Green Approach to the Fertiliser Industry: Low-carbon Fertilisers

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Abstract
Decarbonisation means reducing or ideally eliminating the greenhouse gas emissions by evaluating all processes in a system from a “low-carbon” perspective. This review describes the current state of the fertiliser industry, and the options and recommendations for its decarbonisation. Decarbonisation of the fertiliser industry can be achieved with the developing technologies in terms of raw materials, energy usage, and operating conditions in the fertiliser production processes. Low-carbon fertilisers can be realised with the improvements that can be made in the life cycle of the fertiliser, from the derivation of the raw materials to the formation of the final products. Today, many decarbonisation studies with new technologies that can be created in ammonia production, which is the most energy-intensive process in the fertiliser industry, are at the research stage. This paper reviews the use of hydrogen source in ammonia production and achieving biomass gasification or electrolysis with low carbon footprints, reducing greenhouse gas emissions in nitric acid production, integrating carbon capture and storage technologies into the fertiliser processes, and increasing the efficiency of low-carbon agricultural practices.

Keywords
Fertiliser industry, green ammonia, Haber-Bosch process, decarbonisation, carbon capture

1 Introduction
Decarbonisation means reducing or ideally clearing off greenhouse gas emissions that include mainly carbon dioxide and methane in the activities that run our global economy. According to the Paris Agreement, the aim is to reduce the world’s greenhouse gas emissions by at least 40 % by 2030 compared to 1990 levels. To achieve this challenging goal, it is necessary to reduce the amount of greenhouse gases emitted by human activity to levels that trees, soil, and oceans can absorb naturally, with a goal of net zero emissions by the end of the century. This decline is not a target that can be realized in a short time. Recent studies of the World Meteorological Organization show that the pace of climate change is accelerating, and the global mean surface temperature increases as greenhouse gas concentrations increase, with data indicating that the last ten years (2011–2020) were the hottest years, and 2020 was one of the three hottest years on record. In 2019, greenhouse gas emissions had around 400 ppm concentration of CO₂ that is 148 % of pre industrial levels. Despite COVID-19 causing worldwide industrial shutdowns, global greenhouse gas emissions increased in 2020. Given this advancing state of climate change, the major changes that can be made in industry for the transition to a global decarbonised economy will have a significant impact on our economies and societies.

Industrial manufacturers have the responsibility to research sustainable and ecologically non-toxic production methods. It is no longer an adequate engineering perspective for a process to reach the most efficient product with the least number of resources. Ideally, it is possible to achieve more sustainable production while improving economic returns. The chemical sector is in the industry as the largest consumer of both oil and natural gas. Despite being the largest consumer of industrial energy, it ranks third in terms of direct CO₂ emissions after iron and steel, and cement. The largest energy consumption comes from the demand for a wide variety of chemical raw materials. High-value chemicals, ammonia and methanol, the demands for which have increased strongly in recent years, are the leading in these raw materials. Ammonia, the chemical that forms the basis of all synthetic nitrogen fertilisers, is an important raw material for composite fertilisers that provide potassium and phosphate, which is critical for modern agricultural systems. It is predicted that their demands will increase with the widespread use of sustainable agricultural practices. With the increase in demand for chemical products, studies to reduce the emission intensity of production and research on this subject have become important. Reducing the share of production for fossil fuel-based feedstocks, incorporating renewable resources into production, and adopting innovative processes that support the waste cycle, such as electrolyte or biomass, can help.

The Green Deal, which the European Union designed not only as a climate policy but also as an economic transformation program and published in December 2019, also includes the policy areas of Clean Energy and Sustainable Industry. Low-carbon fertilisers could take an important place in the adaptation and improvement studies of the Carbon Border Adjustment Mechanism, which will adapt to the climate and economic policies of the future, and be desired to be carried out in priority sectors such as energy and fertiliser, according to these policies. Along with the production of cement, steel, and ethylene, it is one of the “big four” industrial processes that must develop and implement a decarbonisation plan to meet the net zero carbon emissions target by 2050.
According to 2019 data from US Environmental Protection Agency, CO₂ emissions by certain sectors are given in Fig. 1a. In the industry, the percentage of processes related to the fertiliser industry is also given in Fig. 1b. The largest source of greenhouse gas emissions is the use of fossil fuels such as coal, natural gas, and petroleum products. These resources are generally consumed for energy, transportation and certain industrial processes that depend on these fuels.⁶

The fertiliser sector is in the middle of the agriculture and food sectors, where green transformation is primarily desired. As it is known, in order to meet the food needs of the increasing population, significant changes in the food chain must be made in a sustainable way. The food and agriculture industry involves converting raw agricultural products into their final products. Fertilisers are important inputs of the food chain and are produced from basic raw materials with a high carbon footprint in the chemical industry. For this reason, the fertiliser sector is the place where decarbonisation is seen as a priority in the food chain.⁷,⁸

