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# Feasibility study of a small-scale fertilizer production facility based on plasma nitrogen fixation

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## ABSTRACT

Over the last century, the nitrogen fertilizer production sector has been dominated by the Haber-Bosch process, used to convert inert $N_2$ into more reactive $NH_3$. This process, coupled with steam methane reforming for $H_2$ production, currently represents the cheapest and most efficient technology in the sector but is recognized as environmentally impacting. Recently, non-thermal plasma-based nitrogen fixation gained some interest as its theoretical minimum energy cost for $N_2$ fixation into NO and $NO_2$ has been estimated to be 0.2 MJ/mol N, lower than the current best available Haber-Bosch-based technology energy cost of 0.49 MJ/mol N and because this technology allows for implementation in small-scaled facilities with modest impact on the cost of the final product. Thus far, a lower energy cost than the Haber-Bosch process has however not been reached yet. Therefore, it is important to evaluate if the benefit of small-scale facilities is significant for the development of plasma-based technologies. This work focuses on studying whether a hypothetical small-scale fertilizer production facility based on a rotating gliding arc plasma for nitrogen fixation can be a local competitive alternative to a classical Haber-Bosch and steam methane reforming based facility. Capital expenditures, gas price, $CO_2$ allowances, levelized cost of energy and transport costs are considered in this comparative model which is used to understand the impact of such parameters on the fertilizer production costs. As the energy cost for plasma-based nitrogen fixation is currently the main drawback to the industrial implementation of the technology, the energy cost requirement for a plasma-based facility to be an economically viable alternative in the upcoming years is studied as a function of the prices of energy and natural gas.

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## 1. Introduction

As both the world population and the per capita food consumption increase, the nutrient demand on the agricultural sector follows accordingly. Such demand is met by increasing the food production per acre of arable land by enriching the soil with both organic and inorganic fertilizers. While the use of organic fertilizers did not record a significant increase in the last 50 years, the industrially produced inorganic fertilizer sector constantly grew with an average compound annual growth rate (CAGR) of 6.3 % from 1961 to 1988 and of 1.6 % from 1994 [1]. According to Allied Market Research, the global fertilizer industry generated 184.6 billion $ in 2021 and an increase of the CAGR up to 3.55 % is forecasted [2]. Inorganic fertilizers are classified according to the percentage in weight of the main nutrient, usually nitrogen (N), phosphorus (P) or potassium (K). Nitrogen fertilizers are the most commonly used accounting for 59 % of the global fertilizer production, especially in the EU where 73 % of the inorganic fertilizers produced are nitrogen-based [3]. The average consumption per hectare of cropland strongly varies from approximately 60 kg/ha of N in the southern member states (Portugal, Italy, Greece and Spain) up to 200 kg/ha of N in the Benelux region [4]. As molecular nitrogen $N_2$, abundantly found in air, is inert due to the high energy needed to break its strong triple bond (9.756 eV bond dissociation energy [5]) it needs to

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be converted into nitrogen-based compounds in order to be accessible to living organisms. Common nitrogen-based fertilizers usually consist of ammonium nitrate ($NH_4NO_3$ - 35 %N), urea ($CO(NH_2)_2$ - 47 %N) or urea ammonium nitrate (UAN - 28-32 %N) which is a solution of the two in water. To produce the listed nitrogen compounds, molecular nitrogen is usually converted to ammonia ($NH_3$). This process is known as "nitrogen fixation" (NF). The demand for ammonia is met via the Haber-Bosch (HB) process, which requires $N_2$ and $H_2$.

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3 \tag{1}$$

In its most commonly implemented design, it uses iron catalysts that require temperatures of 650 K-750 K and high pressures of about 150-300 bar in order to be efficient [6]. Molecular hydrogen ($H_2$) is most commonly produced from natural gas through Steam Methane Reforming (SMR),

$$CH_4 + H_2O \longrightarrow CO + 3\,H_2 \tag{2}$$

where an additional $H_2$ molecule is released through the water gas shift reaction.

$$CO + H_2O \longrightarrow CO_2 + H_2 \tag{3}$$

The waste $CO_2$ can be partially captured preventing its release into the atmosphere. When combined, both processes are however responsible for most of the nitrogen-based fertilizer production energy costs and $CO_2$ emissions. On average 32.4 GJ per ton of ammonia are required, corresponding to 0.55 MJ/mol of fixated nitrogen (MJ/mol N), and 1.8 t of $CO_2$ are emitted [7, 8]. However, with the best available technology, the energy cost can be lowered to 0.49 MJ/mol N. [7, 6]. In 2019, 185 Mt of $NH_3$ have been produced and the nitrogen-based fertilizer industry was recorded to be globally responsible for approximately 1% of the world energy consumption and 1% of the world $CO_2$ emissions [7]. As the energy cost for the HB process is strongly affected by its production scale, the process is currently performed in large-scale facilities in order to optimize its efficiency [9, 10]. A typical ammonia plant, performing both SMR and HB processes, produces between 200 kt and 1200 kt of $NH_3$ per year [7], which is enough to supply an order of magnitude of 100 000 $km^2$ of cropland in the EU. In a nitrogen-based fertilizer production facility all the production steps are covered. The $NH_3$ is then either converted to urea or undergoes the Ostwald process where ammonia is first converted into NO.

$$4\,NH_3 + 5\,O_2 \longrightarrow 4\,NO + 6\,H_2O \tag{4}$$

Then, NO is cooled and oxidized into $NO_2$,

$$2\,NO + O_2 \longrightarrow 2\,NO_2 \tag{5}$$

which is finally absorbed into water to form nitric acid ($HNO_3$).

