# Ammonia, production, applications, and the effect of its phase-out

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Dec. 2022

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# 1- Ammonia

Ammonia with the formula NH<sub>3</sub> is a colorless gas with a distinct pungent smell. Ammonia is a chemical found in trace quantities in nature, being produced from nitrogenous animal and vegetable matter. The kidneys also secrete ammonia to neutralize excess acid. Biologically, it is a common nitrogenous waste, particularly among aquatic organisms, and it contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to 45 percent of the world's food and fertilizers. The boiling point of NH<sub>3</sub> is at around -33 °C under atmospheric pressure, which makes it easier to handle than LNG which has its boiling point at about -161 °C <sup>1</sup>, <sup>2</sup>.

Ammonia is one of the seven basic chemicals used to produce all other chemical products. It is the second most produced chemical by mass, after sulphuric acid. Around four-fifths of all ammonia is used to produce nitrogen fertilizers, such as urea and ammonium nitrate; as such, it supports food production for around half of the global population <sup>3</sup>. Most ammonia goes into nitrogen fertilizers but other uses include diesel exhaust fluid AdBlue and engineering plastics <sup>4</sup>. Due to its critical role in the production of food, ammonia has often been treated by national governments as a strategic asset, according to a recent study published by Fertilizers Europe. As a result, the European fertilizer industry has more than 120 production sites. Currently, Europe has about 19 Mt<sup>1</sup> of annual ammonia production capacity <sup>5</sup>, <sup>6</sup>. Worldwide production of ammonia was 183 million tons (Mt) in 2020, and existing markets are expected to increase demand to 223 Mt by 2030 and reach 333 Mt by 2050 in a 1.5°C scenario <sup>3</sup>. By 2050, global ammonia demand is estimated to reach 688 Mt in a 1.5°C scenario, more than three times the demand expected in 2025 <sup>3</sup>.

Subsidized green ammonia projects could match the blue ammonia cost curve from 2035 onwards, but will require significant cost progress. However, further regulatory support and subsidies for green ammonia are required. Blue ammonia will be the key immediate focus for the unit before economics improve for green ammonia <sup>5</sup>.

<sup>&</sup>lt;sup>1</sup> Mt = million tons

The Haber–Bosch process to produce ammonia from the nitrogen in the air was developed by Fritz Haber and Carl Bosch in 1909 and patented in 1910<sup>-1</sup>. It was first used on an industrial scale in Germany during World War I, following the allied blockade that cut off the supply of nitrates from Chile. The ammonia was used to produce explosives to sustain war efforts <sup>7</sup>. Before the availability of natural gas, hydrogen as a precursor to ammonia production was produced via the electrolysis of water or using the chlor-alkali process <sup>7</sup>. With the advent of the steel industry in the 20th century, ammonia became a byproduct of the production of coking coal <sup>8</sup>. Ammonia, either directly or indirectly, is also a building block for the synthesis of many pharmaceutical products and is used in many commercial cleaning products <sup>9</sup>. The global industrial production of ammonia in 2018 was 175 million tons, with no significant change relative to the 2013 global industrial production of 175 million tons. In 2021 this was 235 million tons <sup>10</sup>. Industrial ammonia is sold either as ammonia liquor (usually 28% ammonia in water) or as pressurized or refrigerated anhydrous liquid ammonia transported in tank cars or cylinders <sup>11</sup>, <sup>12</sup>.

#### 1-1- Ammonia demand

Ammonia makes an indispensable contribution to global agricultural systems through its use as a precursor for fertilizers <sup>13</sup>. About 70% of ammonia is used for fertilizers, while the remainder is used for various industrial applications, such as plastics, explosives, and synthetic fibers. While the use of ammonia as a fuel shows promise in the context of clean energy transitions, this application currently remains nascent <sup>13</sup>.

In the future, the world will need more ammonia but with fewer emissions. An increasingly numerous and affluent global population will lead to growth in ammonia demand, during a period in which governments around the world have declared that emissions from the energy system must head toward net zero <sup>13</sup>. Annual ammonia production is expected to grow from its current 183 Mt to more than 200 Mt by 2025. With its adoption in energy applications, the total annual demand for ammonia is expected to reach 688 Mt by 2050 in a  $1.5^{\circ}$ C scenario <sup>3</sup>. However, urea, which accounts for around 55% of current ammonia demand, requires both ammonia and CO<sub>2</sub>, which is currently supplied as a by-product of fossil-based hydrogen production in an integrated ammonia-urea plant. As such, fossil-based ammonia for urea production cannot simply be substituted with

renewable ammonia using electrolyzers <sup>3</sup>. Ammonia-based fertilizers are suitable for slow growing, long duration crops <sup>14</sup>. Using urea yields faster growth rates and more production in less time. In the past 10 years, urea fertilizer has surpassed and nearly entirely replaced ammonium nitrate in fertilizer use. Ammonia is usually upgraded on site to urea as urea production requires  $CO_2$  which is a by-product of the ammonia production <sup>15</sup>. Circular carbon sources will need to be utilized, such as biomass or direct air capture, and a shift away from urea toward nitrates may be expected <sup>3</sup>. Notably, a biomass-to-urea process would produce more  $CO_2$  than is required for urea production, creating an opportunity for scalable bioenergy with carbon capture and storage (BECCS) and carbon-negative ammonia and fertilizers <sup>3</sup>.

The introduction of renewable ammonia would facilitate the transition to a sustainable circular economy in the chemical, power, transport, and other energy-related sectors. Energy markets will be supplied with renewable ammonia from areas with low-cost solar and wind <sup>3</sup>.



Figure 1- Green ammonia, Urea, and nitric acid production process <sup>5</sup>

#### **1-2-** Ammonia in agriculture: The engine of plant growth

About 50 percent of the world's food production depends on mineral fertilizer application. Due to the increasing world population and changing diets to more meat, there is a constant growth in fertilizer consumption <sup>16</sup>.

Today, roughly 80% of the annually produced ammonia is used for fertilizer production. Fertilization improves plant nutrition, promotes plant growth, improves crop quality, and ultimately maintains and even enhances soil fertility <sup>16</sup>.

Agricultural crops may require about 20-350 kilograms of nutrients per hectare throughout their development <sup>16</sup>.

The controlled release of nutrients reduces the emission of nitrates into the groundwater and optimizes the use of fertilizers and their application. The fertilizer with the highest nitrogen content is urea with 46%. Treating urea fertilizers with urease inhibitors or covering fertilizers with coating material allows the long-term release of nutrients to the ground over the entire period of crop growth <sup>16</sup>.

#### **1-3-** Ammonia for energy

Ammonia is an ideal carbon-free energy storage material due to its high energy density (4.32 kWh/L), high weight fraction of hydrogen (17.65%), and ease of liquefaction under mild conditions  $^{17}$ .

Energy storage in the ammonia chemical bonds would enable a much greater uptake of intermittent renewable power sources such as solar, tidal, and wind, helping to balance the seasonal energy demands in a carbon-free society and distributed ammonia production will find diverse applications <sup>18</sup>.

The key potential of  $NH_3$  as an energy carrier lies in its high volumetric energy density (15.6 MJ/L) which is 9 times more than that of Li-ion batteries (1.73 MJ/L) and almost 3 times that of compressed H<sub>2</sub> (5.5 MJ/L at 70 MPa). This opens an opportunity to use  $NH_3$  as a low-carbon energy storage medium that can be traded globally <sup>18</sup>.

At ambient temperature,  $NH_3$  can be readily liquefied if a pressure of about 10 bar is maintained or by cooling to -33 °C at atmospheric pressure. Consequently, the cost associated with the storage and transportation of liquid  $NH_3$  is expected to be lower than that for compressed hydrogen (H<sub>2</sub>) at 700 bar <sup>18</sup>.

#### 1-4- Ammonia as precursor for other products

Starting from natural gas ammonia is produced, and converted to nitric acid and urea and further processed to give final products like fertilizers (NPK and CAN), melamine or urea products (e.g. AdBlue®). Annually production capacities are approximately <sup>19</sup>:

- 545,000 t ammonia
- 420,000 t urea
- 600,000 t nitric acid
- 1,100,000 t fertilizers (NPK and CAN)
- 54,000 t melamine

# 2- Energy requirements and costs of ammonia production

The energy requirements of the highly optimized Haber–Bosch process at a scale of 1000 t/d is about 7.9 kWh/kg<sub>NH3</sub>. The source of energy for the conventional Haber–Bosch process is fossil fuels. The energy shares of pressurization, heating, and pumping at this process is 2.0 kWh/kg, and this value increases by decreasing the scale of production  $^{20}$ . The stored chemical energy in ammonia molecules is equal to 18.6 GJ/t<sub>NH3</sub> based on the lower heating value of ammonia.

The theoretical minimum energy input for methane fed process is  $22.2 \text{ GJ/t}_{NH3}$ . The share of heat for producing syngas is  $4.5 \text{ GJ/t}_{NH3}$  and process heat requirements for final NH<sub>3</sub> conversion is 17.7 GJ/t<sub>NH3</sub> <sup>21</sup>. The energy efficiency of the ammonia production process via natural gas feed is 65% <sup>22</sup>, not taking into account all the upstream losses.

The overall reaction of ammonia synthesis from  $N_2$  and  $H_2$  is exothermic, the dissociation of dinitrogen is considered the rate-limiting step due to the high dissociate energy (9.8 eV). Therefore,

high temperature and high pressure are used in the conventional thermal catalysis approach to improve the kinetics and shift the equilibrium in favor of ammonia respectively <sup>23</sup>.

The estimated 2018 global production of renewable wind and solar energy of 2480 TWh is sufficient to produce the current global demand of ammonia estimated as 140 Mt y1 for 2014 requiring 1556 TWh of electricity <sup>21</sup>.

Furthermore, the energy requirement of  $NH_3$  production via direct electrochemical synthesis is 19.9 GJ/t<sub>NH3</sub><sup>21</sup>. Direct ammonia production via electrochemical routes by utilizing H<sub>2</sub>O and N<sub>2</sub> has several benefits such as low temperature and pressure conditions. However, the technology is not commercially ready yet and requires further development. At present, ammonia production via the electrochemical synthesis process has a low selectivity in comparison to the H-B process. Hence, the process-related energy consumption is higher in electrochemical synthetizing routes <sup>21</sup>. Moreover, the energy cost of ammonia production via electrochemical routes is twice that of the conventional H-B process with methane feed. Since the cost of renewable electricity generation is rapidly decreasing and scientists are making significant advances in electro-catalysts, ammonia synthesis by green H<sub>2</sub> will become economically viable <sup>10</sup>.