Low-carbon fertiliser is obtained with the use of low-carbon raw materials (ammonia, nitric acid, etc.) and energy, so that minimum carbon emissions are made during production. A low-carbon fertiliser is based on minimal greenhouse gas emissions from fertiliser production processes and agricultural activities. To achieve this, it should be based on the integration of fertiliser production technologies of the future, low energy consumption in existing processes, low pollutant and low carbon emissions, and the use of carbon pools. It should also require minimal human, material, and financial resource input. The development of low-carbon fertiliser technologies can play a key role in promoting global low-carbon activities. Low-carbon fertiliser can offset 80% of industrial greenhouse gas production, and appears to be an important step towards solving the food security and environmental problems caused by climate change.⁹ The main reason why fertiliser production needs to be reviewed and regulated with a green approach is that it is highly dependent on ammonia. Synthetic ammonia-based fertilisers will continue to be essential to feeding a significant and growing proportion of the world’s population. Carbonisation of the synthesis of ammonia, will allow the production of low-carbon fertilisers instead of fertilisers with high carbon emissions.

Ammonia, the most important source of carbonless nitrogen, one of the most common components of food production and human nutrition, is produced largely from hydrogen obtained from natural gas. This constitutes about 5% of global natural gas consumption.¹⁰ This indicates that ammonia production is the most energy-consuming process in the fertiliser sector.⁶ Food and agricultural production are dependent on ammonia in a chain similar to that in Fig. 2. This means that improvements that can be made in ammonia production will lead to robust improvements in the global food chain.¹⁰ The increasing need for food in parallel with the increasing world population creates expectations for improvement, sustainability, and efficiency in many industrial processes, from agriculture to food.⁷

Ammonia is an essential substance for various industries, and due to its very low boiling point (−33 °C at 1 atm), specially designed equipment is required for its storage and transfer.¹¹ It is produced by the Haber-Bosch (HB) process, which involves synthesis reactions of hydrogen and nitrogen with specific catalysts, and is known for emitting high CO₂ emissions. In addition, the hydrogen used in the HB process is produced by steam reforming of natural gas, which emits high amounts of greenhouse gases.¹² Each of these processes is defined as “a high purity source” in the technology roadmap report prepared by the International Energy Agency, as it contains high carbon dioxide emissions and energy consumption.¹³ Ammonia, which is primarily used for the fertiliser sector, increases the carbon credits of both fertiliser and indirectly the food sector, due to the aforementioned process conditions. Ammonia production, which is responsible for 1.2% of the amount of carbon dioxide emitted due to human-made practices, needs to be reviewed.¹⁴ For this reason, it is very important to put the ammonia process at the centre of the studies to be carried out for the decarbonisation of the fertiliser and food sectors. In addition, it is significantly responsible for the largest carbon dioxide emissions in the chemical industry (Fig. 3).
By producing ammonia with the support of renewable energy and removing carbon emissions from the process, the food and fertiliser sectors, which account for a large part of the world’s carbon emissions, will gain momentum in climate improvement efforts. The most basic way is to obtain hydrogen, which is the source of ammonia production, by low-carbon processes. Hydrogen production by a low-carbon chain is an important research topic for the future scenarios aiming to maintain low-carbon fertilisers. Therefore, hydrogen sources with a lower CO₂ footprint (green or blue hydrogen) can be produced on-site or supplied from external sources to ammonia plants. Alternatively, ammonia plants produce large streams of nearly pure CO₂ gas, potentially well-suited for carbon storage. The use of a clean hydrogen source in ammonia production provides the production of ammonia types coded as green and blue, similarly. These are simply environmentally friendly processes that can replace traditional ammonia production with sustainable and clean production in terms of resources and technology. Ammonia production types with environmentally friendly technology can greatly reduce carbon emissions, unlike the method used worldwide today. It can also help promote green technologies in industries such as fertilisers that use ammonia as a raw material. Instead of using fossil fuel, it offers a great opportunity to make a significant improvement in the future of the fertiliser and energy markets. The use of green or blue ammonia is seen as an important step in reducing the carbon footprint in the life cycle of all fertiliser processes. In addition, the spread of green sources in industries directly affects both the carbon credit of fertilisers and the food chain in the world.

The use of hydrogen with a low carbon footprint, such as green ammonia, blue ammonia, or turquoise ammonia, or produced by gasification of biomass, are some of the options for low-carbon sources for fertiliser production. In addition, carbon capture systems (CCS) can be integrated into the process to keep the carbon dioxide emissions of existing systems in fertiliser production processes. As an alternative, energy-efficient technology can be preferred. With appropriate scrubbing towers, the release of nitrogen oxides can be prevented. Clean energies such as biogas, solar and wind energy can be integrated. Fertiliser types, including organic base obtained by waste recycling, can be developed. Developing fertilisers to increase their effectiveness with slow release and different coating technologies, and to prevent losses to air and water in agricultural applications are also decarbonisation studies that can be done on the final product.