$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO \tag{6}$$

The NO is then recycled and re-injected into the oxidation phase. Finally, $HNO_3$ is combined with $NH_3$ in order to obtain $NH_4NO_3$ by pressure neutralization.

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3 \tag{7}$$

Which is then sold to retail sellers as a fertilizer in the form of pellets.

In its current state, the nitrogen-based fertilizer industry faces several challenges. Firstly, there is the urge to reduce $CO_2$ emissions both as a consequence of the Paris Agreement and of the EU decarbonization policy goal of reaching carbon neutrality by 2050. Additionally, the recent disruptions in the energy and gas supply chains, consequent to the Russian invasion of Ukraine, caused food and fertilizer prices to increase and highlighted the importance of diversification for both the energy sources and suppliers.

In this context, alternative methods for NF are being studied. Among them, plasma-based NF is promising thanks to the possibility of selectively channeling the energy to the most efficient processes for the production of nitrogen compounds [11]. The best results have been thus far obtained for nitrogen oxidation from $N_2$ and $O_2$ into NO and $NO_2$, whose theoretical energy cost for non-thermal plasmas has been evaluated to be 0.2 MJ/mol N, lower if compared to $NO_2$ obtained through the SMR, HB and Ostwald processes combined from $N_2$ and natural gas [6].

Rotating gliding arc (RGA) plasmas and microwave discharges operating at atmospheric pressure are known to to be efficient for plasma-based NF because the reduced electric field at which they operate is optimal to transfer energy to excitation channels which are beneficial to break the triple bond in $N_2$ [12]. However, the current best results for these technologies are an order of magnitude higher than the theoretical lower energy cost. These include a RGA achieving an energy cost of 2.1 MJ/mol N and a $NO_x$ yield of 5.9 % [13], which performance was improved to 1.8 MJ/mol N by operating at 4 atm [14] and a microwave discharge operating at atmospheric pressure with an energy cost of 2.0 MJ/mol N and a $NO_x$ yield of 3.8 % [15]. Among the two, RGAs are considered relatively easier to upscale thanks to their simple design. These results were obtained without the introduction of catalysts which, if successfully implemented, could further reduce the energy cost as for dielectric barrier discharges [16]. Other types of plasma reactors are also subject of study. Most notably dielectric barrier discharges are also widely studied for gas conversion. However, for NF the current best result in terms of energy cost known to the authors is 18 MJ/mol N [17]. With the currently available technology, the main advantage of plasma-based NF is that the process can be implemented at a much smaller and local scale compared to HB-based fertilizer production plants [18, 19], thus reducing transportation costs. A recent noteworthy result was achieved with a pulsed plasma jet, achieving an energy cost of 0.42 MJ/mol N [20], although with a low $NO_x$ yield of 0.02% that would be an obstacle to the upscaling of the technology.

In this work, the $NH_4NO_3$ production cost in a hypothetical plasma-based facility is studied. The result is compared with a state of the art HB-based fertiliser facility. The requirements for such a hypothetical facility to be economically competitive are described taking into account capital expenditures, natural gas price evolution and energy production costs. Additional focus is put into understanding how transport costs and $CO_2$ emission allowances affect the results. As the comparison depends on many factors that can strongly vary with time, a sensitivity analysis is also presented to appreciate how the results can evolve due to different market conditions.

## 2. Methodology

Production costs can be divided into two main categories, capital expenditures (CapEx) and operational expenditures (OpEx). The CapEx mainly includes the expenditures to engineer, construct, maintain or improve physical assets such as, for example, properties, plants and equipment (PPE costs) of any kind. These are usually "one-time" expenses and their effect on the production cost is normalized by the $NH_4NO_3$ annual production ($P_a$) and its depreciation period ($d$), i.e. the number of years the asset is estimated to be able to operate. In this work, the following definition of (annual) CapEx [21], expressed in euro per metric ton of $NH_4NO_3$ ($€/t_{NH_4NO_3}$), is used:

$$CapEx = \frac{\text{PPE costs}[€]}{d[y] \cdot P_a\left[\frac{t_{NH_4NO_3}}{y}\right]} \cdot (1+r_p) + \frac{\text{M}\left[\frac{€}{y}\right]}{P_a\left[\frac{t_{NH_4NO_3}}{y}\right]} \quad (8)$$

where M is the annual maintenance cost and $r_p$ is the project interest rate. For both the plasma-based and SMR-HB fertilizer production facilities, a depreciation period of 20 years is assumed. It should be noted that this definition, for the sake of simplicity, does not take into account permits or legal costs. The annual maintenance cost (M) is usually assumed to be between 2 % and 5 % of the replacement asset value (RAV). In this work an intermediate estimation of 3 % is used. Additionally, as the prices for the PPE costs reported in this work, mainly account for plants and equipment, for the estimation of the maintenance costs the RAV is assumed to be, approximately equal to the PPE costs reported. $r_p$ is evaluated according to equation 9 [22]

$$r_p = \frac{r_c}{(1 - (1 + r_c)^{-d[y]})} \quad (9)$$

where $r_c$ is the cost of capital, which includes the costs of equity and debt. The $r_p$ is assumed to be a constant amount over an amount of years equal to $d$. In this work $r_c = 9\%$ is assumed [23], thus, resulting in an $r_p$ of 11%.

The estimations of the PPE costs discussed in this work are based either on cost reports for existing chemical facilities or from other feasibility studies. The PPE costs are then scaled according to the annual production $P_a$ according to equation 10 [21],

$$\frac{\text{PPE costs}}{(\text{PPE costs})_{ref}} = \left(\frac{P_a}{P_{a,ref}}\right)^c \quad (10)$$

where, the subscript $ref$ indicates the reference values and $c$ is the scaling exponent which depends on the type of chemical facility [21]. This work uses the values reported by Peters et al. [21] of 0.6 and 0.65 for the $HNO_3$ and $NH_4NO_3$ facilities, respectively. As for the $NH_3$ production step $P_a = P_{a,ref}$, equation (10) was not used in that case.

