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Research paper

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 $0.2\,\mathrm{MJ/mol}$ N, lower than the current best available Haber-Bosch-based technology energy cost of $0.49\,\mathrm{MJ/mol}$ 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.

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 $60\,\mathrm{kg/ha}$ of N in the southern member states (Portugal, Italy, Greece and Spain) up to $200\,\mathrm{kg/ha}$ 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 ($9.756\,\mathrm{eV}$ bond dissociation energy [5]) it needs to 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

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as “nitrogen fixation” (NF). The demand for ammonia is met via the Haber-Bosch (HB) process, which requires N_2 and H_2.

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

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),

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

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. [6,7]. 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.

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

Then, NO is cooled and oxidized into NO_2,

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

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

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

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 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 fertilizer 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:

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

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

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]

maintenance costs the RAV is assumed to be, approximately equal to the PPE costs reported. r_p is evaluated according to Eq. (9) [22]

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

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 Eq. (10) [21],

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

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 $P_a = P_{a,ref}$, Eq. (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 [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 Eq. (5) and then absorbed in an absorption column with a water sprayer to form HNO_3 according to Eq. (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 Fig. 1.

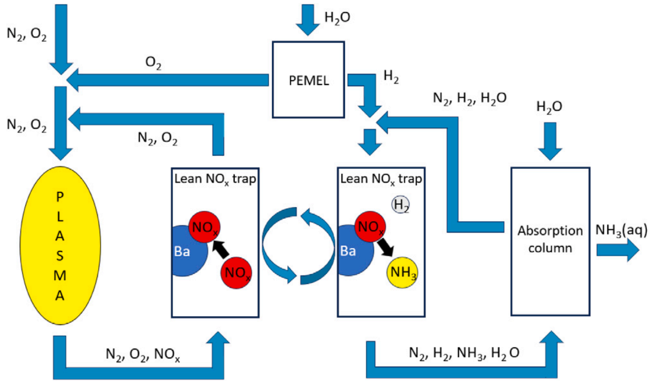


Fig. 1. Scheme of the plasma-based production chain for the synthesis of NO_x and NH_3, from the polymer exchange membrane electrolyzers (PEMEL) to the absorption column, readapted from [26,27].

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].

$$3NO_2 + BaO \longrightarrow Ba(NO_3)_2 + NO \tag{11}$$

$$Ba(NO_3)_2 + 5H_2 \longrightarrow BaO + N_2 + 5H_2O \tag{12}$$

$$Ba(NO_3)_2 + 8H_2 \longrightarrow BaO + 2NH_3 + 5H_2O \tag{13}$$

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 [13,15,29–31].

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

Table 3

Summary of the NH_4NO_3 production costs for a SMR-HB facility.

Name	Price ($e/t_{NH_4NO_3}$)	References
CapEx (d = 20 years)	131	[7,34]
Natural gas	160	[6,7]
CO_2 allowances	111	[7,8]

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.

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 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. The production costs for a SMR-HB facility are summarized in Table 3.

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 [36], 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 Eqs. (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 [37].

Table 4

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

Name	PPE cost (million €)	References
Power supply	5.3	[9,39,40]
PEMEL	4.7	[38]
NH_4NO_3 plant	17–22	[34,35]

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

where P is the power required and $P_a(\mathrm{H_2})$ 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 [38], 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. [38] 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 [9,39]. However, the lowest reported price for a power supply was found to be 0.2 €/W for a 1 GW power supply [40]. The described facility would require 9200 t of NO_2 to be produced yearly, which corresponds to 2×10^8 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 4, 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.

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. The production costs for a plasma NF-based

Table 5

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 $(e/t_{NH_4NO_3})$	References
CapEx (d = 20 years)	288–342	[9,34,35,38,42,43]
Electricity (PV_{2020} prediction)	1060	[13,26]
(PV_{2030} prediction)	560	[13,26]
(PV_{2050} prediction)	395	[13,26]

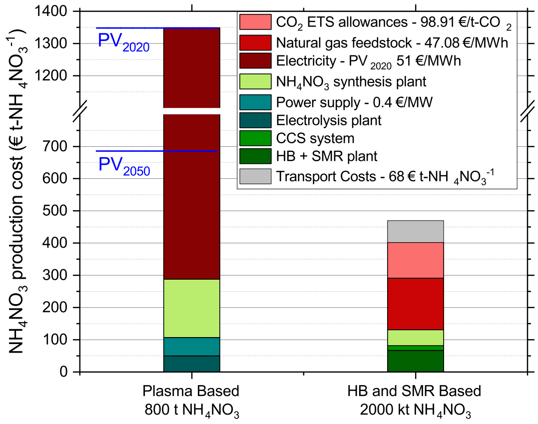


Fig. 2. NH_4NO_3 production cost comparison using plasma-based NF and SMR-HB divided into its CapEx (green) and OpEx (red) components. With the 2050 predictions for the LCOE, the price for plasma-based NF would evolve to approximately half of the current estimation.

facility are summarized in Table 5). 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 [41] 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 $100\,000\,\mathrm{km}^2$ of arable land. Thus, two typical distances of $100\,\mathrm{km}$ and $1000\,\mathrm{km}$ 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 [41], 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

Fig. 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 Figs. 3(a) and 3(b) 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 Eq. (15).