The presented study examines the economic and environmental effects of using green technologies in the fertiliser industry, which is heavily dependent on natural gas as a raw material. It aims to present low-carbon technologies, which have been very interesting recently, together with applications that affect the fertiliser industry and reduce carbon emissions in fertilisers. With a green approach to the fertiliser industry, potential systems, options, and recommendations for the incorporation of low-carbon processes in the life cycle of fertiliser production processes have been compiled. In addition, it was desired to create a roadmap for the important points of carbonisation steps in fertiliser production for researchers in the fertiliser industry who want to make improvements in line with future environmental and economic requirements. In the prepared study, the aim was to reveal the place and importance of low-carbon fertilisers in the improvements needed by the global food chain in climate improvement efforts.

2 Main processes in fertiliser industry

Throughout human history, fertiliser has been the basic input of nutrients for crop production. With the development of agricultural production and the increase in food demand, methods have been sought to increase crop productivity. Increasing urbanisation has necessitated the development of commercial fertilisers. Fertiliser application increases the development of the plant and thus the yield. Therefore, fertilisers contribute to addressing the greatest challenge of feeding the growing world population. Various production units such as ammonia production, nitric acid production, urea production, and granular compound fertiliser production can be found in the mineral fertiliser industry. Fertilisers are basically defined by their macro plant nutrients content (nitrogen, phosphorus, potassium). Fertiliser production processes vary according to their chemical content and designed particle forms. Fig. 4 simply describes the process steps of the basic fertiliser types.

The global production of nitrogenous fertiliser is about 450 million tons/year. In general, a high level of energy is required in fertiliser production. About 1.2 % of the world’s energy is used in the fertiliser sector, of which 93 % is nitrogen-based. Almost all nitrogenous fertilisers are manufactured using the HB process, which is a traditionally rooted process. The HB process, which converts hydrogen and nitrogen into ammonia, made nitrogen fertilisers widely available as one of the most important in-

Fig. 3 – Direct CO₂ emissions from primary chemical production⁴

![Graph showing Direct CO₂ emissions from primary chemical production](image-url)
When nitrogen fertilisers are evaluated in determining the carbon footprint of the production processes of different fertiliser products, the CO₂ emission per kg N can be calculated. In a previous study, the carbon footprint values for ammonium nitrate, urea, and urea ammonium nitrate, for production according to European standards, were found to be very close to each other, around 3.5 kg CO₂ eq/kg N. Here, the CO₂ released during the rapid decomposition and hydrolysis of urea after it is applied to the soil is also included in the calculation. From this point of view, studies on slow release of urea and specially coated products produced in this field can be considered as one of the steps taken toward low-carbon fertiliser production.

Fertiliser production is a significant contributor of greenhouse gas emissions to the carbon footprint of agricultural products. When evaluating the carbon footprint of fertilisers, it is even more important to consider all life cycle emissions to account for all additional sources of greenhouse gas emissions beyond the production stage. This applies mainly to nitrogen fertilisers, as their use in agriculture can lead to N₂O emissions in different ways. In addition, the use of most N fertilisers acidifies the soil; this is usually offset by the application of CO₂, which releases lime in the soil after conversion. For example, when the locations are compared in fertiliser production such as Europe, Russia and/or China, it is seen how the differences in carbon emissions vary according to the facilities. The impact factor here is whether the facilities are integrated with CCS or not, the differences in green technology percentages. This situation is shaped by the presence of nitrogen dioxide in nitric acid production, absorption percentage, energy reuse percentage or the use of fossil fuels in ammonia production.

### 3.1 Decarbonisation of ammonia production

The annual production of ammonia is about 145–160 million tons per year, around 80 % of which is used by the fertiliser industry, supplying to feed over 70 % of the world population. Therefore, most of the nitrogen found in the human body has passed by the HB process. According to 2019 data, 144 million tons of ammonia was produced worldwide, and was generally used for derivatives such as urea, ammonium nitrate, nitric acid, ammonium phosphates, and ammonium sulphate. Approximately 88 % of apparent domestic ammonia consumption is for fertiliser use, including anhydrous ammonia, urea, ammonium nitrates, ammonium phosphates, and other nitrogen compounds for direct application, and about 50 % of the world’s food production relies on ammonia fertiliser. The rest of ammonia is used to produce explosives, pharmaceuticals, plastics, synthetic fibres and resins, and numerous other chemical compounds.