The OpEx includes the expenses for consumable goods. This work mainly focuses on electricity, natural gas and $CO_2$ emission allowances prices. The natural gas price is taken from the Dutch TTF index and expressed in €/MWh. The $CO_2$ emission allowances price considered is the current market price for a ton of $CO_2$ in the EU emission trading system (EU ETS). Table 1 summarizes the prices which are assumed in this work. As for electricity, the prices in European markets (EPEX, IPEX, OMIE) are generally higher and much more volatile than the reported energy production cost from renewable sources. Thus, this work considers the levelized cost of energy (LCOE) for photovoltaic plants (PV) as discussed and studied in an article by Sens et al. [24]. Among other renewable energy sources, on-shore and off-shore wind power generation are not included in the model as they are associated with a higher LCOE prediction for 2050

**Table 1**
Market prices for gas and $CO_2$ allowances assumed in this work.

| Parameter | unit | price | reference |
|---|---|---|---|
| Natural gas | €/MWh | 47.08 | Dutch TTF (01 mar 2023) |
| $CO_2$ allowances | €/$t_{CO_2}$ | 98.91 | EU ETS (01 mar 2023) |

**Table 2**
LCOE for photovoltaic electricity production in 2020 and the predictions for its evolution in 2030 and 2050.

| Parameter | LCOE (€/MWh) | reference |
|---|---|---|
| PV (2020) | 51 | [24, 25] |
| PV (2030 prediction) | 27 | [24] |
| PV (2050 prediction) | 19 | [24] |

[24]. The LCOE is defined as the sum of costs over the power plant lifetime normalized by the energy produced in the same timeframe. The values reported in the study are shown in table 2. Especially for small and localized producers this approximation offers a baseline for the evaluation of the energy cost. Its accuracy is influenced by the degree of electric self-sufficiency and the contract agreements on selling the energy in excess during the daytime, when PV production peaks, to the grid and buying it during nighttime. It should be noted that the PV LCOE should be intended as a reference on the minimum LCOE that is currently predicted for 2022. For this reason, the cost comparison discussed in section 5 treats the LCOE as a variable parameter. Additional entries that would affect the OpEx, such as salaries, are not included in the model.

## 3. Plasma nitrogen fixation setup

To synthesize $NH_4NO_3$, both $HNO_3$ and $NH_3$ are required. This work considers plasma NF to $NO_x$ as the first step for the production of both chemicals. The use of an RGA operating at atmospheric pressure is considered with an energy cost of 2.1 MJ/mol [13]. Such a system was tested with an input gas flow rate ranging from 1 slm to 10 slm and provided $NO_x$ concentrations up to 5.9 % when set at 2 slm. Two lower energy cost values were reported for plasma-based NF, as mentioned in the introduction, however, to simplify the CapEx evaluation, this work focuses on atmospheric pressure plasmas and chooses an RGA as it has a simpler and cheaper design. Nevertheless, in later sections, a range of energy costs is discussed to evaluate the, more general, requirements for plasma-based NF technology. Half of the produced $NO_x$ would follow a similar process to what has been discussed for SMR-HB facilities: the NO is further oxidized to $NO_2$ as described in equation 5 and then absorbed in an absorption column with a water sprayer to form $HNO_3$ according to equation 6. As for the plasma $NH_3$ synthesis, this work considers a setup proposed and tested by Hollevoet et al. in 2020 [26] and in 2022 [27], respectively, which is schematized in figure 1.

The RGA plasma exhaust is connected to a lean $NO_x$ trap where the produced $NO_x$ contained in the gas mixture is absorbed. The lean $NO_x$ trap is then fed with $H_2$ in $N_2$ carrier gas for the trapped $NO_x$ to be reduced to $NH_3$. A $Pt/BaO/Al_2O_3$ catalyst can be used in the lean $NO_x$ trap to favor the reduction to $NH_3$ [28].

$$3\,NO_2 + BaO \longrightarrow Ba(NO_3)_2 + NO \qquad (11)$$

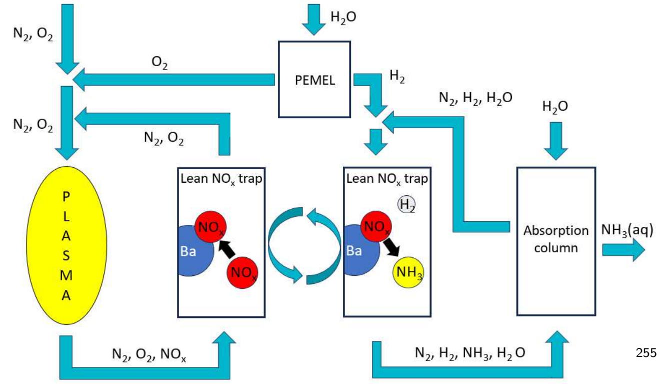


**Figure 1:** Scheme of the plasma-based production chain for the synthesis of $NO_x$ and $NH_3$, from the polymer exchange membrane electrolyzers (PEMEL) to the absorption column, readapted from [26, 27].

$$Ba(NO_3)_2 + 5\,H_2 \longrightarrow BaO + N_2 + 5\,H_2O \qquad (12)$$

$$Ba(NO_3)_2 + 8\,H_2 \longrightarrow BaO + 2\,NH_3 + 5\,H_2O \quad (13)$$

Where, according to the choice of the $Pt/BaO/Al_2O_3$ catalyst, the selectivity towards $NH_3$ can vary between 75% and 87%. However, as part of the $H_2$ is lost in $H_2O$, 4.6 mol $H_2$ are needed to produce 1 mol $NH_3$ [26]. Switching between a series of lean $NO_x$ traps is proposed in order to allow the system to operate continuously. The produced $NH_3$ can then be extracted as an aqueous solution in a spray column. Finally, $HNO_3$ and $NH_3$ would combine to form $NH_4NO_3$ following the same process used for SMR-HB facilities. In this work, water electrolysis is assumed to be used for $H_2$ production. The $O_2$ obtained as a byproduct can be used, together with air, as the gas feed input for the RGA because $O_2$-enriched air typically increases $NO_x$ yields and lowers the energy cost [13, 15, 29, 30, 31].