The price of feedstocks is the determining factor of ammonia cost. The cost of natural gas covers 70-85% of ammonia costs and is equal to  $80.36 \in_{2019^2}/t_{Ammonia}$ . Once the green hydrogen is supplied from the electrolysis of water, the costs are higher and reach 199.11  $\notin_{2019}/t_{Ammonia}$ <sup>24</sup>, <sup>20</sup>. However, electrolysis-aided ammonia production enables small-scale and agile processes due to modular electrolysis units and the quick-started/stopped performance. Small-scale production and agile production and agile production are important for local ammonia production by integrating green electricity <sup>21</sup>.

Capital investment for conventional Haber–Bosch facilities are essentially equivalent at 276.11<sup>3</sup>  $M \in_{2017}$  for 2000-tpd capacity. Grundt et al. estimated capital expenses of 176.99  $M \in_{2017}$  for a 1000 tpd ammonia facility <sup>25</sup>.

<sup>&</sup>lt;sup>2</sup> Converted from Dollars to Euros,  $1 \in 2019 = 1.12 \$ 2019^{93}$ 

 $<sup>^3</sup>$  Con-verted from Dollars to Euros,1  ${\rm \in}_{\rm 2017}{\rm =}\,1.13$  \$  $_{\rm 2017}$ 

# 3- The effect of Ammonia cost on other products in chain

Ammonia plays a key role in the manufacturing of fertilizer, engineering plastics, and diesel exhaust fluid. Its production also yields high-purity carbon dioxide ( $CO_2$ ) as a byproduct, which is needed by the meat and fizzy drinks industries <sup>4</sup>.

Curtailed ammonia output means less fertilizer for agriculture. So, food production may be impacted <sup>26</sup>. Russia's squeeze on flows of gas -- a key feedstock for fertilizers and source of power for heavy industries in Europe -- is hitting everything from aluminum smelters to sugar refineries <sup>27</sup>.

Soaring ammonia prices are giving European producers the incentive to restart idled capacity as supply shortages keep prices elevated. Sanctions on several Russian oligarchs associated with fertilizer production have cut most of the supply from Baltic Sea producers including EuroChem and Uralchem <sup>28</sup>.

Nitrogen fertilizer prices are high and likely will go higher due to repercussions from The war in Ukraine <sup>29</sup>. Fertilizer prices have been rising since 2020, reaching extremely high levels in the fall of 2021 (see Figure 2). According to the Agricultural Marketing Service, farmer-paid prices for anhydrous ammonia were  $428 \in_{2020} {}^{30}$  per ton in 2020, increasing to  $631 \in_{2021} {}^{4}$  per ton by July 2021. Concerns about nitrogen fertilizers will continue as the Russia-Ukraine war shocks the natural gas and fertilizer markets. Europe undertook policies to replace fossil fuels that increased reliance on natural gas and Russia as a natural gas supplier. Most recently, the Ukraine-Russia war has pressured natural gas and fertilizer supplies <sup>29</sup>.

The price continued to grow, reaching over  $845.8 \notin_{2021} {}^5$  per ton in October 2021. Illinois ammonia prices continued to increase to  $1,267 \notin_{2021} {}^6$  on February 10 and  $1,271 \notin_{2021} {}^7$  on 24 February 2021,

<sup>&</sup>lt;sup>4</sup> 746 \$<sub>2021</sub> = 631 €<sub>2021</sub>; Average exchange rate in 2021: 1 \$ =  $0.8458 \in {}^{94}$ .

<sup>&</sup>lt;sup>5</sup> 1,000  $\$_{2021} = 845.8 €$ 

<sup>&</sup>lt;sup>6</sup> 1,498 \$2021

<sup>7 1,503 \$2021</sup> 

the day Russia invaded Ukraine. On March 23, the ammonia price was  $1,282 \in_{2021} {}^{8}$ per ton, increasing little from the reference point before the invasion  ${}^{29}$ .



Figure 2. Anhydrous ammonia prices per ton in Illinois from 2008 to 2021 <sup>29</sup>

Norway's Yara (YAR.OL), one of the world's largest fertilizer makers, is slashing ammonia production due to soaring gas prices <sup>26</sup>. Yara is a significant producer of nitrogen fertilizers <sup>29</sup>. Europe's fertilizer crunch tightened after Yara International ASA cut output in the face of soaring gas prices, putting more pressure on food supplies as a cost-of-living crisis intensifies <sup>31</sup>. Consumers, already feeling the pain of higher energy bills, are likely to be hit again as shrinking fertilizer supplies boost the cost of farm inputs and lower productivity by curbing the use of key crop nutrients. That could reignite food inflation <sup>27</sup>, <sup>31</sup>.

As a result of much higher natural gas prices, nitrogen fertilizer production was curtailed in Europe <sup>31</sup>. Through October 2021, ammonia price increases were explained reasonably well by increases in corn and natural gas prices, with corn prices having more impact than natural gas prices. Corn represents the crop with the single highest nitrogen use in North America (soybeans generally do not need additional nitrogen fertilizers, while wheat and other grasses would use nitrogen). As a result, increases in corn prices may signal increased demand for nitrogen fertilizers that pushes fertilizer prices higher <sup>29</sup>.

From September to November 2021, Yara reduced European production of nitrogen fertilizer by 30%, sourcing that nitrogen from its global network outside of Europe. Reductions by Yara and other European producers reduced world supply and increased prices around the world including in the U.S<sup>29</sup>. The cutbacks by Yara come a day after CF Industries announced it will stop ammonia production at its remaining UK plant. Hungary's sole producer, Nitrogenmuvek Zrt., stopped output in early August. Grupa Azoty, Poland's largest chemical company, also trimmed ammonia output, and Anwil, a unit of oil company PKN Orlen SA, halted production <sup>31</sup>. Achema AB, Lithuania's top fertilizer company has also halted ammonia output in September 2022 <sup>32</sup>.

Half of Europe's ammonia capacity is out by the second half of 2022 <sup>27</sup>. Yara is going to cut its ammonia utilization to about 35%. Imported ammonia is currently much cheaper than than producing it in the EU <sup>27</sup>. Still, Yara's second-quarter profit rose 23% to  $652 \in_{2022} 9$  million thanks to higher fertilizer prices. Farmers without access to credit, subsidies, or cash reserves to pay the higher nutrient prices will be the first to suffer, according to Alexis Maxwell, a Bloomberg Intelligence analyst <sup>31</sup>. Ammonia plays a key role in the manufacturing of fertilizer. Without it, crop yields will deteriorate because nutrients removed from soil during harvesting are not replenished <sup>26</sup>.

Russia also is also a significant producer of fertilizer ingredients, including nitrogen, accounting for 23% of ammonia exports. Russia has announced plans to restrict fertilizer exports, and sanctions against Russia could further heighten export barriers. Eliminating 23% of worldwide nitrogen exports will severely affect the nitrogen market. As a result, countries that rely on Russia will need to find alternative sources of nitrogen, including Brazil <sup>29</sup>.

Yara has repeatedly warned the world faces an extreme food supply shock due to a combination of high gas prices, the war in major grains producer Ukraine, and sanctions on fertilizer producer Russia. Fertilizers require large amounts of energy to be produced. Manufacturers such as Yara use gas for the process. Gas prices have surged almost 40% in August and nearly 300% this year <sup>26</sup>.

<sup>&</sup>lt;sup>9</sup>  $664 = 651.81 \in_{2022}$ ; 1 €<sub>2022, Aug.</sub> = 1.0187  $$_{2022, Aug.}$ 

Fertilizer makers in Europe have been hit hardest because of the region's reliance on Russian gas. The industry must also contend with US and European Union sanctions on potash sales from Belarus and China's move to rein in its shipments. Trade in Russian nutrients has suffered from many shippers, banks and insurers which fall under sanctions, leading to difficulties in servicing exports from Russia, as a large supplier of every major type of crop nutrient <sup>31</sup>. The impact of a continued crunch will stress wheat and corn farmers and potentially constrain acreage and yield potential <sup>31</sup>.

# 4- CO<sub>2</sub> emission from ammonia production and its reduction pathways

The ammonia production leads to annual emissions of 0.5 gigatons (Gt) of carbon dioxide (CO<sub>2</sub>), representing around 1% of global CO<sub>2</sub> emissions and 15-20% of the chemical sector's CO<sub>2</sub> emissions. Addressing emissions from ammonia production is therefore a key component of the decarbonization of the chemical and agricultural sectors <sup>3</sup>.

By the year 2022, the direct  $CO_2$  emission from ammonia production was 450 Mt  $CO_2$  that is equal to the emission from total energy system in South Africa. The indirect  $CO_2$  emission (170 Mt/y) comes from applying urea-based fertilizers to the soil. The consumed electricity and chemical reactions during the implementation of fertilizer are the source of this indirect carbon emission. "Ammonia is one of the most emissions-intensive commodities produced by heavy industry, despite coal accounting for a much smaller share of its energy inputs than in other sectors. At around 2.4 t  $CO_2$  per ton of production, it is nearly twice as emissions-intensive as crude steel production and four times that of cement, on a direct  $CO_2$  emissions basis" <sup>13</sup>.

The global production share of ammonia is 30% in China and 8-10% for each of the EU, Russia, India, and the Middle East. 10% of ammonia production is also being traded globally. The share of global urea trade is around 30%. Production of ammonia severely depends on the availability of feedstock and process energy. In China, low-cost coal provides the required energy for 85% of ammonia production <sup>13</sup>. Ammonia production will increase around 40% by the year 2050 due to population and economic growth, while the emissions will decrease by 10% <sup>13</sup>.

The lifetime of ammonia production plant and facilities are around 50 years. The current installed capacity age is 25 years in average. Distribution of the ammonia plant's age are 40 years in the EU and 12 years in China. Currently, China owns 30% of global ammonia production. The remaining lifetime of the global ammonia production plants imposes 15.5 Gt  $CO_2$  emission <sup>13</sup>.



Figure 3. Projected emissions from existing ammonia plants under different lifetime assumptions, 2020-2070<sup>13</sup>

"In addition to  $CO_2$  emissions, the production of nitrogen fertilizers also results in nitrous oxide emissions. Nitrous oxide and  $CO_2$  are also generated in the use phase during and after fertilizer application. While exact quantities are hard to measure accurately, it is estimated that use-phase emissions are upwards of 70% of the total life-cycle greenhouse gas emissions of nitrogen fertilizers" <sup>13</sup>.