The main goal in the HB process is to produce liquid ammonia by bonding atmospheric nitrogen with hydrogen at high temperature and high pressure through a catalytic reaction. The high energy that needs to reach high heating is generally provided by natural gas. About 3–5 % of the global natural gas consumption is realized by the fertiliser sector yearly. Approximately 65 % of the natural gas used in the process is the main source of hydrogen required for the formation of ammonia. The remaining 35 % is used to provide the heating required for the process. Therefore, it

### 3 Green technologies for low-carbon fertilisers

During the study on carbon emissions in the fertiliser industry, the reported data include energy consumption in ammonia synthesis via HB process, and NOx emissions from nitric acid production, as well as other CO₂ sources due to energy consumption for the synthesis of urea and nitrate products, prilling and granulation of final products, etc.
can be stated that natural gas is one of the high-priced and valuable inputs in the fertiliser industry as well as ammonia. Due to its high energy requirement, the HB process has a huge carbon footprint because the reaction operating at temperatures around 500 °C and pressures up to about 20 MPa consume about 1–2 % of the world’s total energy consumption. Approximately 420 million tons of CO₂ gas is emitted annually in ammonia production. This total accounts for roughly 1.2 % of global anthropogenic CO₂ emissions, more than any other industrial chemical production reaction.¹⁴,²⁹

Current commercial ammonia production, which is called brown ammonia, heavily relies on the HB process (Fig. 5). This reaction includes the catalytic reaction of hydrogen and nitrogen at high temperature and pressure. In general, brown ammonia production is energy-intensive, consuming 8 MWh per ton of ammonia. However, most of the energy consumption and about 90 % of carbon emissions come from hydrogen production. Nitrogen is obtained from compressed air or an air separation unit.³⁰

![Diagram](image_url)

Fig. 5 – Schematic of brown ammonia production process.¹⁷,²⁶

Ammonia synthesis is carried out with HB reaction. However, before the ammonia synthesis step takes place, there is the preparation process of the raw material, namely natural gas. Thus, ammonia production takes place with the listed steps. There exist six steps during the catalytic steam reforming method: 1) natural gas purification, 2) catalytic steam reforming, 3) carbon monoxide shift, 4) carbon dioxide removal, 5) methanation, and 6) ammonia synthesis.¹¹,²²

Most natural gas requires a purification step for the removal of CO₂, sulphur compound, and depending on the source, it should be filtered or separated to remove the droplets containing oil or water.²⁰ Also, since the catalyst used in the steam reforming process is highly sensitive to sulphur compounds, the sulphur content of the natural gas must be removed. The aim of the first step in the ammonia production process is therefore to remove the sulphur. To reduce sulphur concentration in natural gas to 0.15 mg m⁻³, feeding natural gas is preheated to 350–400 °C. Next, hydrogen gas is added, which reacts with sulphur compounds to form hydrogen sulphide.²² Likewise, sulphur can be removed by adsorption with active carbon or hot zinc oxides.²⁰

The second step is the reforming process, which takes place in two stages. In the primary stage, sulphur-free natural gas enters the reformer at a temperature of 400–600 °C and is mixed with steam to achieve 60 % conversion, according to Eq. (1).

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H = +206 \text{ kJ mol}^{-1}
\]  

(1)

Next, the gas mixture enters the secondary reformer, where the air required for ammonia production is supplied. About 99 % of the hydrocarbons are converted in the secondary reformer at a temperature of 500–600 °C. The gas mixture is then passed through catalysts containing nickel. The gas outlet temperature is 1000 °C, therefore, the heat is removed, and the gas is cooled to approximately 330–380 °C.¹⁴,²² In the third step, the shift reaction (Eq. (2)) is carried out to convert CO and produce hydrogen gas by using copper-based catalyst.

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H = -41 \text{ kJ mol}^{-1}
\]  

(2)

After leaving the shift conversion step, the gas should be removed by the remaining CO₂ (Hocking, 2006). Both physical and chemical absorption processes are used to remove carbon using solvents such as mono ethanolamine, activated methyl diethanolamine or in a physical absorption process such as glycol dimethylethers.¹⁴,²² The gas leaving the CO₂ adsorption process may still contain around 0.3 % or less CO₂. This remaining content should be removed completely because it can cause ammonium carbamate pollution by reducing the activity of the catalysts in the ammonia synthesis step.²⁰ For this purpose, methanation steps are carried out. The remaining carbon dioxide residues and the remaining carbon monoxide are then catalytically treated with hydrogen in these methanation steps of the gas to remove the last traces of the oxygen-containing components, according to Eqs. (3) and (4).²³

\[
\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H = -206 \text{ kJ mol}^{-1}
\]  

(3)

\[
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H = -165 \text{ kJ mol}^{-1}
\]  

(4)

Ammonia is produced according to the Eq. (5).

\[
\text{N}_2(\text{atmospheric}) + 3\text{H}_2(\text{from natural gas source}) \rightarrow 2\text{NH}_3(\text{g}) \\
\quad \Delta H = -91.8 \text{ kJ mol}^{-1}
\]  