The work in which this setup is first proposed reports an energy cost of 4.61 MJ/mol $NH_3$, four times lower than the current best available technology for direct plasma-catalytic $NH_3$ synthesis [26]. This result can be lowered to 3.9 MJ/mol $NH_3$ if the use of a better performing RGA is assumed [13] and by including polymer exchange membrane electrolyzers (PEMEL) with 70 % efficiency. In terms of the final product, this would translate in 20.9 MWh/$t_{NH_4NO_3}$, of which 6.25 MWh are required for $H_2$ production and 14.6 MWh for NF. Further tests have been performed using a Soft Jet plasma [27] obtaining the lowest energy cost of 2.1 MJ/mol $NH_3$. However, such a result is currently limited by the relatively low $NO_x$ concentration and input gas flow rate, 0.12 % $NO_x$ and 0.2 L/m respectively. Thus, this result was not considered for this analysis due to concerns about its compatibility with high-scale production.

**Table 3**
Summary of the $NH_4NO_3$ production costs for a SMR-HB facility.

| name | price (€/$t_{NH_4NO_3}$) | references |
|---|---|---|
| CapEx (d = 20 years) | 131 | [7, 34] |
| Natural gas | 160 | [6, 7] |
| $CO_2$ allowances | 111 | [8, 7] |

Finally, the energy costs associated to the production of $HNO_3$ and $NH_4NO_3$ are estimated, according to different reports [32, 33], to be of the order of a few tens of kWh/$t_{NH_4NO_3}$ and are, thus, neglected.

## 4. Cost evaluation

### 4.1. SMR-HB facility

This work considers as a reference for comparison a SMR-HB facility with a $P_a$ of 2000 kt/year of $NH_4NO_3$, which corresponds to an $NH_3$ annual production of 850 kt/year. The price for the SMR and the $NH_3$ plants, according to evaluations from IEA's ammonia technology roadmap [7], can be estimated to be 1570 million €, which can increase by 380 million € if a CCS system is included. The price for

**Table 4**
Summary of the $NH_4NO_3$ production costs for the plasma NF-based facility discussed in this work. The electricity expenses are based on the LCOE for PV listed in table 2.

| name | price (€/$t_{NH_4NO_3}$) | references |
|---|---|---|
| CapEx (d = 20 years) | 288-342 | [9, 34, 35, 36, 37, 38] |
| Electricity ($PV_{2020}$ prediction) | 1060 | [13, 26] |
| ($PV_{2030}$ prediction) | 560 | [13, 26] |
| ($PV_{2050}$ prediction) | 395 | [13, 26] |

building the $HNO_3$ and the $NH_4NO_3$ plants is evaluated to be 1150 million €. Such an estimation is based on the reported upgrade costs for two existing facilities [34, 35] which have been adjusted for inflation and have been rescaled to meet the reference quota using equation 10. These contributions sum to 3100 million €, thus, using equation 8 the CapEx is estimated to be 131 €/$t_{NH_4NO_3}$.

The main contributor to the OpEx is natural gas as 0.49 MJ/*mol* N are currently required [6, 7]. Natural gas is used both as a feedstock for the SMR process and as a fuel for the facility. This translates into 3.4 MWh/$t_{NH_4NO_3}$ which, taking into account the price for natural gas, results in an OpEx contribution of 160 €/$t_{NH_4NO_3}$. Additional costs come from the $CO_2$, which is mainly emitted during the SMR process. Assuming a CCS system is implemented to reduce the $CO_2$ emissions, the estimation of the average $CO_2$ emissions per ton of $NH_4NO_3$ is 1.12 t according to the GREET 2021 database [8] which corresponds to an OpEx contribution of 111 €/$t_{NH_4NO_3}$ according to the EU ETS allowances price.

## 4.2. Plasma-based NF facility

In this work, a plasma-based facility with the setup discussed in section 3 is proposed. As previously stated, a hypothetical plasma-based fertilizer production facility would not require the upscaling needed for the typical SMR-HB plant to be economically advantageous. This, combined with the generally higher requirements in terms of energy, pushes for plasma alternatives to be more interesting on a small scale. Therefore a $P_a$ of 8000 t/year of $NH_4NO_3$ is used as reference. This quota would sustain between 30 and 100 $km^2$ of arable land. Considering that the average farm in the EU has an area of 0.17 $km^2$ [39], this would correspond to 180-600 average-sized farms. Such a reference quota was arbitrarily chosen as it would supply an area considered "local" by the authors. Based on the molar weights, such an amount would require 1700 t/year of $NH_3$ and 6300 t/year of $HNO_3$. As previously mentioned, 4.6 mol $H_2$ are required to produce 1 mol $NH_3$ [26] since, during the NO reduction to $NH_3$, part of the $H_2$ is lost due to conversion in $H_2O$ as shown in equations 12 and 13. In order to meet the production quota, 920 t/year of $H_2$ should be produced through water electrolysis. Using the higher heating value for $H_2$ (HHV = 142 MJ/kg) and assuming a production efficiency $\epsilon = 70\%$, a 5.9 MW electrolysis plant is required to meet the quota based on the following equation [40].