Across the EU no universal path exists for decarbonizing of ammonia production. Moreover, novel arising technologies should consider the availability of local resource <sup>6</sup>. By 2022, the annual ammonia production capacity was about 19 million tons. Assuming average process emissions of 1.9 tons of  $CO_2$  per ton of ammonia, this results in about 36 million tons of  $CO_2$  produced from

the ammonia production process, if all capacity is utilized. The best case scenario shows about 3 million tons of  $CO_2$  reduction by capturing process  $CO_2$  emissions across the sector. Furthermore, the authors found that ammonia with  $CO_2$  capture and storage will be cost-competitive with conventional ammonia, (i.e. without carbon emission mitigation) by 2030 due to rising carbon prices. Other technologies, such as electrolysis-based hydrogen from renewable electricity or a low carbon grid, and methane pyrolysis-based hydrogen account for the remainder of carbon mitigation <sup>6</sup>.

Furthermore, various types of hydrogen-derived carriers from a range of supply regions will be able to provide cost-competitive renewable energy and raw materials by 2030-2035. The most promising green energy carriers are ammonia, methanol, and synthetic methane <sup>33</sup>. Ammonia is more cost-effective and easier to store and transport in large quantities than hydrogen due to its higher energy density. The chemical compound can also be used directly as fuel by ships <sup>34</sup>. However, there are cost uncertainty during dehydrogenation of imported ammonia once considering it as a hydrogen carrier. Ammonia will be the fuel of the future in shipping. Shipping could provide a positive surprise by carrying out its transition to green fuels more quickly than expected – and green ammonia is an obvious candidate for being the most important green fuel for ships in the future <sup>35</sup>. However, ammonia leakage during transport or bunkering and NO<sub>x</sub> emissions when burning can have considerable environmental impacts <sup>36</sup>, <sup>37</sup>.

Unlike several other sectors, hard-to-abate sectors such as shipping, agriculture, and industrial applications cannot be directly electrified. Large-scale production of green alternatives to the agriculture and shipping sectors, along with strong partnerships, are vital success factors in the transition of these fossil fuel-reliant industries <sup>38</sup>. Ammonia is also proposed as a carbon-free fuel and hydrogen carrier. However, ammonia is currently not used for these applications beyond research, development, and demonstration projects <sup>3</sup>.

European industry has the ambition to advance even faster in the green transition. But to enable a higher pace of investments, the fertilizer sector calls for a regulatory framework that supports investments in clean technologies, improves access to abundant and affordable renewable energy, and provides financial support. All these elements are a prerequisite for the industry to deliver on the objectives of the green transformation in Europe <sup>6</sup>.

Switching the hydrogen production method from methane to hydropower-electrolysis reduces the  $CO_2$  emissions from 1.5 to 0.38 t<sub>CO2-eq</sub>/t<sub>NH3</sub> (75% decrease)<sup>21</sup>. 76% of the methane consumed in the process is associated with the production of hydrogen via the SMR reaction and the remaining 24% of the methane is consumed as fuel to provide reaction heat for the endothermic reforming reaction and to raise the necessary process steam <sup>21</sup>.

Assuming that the electrically-driven Haber-Bosch process requires a 38.2 GJ/t<sub>NH3</sub> (35.5 GJ/t<sub>NH3</sub> for hydrogen production assuming 60% efficient electrolyzer and approximately 2.7 GJ/t<sub>NH3</sub> for the N<sub>2</sub> separation and Haber–Bosch loop compressors), a wind-powered ammonia process will have a carbon intensity of 0.12–0.53 t<sub>CO2-eq</sub>/t<sub>NH3</sub> <sup>21</sup>.

For developing a carbon-free ammonia production three main steps are required. First, the decoupling of plant from methane reforming e.g. by implementing of high efficient water electrolysis; second, replacement of condensing steam turbine compressors by electric compressors; third, alternating ammonia separation techniques to the decreased operating pressure ones <sup>21</sup>.

# 5- Renewable ammonia production lines

Ammonia is expected to be a zero-carbon energy carrier in the future, like being a fuel for automobiles, ships, aircraft, and other engines, and replacing gas/oil as a fuel for industrial boilers or civil stoves <sup>39</sup>.

Although renewable ammonia's use as a carbon-free fuel and hydrogen carrier has been proposed, this has not yet been implemented at a significant scale. Renewable ammonia has been produced at an industrial scale using hydropower since 1920; however, most ammonia today is produced from natural gas (72%) and coal (22%)<sup>3</sup>.

The global industrial production of ammonia in 2018 was 175 million tons of which China produced 31.9% of the worldwide capacity, followed by Russia with 8.7%, India with 7.5%, and the United States with 7.1%. There are numerous large-scale ammonia production plants worldwide. In conclusion, ammonia is one of the most highly produced inorganic chemicals <sup>39</sup>.

The importance of ammonia is self-evident. It is not only an important chemical raw material for modern industry and agricultural fertilizers, but also one of the main carriers of hydrogen energy. However, 98% of the feedstock for ammonia production comes from fossil fuels <sup>39</sup>.

Nearly all nitrogen-based fertilizers rely on ammonia and nitric acid as feedstocks, and thus the demand for these chemicals is heavily dependent on the global population and food demand <sup>39</sup>. If the current approaches for manufacturing ammonia and nitric acid remain constant, carbon emissions from the production of fixed fertilizer feedstocks could exceed 1300  $Mt_{CO2eq}/yr$ , prompting a strong need for green alternatives <sup>39</sup>.

"Green ammonia" is ammonia produced by using green hydrogen (hydrogen produced by electrolysis), whereas "blue ammonia" is ammonia produced using blue hydrogen (hydrogen produced by steam methane reforming where the carbon dioxide has been captured and stored).

Regions with abundantly available renewable energy are not necessarily the same as those with a high population density and high energy consumption. Therefore, renewable energy can be produced in optimal climate conditions with a remote renewable hub and transported to these population-dense regions. To establish this energy transport, ammonia provides a flexible, easy-to-handle energy carrier, which already showed a viable option for transporting energy from Australia to Japan<sup>40</sup>.

Green ammonia production is where the process of producing ammonia is 100% renewable and carbon-free. One way of producing green ammonia is by using hydrogen from water electrolysis and nitrogen separated from the air<sup>41</sup>. Therefore, power-to-X solutions are key if these sectors are to reach carbon neutrality in 2050. Through power-to-X processes it is viable to use green ammonia as feedstock for fertilizer production and as green fuel in the maritime industry <sup>41</sup>.

The local production provides for higher and robust Power-to-ammonia energy efficiencies (53.6% in mean and 0.1% in standard deviation), while the remote production is less efficient and more sensitive to uncertainties (47.9% in mean and 1.53% in standard deviation). Both objectives are highly influenced by the capacity of the photovoltaic arrays and the electrolyzers, where in the case of Morocco, the fuel cell capacity plays a major role in the efficiency of the system <sup>40</sup>.

Projects across the world (between Japan and Australia, in Germany and Korea) examine the advantage of renewable ammonia and its possibility to transport this energy vector via ship or pipelines to other countries or continents in the future. Another advantage for considering import over local NH<sub>3</sub> production is the additional electric load on the electricity grid when renewables are not sufficient to cover the PtA<sup>10</sup> system base load <sup>42</sup>, <sup>40</sup>, <sup>43</sup>.

In the case of Belgium, renewable energy sources are scarce compared to other regions in Europe with higher wind speed (north of Scotland) and solar irradiance (south Europe), therefore Belgium cannot rely on only domestic renewable energy supply in the future <sup>42</sup>, <sup>44</sup>, <sup>45</sup>.

The hydrogen import coalition showed the economic feasibility of importing renewable energy to Belgium over the sea through the use of energy carriers. These energy carriers included hydrogen, ammonia, methane, methanol, and liquid organic hydrogen carriers, where producing ammonia and methanol in Chile, Oman and Morocco were competitive against different hydrogen production sites in Belgium <sup>46</sup>, <sup>47</sup>.

One promising solution to the decarbonization of ammonia production is to generate hydrogen from water electrolysis using electricity originating from solar or wind sources <sup>10</sup>. Electrolysis is the most energy-intensive part of the process, which if run continuously, has a specific energy consumption of 10.43 kWh/kg-NH<sub>3</sub> and an electric process efficiency of 37.4% <sup>48</sup>.

Green Ammonia could help Europe directly meet almost 30% of the 341.93 TWh<sup>11</sup> savings the EU hopes to achieve in the industry by 2030 in its newly presented "REPowerEU" plan <sup>12</sup>. The REPowerEU plan aims to domestically produce several million tons of renewable hydrogen based on ammonia. It also wants to import from outside the EU no less than 4 million tons of renewable hydrogen-based ammonia in the coming years. But of course, this high import target would mean Europe risks jumping from one dependency into another. And that might not chime with its broader

<sup>&</sup>lt;sup>10</sup> Power to Ammonia

<sup>&</sup>lt;sup>11</sup> 35 bcm of natural gas (Billion cubic meters of natural gas (bcm) is a unit of energy, specifically natural gas production and distribution)

<sup>&</sup>lt;sup>12</sup> REPowerEU: A plan to rapidly reduce dependence on Russian fossil fuels and fast forward the green transition, https://ec.europa.eu/commission/presscorner/detail/en/ip\_22\_3131

agenda of strategic autonomy, where the EU wants to become more self-sufficient when it comes to critical raw materials and other means  $^{49}$ .

While the EU should certainly look for secure ways to source green ammonia from foreign sources, it should also look deeper within. And it has a big capacity to do so. For example, First Ammonia applied for funding under the Innovation Fund of the EU Emissions Trading System (EU ETS). So far, a 300-megawatt plant in Brunsbüttel, Germany, is planned to produce green ammonia with a first-of-a-kind, industrial-scale "solid oxide" electrolyzer (SOEC). This innovative system, which produces green ammonia in-line with the production of green hydrogen, is significantly more efficient than current production technology and is designed as a modular unit that can easily scale. Hence, efficient use of renewable power is significant as Europe only has a limited capacity to generate renewables and a big number of end uses <sup>49</sup>.

# 6- Ammonia production with 100% renewable energy

As a practical case, Ola Osman et. al. has optimized the design of an industrial-scale ammonia plant (1840 Mt/day) that utilizes 100% renewable energy. They concluded that electrolysis was the most energy-intensive part of the process, which if run continuously, has a specific energy consumption of 10.43 kWh/kg-NH<sub>3</sub> and an electric process efficiency of 37.4% <sup>48</sup>.

To adapt the ammonia production process to the variable renewable energy supply, energy storage is needed, namely batteries, thermal storage, nitrogen, and hydrogen to support the ammonia synthesis that would need to be operated continuously. This storage is also used to address process limitations (limited modulation capability for the air separation unit) or as buffers for systems that can operate variably (desalination and electrolysis)<sup>48</sup>.

