (one acting as an anode, where the oxidation of hydrogen or water takes place and the other – a cathode – where the reduction of nitrogen takes place) with a membrane permeable to proton transport placed between them. These electrodes usually consist of electrocatalysts to facilitate the reaction, for example, for the anode, elements such as iron (Fe), ruthenium (Ru), palladium (Pd), titanium (Ti), platinum on carbon (Pt/C), and zirconium (Zr), and for the cathode, typical oxidising elements such as iron, ruthenium, tungsten (W), and nickel (Ni). Thus, by applying a current with a certain voltage to the electrochemical system, ammonia is produced thanks to the electrolyzer.

In this type of catalysis, nitrogen molecules are adsorbed (i.e., bonded) to the surface of the electrolyser cathode, weakening the nitrogen triple bond and even dissociating the molecule. The oxidation of hydrogen or water then releases the necessary protons into the medium to react with the nitrogen atoms to form ammonia. The advantages of this technology over the conventional Haber–Bosch process include the ability to work with reagents of lower purity, production at atmospheric pressure and moderate temperatures, and most importantly, the fact that the reaction is activated by the application of an electrical current, which can be generated from renewable energy sources.

Light-induced ammonia production (photocatalysis). The strategy of using sunlight to produce chemical reactions involves the use of semiconductor materials. As in the previous case, catalysts using semiconductors facilitate the reactions of nitrogen with hydrogen or water, favouring the formation of ammonia. In photocatalytic processes, light strikes these materials and causes the formation of the electron vacuum pair that separates their electrical charges (Nguyen et al., 2021). Once the physical adsorption of the nitrogen molecules takes place, the formed electric charges migrate towards the surface where the redox reactions of nitrogen reduction and hydrogen or water oxidation occur.

The most commonly used photocatalysts for these reactions are based on titanium oxide or iron oxide semiconductors, metal sulphides, or graphene, among others. Again, published work using this strategy demonstrates the possibility of synthesising ammonia from gaseous nitrogen at an ambient pressure and temperature. However, higher temperatures and pressures help to make the reaction more efficient, which could be achieved by using light concentrators – reflective devices that collect solar energy over a small area – directly on the photoreactor. The main strength of this method is the use of sunlight as the sole energy source.

Plasma-assisted catalysis for ammonia formation. In this method, plasma is created by ionising gas molecules by applying a high-intensity potential difference. The electrons in the gas molecules – in this case both hydrogen and nitrogen – are stripped away, turning the molecules into positively charged ions. The free electrons then circulate through the plasma cloud, chemically activating the nitrogen molecules. Plasma is produced by lightning during a thunderstorm and research teams can now use it to synthesise chemicals. This has two main advantages: firstly, it is possible to electrify the chemical reaction, and secondly, much lower pressures can be used than in the industrial process.

Cold or non-thermal plasma technology is considered a promising alternative for sustainable ammonia production in the medium to long term (Peng et al., 2018). In addition to ionisation of the gaseous reactants, the presence of other catalytic elements is common in this case. Moreover, alkali cations such as cesium (Cs), potassium (K), or magnesium or calcium oxides have been widely used as activators in these systems. Other catalysts that provide a metal surface capable of promoting nitrogen hydrogenation, such as nickel, platinum, palladium, or ruthenium, have also been widely used in this area of research.

«The energy dependence of the current system conceals other serious problems, such as the growing scarcity of other essential soil nutrients that cannot be produced industrially, such as phosphorus»

Ammonia synthesis by chemical looping reactions. Chemical looping processes use interconnected reactor systems that allow complementary chemical reactions to be carried out alternately on a continuous basis. These dual fluidised bed reactor systems can carry out the ammonia formation reaction in a similar way to the Haber–Bosch process, but at atmospheric pressure, thereby significantly reducing the complexity and cost of the method, while still achieving substantial yields (Brown & Hu, 2023). In these systems, the nitrogen typically reacts with a metal catalyst in a first step, usually forming nitrides. The chemical species formed can also activate the next stage, during which hydrogenation with hydrogen or water occurs and the desired ammonia is formed. Once the reaction has taken place, the metal catalysts are returned to the first reaction chamber to restart the cycle. In chemical loop reactions, metal nitrides of nickel, manganese (Mn), iron, or cobalt (Co) are commonly used as catalysts for the formation of ammonia.