$$P[MW] = \frac{P_a(\mathrm{H_2})[\frac{t_{H_2}}{y}] \cdot HHV_{\mathrm{H_2}}[\frac{MJ}{kg}]}{\epsilon} \frac{1000}{365 \cdot 24 \cdot 3600} \tag{14}$$

where P is the power required and $P_a(H_2)$ is the $H_2$ production quota of $H_2$. If the use of PEMELs is assumed, the production price can be expected to be around 800 €/kW [36], resulting in a total price of 4.7 million €. This price per unit of power is based on a recent study by Reksten et al. [36] which analyses and models the price dependency of different water electrolyzer technologies as a function of the annual production and of the year of commission. As for the RGA, the main contribution to the CapEx comes from the power supply. Considering the scale of the facility, a wide price range between 0.9 €/W and 0.05 €/W is often assumed [9, 41]. However, the lowest reported price for a power supply was found to be 0.2 €/W for a 1 GW power supply [42]. The described facility would require 9200 t of $NO_2$ to be produced yearly, which corresponds to $2 \times 10^8$ mol N each year. Assuming the plant to be operational throughout the year and an energy consumption of 2.1 MJ/mol N, an average power of 13.3 MW is required. Considering the scale, a price of 0.4 €/W is assumed, resulting in 5.3 million € as the cost estimation for such power supply. As the cost of power supplies is an important component of the CapEx, it becomes clear how reducing energy cost for NF is crucial, not only to lower the OpEx but the CapEx as well, because a lower power supply would be required to meet the same quota. Finally, a small-sized plant for the synthesis of $HNO_3$ and $NH_4NO_3$ would be required. As the reports for a plant with an annual production close to the target quota are not available, the estimation is based on the downscaling, using equation 10, of facilities with an annual production which is of 3-4 orders of magnitude higher [34, 35] and, as such, might suffer from an overestimation. Additionally, as the plasma-based NF facility proposed would directly produce $NO_2$, the Oswald process, which is one of the two processes normally covered in an $HNO_3$ plant, is not necessary. From these considerations, a cost range between 17 and 22 million € is assumed. The costs for the RGA structure and the lean $NO_x$ trap are assumed to be negligible compared to the other prices listed. The sum of these contributions, which are summarized in table 5, give a PPE cost of 28.6-31.6 million € Using equation 8 a CapEx between 288 $€/t_{NH_4NO_3}$ and 342 $€/t_{NH_4NO_3}$ is estimated.

**Table 5**
Summary of the PPE costs for the plasma NF-based facility discussed in this work.

| name | PPE cost (million €) | references |
|---|---|---|
| Power supply | 5.3 | [9, 41, 42] |
| PEMEL | 4.7 | [36] |
| $NH_4NO_3$ plant | 17-22 | [34, 35] |

As listed at the end of section 3, the main contribution for the OpEx is electricity as, per ton of $NH_4NO_3$, 6.25 MWh are required for $H_2$ production and 14.6 MWh for NF. The OpEx is evaluated as the energy cost per ton of $NH_4NO_3$ times the LCOE. Therefore, the LCOE is of primary importance for the determination of the OpEx. If the photovoltaic generation LCOE in 2020 shown in table 2 is assumed, the OpEx would be approximately 1060 $€/t_{NH_4NO_3}$ which, alone, would not make plasma-based NF an interesting option in 2020 with the current performances. The cost predictions become more interesting as photovoltaic technology develops and the LCOE from renewable sources decreases. Using the LCOE listed in table 2, the OpEx would be expected to diminish to 560 $€/t_{NH_4NO_3}$ in 2030 and to 395 $€/t_{NH_4NO_3}$ in 2050. However, as previously mentioned, these energy costs should be considered as a lower limit for the OpEx as, in order to sustain a continuous $NH_4NO_3$ production, a mix of different energy sources, as well as a grid integration to sell the energy excesses and buy when needed, should be preferred. The implications of cheaper renewable energy are further discussed in section 5.

### 4.3. Transport costs analysis

Due to the large production scale, transportation costs for the final product to be delivered to retail sellers should be taken into account for the classical SMR-HB facility. This is not the case for the plasma-based NF facility since its production scale is meant to be sufficient to only meet the demand of the local farmers. The transport costs are based on a market report from Upply [43] which shows the relation between the average freight rate, expressed in €/km, and the journey length. As stated in the introduction, the typical HB-based plant can produce enough fertilizer to meet the demand of an order of magnitude of 100 000 km$^2$ of arable land. Thus, two typical distances of 100 km and 1000 km are studied to understand the effects of shipments on $NH_4NO_3$ prices. The average reported price is between 300 € and 1500 € for a standard 22t cargo [43], increasing the final price by 14 to 68 $€/t_{NH_4NO_3}$. The estimation presented might suffer from an underestimation as $NH_4NO_3$ requires additional safety procedures whose impact on the transport cost is difficult to quantify.