The HØST plant (in Esbjerg, Denmark) is an example of how electricity from renewables is used to produce green ammonia for fertilizers and fuel through power-to-X. Once finished, the plant will produce approx. 600,000 tons of green ammonia. The plant will operate flexibly adapting to the available power production from renewables, which is converted into hydrogen and stored as ammonia. The flexible operation will ensure efficient use of the electricity being fed into the Danish energy system from the planned 10GW offshore wind build-out in the North Sea.

Furthermore, the process heat from the production of hydrogen and ammonia will be used for district heating of 15,000 households by the local utility company <sup>38</sup>.

Moreover, using semiconductors with sunlight to drive photocatalytic reactions in a Solar Ammonia Refinery is another approach being pursued to realize environmentally friendly ammonia synthesis <sup>10</sup>. As a case in point, nanostructured metals with localized surface plasmon resonance effect, including ammonia synthesis metals Fe and Ru<sup>13</sup>, can concentrate the diffused solar flux to generate heat in a small volume workable for N<sub>2</sub> dissociation. The novel catalyst could kinetically reduce the energy barrier of ammonia synthesis <sup>50</sup>.

Furthermore, plasma, generated by the ionization of gases, provides a unique way to synthesize ammonia or nitric oxide from  $N_2$ . In this process,  $N_2$  and  $H_2$  molecules dissociate into free radicals in the plasma.

# 7- Biosynthesis of ammonia

In certain organisms, ammonia is produced from atmospheric nitrogen by enzymes called nitrogenizes. The overall process is called nitrogen fixation. Intense effort has been directed toward understanding the mechanism of biological nitrogen fixation; the scientific interest in this problem is motivated by the unusual structure of the active site of the enzyme, which consists of an  $Fe_7MoS_9$  ensemble.

Ammonia is also a metabolic product of amino acid deamination catalyzed by enzymes such as glutamate dehydrogenase. Ammonia excretion is common in aquatic animals. In humans, it is quickly converted to urea, which is much less toxic, particularly less basic. This urea is a major component of the dry weight of urine. Most reptiles, birds, insects, and snails excrete uric acid solely as nitrogenous waste.

Biomass-to-ammonia - The ammonia production fuel decarbonization is possible through CCS, beside the usage of renewable energies and resources such as biomass <sup>22</sup>. Ligno-cellulosic biomass can be used as a source of hydrogen for ammonia production <sup>51</sup>. A biomass-to-ammonia production

<sup>&</sup>lt;sup>13</sup> Fe: Iron, a metal; and, Ru: Ruthenium, a rare transition metal belonging to the platinum group

pathway with inputs of  $N_2$  from air and  $H_2$  from gasification of biomass is shown in Figure 4. The proportion of land area required for highly productive biomass species is only a small fraction (1–5%) of the grower's acreage. Thus, a small investment in land for a bioenergy crop could produce the ammonia to increase crop yield greatly on the remaining 95% of acreage <sup>51</sup>.

The other option is the development of alternative methods of production such as plasma reactions and electrochemical processes  $^{52}$ . Moreover, getting inspired from nature, chemists are developing transition-metal–dinitrogen complexes to enable the reduction of  $N_2$  to ammonia under mild reaction conditions  $^{10}$ .



Figure 4. Simplified flow diagram of the biomass to ammonia production process <sup>51</sup>.

# 8- Ammonia production in Europe

Figure 5 shows the location and production capacity of ammonia plants in the European Union and Norway.



Figure 5. Location and production capacity of ammonia plants in the European Union and Norway 53.

BASF Antwerp Complex has an active annual capacity of 64.83 t/y Ammonia <sup>54</sup>.



Figure 6. Belgium Ammonia production by year (2003 – 2012)  $^{55}$ 

Year	Production	duction Unit of Measure				
2003	873.5	Thousand metric tons of contained nitrogen	NA			
2004	856.5	Thousand metric tons of contained nitrogen	-1.95%			
2005	860	Thousand metric tons of contained nitrogen	0.41%			
2006	850	Thousand metric tons of contained nitrogen	-1.16%			
2007	850	Thousand metric tons of contained nitrogen	0.00%			
2008	830	Thousand metric tons of contained nitrogen	-2.35%			
2009	830	Thousand metric tons of contained nitrogen	0.00%			
2010	830	Thousand metric tons of contained nitrogen	0.00%			
2011	830	Thousand metric tons of contained nitrogen	0.00%			
2012	830	Thousand metric tons of contained nitrogen	0.00%			

Table 1. Tabulated data of Belgium Ammonia production by year <sup>55</sup>

# 9- The effect of Natural gas pricing on Ammonia production curtailment

Ammonia production currently (by 2022) relies heavily on fossil fuels. Global ammonia production today accounts for around 2% (8.6 EJ) of total final energy consumption. Around 40% of this energy input is consumed as feedstock – the raw material inputs that supply a proportion of the hydrogen in the final ammonia product – with the rest consumed as process energy, mainly for generating heat. Just over 70% of ammonia production is via natural gas-based steam reforming, while most of the remainder is via coal gasification, leading to 1,660.81 TWh<sup>14</sup> of natural gas demand (20% of industrial natural gas demand) and 75 Mtce<sup>15</sup> of coal demand (5% of industrial coal demand). Oil and electricity combined account for just 4% of the sector's energy inputs <sup>13</sup>.

Under normal circumstances, ammonia production accounts for about 4.5 percent of the natural gas used by German industries <sup>4</sup>. The EU's ammonia sector uses about 97.69 TWh<sup>16</sup> of natural gas annually, mostly as a feedstock to make fertilizers. And of course, Europe can't just stop using fertilizers because they are essential to help guarantee food security for the EU and the world <sup>49</sup>.

<sup>&</sup>lt;sup>14</sup> Equal to 170 bcm

<sup>&</sup>lt;sup>15</sup> Mtce: Megatonne of Coal Equivalent

<sup>&</sup>lt;sup>16</sup> 10 bcm

Most ammonia goes into nitrogen fertilizers but other uses include diesel exhaust fluid AdBlue and engineering plastics <sup>56</sup>.

A global food crisis could spell a bigger catastrophe than Vladimir Putin's war. For the past three generations, mineral fertilizer has played a decisive role in alleviating global famine. According to the UN, since 1960, global food production has skyrocketed by 211 percent. The clear reason for this is the industrialization of ammonia production, the game-changer in terms of the world feeding itself. Today, roughly half of the world's population (48 percent) depends on fertilizer use. Limiting the fertilizer supply could lead to the threat of crop failures and famine in the most fragile countries in the tottering Middle East and North Africa, with catastrophic consequences for Europe itself. Refugees could then well flood across the Mediterranean, leading to further political radicalization in an already shaky southern Europe <sup>57</sup>.

Recent developments have resulted in high gas prices within Europe, causing most European ammonia plant operators to curtail production, or even shut down entirely. Relatively expensive LNG is considered an alternative to provide natural gas to European ammonia plants. This will increase the cost of fossil-based ammonia production, with or without carbon mitigation, as compared to standard cost levels. Should the high natural gas prices in Europe persist, electrolysis-based hydrogen production may become increasingly competitive <sup>6</sup>.

Ammonia production would be a prime candidate for cuts to cushion any gas supply squeeze over the second half of 2022 <sup>56</sup>. Due to the recent rise in natural gas prices in Europe, the economics of operating an ammonia plant in the region has become extremely challenging. During normal times, ammonia production accounts for about 4.5% of the natural gas used by the German industry <sup>56</sup>. Due to the rise in natural gas prices in Europe in the first half of 2022, the economics of operating an ammonia plant in the region has become extremely challenging <sup>58</sup>.

Despite the short-term fluctuations, businesses and private consumers must adapt to significantly higher gas prices. While the lower prices on the spot market are a good thing, changes only affect consumers with a time lag. The high price level will, of course, continue to be a burden. Consumers and industries must continue to conserve energy to avert a supply shortage <sup>59</sup>.

Gas-intensive industries are already struggling. German chemical manufacturing giant BASF — whose plant on the Rhine River uses more gas than Switzerland — would be permanently downsizing in Europe, citing rising energy prices that make the region uncompetitive <sup>59</sup>. As a result, BASF has curtailed its ammonia production at its production sites in Antwerp and Ludwigshafen. BASF will continuously monitor the gas price development and adjust its ammonia production accordingly <sup>58</sup>.

Chemical companies are the biggest industrial natural-gas users in Germany and ammonia is the single most gas-intensive product within that industry <sup>4</sup>. Approximately, 9 MWh of natural gas is being consumed to produce one metric ton of ammonia. For German as the biggest ammonia producer in the EU, a permanent reduction of ammonia production by 40%, can save annual natural gas demand by about 10 TWh or 3% <sup>60</sup>. FRANKFURT, July 27 (Reuters) <sup>56</sup>, <sup>4</sup>.

Both SKW and BASF cut ammonia production in September 2021, because of a surge in gas prices <sup>56</sup>. Germany's biggest ammonia maker SKW Piesteritz and number four Ineos also said they could not rule out production cuts as the country grapples with disruption to Russian gas supplies <sup>56</sup>. SKW, which at the time cut output by 20%, resumed normal production when customers accepted price mark-ups <sup>56</sup>.

BASF's production network, in particular, does not rely on ammonia as much as it does on other basic chemicals for onward use in more specialized downstream chemicals <sup>56</sup>. In the first nine months of 2022, the additional costs for natural gas at BASF's European sites amounted to around  $\in 2.2$  billion compared with the same period in 2021 <sup>59</sup>.

CF Fertilisers UK, a subsidiary of CF Industries Holdings, Inc. (NYSE: CF), on 24 August 2022, announced its intention to temporarily halt ammonia production at the Billingham Complex due to market conditions <sup>61</sup>. CF Fertilisers UK intends to use the site's capability to import ammonia to enable it to continue to run its ammonium nitrate (AN) and nitric acid upgrade plants. The Company expects to fulfill all ammonia and nitric acid contracts and all orders of AN contracted for delivery in the coming months <sup>61</sup>.

Unlike many European countries, Germany just started to build up liquefied natural gas (LNG) port terminals to replace Russian pipeline gas <sup>62</sup>. That means companies are under political and

commercial pressure to reduce gas-intensive activities if gas deliveries are cut further <sup>56</sup>, <sup>4</sup>. Production lines for raw material syngas, a mixture of carbon monoxide and hydrogen, and basic petrochemical acetylene were also candidates for cutbacks to save on gas <sup>56</sup>.