(5)

HB reaction is both reversible and exothermic, and it causes a decrease in entropy. According to Le Chatelier’s principle, lower temperatures and higher pressures are required to reach the reaction equilibrium and produce as much ammonia as possible. However, at the lower temperatures, the reaction rate is slower, and to achieve sufficient catalytic activity, higher temperatures are required. However, increase in temperature leads to lower equilibrium yields. Therefore, high pressure conditions are applied, and this creates extra cost because of the need for special types of equipment such as strong vessels and pipes.²⁹,³³ Therefore, the HB reaction is carried out in contact with the magnetite iron catalyst to bond nitrogen and hydrogen, mixed in a 1 : 3 ratio, at 100–250 bar, which is an optimum pressure chosen for convenient costs, and 450 – 600 °C as a compromise temperature obtaining a reasonably high propor-
tion of ammonia such as 15%. In addition, these hard reaction conditions are needed for breaking the triple bonds in diatomic nitrogen molecules which are extremely strong (bond dissociation energy of 941 kJ mol\(^{-1}\)). Finally, the HB reaction is an inefficient, and energy-intensive process. Also, the efficiency of the HB process is not high, and the ammonia must be continuously separated and extracted in order for the reaction to proceed at a suitable rate.\(^{14,35}\)

More than 90% of ammonia production globally is produced from fossil fuels using the HB process.\(^{36}\) The HB process operates in the presence of an iron or ruthenium-rich catalyst at high temperatures and pressures. Approximately 96% of the hydrogen required for this process is obtained from fossil fuels by the steam reforming process. The fossil fuel here is usually natural gas. Each ton of hydrogen produced by a typical steam methane reforming process produces 9–10 tons of CO\(_2\) equivalent emissions. The hydrogen required for ammonia synthesis is commonly produced from fossil-based hydrocarbons. In the 1920s, hydrogen was produced primarily by steam reforming coal and lignite. However, the introduction of low-cost and cleaner (lower chlorine and sulphur content) natural gas has shifted hydrogen production more towards steam methane reforming.\(^{7}\) The most important and fundamental point for improvement in ammonia production is to find an economically viable, energy-efficient, and more sustainable way to produce hydrogen.\(^{26}\) An overview of the various production routes of hydrogen to be used in the production of ammonia is shown in Fig. 6.

Various methods of ammonia production are defined in different terms according to the use of raw materials and sustainable technology in the production process. High-carbon-containing ammonia produced using fossil fuels by the HB process conventionally is called “brown ammonia” (also called grey ammonia). In the brown production process, if there is a carbon capture and storage technology applied to the process, the low-carbon ammonia produced here is called “blue ammonia”. Blue ammonia is reducing climate change effects compared with brown ammonia. Another one is zero-carbon ammonia called “green ammonia” by using sustainable sources, namely, electricity, water, and air. Actually, in green ammonia production, the hydrogen that is used is produced from renewable sources. The last one is turquoise ammonia that is derived from methane. In this process, methane is pyrolysed for transforming to pure carbon and hydrogen that is used as a hydrogen resource. While the ammonia produced from all systems is the same, the amounts of carbon emissions from the processes are different.\(^{14,37}\)

### 3.2 Green ammonia

In the green ammonia system, hydrogen is obtained by electrolysis of water (Fig. 7). The electrolyser is mostly set up as an alkaline system, which is able to produce 485 N m\(^{-3}\) h\(^{-1}\) of hydrogen with an energy consumption of 4.85 kWh N\(^{-1}\) m\(^{-3}\) of hydrogen.\(^{37}\) The energy used in the system is electricity obtained from sustainable sources such as wind or sun. The carbon emission is zero during the hydrogen production of the process, and thus during the ammonia production in the HB process.\(^{36}\)

![Fig. 7 – Schematic of green ammonia production process](image-url)

Technologies for industrial ammonia production commonly consist of processes that require high energy or high water consumption, thus causing large carbon dioxide emissions and resource consumption. The most common ammonia production method is the HB process, which, due to its high operating pressure and temperature, releases roughly 1.2% of global anthropogenic carbon dioxide emissions, and has disadvantages such as high energy use. The most common technology adopted for sustainable and environmentally friendly ammonia production is water electrolysis, which is integrated with renewable technologies such as wind and solar energy to produce hydrogen. In general, a water electrolyser requires a continuous stream of pre-treated water to operate, brought to high levels of purity. According to the calculations, previous studies reported that 9 t of water is needed to produce 1 t of hydrogen. Therefore, water electrolysis is a process that causes high water consumption.\(^{40}\) Based on ammonia production data in 2019, approximately 230 million tons of water is needed to produce the same amount of ammonia via water electrolysis.\(^{25}\)
3.2.1 Carbon capture and storage in ammonia plants