## 5. Cost comparison

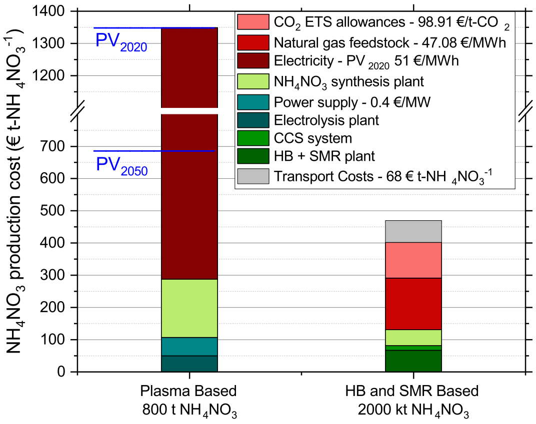


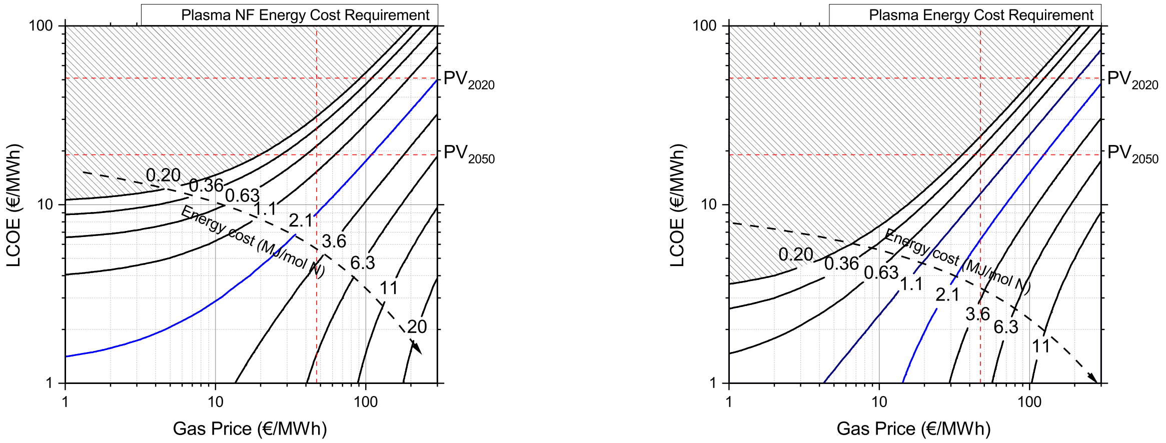
**Figure 2:** $NH_4NO_3$ production cost comparison using plasma-based NF and SMR-HB divided into its CapEx (green) and OpEx (red) components. With the 2050 predictions for the LCOE, the price for plasma-based NF would evolve to approximately half of the current estimation.

Figure 2 summarizes the costs per ton of $NH_4NO_3$. With the assumptions of this work, in both cases, the OpEx is responsible for most of the $NH_4NO_3$ production cost. While the CapEx is expected to be only slightly higher for a plasma-based facility, the Opex of the HB-based plant is currently expected to be lower by a factor of 4, effectively making plasma-based NF nonappealing even if transport costs are considered. As, for a hypothetical plasma-based NF facility, the largest contribution by far is due to the electricity, the OpEx needs to be reduced by improving the energy cost of plasma-based NF and by lowering the LCOE. While the predicted decrease in the LCOE from renewable sources would result already in a reduction of the production cost from 1348 to 683 $€/t_{NH_4NO_3}$ by 2050, the plasma-based NF production cost would still be higher with the current natural gas price.

More generally, as the LCOE from renewable sources is predicted to decrease and the natural gas price fluctuates, the plasma-based NF energy efficiency needed to obtain an economically competitive alternative evolves accordingly. This is shown in figures 3a and 3b where, for different values of the energy cost for plasma NF into $NO_x$, each line represents the LCOEs and gas prices for which the plasma NF-based $NH_4NO_3$ production cost is equal to its classical SMR-HB counterpart according to equation 15.

$$\begin{aligned} (CapEx + OpEx)_{plasma} &= \\ = (CapEx + OpEx)_{SMR-HB} &+ \text{transport costs} \end{aligned} \tag{15}$$

The transport cost is assumed to be 68 $€/t_{NH_4NO_3}$ in figure 3a and 14 $€/t_{NH_4NO_3}$ in figure 3b. The current gas price and photovoltaic LCOE, as in tables 1 and 2 respectively, are highlighted with a red dashed line. The current plasma NF energy cost is plotted in blue. The region that would require a plasma NF energy cost below its theoretical limit is excluded (upper left corner). It should be noted that the energy cost for



(a) (b)

**Figure 3:** LCOE required for Plasma NF $NH_4NO_3$ production cost to be equal to SMR-HB as a function of the gas price and for different plasma NF energy efficiencies (black contour lines). The blue contour line indicates the best plasma-based NF EC reported so far at atmospheric pressure [13], while the red dashed lines indicate the LCOE for 2020, its predicted evolution in 2050 and the current market price for natural gas. The transport costs are assumed to be 68 $€/t_{NH_4NO_3}$ (a) and 14 $€/t_{NH_4NO_3}$ (b).

NF also affects the CapEx by determining the requirements for the power supply.

The effect of the transport cost, as expected, becomes more noticeable as both the LCOE and gas prices decrease, especially as electricity is the main responsible for the production costs of a plasma-based NF facility. It should be noted, when discussing figures 3a and 3b, that the lower the LCOE and the gas price are, the more the model is sensitive to the assumptions done when evaluating the CapEx. From figure 3a considering the current plasma-based-NF performances (i.e. 2.1 MJ/mol N [13]), the hypothetical facility discussed in this work would be an economically viable alternative only if LCOE dropped to 9 €/MWh or if natural gas was sold at more than 300 €/MWh. This LCOE is a factor of five lower than the LCOE for PV electricity production in 2020 and approximately 50% lower than the LCOE for PV electricity production predicted for 2050, while the gas price of 300 €/MWh is at least six times higher than the current price. The result is worse if the lower extreme of the transport costs range proposed is considered, as in figure 3b, where the required LCOE would be 7 €/MWh. For the current market scenario, the implementation of the plasma-based setup proposed is thus not a viable option regardless of its energy cost. This is caused by the cost of $H_2$ production. While a SMR-HB facility requires 3 mol $H_2$ per mol of $NH_4NO_3$, for the proposed plasma facility 4.6 mol $H_2$ are required for the same amount of $NH_4NO_3$ despite producing only half of the $NH_3$ [26]. As it is clear by crossing the corresponding red dashed lines in figure 3a, however, based on the LCOE estimations of 2050 and a natural gas price of 47 €/MWh, an energy cost lower than approximately 0.8 MJ/mol N would allow plasma-based NF to be a viable alternative depending on the transport costs. This estimation assumes the same $CO_2$ allowances price. While the market value for the natural gas is hard to predict, the $CO_2$ allowances price is likely to increase according to the current EU carbon policy, effectively resulting in plasma-based NF to be favored on SMR-HB despite its higher energy cost.