Companies that reduce ammonia production may lose market share to imports from overseas suppliers with access to cheap gas, or in Germany might accept compensation payments under a potential gas rationing program to encourage manufacturers to quickly scale back production to balance out supply cuts <sup>56</sup>. BASF would purchase some ammonia from external suppliers to fill gaps but warned farmers would face soaring fertilizer costs next year <sup>56</sup>. A close look at German fertilizer production, which heavily relies on natural gas as fuel and feedstock to produce ammonia as an intermediate product, reveals that increased ammonia imports have allowed domestic fertilizer production to remain remarkably stable <sup>60</sup>.

Until August 2021, ammonia prices were high compared to European gas prices, making exports attractive. After natural gas prices surged in the fall of 2021, the situation reversed, and domestic German ammonia production became uncompetitive <sup>60</sup>.

The industry is responding to high natural gas prices in the current energy crisis, and the response of the ammonia industry alone is significant. Downstream industries, such as fertilizer production, do not necessarily need to break down because intermediate products may be substituted by imports <sup>60</sup>.

Fertilizer giant Yara (YAR.OL), which runs Germany's third-largest ammonia production site in the northern town of Brunsbuettel, said its output across Europe was currently (July 27, 2022) 27% below capacity due to the surge in gas prices <sup>56</sup>.

In the northern hemisphere, nitrogen fertilizer is applied primarily during the spring. It can also be produced in the United States and shipped to Europe while adding  $CO_2$  supply for the food industry could prove a thorny issue <sup>56</sup>.

Even before the war in Ukraine, reduced ammonia production due to rocketing natural gas prices in Britain last year caused CO<sub>2</sub> shortages in the meat and drinks industries <sup>56</sup>. That forced the UK

government in September to provide financial support for ammonia maker CF Industries (CF.N) to restart production <sup>56</sup>.

A Russian gas embargo might be less of an issue for BASF's Antwerp Verbund site as Belgium in general only has 5-10% Russian gas exposure and, therefore, Antwerp's ammonia production might not be at risk in the case of Russian supply issues <sup>63</sup>.

# **10-** Applications of ammonia:

Ammonia has several applications mainly in chemical production chains and fertilizers. About 88% of the total production of this substance is used in the production of agricultural fertilizers. 16 to 25% of it (of ammonia) is used to produce nitric acid  $^3$ .

Nitrogen fertilizers account for around 80% of today's total ammonia demand. Other markets include the manufacturing of chemicals, plastics, and textiles (acrylonitrile, melamine); the mining industry (low-density ammonium nitrate explosives, metals brightening processes), pharmaceuticals; refrigeration; waste treatment; and air treatment, such as abatement of nitrogen oxide (NO<sub>X</sub>) <sup>3</sup>.

Ammonia is used in the ammonia-soda process (Solvay process) to produce soda ash,  $Na_2CO_3$ . Ammonia is also used in the preparation of hydrazine,  $N_2H_4$ , a colorless liquid used as a rocket fuel and in many industrial processes.

Ammonia can act as a ligand in transition metal complexes. It is a pure  $\sigma$ -donor, in the middle of the spectro-chemical series, and shows intermediate hard-soft behavior. For historical reasons, ammonia is named ammine in the nomenclature of coordination compounds. Some notable ammine complexes include tetraamminediaquacopper(II) ( $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ), a dark blue complex formed adding ammonia solution of copper(II) by to a salts. Tetraamminediaquacopper(II) hydroxide is known as Schweizer's reagent and has the remarkable ability to dissolve cellulose. Several applications of ammonia are explained as follows.

#### 10-1- Solvent

Liquid ammonia is the best-known and most widely studied non-aqueous ionizing solvent. Its most conspicuous property is its ability to dissolve alkali metals to form highly colored, electrically conductive solutions containing solvated electrons. Apart from these remarkable solutions, much of the chemistry in liquid ammonia can be classified by analogy with related reactions in aqueous solutions. The ionic self-dissociation constant of liquid NH<sub>3</sub> at -50 °C is about  $10^{-33}$ .

#### 10-2- Fuel

Ammonia may also be used as stationary fuel in, for example, Europe and North America, as ammonia offers an alternative to natural gas for peaker plants<sup>17</sup> for full decarbonization of the electricity grid. Currently, hydrogen is considered for such applications, although due to the storage challenges of hydrogen <sup>3</sup>.

Ammonia is sometimes proposed as a practical alternative to fossil fuel for internal combustion engines. Its high octane rating of 120 and low flame temperature allows the use of high compression ratios without a penalty of high  $NO_x$  production. The principle is similar to that used in a fireless locomotive, but with ammonia as the working fluid, instead of steam or compressed air. During World War II ammonia was used to power buses in Belgium. Since ammonia contains no carbon, its combustion cannot produce carbon dioxide, carbon monoxide, hydrocarbons, or soot. However, ammonia cannot be easily used in existing Otto cycle engines because of its very narrow flammability range, and there are also other barriers to widespread automobile usage.

The raw energy density of liquid ammonia is 11.5 MJ/L, which is about a third that of diesel. There is the opportunity to convert ammonia back to hydrogen, where it can be used to power hydrogen fuel cells, or it may be used directly within high-temperature solid oxide direct ammonia fuel cells to provide efficient power sources that do not emit greenhouse gases.

The combustion of ammonia to form nitrogen and water is exothermic:

<sup>&</sup>lt;sup>17</sup> Peaker plants are power plants that generally run only when there is a high demand, known as peak demand, for electricity

4 NH<sub>3</sub> + 3 O<sub>2</sub>  $\rightarrow$  2 N<sub>2</sub> + 6 H<sub>2</sub>O(g),  $\Delta$ H°r = -1267.20 kJ (or -316.8 kJ/mol if expressed per mol of NH<sub>3</sub>)

The combustion of ammonia in air is very difficult in the absence of a catalyst (such as platinum gauze or warm chromium(III) oxide), due to the relatively low heat of combustion, a lower laminar burning velocity, high auto-ignition temperature, high heat of vaporization, and a narrow flammability range. However, recent studies have shown that efficient and stable combustion of ammonia can be achieved using swirl combustors, thereby rekindling research interest in ammonia as a fuel for thermal power production.

Compared to hydrogen as a fuel, ammonia is more energy efficient, and could be produced, stored, and delivered at a lower cost than hydrogen, which must be kept compressed or as a cryogenic liquid. However, ammonia production, shipping, storage etc. will further decrease the overall efficiency and comes with safety risks. Rocket engines have also been fueled by ammonia. The Reaction Motors XLR99 rocket engine that powered the X-15 hypersonic research aircraft used liquid ammonia. Although not as powerful as other fuels, it left no soot in the reusable rocket engine, and its density approximately matches the density of the oxidizer, liquid oxygen, which simplified the aircraft's design.

#### **10-3-** Fertilizer and Precursor to nitrogenous compounds

In the US as of 2019, approximately 88% of ammonia was used as fertilizers either as its salts, solutions, or anhydrous. When applied to soil, it helps provide increased yields of crops such as maize and wheat. 30% of agricultural nitrogen applied in the US is in the form of anhydrous ammonia and worldwide 110 million tons are applied each year.

Ammonia is directly or indirectly the precursor to most nitrogen-containing compounds. Virtually all synthetic nitrogen compounds are derived from ammonia.

#### 10-3-1- Urea

 $CO_2$  from the SMR of a nearby ammonia plant is usually used on-site to produce urea and the reaction of ammonia and gaseous carbon dioxide takes place (Eq. 1) in a synthesis reactor,

operating at relatively high pressures (150 bar) and elevated temperatures (180-210°C) to produce ammonium carbamate. This intermediate product reacts further to urea and water (Eq. 2).

 $2 \text{ NH}_3 + \text{CO}_2 \leftrightarrow [\text{NH}_2\text{COO}][\text{NH}_4] \qquad (\text{Eq. 1})$  $[\text{NH}_2\text{COO}][\text{NH}_4] \rightarrow \text{H}_2\text{O} + (\text{NH}_2)_2\text{CO} \qquad (\text{Eq. 2})$ 

The product mixture, consisting of ammonium carbamate and urea, is stripped of ammonia with the resultant solution and fed through several decomposers operating at reduced pressures. The urea solution is concentrated by evaporation or crystallization and the crystals melted or granulated to yield pure urea in the form of pills or granules. Unconverted carbamate is decomposed back to ammonia and carbon dioxide and recycled into the reactor <sup>53</sup>.

#### 10-3-2- Nitric acid

An important derivative is nitric acid. This key material is generated via the Ostwald process by oxidation of ammonia with air over a platinum catalyst at 700–850 °C (1,292–1,562 °F),  $\approx$ 9 atm. Nitric oxide is an intermediate in this conversion:

 $NH_3 + 2 O_2 \rightarrow HNO_3 + H_2O$ 

Nitric acid, the main feedstock for fertilizer production, is one of the largest sources of  $N_2O$  emissions in the European chemical industry. Nitric acid is also used for the production of explosives and many organo-nitrogen compounds <sup>53</sup>.

#### 10-3-3- Other products

Ammonia is also used to make the following compounds:

- Hydrazine, in the Olin Raschig process and the peroxide process
- Hydrogen cyanide, in the BMA process and the Andrussow process
- Hydroxylamine and ammonium carbonate, in the Raschig process
- Phenol, in the Raschig-Hooker process
- Amino acids, using Strecker amino-acid synthesis

• Acrylonitrile, in the Sohio process

Ammonia can also be used to make compounds in reactions that are not specifically named. Examples of such compounds include: ammonium perchlorate (NH<sub>4</sub>ClO<sub>4</sub>), ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), formamide (CH<sub>3</sub>NO), dinitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>), alprazolam (C<sub>17</sub>H<sub>13</sub>ClN<sub>4</sub>), ethanolamine (C<sub>2</sub>H<sub>7</sub>NO), ethyl carbamate (CH<sub>3</sub>CH<sub>2</sub>OC(O)NH<sub>2</sub>), hexamethylenetetramine ((CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>), and ammonium bicarbonate ((NH<sub>4</sub>)HCO<sub>3</sub>). Moreover, ammonia is used in the ammonia-soda process (Solvay process) to produce soda ash (Na<sub>2</sub>CO<sub>3</sub>).

#### 10-4- Remediation of gaseous emissions

Ammonia is used to scrub  $SO_2$  from the burning of fossil fuels, and the resulting product is converted to ammonium sulfate for use as fertilizer. Ammonia neutralizes the nitrogen oxide ( $NO_x$ ) pollutants emitted by diesel engines. This technology, called SCR (selective catalytic reduction), relies on a <u>vanadia</u>-based catalyst. Ammonia may be used to mitigate gaseous spills of phosgene.