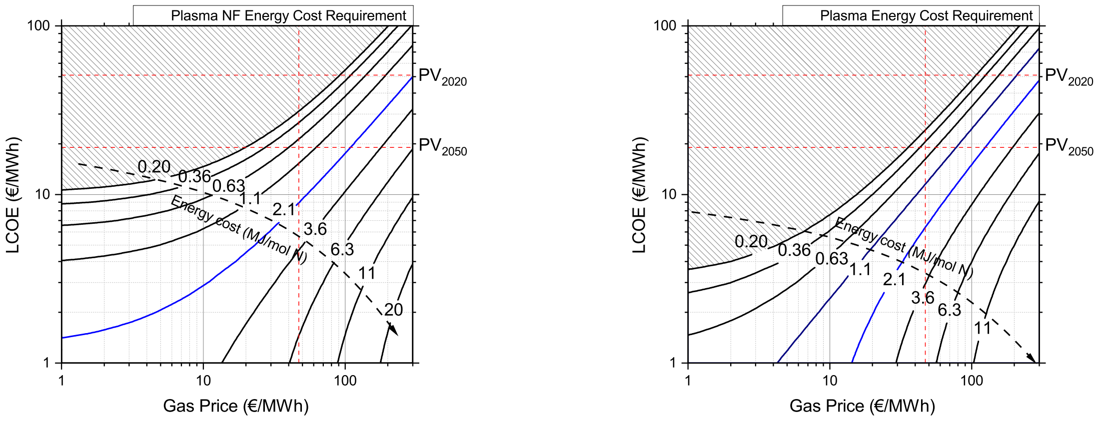
$$
\begin{aligned}
&(CapEx + OpEx)_{plasma} = \\
&= (CapEx + OpEx)_{SMR-HB} + \text{transport costs}
\end{aligned}
\tag{15}
$$

The transport cost is assumed to be 68 $€/t_{NH_4NO_3}$ in Fig. 3(a) and 14 $€/t_{NH_4NO_3}$ in Fig. 3(b). 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 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 Figs. 3(a) and 3(b), 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 Fig. 3(a) considering the current plasma-based-NF performances (i.e. $2.1\,\mathrm{MJ/mol}$ 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 Fig. 3(b), 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 Fig. 3(a), however, based on the LCOE estimations of 2050 and a natural gas price of 47 €/MWh, an energy cost lower than approximately $0.8\,\mathrm{MJ/mol}\ N$ 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 $0.59\,\mathrm{MJ/mol}$ 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



(a)

(b)

Fig. 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).

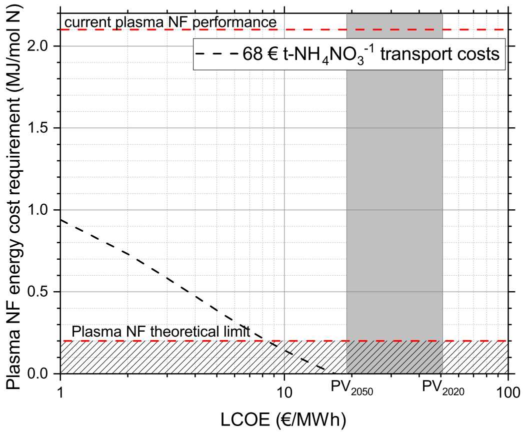


Fig. 4. Plasma NF energy cost required for NH_4NO_3 production cost based on the discussed setup to be equal to HB_{el} as a function of the LCOE.

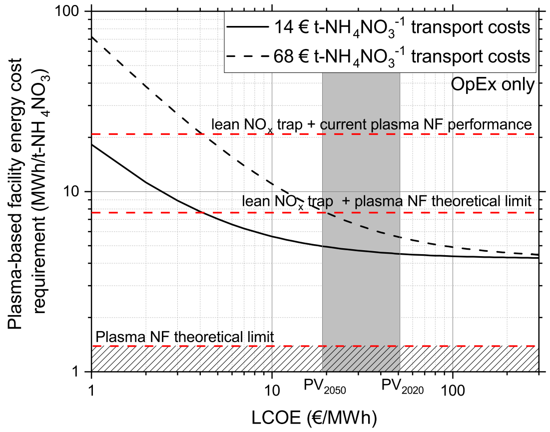


Fig. 5. Energy cost required for a general plasma-based facility to equal the OpEx of an HB_{el} facility as a function of the LCOE.