Since the green hydrogen source will not be produced in significant quantities to support the hydrogen market in a short time, it is also important to develop the hydrogen production infrastructure using known systems such as steam methane reforming system as a hydrogen source as long as there is no CO₂ presence. As mentioned previously, steam reforming of natural gas, including mainly methane, causes a large amount of carbon emissions. This large amount of carbon release can be controlled and collected by some CCS systems. Thus, a low-carbon hydrogen production system is created. Another system in which methane is converted to hydrogen apart from reformation is pyrolysis. In pyrolysis, CH₄ is broken down into hydrogen and carbon by thermal energy. Unlike steam methane reforming, auto-thermal reforming or electrolysis of water, pyrolysis is a dry process. Not wasting water is economically important. It is a hydrogen production system that can be integrated with capture carbon systems like others.

The hydrogen produced from this low-carbon emission system is fed to the HB process as a raw material to obtain blue ammonia. Blue ammonia is a carbon-clean system, but it has high costs. This is because more natural gas is needed in hydrogen production, and operating conditions are more expensive. With a simple estimation, integrating the CCS system creates an additional cost of 0.40 euro per hydrogen. However, according to International Energy Agency data, this cost is found to be cheaper when compared to other carbon capture systems. In order for CO₂ to be captured, it must be extracted as a pure stream from the system in which it is produced. A typical CCS system uses an amine solvent for ammonia production to treat the gas from the reformer. On average, 1.27 t of carbon dioxide is captured per 1 t of amine in modern facilities.

Ammonia plants have gas outlets consisting of high concentrations of nearly pure CO₂ gases that are well suited for CCS. The CO₂ is already separated as a separate stream in the generating unit. Therefore, only one system is sufficient for compressed storage. Some of the carbon emissions from ammonia production can already be used as feedstock for urea production or other downstream uses. The costs of CCS are lower when the source of emissions is larger, and the CO₂ flow is more intense. Steam methane reforming or auto-thermal reforming processes are commonly used to convert methane to hydrogen. The large volumes of carbon dioxide, formed as a result of these processes, need to be captured and stored, and the processes should be decarbonised. Both processes can reach a CO₂ capture of 95% and more.

While carbon capture technology can be designed in large capacities and there are no major barriers to integrating it into the required systems, the main problem with the decarbonisation of natural gas via steam methane/auto-thermal reforming is that the large volumes of CO₂ produced are transported to storage rather than captured. Carbon dioxide can be transported as a gas in piping systems or as a liquid by ships to storage areas. Pipeline CO₂ transport, in the context of using CO₂ for advanced oil recovery, is a technology especially used in the USA, although some European countries have very restrictive CO₂ storage and transport laws, and the only realistic option is to ship CO₂ in liquid form. Very large facilities are needed because the gas transported at a location close to atmospheric pressure occupies a very large volume. By compressing the gas, the volume can be reduced, and the compressed gas is transported by pipeline. The volume can be further reduced by liquefaction, solidification or hydration. Liquefaction technologies such as liquefied petroleum gas and liquefied natural gas can be transferred to liquid CO₂ transport. Solidification is disadvantageous in terms of cost and energy compared to other options. The deployment of CCS systems with the decarbonisation of processes will require an extensive pipeline network. As growth continues, securing rights of way for pipelines may become more difficult, especially in highly populated areas that produce large amounts of carbon dioxide. Current experience has shown that regions with low population density are more suitable. In densely populated areas, security issues will become more complex.

3.2.2 Biomass to ammonia production

The production of ammonia-based N-fertiliser from biomass gasification emphasises an important potential for industrial decarbonisation. Biomass as a feedstock is gasified to obtain a hydrogen-rich syngas to be used instead of the natural gas during the steam reforming step of ammonia synthesis. Therefore, a low-carbon, bioderived ammonia is produced as raw material for nitric acid as well as ammonium nitrate fertiliser. Biomass gasification provides important environmental impacts and a carbon saving of 70–80%. On the other hand, biomass-based hydrogen production with a carbon capture storage system can be an alternative for electrolysis in green ammonia synthesis. Biomass conversion needs more energy according to electrolysis systems. In general, biomass-related facilities have logistical constraints due to biomass access and transfer. The main measure for the cost of hydrogen produced from biomass is largely dependent on the properties of the biomass, such as moisture, hardness, particle size, which affect its processing, and where it is collected. Technologies that can synthesise hydrogen from biomass are thermochemical and biochemical processes that can be listed as carbonisation, gasification, anaerobic or aerobic fermentation. Hydrogen yields close to 60% are obtained by gasification. In other processes, gas product yield is low as there will be more output of solid products such as char, compost, and liquid products such as bio-oil than gas products. For this reason, the gasification process comes to the fore in the biomass cycle to produce hydrogen.