#### **10-5-** As a hydrogen carrier

Due to its attributes, being liquid at ambient temperature under its vapor pressure and having high volumetric and gravimetric energy density, ammonia is considered a suitable carrier for hydrogen, and may be cheaper than the direct transport of liquid hydrogen despite uncertainties in costs for the dehydrogenation step.

Among the carriers for hydrogen, ammonia is quickly standing out as one of the most popular choices. Ammonia benefits from having the existing infrastructure in place for global trade, as well as a healthy demand of 150 million tons per annum from the fertilizer industry <sup>64</sup>.

#### 10-6- Cleansing agent

Household "ammonia" (also incorrectly called ammonium hydroxide) is a solution of  $NH_3$  in water and is used as a general-purpose cleaner for many surfaces. Because ammonia results in a relatively streak-free shine, one of its most common uses is to clean glass, porcelain, and stainless steel. It is also frequently used for cleaning ovens and soaking items to loosen baked-on grime. Household

ammonia ranges in concentration by weight from 5 to 10% ammonia, is used as household cleaners, particularly for glass.

#### **10-7-** Fermentation

Solutions of ammonia ranging from 16% to 25% are used in the fermentation industry as a source of nitrogen for microorganisms and to adjust pH during fermentation.

#### 10-8- Antimicrobial agent for food products

As early as in 1895, it was known that ammonia was strongly antiseptic, it requires 1.4 grams per litre to preserve beef tea (broth). Anhydrous ammonia is currently used commercially to reduce or eliminate microbial contamination of beef.

#### **10-9- Refrigeration – R717**

Because of ammonia's vaporization properties, it is a useful refrigerant. It was commonly used before the popularisation of chlorofluorocarbons (Freons). Anhydrous ammonia is widely used in industrial refrigeration applications and hockey rinks because of its high energy efficiency and low cost. It suffers from the disadvantage of toxicity and requires corrosion-resistant components, which restricts its domestic and small-scale use. Along with its use in modern vapor-compression refrigeration, it is used in a mixture along with hydrogen and water in absorption refrigerators. The Kalina cycle, which is of growing importance to geothermal power plants, depends on the wide boiling range of the ammonia–water mixture. Ammonia coolant is also used in the S1 radiator aboard the International Space Station in two loops which are used to regulate the internal temperature and enable temperature-dependent experiments.

The potential importance of ammonia as a refrigerant has increased with the discovery that vented CFCs and HFCs are extremely potent and stable greenhouse gases.

#### **10-10- Textile**

Liquid ammonia is used for the treatment of cotton materials, giving properties like mercerisation, using alkalis. In particular, it is used for prewashing wool.

#### 10-11- Lifting gas

At standard temperature and pressure, ammonia is less dense than the atmosphere and has approximately 45–48% of the lifting power of hydrogen or helium. Ammonia has sometimes been used to fill balloons as a lifting gas. Because of its relatively high boiling point (compared to helium and hydrogen), ammonia could potentially be refrigerated and liquefied aboard an airship to reduce lift and add ballast (and returned to gas to add lift and reduce ballast).

#### **10-12-** Fuming

Ammonia has been used to darken quarter sawing white oak in Arts & Crafts and Mission-style furniture. Ammonia fumes react with the natural tannins in the wood and cause it to change colors.

### 10-13- Physiology and excretion

Ammonia plays a role in both normal and abnormal animal physiologies. It is biosynthesized through normal amino acid metabolism and is toxic in high concentrations. The liver converts ammonia to urea through a series of reactions known as the urea cycle. Ammonia is important for normal animal acid/base balance. The 9 essential amino acids are histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine.

Furthermore, Ammonium ions are a toxic waste product of metabolism in animals. Ammonium is excreted in the urine, resulting in a net acid loss. Ammonia may itself diffuse across the renal tubules, combine with a hydrogen ion, and thus allow for further acid excretion. In fish and aquatic invertebrates, Ammonia is excreted directly into the water. In mammals, sharks, and amphibians, it is converted in the urea cycle to urea, which is less toxic and can be stored more efficiently. In

birds, reptiles, and terrestrial snails, metabolic ammonium is converted into uric acid, which is solid and can therefore be excreted with minimal water loss.

Table 2. A summary	of	ammonia	applications
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Products from (or	Chemical formula	Applications					
related to)							
Ammonia							
nitric acid	HNO <sub>3</sub>	Nitric acid is used in the production of ammonium					
		nitrate for fertilizers, making plastics, and in the					
		manufacture of dyes.					
Nitrates (salts and	NO <sub>3</sub> <sup>-18</sup>	Nitrates are common components of fertilizers and					
esters of nitric acid)		explosives.					
Hydrazine	N <sub>2</sub> H <sub>4</sub>	rocket fuel and in many industrial processes					
Sodium carbonate <sup>19</sup>	Na <sub>2</sub> CO <sub>3</sub>	dermatitides, mouthwash, emergency emetic, vaginal					
		douche, and veterinary medicine					
Sodium bicarbonate	NaHCO <sub>3</sub>	Antacid (medical utilization), manufacture of glass,					
*		soap and paper, used to relieve heartburn acid					
		indigestion, and sodium compounds, etc.					
Hydrogen cyanide	HCN	Antiseptic agent to kill rodents and other pests in					
		green beans**					
Hydroxylamine	NH <sub>2</sub> OH	Nylon-6 production					
Urea	CO(NH <sub>2</sub> ) <sub>2</sub>	Fertilizer and a starting material for the manufacture					
		of plastics and drugs (mainly urea-formaldehyde resin					
		and barbiturates).					
Amino acids	The elements present in						
	every amino acid are						
	carbon, hydrogen,						
	oxygen, and nitrogen						
	(CHON)						

<sup>&</sup>lt;sup>18</sup> Salts containing this ion are called nitrates.

<sup>&</sup>lt;sup>19</sup> Ammonia is used in the <u>ammonia-soda process</u> (Solvay process) to produce soda ash Na<sub>2</sub>CO<sub>3</sub>

Acrylonitrile	CH <sub>2</sub> CHCN		for	the	manufacture	of	useful	plastics	such	as
			poly	acry	lonitrile					
Ammonium salts***	Such as	(NH4)2CO3,								
	NH <sub>4</sub> Cl, NH <sub>4</sub> N	NO3,								

\* (IUPAC name: sodium hydrogencarbonate), commonly known as baking soda or bicarbonate of soda. Bicarbonate of Soda

\*\* The annual production of hydrogen cyanide is estimated to be around 1.4 million tons worldwide. Hydrogen cyanide is produced in large quantities through the metal processing industries, electroplating of metals to make metals hard and resistant, extraction of gold and silver from mines, and flue gasses of ships. Wheat silos, flour production factories, coal gasification production, iron and steel production factories, and chemical production industries also discharge hydrogen cyanide to water sources.

\*\*\* Ammonium carbonate ((NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>), ammonium chloride (NH<sub>4</sub>Cl) and ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>).

# 11- Storage, transport and distribution of ammonia

Ammonia has been handled in large quantities for many decades, and there is a high maturity of storage, transport, and distribution technologies, as well as training, industry codes and standards, and regulations that must be observed to ensure safety and security. Ammonia can be transported by pipeline, and both natural gas pipelines and liquids pipelines can be retrofitted for this purpose. Ammonia is transported by road, train, ship, and pipeline. In total, around 25-30 Mt of ammonia is transported annually <sup>3</sup>.

Yara's Tertre site has invested  $\notin$ 40 million in the construction of a new ammonia tank. Inaugurated on 2 October 2020, the new tank will improve safety and optimize the production process. Another advantage is that the new storage significantly reduces the site's energy consumption. With a capacity of 15,000 tons, the new tank avoids unit shutdowns and restarts. It also optimizes the company's energy consumption and is equipped with cutting-edge technology that increases the safety of site <sup>65</sup>.

# **12-** Recent prices changes

### 12-1- The third quarter of 2022

Across the continent, governments and businesses have aggressively replenished how much gas they are holding in storage. At the urging of European Union officials and a high cost, energy companies and governments have filled underground caverns and other facilities to more than 90 percent of capacity, compared with less than 80 percent a year ago <sup>66</sup>.

Companies that sell natural gas, driven by the high prices, flooded the European market. Special ships with huge amounts of liquefied natural gas, or L.N.G., raced to Europe from the United States, Qatar, and other countries (including Russia) that produce large amounts of gas <sup>66</sup>.

The rush to sell to Europe was so great that vessels are now loitering off the coast waiting for slots at crowded terminals to unload their cargoes. One illustration of the glut: In recent days, at least one L.N.G. carrier heading from Algeria to Europe appears to have diverted to Asia in search of a better price, according to Laura Page, an analyst at Kpler, a research firm <sup>66</sup>.

European ammonia producers are restarting as gas prices have declined significantly due to milder temperatures across Europe, near full storage, and an improving supply situation in the short to medium term on the back of solid LNG volume arrivals <sup>67</sup>. Europe's gas prices fall below  $\in$ 100 MWh for the first time since mid-June <sup>68</sup>. Moreover, fertilizer producers are restarting as gas prices have declined by 80% in October 2020.

The Dutch Title Transfer Facility (TTF), Europe's leading trading hub, a futures contract for November closed at  $\notin$ 99.17 per megawatt-hour (MWh) on 25<sup>th</sup> October 2022. Moreover, the final bills contain extra costs related to network maintenance, taxes, and operational fees <sup>68</sup>. The TTF broke records when it reached  $\notin$ 349 MWh in August 2022 <sup>68</sup>.



Figure 7. Gas price at the Dutch TTF<sup>68</sup>

European gas prices may have dropped to levels not seen in more than four months, but this is far from being the end of the energy crisis, four industry analysts told CNBC. The latest data compiled by industry group Gas Infrastructure Europe shows that the EU's overall storage levels are at an average of nearly 94% full. That's comfortably above the 80% target the bloc had set for countries to reach by the start of November <sup>69</sup>.

Unseasonably mild weather is largely responsible for the dramatic change in fortune. Countries like Italy, Spain, and France, have temperatures and gas consumption closer to August and early September levels in October 2022. Even in countries in the Nordics, the UK, and Germany, consumption is way below the average for this time of the year. The European Union has also built substantial buffers against any further supply cuts by filling gas storage facilities close to capacity. Stores are now almost 94% full, according to data from Gas Infrastructure Europe. That's well above the 80% target the bloc set countries to reach by November 2022<sup>70</sup>.