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 Eq. (16), the energy cost requirement for plasma-based NF can be obtained as a function of the LCOE, as shown in Fig. 4.

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

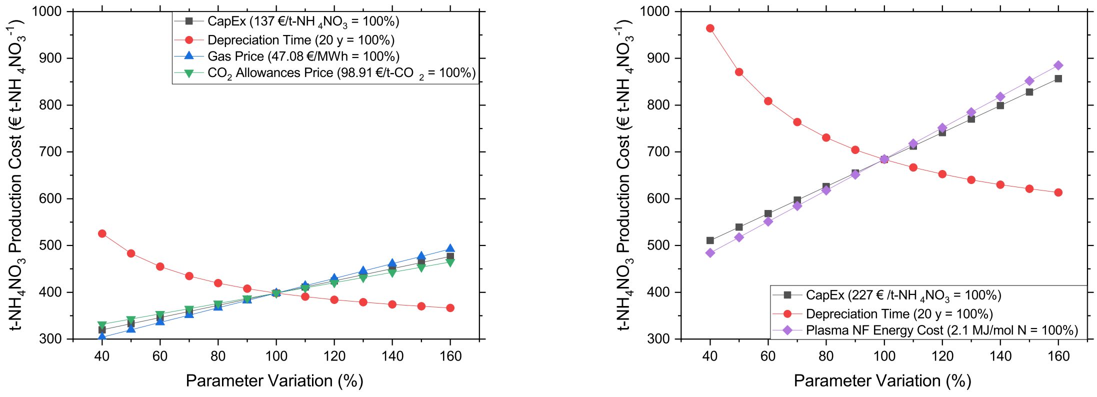
Where, for the HB_{el}, transport cost 68 $€/t_{NH_4NO_3}$ is assumed. When expanding equation (16), it should be noted that the energy cost for NF also affects the requirements for the power supply, and thus the CapEx. This result shows that, with the current LCOE predictions for the upcoming decades and the assumptions made in this work, the proposed setup will not 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 Fig. 4, the $CapEx_{plasma}$ 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 Eq. (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 Eq. (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 Fig. 5.

As expected, the impact of the transport costs on the plasma-based NF energy cost required becomes more noticeable 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 Fig. 4, with the implementation of a lean NO_x trap, would only be possible when plasma-based NF reaches its theoretical limit for



(a) (b)

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

the energy cost. This highlights how, for the production of NH_4NO_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. [42]).

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_4NO_3 production costs is affected by variation on the initial assumptions has been conducted and is shown in Figs. 6(a) and 6(b) for the classic SMR-HB and the plasma-based NF facilities respectively.

Unsurprisingly, Fig. 6(a) 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 Fig. 6(b) 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 Fig. 6(a). 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_4NO_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 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 [42]. 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].

CRediT authorship contribution statement

Filippo Manaigo: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Kevin Rouwenhorst:** Writing – review & editing, Methodology, Data curation. **Annemie Bogaerts:** Writing – review & editing, Supervision, Funding acquisition. **Rony Snyders:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

[1] Daramola DA, Hatzell MC. ACS Energy Lett 1493–501.

[2] Bloomberg. Fertilizer market to garner $251.57 Billion, globally, by 2030 at 3.55% CAGR, says allied market research. 2022, Bloomberg.

[3] Fertilizers Europe. Forecast of food, farming & fertilizer use in the European Union 2022–2032. Technical Report, Fertilizers Europe; 2022.

[4] Food and Agriculture Organization of the United Nations. FAOSTAT statistical database. 2023.

[5] Frost DC, McDowell CA, Bawn CEH. Proc R Soc Lond Ser A Math Phys Eng Sci 1956;236(1205):278–84.

[6] Cherkasov N, Ibhadon A, Fitzpatrick P. Chem Eng Process 2015;90:24–33.

[7] IEA. Ammonia technology roadmap. Technical Report, IEA; 2021.

[8] Wang M, Elgowainy A, Lu Z, Bafana A, Banerjee S, Benavides PT, et al. Greenhouse gases, regulated emissions, and energy use in technologies Model (2021 .Net). 2021, Computer Software.

[9] Rouwenhorst KHR, Lefferts L. Catalysts 2020;10(9).

[10] Clomburg JM, Crumbley AM, Gonzalez R. Science 2017;355(6320):aag0804.

[11] Patil B, Wang Q, Hessel V, Lang J. Catal 2015;256:49–66, Plasmas for enhanced catalytic processes (ISPCEM 2014).