### 5.1. HB electrification

If the market effectively evolves towards a scenario where the LCOE is consistently lower than the natural gas price, it is safe to assume that the fertilizer manufacturing industry will progressively electrify. With the current best available technology an energy cost of 0.59 MJ/mol N has been achieved [7, 44], corresponding to 4.1 $\mathrm{MWh}/t_{NH_4NO_3}$. According to IEA's ammonia technology roadmap [7] an electrified HB facility would require a similar investment as a classic SMR-HB one, resulting in the same CapEx for the two.

In such a scenario, $NH_4NO_3$ production costs for plasma-based NF and $HB_{el}$ should be compared. By studying the case in which the production costs are equal, described by equation 16, the energy cost requirement for plasma-based NF can be obtained as a function of the LCOE, as shown in figure 4.

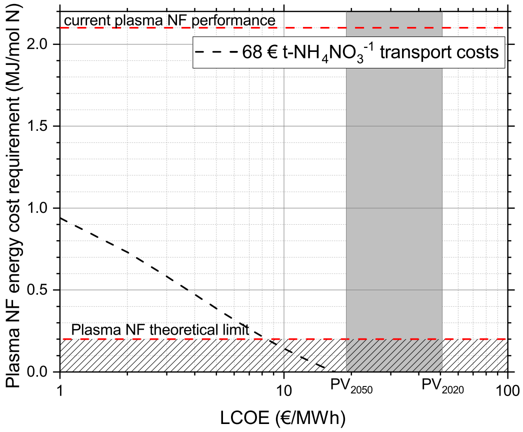


**Figure 4:** Plasma NF energy cost required for $NH_4NO_3$ production cost based on the discussed setup to be equal to $HB_{el}$ as a function of the LCOE.

$$\begin{aligned}(CapEx + OpEx)_{plasma} &= \\ = (CapEx + OpEx)_{HB_{el}} &+ \text{transport costs}\end{aligned} \tag{16}$$

Where, for the $HB_{el}$, transport cost 68 $€/t_{NH_4NO_3}$ is assumed. When expanding equation 16, it should be noted that the energy cost for NF also affects the requirements for the power supply, and thus the CapEx. This result shows that, with the current LCOE predictions for the upcoming decades and the assumptions made in this work, the proposed setup won't be able to provide an economically competitive source of $NH_4NO_3$ until the energy cost for plasma-based NF approaches its theoretical limit and in a scenario characterized by high transport costs. If the lower extreme for the transport costs of 14 $€/t_{NH_4NO_3}$ is assumed, which is not shown in figure 4, the $\mathrm{CapEx}_{plasma}$ alone would be higher than the $NH_4NO_3$ production cost with $HB_{el}$ and the transport costs.

Considering that the high amount of losses of $H_2$ in the catalytic process of the proposed design greatly affects the performance of a plasma-based NF facility, it can be interesting to study what are the requirements for a general small-scale plasma-based facility to produce economically competitive $NH_4NO_3$. As the CapEx would depend on the design, the condition described by equation 16 cannot be studied directly. Therefore, a case study can be proposed by assuming the same CapEx for the two facilities, thus, resulting in a comparison between the OpEx as in equation 17.

$$OpEx_{plasma} = OpEx_{HB_{el}} + \text{transport costs} \tag{17}$$

Both the transport costs of 14 $€/t_{NH_4NO_3}$ and 68 $€/t_{NH_4NO_3}$ are considered for the $HB_{el}$. From this equation, the energy cost required for the whole plasma-based NF facility (thus, including the cost for $H_2$ production) can be obtained and studied as a function of the LCOE as shown in figure 5. As expected, the impact of the transport costs on the plasma-based NF energy cost required becomes more noticeable

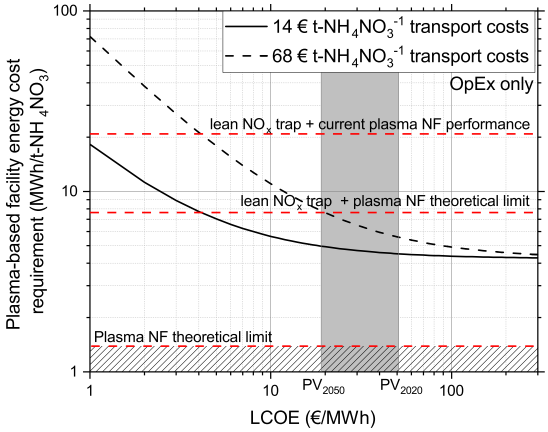


**Figure 5:** Energy cost required for a general plasma-based facility to equal the OpEx of an HB$_{el}$ facility as a function of the LCOE.

as the LCOE decreases. Considering the proposed scenario for 2050 energy production and if a transport cost of 68 €$/t_{NH_4NO_3}$ is assumed, it is shown that an energy cost below 8 MWh$/t_{NH_4NO_3}$ would be required for plasma-based NF alternatives to be economically viable. This, with the current LCOE predictions and in agreement with the results previously discussed with figure 4, with the implementation of a lean NO$_x$ trap, would only be possible when plasma-based NF reaches its theoretical limit for the energy cost. This highlights how, for the production of NH$_4$NO$_3$, optimizing the energy cost for plasma-based NF and limiting the losses of H$_2$ in the conversion from NO$_x$ to NH$_3$ are equally important.