Europe's efforts to secure as much fuel ahead of winter as possible has caused a backlog of LNG tankers at European ports, made worse by a shortage of LNG import terminals. The bloc has ramped up imports of LNG from the United States and Qatar as natural gas imports from Russia

plummeted. And despite the fact that Russia's share of Europe's total gas imports has fallen from 40% to just 9%, the region could be in a difficult spot next summer as it tries to replenish its stores ahead of the following winter  $^{70}$ .

Some of the LNG (liquefied natural gas) orders made during the summer are arriving now, when storage is full, representing an oversupply. Temperatures in the region have also been unusually warm, with some nations currently experiencing 20 degrees Celsius (68 degrees Fahrenheit) heat. high output from wind power and political agreement within the EU on cooperative measures to reduce gas prices and consumption have contributed to lowering gas prices. But Europe's energy crisis isn't over, and analysts are warning European policymakers against complacency <sup>69</sup>.

Once it gets cold, inventories will draw down. If there's a late winter cold snap when stocks have been reduced, thigs could get pretty tight in early 2023, meaning possible price spikes and potential energy shortages <sup>69</sup>.

Before Russia invaded Ukraine, the EU was obtaining about 40% of all its natural gas from Moscow. That has now fallen below 10%. Forward pricing indicates that high prices will soon return: ICIS data shows gas for delivery in January is more than four times the price of spot gas at the TTF <sup>69</sup>.

Several experts have warned that Europe's high storage levels were to a large extent achieved with Russian gas. Even if this winter ends up being mild, next winter also remains a supply concern <sup>69</sup>.

The European Union as a whole also met a target for refilling gas storage sites to 80% by Nov. 1 ahead of time. Storage facilities are currently 93% full, compared with 77% this time last year, Gas Infrastructure Europe data shows <sup>71</sup>.

#### 12-2- Higher prices next year

Despite the recent slump, at around  $\in 100 \ (\$100)^{20}$  per megawatt hour European natural gas futures are still 126% above where they were last October when economies started to reopen from their pandemic lockdowns and demand spiked.

Prices could rise sharply again in December and January as the weather turns colder, providing an incentive for some of those tankers to wait offshore a while longer before coming into port to unload.

Prices are expected to hit  $\in$ 150 (\$150) per megawatt hour by the end of 2023, said Bill Weather burn, a commodities economist at Capital Economics. "Filling storage ahead of next winter will require the EU to import even more LNG because there is a need to replace lost Russian gas imports for an entire year <sup>70</sup>.

#### **12-3-** Tips to manage the situation

The battle for fertilizer, a vital commodity for food production, has emerged as one of the byproducts of the Russia/Ukraine conflict, leaving states in Europe and elsewhere scrambling for alternative suppliers.

#### 12-3-1- Import Ammonia

Europe can only achieve its climate and energy security goals with a rapid deployment of imported "green" hydrogen and ammonia made from renewable energy. With the current (26 August 2022) and expected natural gas prices, green ammonia imports are cheaper than fossil-based "gray" ammonia and can be deployed in the shipping sector as a green bunker fuel as well as in established chemical industries. Including green hydrogen and ammonia in trade policy with renewables-rich countries like Australia, Brazil, Chile, and North African nations will enable imports to reach the continent as early as 2024<sup>72</sup>.

<sup>&</sup>lt;sup>20</sup> 1  $\in_{Nov.2022} = 1$   $_{Nov.2022}$ 

The EU market for certain nitrogen fertilizer inputs depends significantly on imports from third countries, with Russia being the second largest supplier. In 2021, the EU imported 2.9 million tons of ammonia and 4.7 million tons of urea for the production of nitrogen fertilizers. Prices for those products increased in 2021 and have further risen during 2022 after the military aggression of Russia against Ukraine. This has had a profound negative impact on the production of nitrogen-based fertilizers in the EU <sup>73</sup>.

Oslo-based Yara said that, where possible, it will use its global sourcing and production system to optimize operations and meet customer demand, which includes using imported ammonia when feasible. It's currently much cheaper to import ammonia into Europe than to make it there, according to CRU <sup>31</sup>.

By constructing an ammonia terminal in the port of Antwerp, Fluxys hopes to transform Belgium into a hub for the import and transit of green ammonia across Europe. It is collaborating with logistics specialists Advario and Stolthaven to achieve this. The terminal could provide corporations with direct storage and transit services via rail, road, ship, or pipeline. The ammonia might potentially be transformed back into hydrogen with an extra installation. The firms want to have it functioning by 2027. It would require "hundreds of millions" of euros in investment <sup>35</sup>.

Andreas Gocke, global lead for chemicals at Boston Consulting Group (BCG), said that before the war, the entire cash cost of ammonia production in Europe was bad, but with current gas prices, there is a brutal translation. There is no chance anymore for the cost-competitive production of ammonia in Europe. This will have an impact not only on fertilizers production, but also on downstream products such as polyamide 6 (PA6) or by-products from ammonia production such as carbon dioxide (CO<sub>2</sub>), which is used in a variety of industrial sectors, not least the food and drinks sector <sup>74</sup>.

European Commission proposes to temporarily scrap tariffs on goods used to produce fertilizer. On 19<sup>th</sup> July 2022, the Commission proposed to suspend tariffs on inputs used for the production of nitrogen fertilizers until the end of 2024. The objective of this proposal is to help alleviate costs for EU fertilizer producers and EU farmers <sup>73</sup>.

In addition to lowering costs for EU producers and farmers, the proposal will help increase the stability and diversification of supply by fostering imports from a wider range of third countries, while excluding Russia and Belarus from the suspension of tariffs. The proposal will now be discussed by Member States in the Council because of its adoption <sup>73</sup>.

Already before the Russian invasion of Ukraine, commodity markets were witnessing a significant price surge, which agricultural markets felt through the increases in energy and fertilizer costs, and a consequent increase in farm product prices. The invasion of Ukraine and a global commodity price hike have further driven up prices in agricultural product markets and are exposing the vulnerabilities of the Union's food system which is partially reliant on imports of fertilizers<sup>75</sup>.

The Communication stresses that, in the short term, the cost and availability of mineral fertilizers must be a priority, pending the transition to the use of sustainable types of fertilizers or methods of fertilizing. During that period, the fertilizer industry in the EU must be able to access the necessary imports, including inputs to produce fertilizers within the EU itself <sup>75</sup>.

Of the three main fertilizer types used by farmers, nitrogen-based fertilizer is the one subject to common customs tariff duties applicable to intermediate inputs that are key to its production, as opposite to potash and phosphorus, where key inputs are subject already to a zero-duty common customs tariff rate. Nitrogen-based fertilizers are also the widest consumed fertilizers type in the EU, and also the one where prices have increased the most since 2021. Therefore, the proposed measures focus on inputs for nitrogen-based fertilizers <sup>75</sup>.

Currently, third countries that benefit from duty-free preferential access to the Union market according to Free Trade Agreements are the main suppliers of these goods to the EU market <sup>75</sup>.

Nevertheless, the EU imports a large volume of inputs for nitrogen fertilizers originating in countries subject to the Common Customs Tariff, with tariff rates currently ranging between 5,5 and 6,5%. To increase the stability of supply, it is appropriate to temporarily enlarge the geographical scope of supplying countries beyond those who benefit from a free-trade agreement, as supply is currently concentrated in a relatively small number of preferential suppliers. However, unlike for access via preferential trade agreements, the proposed measures for tariff suspensions under this proposal are temporary <sup>75</sup>.

In 2021, the total value of imports of CN codes 2814 10 00 amounted to 1,3 billion €. The conventional rate of duty for this CN code is 5,5%. Most of these imports (68%) were duty-free as a result of the implementation of Free Trade Agreements. Aa additional 29% were imported from Russia, which will not be subject to tariff reduction. The estimated uncollected duties are therefore 2,1 million  $\in$  <sup>75</sup>.

In 2021, the total value of imports of CN codes 3102 10 10 and 3102 10 90 amounted to 1,8 billion €. The conventional rate of duty for this CN code is 6,5%. Most of these imports (65%) were duty-free as a result of the implementation of Free Trade Agreements. Additional 24% were imported from Russia and Belarus, which will not be subject to tariff reduction. The estimated uncollected duties are therefore 12.9 million  $\in$  <sup>75</sup>.

Based on the above, the impact on the loss of revenue for the EU budget resulting from this Regulation is estimated at 11,25 Mio  $\in$  per year [(12,9 Mio  $\in$  + 2,1 Mio  $\in$  = 15 Mio  $\in$  gross amount, including collection costs) x 0,75]. For 2022 the impact of the loss of traditional own resources revenue for the EU budget is estimated as one-third of the above amount. i.e. 3.8 million €. The loss of revenue in traditional own resources will be compensated by Member States Gross National Income (GNI) based on resource contributions<sup>75</sup>.

OCI Chemical industry company is aiming to triple ammonia throughput in its import terminal at the Port of Rotterdam to 1.2m tons/year by 2023. The expansion's first phase will have capital expenditure (Capex) of 19.63 m€<sub>2022, Aug.</sub><sup>21 76</sup>. OCI's move would help the key petrochemicals hub of Amsterdam-Rotterdam-Antwerp (ARA) to become a greener logistics hub <sup>76</sup>. In 2020, Belgium exported 5.43 M $\in_{2020}$  <sup>22</sup> in Ammonia in aqueous solution, making it the 6th largest exporter of Ammonia in aqueous solution in the world. In the same year, Ammonia in aqueous solution was the 2274<sup>th</sup> most exported product in Belgium <sup>77</sup>.

The additional advantage of ammonia as a fertilizer, row material for other products, and hydrogen carrier is that the ammonia trade already exists. Infrastructure and regulations are already largely in place.' Even the storage tanks are already there. Gasunie will be using its peak shaver (shortterm LNG storage) facilities already in place at its Maasvlakte location <sup>78</sup>.

 $<sup>^{21}</sup>$  1  $\pounds_{2022,\,Aug.}$  = 1.0187 \$2022, Aug.  $^{22}$  6.19 M\$2020; 0.877  $\pounds_{2020}$  = 1 \$2020, Sep  $^{30}$ 

Gasunie and Fluxys are working on the development of national hydrogen networks in the Netherlands and Belgium respectively. These networks will be interconnected in the North Sea Port area, which stretches from Ghent to Vlissingen and Terneuzen. In the future, the Dutch-Belgian connection will supply hydrogen to companies in the 60-kilometer-long port area. Gasunie, Fluxys, and North Sea Port made agreements about this on Tuesday 17 May 2022<sup>79</sup>.