[12] Bogaerts A, Neyts EC. ACS Energy Lett 2018;3(4):1013–27.

[13] Van Alphen S, Ahmadi Eshtehardi H, O'Modhrain C, Bogaerts J, Van Poyer H, Creel J, et al. Chem Eng J 2022;443:136529.

[14] Tsonev I, O'Modhrain C, Bogaerts A, Gorbanev Y. ACS Sustain Chem Eng 2023;11(5):1888–97.

[15] Kelly S, Bogaerts A. Joule 2021;5:3006–30.

[16] Zhang J, Li X, Zheng J, Du M, Wu X, Song J, et al. Energy Convers Manag 2023;293:117482.

[17] Patil B, Cherkasov N, Lang J, Ibhadon A, Hessel V, Wang Q. Appl Catal B 2016;194:123–33.

[18] Sarafraz MM, Tran NN, Nguyen H, Fulcheri L, Burton R, Wadewitz P, et al. J Adv Manuf Process 2021;3(2):e10081.

[19] Olabi A, Abdelkareem MA, Al-Murisi M, Shehata N, Alami AH, Radwan A, et al. Energy Convers Manage 2023;277:116594.

[20] Vervloessem E, Gorbanev Y, Nikiforov A, De Geyter N, Bogaerts A. Green Chem 2022;24:916–29.

[21] Peters M, Timmerhaus K, West R, Peters M. Plant design and economics for chemical engineers. fifth ed.. McGraw-Hill Education; 2002.

[22] Queensland Competition Authority. Issues in the application of annuities. 2014.

[23] Damodaran A. Cost of equity and capital (US). 2023, data retrieved from NYU Stern School of Business, https://pages.stern.nyu.edu/~adamodar/New_Home_Page/datafile/wacc.html.

[24] Sens L, Neuling U, Kaltschmitt M. Renew Energy 2022;185:525–37.

[25] IRENA: International Renewable Energy Agency. Renewable power generation costs in 2020. 2021.

[26] Hollevoet L, Jardali F, Gorbanev Y, Creel J, Bogaerts A, Martens JA. Angew Chem Int Edn 2020;59(52):23825–9.

[27] Hollevoet L, Vervloessem E, Gorbanev Y, Nikiforov A, De Geyter N, Bogaerts A, et al. ChemSusChem 2022;15(10):e202102526.

[28] Clayton RD, Harold MP, Balakotaiah V, Wan C. Appl Catal B 2009;90(3):662–76.

[29] Jardali F, Van Alphen S, Creel J, Ahmadi Eshtehardi H, Axelsson M, Ingels R, et al. Green Chem 2021;23:1748–57.

[30] Vervloessem E, Aghaei M, Jardali F, Hafezkhiabani N, Bogaerts A. ACS Sustain Chem Eng 2020;8(26):9711–20.

[31] Wang W, Patil B, Heijkers S, Hessel V, Bogaerts A. ChemSusChem 2017;10(10):2145–57.

[32] Environment Agency Austria - Umweltbundesamt. Production of ammonia, nitric acid, urea and N. fertilizer. 2017.

[33] Ammonia Energy Association. Renewable ammonia projects in Sub-Saharan Africa. 2021.

[34] Koranyi B. Norway's Yara to spend $220 million to rebuild, expand Swedish plant. 2014,

[35] Luck P. World fertilizer magazine. 2021.

[36] EUROSTAT. Farms and farmland in the European Union - statistics. 2022.

[37] Lettenmeier P. Ammonia technology roadmap. Technical Report, Siemens; 2021.

[38] Reksten AH, Thomassen MS, Møller-Holst S, Sundseth K. Int J Hydrogen Energy 2022;47(90):38106–13.

[39] van Rooij GJ, Akse HN, Bongers WA, van de Sanden MCM. Plasma Phys Control Fusion 2017;60(1):014019.

[40] Noordende H, Ripson P. Gigawatt green hydrogen plant, State-of-the-art design and total installed capital costs. Technical Report, Intitute for Sustainable Process Technology; 2020.

[41] Upply. The European road freight rate development benchmark Q2. 2020.

[42] Rouwenhorst KHR, Jardali F, Bogaerts A, Lefferts L. Energy Environ Sci 2021;14:2520–34.

[43] Osorio-Tejada J, van't Veer K, Long NVD, Tran NN, Fulcheri L, Patil BS, et al. Energy Convers Manag 2022;269:116095.

[44] Smith C, Hill AK, Torrente-Murciano L. Energy Environ Sci 2020;13:331–44.

[45] Graves DB, Bakken LB, Jensen MB, Ingels R. Plasma Chem Plasma Process 2019;39:1–19.

[46] Ingels R. Nitrogen enrichment of organic fertilizers with nitrate and air plasma. 2020, Canadian Patent 3116999.