As an alternative approach, the NO$_x$ to NH$_3$ conversion step could be avoided by combining plasma-based HNO$_3$ production with NH$_3$ from HB$_{el}$. In this context, a more encouraging result of 1.1-1.5 MJ/mol N was identified as the necessary energy cost range for plasma-based NF to be an economically viable alternative in another feasibility study by K. Rouwenhorst et. al. (in an update to ref. [37]).

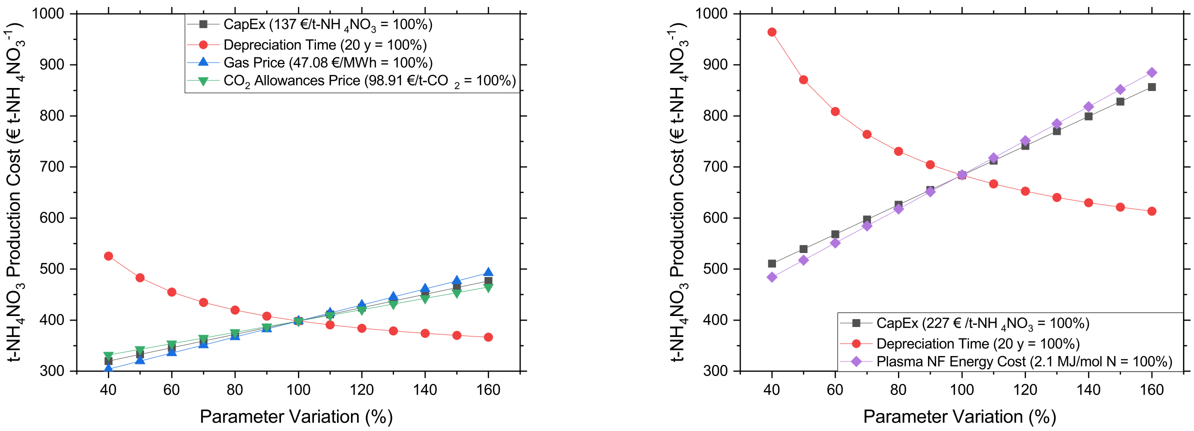
## 5.2. Sensitivity analysis

While the effects of the LCOE are discussed in the previous sections, the analysis presented in this work is based on assumptions on a different range of parameters that can vary or evolve with time: market prices are known to experience strong fluctuations in short time periods and assumptions on the CapEx and the depreciation time can vary based on the location and the year of commission. Therefore, a sensitivity analysis showing how the estimation of NH$_4$NO$_3$ production costs is affected by variation on the initial assumptions has been conducted and is shown in figures 6a and 6b for the classic SMR-HB and the plasma-based NF facilities respectively.

Unsurprisingly, figure 6a shows that production costs are strongly affected by a variation on the gas price, as a 50 % increase would cause the estimated production cost to increase by 19 % from 405 €$/t_{NH_4NO_3}$ to 483 €$/t_{NH_4NO_3}$. A similar effect is determined by a variation of CO$_2$ allowances price and of the CapEx, for which a 50 % increase would cause the final product cost estimation to increase by approximately 14 %. In figure 6b it can be seen that the effects of CapEx and depreciation time are milder in terms of relative increase or decrease on the plasma-based NF facility. However, this is due to the OpEx being responsible for most of the production and, in terms of absolute production cost variation, it is comparable with what is presented in figure 6a. For the same reason, the sensitivity on the energy cost for plasma NF is shown to be crucial, as a 50 % variation would affect the NH$_4$NO$_3$ production costs by up to 24%.

## 6. Conclusions

This work highlights that, in the current state of the art, plasma-based NF is not a viable alternative to the classic combination of HB and SMR due to the high OpEx caused



(a)

(b)

**Figure 6:** Sensitivity analysis of $NH_4NO_3$ production costs for a classical SMR-HB (a) and for a plasma NF-based (b) facility.

by the current energy cost of plasma-based NF and by the higher amount of $H_2$ required to form $NH_3$ from $NO_x$. This might change in a future scenario where a combination of cheaper LCOE and more expensive $CO_2$ allowances in the EU would push the fertilizer industry towards electrification. As a reference, the plasma NF theoretical limit would correspond to 1.39 $MWh/t_{NH_4NO_3}$ and only 2 $MWh/t_{NH_4NO_3}$ of $H_2$ are effectively converted into $NH_3$. This, if a more efficient $H_2$ use is obtained, would fix a milder goal for plasma-based NF compared to reaching the current $HB_{el}$ energy cost of 0.59 MJ/mol N, or even to approaching the theoretical limit of 0.2 MJ/mol N for the technology. In this scenario, plasma-based NF can be designed as a complementary technology to the HB in the $NH_4NO_3$ production industry, supplying regions where high transport costs are necessary for the fertilizer to be delivered.

Until then, alternative implementations of plasma-based NF should be investigated. As an example, plasma-based $NO_x$ production for $HNO_3$ could be combined with $HB_{el}$ to produce $NH_4NO_3$ [37]. Additionally, an application that is recently gaining interest is to combine plasma-based NF into $NO_x$ with $NH_3$ naturally released from manure, effectively avoiding the need for $H_2$ production to obtain $NH_4NO_3$ and tackling the problem of nitrogen air pollution and eutrophication [45, 46].

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