3.3 Decarbonisation of nitric acid production

World nitric acid consumption has increased steadily since 2000. The largest market for nitric acid is for ammonium nitrate and calcium ammonium nitrate fertilisers, accounting for almost 77% of total world nitric acid consumption in 2020. The chemical process of nitric acid production was determined experimentally by Kuhlmann in 1839, but it was not until the 1900s that Ostwald made
it commercially available and economical. Nitric acid is produced almost entirely by the high-temperature catalytic oxidation of ammonia, and the absorption of oxidation products in water to form nitric acid and nitric oxide. Ammonia feed and produced nitric acid ratio is 0.27 t N\textsubscript{H}_3/t HNO\textsubscript{3} and the process efficiency from ammonia to nitric acid is around 94 %.

This process usually consists of three steps: ammonia oxidation, nitric oxide oxidation, and absorption. Since the process involves oxidation reactions that require high energy and cause the release of nitrogen oxides, which are important greenhouse gases, nitric acid production draws attention among the fertiliser production processes that will be re-evaluated with a green approach.

Unlike the reactions for ammonia production steps, all of the reactions in nitric acid production are exothermic. This means that a certain amount of heat, such as 6.3 GJ/t HNO\textsubscript{3}, is released as a result of the reactions. In other words, there is an energy that can be fed back to the system during the process or used in different processes. However, when some energy losses and the efficiency of energy conversion processes are considered, the net energy value will definitely be below this value. First reaction of nitric acid production is ammonia oxidation, Eq. (6). This reaction is important because it depends on ammonia, takes place at high temperature, and produces NO gas. Ammonia is oxidised using a mixture of ammonia and air (9-11 %), and it is passed through platinum-rhodium fine layers at 750 to 800 °C; Eq. (6).

\[
4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} \quad \Delta H = -907 \text{ kJ mol}^{-1} \quad (6)
\]

After oxidation of ammonia to nitrous oxide, nitrogen dioxide is formed by oxidation of nitrous oxide, Eq. (7).

\[
2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \quad (7)
\]

The last step is the absorption process with NO\textsubscript{2} and dimer mixture that is given by Eq. (8). The mixture introduces the bottom of the absorption tower, while water flows to the top of the column. The reaction given below is carried out between the trays through the column and nitric acid is obtained. Finally, if high strength nitric acid (up to 90 % percent concentration) is desired, the weak acid can be concentrated using extractive distillation.

\[
3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \quad (8)
\]

The nitric oxide oxidation, Eq. (7), and water absorption, Eq. (8), reactions are both much slower than the ammonia oxidation, and involve a significant volume reduction. Therefore, the absorbers in which most of these reactions occur must be large to provide sufficient residence time, and must be cooled to maintain equilibrium in the desired direction. With these process steps, a weak nitric acid with a concentration ranging from 30 to 70 % is obtained. To produce high strength nitric acid (that contains more than 90 % nitric acid) from weak nitric acid, process can be combined with dehydrating, bleaching, condensing, and absorption steps.

Nitric acid production is the largest source of industrial NO\textsubscript{x} emissions in chemical processes. The carbon dioxide equivalent of nitrogen oxides formed as a result of oxidation reactions is 310 t of CO\textsubscript{2} per t of nitric acid produced. With nitric acid production, 15.6 million tons of CO\textsubscript{2} eq. per year is released, which corresponds to approximately 5 % of the total industrial greenhouse gas emissions.

There are various technologies in the industry that include absorption and catalytic reduction to control emissions of N\textsubscript{2}O and NO\textsubscript{x} (such as NO, NO\textsubscript{2}). Nitric acid plants are the leakage of NO and NO\textsubscript{2} that can occur from the absorber column. These are defined as important greenhouse gases. Nitric acid plants are not the only source of nitrogen oxides (NO\textsubscript{x}), but if these pollutants are not abated by scrubber towers, they can result in relatively larger emissions of pollution from the use of fossil fuels.

Nitrous oxides are a brown irritant gas in equilibrium with dinitrogen tetroxide under normal ambient conditions, and are dangerous to humans at concentrations above 50 ppm.

Emission control of nitrous oxides is carried out by catalytic reduction reactions using methane (natural gas) or hydrogen. To achieve this, the waste gas leaving the absorption tower is first heated to 4008 °C and mixed with a certain proportion of methane. It is then passed through a platinum or palladium-catalysed filler bed. With this process, the concentration of nitrogen oxides can be reduced by approx. 90 %. This is the only way to achieve true "reduction" that requires additional capital and fuel costs. However, energy conversion can be achieved with technologies such as hot gas turbines that can be integrated into the system.