All of the research results presented in this article indicate the potential of the discipline to achieve sustainability in this process through the development of new production techniques. However, while the results published so far are not insignificant, the

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Transitioning to a model of agricultural production that is truly adapted to the constraints of the planet will require a profound rethink and much more activity than that generated by chemical research. However, the ability to artificially fix nitrogen to provide essential nutrients in a sustainable way can be a powerful tool.

complexity of the process still requires simultaneous advances in several disciplines, such as chemistry and engineering. Moreover, it is not likely that these technologies will be widely applicable in the short term. The most optimistic experts still predict that the milestone of having one of these technologies available will be reached within the next few decades. Nonetheless, the global energy crisis will not allow such timeframes and so we must also assess how the current process can be transformed today.

THE RENOVATION OF AMMONIA PLANTS

Over the last century, the energy efficiency of the Haber–Bosch cycle has improved significantly. Its consumption has fallen from 110 $kWh \cdot kg^{-1}$ to 7.7–10.1 $kWh \cdot kg^{-1}$. However, efforts to make the process renewable have been rather unsuccessful. Therefore, there is still a lot of room for improvement: the process can be made more sustainable by lowering the pressure and temperature conditions at which the reaction takes place, electrifying the plants using renewable energy sources, using green hydrogen as a reagent, and improving the technology to allow the use of less pure reagents.

«Global ammonia production is thought to be responsible for up to 1.5% of all greenhouse gas emissions»

In this respect, the work published by Macfarlane et al. (2020) argues for a gradual transition from the Haber–Bosch process to sustainability through the implementation of different technologies, which would be introduced in three overlapping periods of improvement.

A first generation of innovations, which could be implemented almost immediately, would require electrification of production facilities, on-site carbon capture technology, and the use of solar concentrators as the main source of thermal energy for reactors. This industry could easily adapt to the use of renewable electricity produced by solar panels or wind turbines and it is therefore desirable for most processes to be powered by this form of energy. On the other hand, greenhouse gases produced during hydrogen synthesis can be mitigated by implementing carbon capture, transport, and storage systems (Zhao et al., 2023). The sequestered carbon dioxide can be revalorised by converting it to methane through the Sabatier reaction (Novoa-Cid & Baldovi, 2020).

In a second generation, medium-term improvements would involve the introduction of hydrogen electrolysers into the same plants, allowing this reagent to be produced in situ using renewable energy. Ideally, the electrodes used in these systems should be made from abundant and available materials.

In the third and final generation, long-term technologies would have to replace all parts of the Haber–Bosch process that are, at least for the time being, unavoidable. This transformation would require the implementation of nitrogen electroreduction methods – through catalytic strategies such as those presented in the previous section – to make the overall process sustainable. In addition, such redox reactions are better suited to an intermittent energy supply, as may be the case with renewable energy sources.

«The current challenge is to overcome the energy dependence of the Haber–Bosch process and its associated carbon footprint»

AN ESSENTIAL TOOL FOR GREATER CHANGE

There is no doubt that chemistry is once again destined to play a key role in transforming the global food production system. The alternatives presented in this article are already under development; they are viable technological strategies that allow us to think about the sustainable production of nitrogen derivatives, which would play a fundamental role in achieving agriculture independent of fossil fuels. Nevertheless, it seems unwise to fall prey to the kind of banal techno-optimism that stakes the future of the model on such advances. This is partly because the material and energy dependence of the current system conceals other serious problems, such as the energy consumption of large-scale distribution or the growing scarcity of other essential soil nutrients that cannot be produced industrially, such as phosphorus (Cordell et al., 2009).

The transition to a model of agricultural production that is truly adapted to the constraints of the planet and human lifestyles will require a profound rethink and much more investigation than that currently generated by chemical research. It will demand the collective efforts of a wide range of actors working on a new way of managing resources. However, the ability to artificially fix nitrogen to provide essential nutrients in a sustainable way could be a powerful tool in this transformation.

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