Global fertilizer consumption has remained strong throughout the COVID-19 pandemic. Brazil and the United States have allocated record acreage to soybean (a fertilizer-intensive crop). Demand is also strong in China due to increased feed use, especially maize and soybean meal, as the country is rebuilding its hog herd population following the African swine fever outbreak <sup>80</sup>.

Imported green hydrogen produced from renewable energy — and the green ammonia made with it — are crucial for European industry to eliminate its reliance on Russian natural gas. Imports of these clean energy fuels are already cost-competitive and can substitute most fossil fuels used by heavy industry and transport in the EU within eight years from 2022 <sup>81</sup>.

Incorporating green hydrogen and ammonia into trade policy with renewables-rich countries like Australia, Brazil, Chile, and North African nations will enable imports to reach the continent as early as 2024 <sup>81</sup>.

By strategically deploying green ammonia immediately as a feedstock for fertilizer production and use as shipping fuel, the EU can offset demand for fossil fuels and potentially dissuade costly and shortsighted investments in new gas infrastructure <sup>81</sup>.

The ports of Antwerp, Brunsbüttel, Hamburg, and Rotterdam have committed to building ammonia import capacity and are exploring investments in re-hydrogenation facilities for cracking ammonia into hydrogen upon arrival. Because more than 40% of Europe's fertilizer production, steel production, and petrochemicals manufacturing is concentrated in Belgium, Germany, and the Netherlands, the region is ideally suited to become the EU's primary green hydrogen hub<sup>81</sup>.

Ammonia imports could also bolster the EU's fertilizer sector at a time when food security concerns are top of mind, ensuring a stable supply for the bloc's agriculture industry and potentially creating opportunities for exporting products to countries with diminished stores <sup>81</sup>.

OCI N.V. expands the ammonia import terminal in the port of Rotterdam to meet emerging largescale low-carbon hydrogen and ammonia demand in the energy transition. The expansion will triple capacity at OCI's terminal in Rotterdam to 1.2 million tons per year by 2023 (c.400 ktpa to up to 1.2 million metric tons per year) <sup>82</sup>.

The terminal is strategically located to enable the import of blue and green ammonia from OCI's global operations in the Middle East & North Africa at Fertiglobe and the US, connecting to key infrastructure to serve Europe's future hydrogen deficit. Moreover, it creates sustainable downstream value chains for society and industry, including new applications such as a low-carbon alternative for power generation and industrial feedstocks, which helps reduce Europe's dependence on natural gas <sup>82</sup>.

Air Products and Gunvor Petroleum Rotterdam, a wholly-owned subsidiary of Gunvor Group (Gunvor), have signed a joint development agreement for an import terminal in Rotterdam. It offers strategic access for receiving green ammonia from large-scale green hydrogen production locations operated by Air Products and its partners from projects around the world. The green ammonia will be converted to hydrogen and distributed to markets within Europe, including the Netherlands, Germany, and Belgium<sup>83</sup>. Figure 8 shows the production capacity of ammonia worldwide from 2018 to 2021, with a forecast for 2026 and 2030<sup>84</sup>.

German energy firms Uniper UN01.DE and E.ON EONGn.DE plan to work on deals with Canada's EverWind to buy a total of 1 million tonnes of green ammonia a year from the middle of the decade, in a bid to further diversify away from Russian energy <sup>85</sup>.



Figure 8. Import volume of ammonia worldwide in 2019, by country (in 1000 metric tons)<sup>84</sup>

The ammonia will come from EverWind's planned Point Tupper facility, which is expected to start commercial operation in early 2025. Green ammonia, produced via renewable energy, can be either used in its gas form or turned into green hydrogen to power the local economy <sup>85</sup>.

Egypt-based Mediterranean Energy Partners (MEP) to invest 250  $M \in_{2022}$  <sup>23</sup>to establish a green ammonia plant with a production capacity of 120,000 tons per year. Suez Canal Economic Zone (SCZONE) announced that seven new Memorandums of Understanding (MOU) were signed with international companies to set up green hydrogen and ammonia production facilities in Sokhna <sup>86</sup>.

#### 12-3-2- Other alternatives to meet fertilizer requirements

Corn uses more land than any other crop. It also uses a lot of fertilizer <sup>87</sup>. Recently researchers at the University of Wisconsin–Madison have made a remarkable discovery. They found that an indigenous variety of Mexican corn can fix nitrogen from the atmosphere, instead of requiring synthetic fertilizers <sup>87</sup>.

<sup>&</sup>lt;sup>23</sup> 250 million $$_{2022}$ ; 1  $\in_{2022, Nov.} = 1$ 

The tropical corn discovered in the Sierra Mixe region looks nothing like conventional corn. It can grow more than 16 feet tall, towering over the typical 12-foot-tall conventional varieties. It also grows slowly, taking eight to nine months rather than the three months of conventional corn <sup>87</sup>.

The study found that Sierra Mixe corn obtains 28 to 82 percent of its nitrogen from the atmosphere. To do this, the corn grows a series of aerial roots. Unlike conventional corn, which has one or two groups of aerial roots near its base, nitrogen-fixing corn develops eight to ten thick aerial roots that never touch the ground. During certain times of the year, these roots secrete a gel-like substance or mucilage. The mucilage provides the low-oxygen and sugar-rich environment required to attract bacteria that can transform nitrogen from the air into a form the corn can use <sup>87</sup>.

Researchers are a long way from developing a similar nitrogen-fixing trait for commercial corn, but this is a first step to guide further research on that application. The discovery could lead to a reduction of fertilizer use for corn, one of the world's major cereal crops. It takes 1 to 2 percent of the total global energy supply to produce fertilizer. The energy-intensive process is also responsible for 1 to 2 percent of global greenhouse gas emissions <sup>87</sup>.

In principle, closing the cycle for phosphate is possible by managing the recovery of all phosphate that leaves the agricultural cycle through animal and plant products. The biggest challenge is to organize the return stream from the consumer/city, as that is where most of it is lost <sup>88</sup>.

For nitrogen the losses are much greater, even if you do whatever you can to limit them, and you also need an external supplement if you want to keep the production at the same level. This can be supplemented in two ways: by using nitrogen-fixing crops, such as clover, alfalfa, and legumes, which can fix nitrogen from the air through a symbiosis with rhizobium bacteria. This form of nitrogen supply requires acreage, at the expense of other crops <sup>88</sup>.

The second option is to use artificial nitrogen fertilizer. This costs energy instead of acreage <sup>88</sup>.

The chemical recycling of poly (isosorbide carbonate) (PIC) is presented as a model for the next generation of plastic-recycling systems. PIC, a bio-based polymer known for its excellent physical properties, undergoes a degradation reaction with aqueous ammonia. PIC completely decomposes within 6 h at 90 °C to afford isosorbide and urea <sup>89</sup>.

The generation of fertilizers via polymer degradation it is expected to lead not only to innovative chemical recycling systems to address the environmental problems associated with polymer materials, but also to provide solutions to the food-production problems associated with the growth of the global population <sup>89</sup>.

Ammonia is shown to completely degrade the bio-based polymer PIC to produce urea and the isosorbide monomer (ISB, a sugar). The resulting urea + ISB showed to be an effective fertilizer, with the ISB enhancing plant nitrogen use. PIC, poly (isosorbide carbonate), is a bio-based plastic based on isosorbide (ISB), which is derived from glucose. Tests showed complete degradation of PIC to ISB by reacting with an aqueous ammonia solution at 90°C for 6 hours, without solvent or catalyst. Such ammonolysis (using ammonia to break down polymers) is a known reaction. This study showed that the resulting material, a mixture of urea and ISB monomer, could be directly used as a fertilizer in pot trials with Arabidopsis thaliana (thale cress). The generated material showed the same N-fertilizer effectiveness as commercial urea, and the ICB enhanced the fertilizer effectiveness, presumably acting as a biostimulant. ESPP notes that these results may not transpose to more widely used or synthetic polymers and that it could be considered preferable to re-use the ISB monomer in plastics production rather than putting it on the soil. The title of the paper is misleading in that the nitrogen is not recycled but comes from 'virgin' ammonia <sup>90</sup>.

# 13- Other hydrogen carriers

In addition to liquid hydrogen, the other main hydrogen carriers are methanol, ammonia, and synthetic methane. Shipping enables imports of hydrogen carriers from countries further away from Europe, thus contributing to the diversification of supply. Import terminals for synthetic methane (to be used as hydrogen), ammonia, and methanol are currently either in planning or under construction. Hydrogen carriers can be directly utilized e.g., ammonia as a fertilizer, methanol as a chemical feedstock, or methane covering a wide range of applications in industrial, residential, and transportation sectors. From a demand perspective, gaseous hydrogen is needed across sectors in different regions to decarbonize (e.g., steel industry), while imported renewable or low-carbon ammonia/methanol could be used to replace existing grey ammonia/methanol production close to

the import terminal. Fossil-derived ammonia (liquefied), methanol, and natural gas (for synthetic methane) are currently transported in large quantities with tankers <sup>91</sup>.

Additionally, ammonia and methanol can be used as shipping fuels. However, ammonia-powered vessels must also carry heavy fuel oil or diesel to ensure quick start-up of engines in case of emergency. It should be noted that methanol and ammonia are highly toxic, flammable (especially methanol), and explosive under certain conditions. Stringent safety measures must be ensured for transport and storage tanks <sup>91</sup>.

The current European imports of ammonia reach 4 Mt.32 Many European terminals can potentially contribute to the imports of ammonia, as a hydrogen carrier, to meet REPowerEU 2030 targets. REPowerEU estimates that up to 4 Mt of hydrogen is imported in the form of ammonia or potentially other hydrogen carriers and derivatives. As hydrogen constitutes approximately 18% of the weight of ammonia, the amount of ammonia required is around 31 Mt. To meet the REPowerEU target, 27 Mt of ammonia would need to be imported additionally. Additional ammonia import capacities are currently planned in the Netherlands, Germany, and Belgium. It is important to note that cracking of ammonia back to hydrogen is not yet available at scale. First, large-scale ammonia into green hydrogen. The prototype will use ammonia to deliver 200kg of hydrogen a day. The UK Government estimates that hydrogen could make up to one-third of the UK's energy mix by 2050, but there are challenges with hydrogen storage and transport that need to be addressed to make this viable. The cost of the ammonia cracker prototype is about 4 m€<sub>2021</sub><sup>24</sup> and aims to help tackle the challenges ahead <sup>92</sup>.

<sup>&</sup>lt;sup>24</sup> £3.5m; 1 £<sub>2021</sub> =  $1.1632 \in_{2021} {}^{95}$ 

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