Nitric acid plants can also indirectly produce carbon dioxide and methane emissions by providing the energy used during the process from fossil fuels. This is common for plants with steam-powered systems that require the use of natural gas. At this point, the use of renewable resources is an important step towards the decarbonisation of the process. Energy recovery in nitric acid production is very important, as it is a process that requires high energy. Fuel use can be reduced by recycling the lost heat back into the system. There are two exothermic reactions, oxidation and absorption, that produce more energy than the total production process consumes. Therefore, it is very important that the heat produced here is returned to the system.

The use of selective catalytic reduction units for emission control requires less energy than non-selective catalytic reduction, as they operate at lower temperatures. Approximately 386 GJ kg\textsuperscript{-1} of 100 % nitric acid is produced from the catalytic reactor. The absorption tower produces approximately 86 GJ kg\textsuperscript{-1}. All of this energy can potentially be used for heating. The potential CO\textsubscript{2} equivalent emissions avoided at this level of energy recovery are 0.26 t of CO\textsubscript{2} eq. per ton of 100 % nitric acid.

4 Conclusion

The fertiliser industry (mineral fertilisers), which comprises 50 % of global food production, has an important place in the industry and economy with its production facilities. The fertiliser industry, which can be directly linked to climate policies, needs a set of policy solutions to ensure the transition to a climate-neutral but competitive economy by
2050. By 2050, there should be facilities for the production of ammonia under the right conditions, using low-carbon raw materials, based on decarbonised energy sources, and equipped with clean waste systems.

In the production of nitrogen-based fertilisers, fossil fuels such as natural gas and coal are predominantly used in large quantities; this has a negative impact on the greenhouse gas balance of the food chain. Emission amounts can differ between different types of fertiliser production. As one of the most important inputs used in the fertiliser industry, ammonia is one of the critical substances that affect the carbon emission rate of the food chain. The use of green ammonia instead of traditional ammonia in the fertiliser industry can be an important step towards the decarbonisation of the industry. Instead of producing hydrogen by steam reforming of natural gas, hydrogen production from sustainable sources with renewable energy will provide carbon-zero fertiliser production.17

Compiled here are alternative methods for the decarbonisation of ammonia and nitric acid, which are the two main substances in the production of ammonium nitrate fertiliser that is the main product for fertiliser industry. Ammonium nitrate is a downstream commodity of ammonia and nitric acid. It is produced by neutralising nitric acid with ammonia. Ammonium nitrate is an important form of nitrogen as a vital nutrient for plant life. It is available in many different forms in the fertiliser market, depending on its use. All ammonium nitrate plants produce an aqueous ammonium nitrate solution through the reaction of ammonia and nitric acid in a neutraliser. Prilling and granulation are the most common processes used to produce solid ammonium nitrate. To produce prills, concentrated melt is sprayed into the top of a prill tower. In the tower, ammonium nitrate droplets fall counter-current to a rising air stream that cools and solidifies the falling droplets into spherical prills.52 The hydrogen source used in the previous process of ammonium nitrate production and the fuel used for energy constitute the basic carbon footprint. For the decarbonisation of the fertiliser industry, it should be considered as one with the raw material production systems, because it is an industry that depends on traditional ammonia and nitric acid raw materials, which has a large carbon footprint. Therefore, only improvements that can be made in the production systems of these raw materials can provide low-carbon fertilisers.

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SAŽETAK
Zeleni pristup industriji gnojiva: niskougljična gnojiva
Aysu Kayalioğlu

Dekarbonizacija podrazumijeva smanjenje ili, u idealnom slučaju, potpunu eliminaciju emisija stakleničkih plinova kroz procjenu svih uključenih procesa iz niskougljične perspektive. Ovaj pregledni rad opisuje trenutno stanje u industriji gnojiva, te daje mogućnosti i preporuke za njenu dekarbonizaciju. Dekarbonizacija industrije gnojiva može se postići razvojem tehnologija bilo da se radi o proizvodnji sirovina, korištenju energije ili radnim uvjetima procesa proizvodnje. Niskougljična gnojiva mogu se realizirati kroz poboljšanja tijekom procesa proizvodnje, od dobivanja sirovina do nastanka konačnih proizvoda. Danas se provode istraživanja dekarbonizacije vezana uz nove tehnologije koje se mogu primijeniti kod proizvodnje amonijaka kao energetski najintenzivnijeg procesa u industrijskoj proizvodnji gnojiva. Ovaj rad dotiče izvora vodika u proizvodnji amonijaka te postizanja plinifikacije ili elektrolize biomase s niskim ugljičnim otiskom, smanjenja emisija stakleničkih plinova u proizvodnji dušične kiseline, integriranja tehnologija hvatanja i skladištenja ugljika u procese proizvodnje gnojiva te povećanje učinkovitosti niskougljičnih praksi u poljoprivredi.

Ključne riječi
Industrija gnojiva, zeleni amonijak, Haber-Boschov proces, dekarbonizacija, izdvajanje CO₂

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