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## RESEARCH ARTICLE

# A new route towards green ammonia synthesis through plasma-driven nitrogen oxidation and catalytic reduction

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Supporting information for this article is given via a link at the end of the document.

**Abstract:** Ammonia is an industrial large volume chemical, with its main application in fertilizer production. It also attracts increasing attention as a green energy vector. Over the past century, ammonia production has been dominated by the Haber-Bosch process, in which a mixture of nitrogen and hydrogen gas is converted to ammonia at high temperatures and pressures. Haber-Bosch processes with natural gas as source of hydrogen are responsible for a significant share of the global CO<sub>2</sub> emissions. Processes involving plasma are currently investigated as an alternative for decentralized ammonia production powered by renewable energy sources. In this work, we present the PNOORA process (Plasma Nitrogen Oxidation and Catalytic Reduction to Ammonia), combining plasma-assisted nitrogen oxidation and Lean NO<sub>x</sub> Trap technology, adopted from diesel engine exhaust gas aftertreatment technology. PNOORA achieves an energy requirement of 4.6 MJ/mol NH<sub>3</sub>, which is an over 4-fold energy reduction compared to the state-of-the-art plasma-enabled ammonia synthesis from N<sub>2</sub> and H<sub>2</sub> with reasonable yield (>1%).

## Introduction

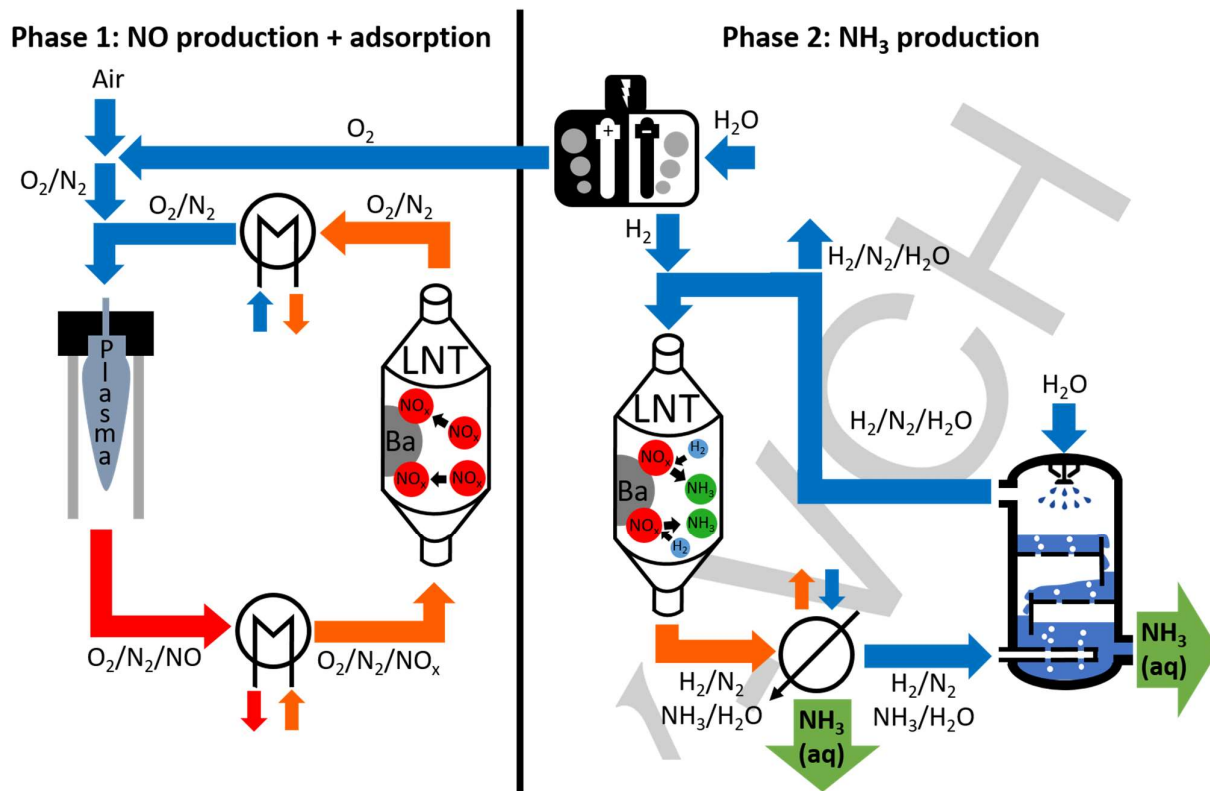
Ammonia is one of the most important globally produced chemicals. It is an essential fertilizer in agriculture and a crucial building block in chemical and pharmaceutical industries. It also emerges as an alternative carbonless renewable fuel.<sup>[1]</sup> The industrial production of ammonia via the Haber-Bosch process amounts to ca. 150 million tons annually. The Haber-Bosch process operated with natural gas results in ca. 1.5 kg CO<sub>2</sub> production per 1 kg of NH<sub>3</sub>.<sup>[2]</sup> Therefore, greener, more sustainable routes towards ammonia production are actively investigated.<sup>[3]</sup> The use of “green”, “blue” or “turquoise” hydrogen in the Haber-Bosch process is an option.<sup>[4,5]</sup> Alternatively, electrification of ammonia synthesis can be achieved with electrocatalysis<sup>[6]</sup> or with plasma technology. Plasma is an ionized gas which consists of electrons, ions, neutral gas molecules, excited molecular species, radicals and atoms, and photons.<sup>[7]</sup> The vast interest in plasma is due to their unique properties. Plasma generates highly reactive species which facilitate N<sub>2</sub> fixation, can be operated under atmospheric pressure,

and can be powered with renewable electricity, which makes it perfectly suited for decentralized and intermittent production.<sup>[8]</sup> The recent advances in employing plasma discharges for NH<sub>3</sub> production are related to direct plasma-driven reaction of N<sub>2</sub> with H<sub>2</sub><sup>[9]</sup>, or even using H<sub>2</sub>O instead of H<sub>2</sub>.<sup>[10,11]</sup> Plasma-assisted (e.g. plasma-electrochemical<sup>[12]</sup> and, especially, plasma-catalytic<sup>[9,13]</sup>) processes have been proposed to enhance the performance. In plasma catalysis a catalyst is introduced in the plasma reactor to favor the desired reaction.

The synthesis of NH<sub>3</sub> from N<sub>2</sub> and H<sub>2</sub> is thermodynamically favored. However, due to sluggish kinetics, large amounts of energy are currently required to activate the relatively inert N<sub>2</sub> molecule. Plasma could overcome this problem, because the applied electric energy mainly heats up the light electrons, which will activate the N<sub>2</sub> molecules by electron impact dissociation, ionization and excitation, creating N atoms, ions and excited species, which easily react into other compounds, such as NH<sub>3</sub>. However, the current state-of-the-art of plasma-catalytic NH<sub>3</sub> synthesis clearly indicates that it suffers from a major drawback: an apparent compromise between either low energy consumption or a large concentration of ammonia in the reaction product. Nevertheless, this is not a physical law, but rather the situation in the current state-of-the-art. More fundamental research, both experimental and computational, is needed to overcome the current limitations.

NH<sub>3</sub> yields in excess of 10 % are accompanied by high energy consumptions exceeding 80 MJ/mol NH<sub>3</sub>.<sup>[14]</sup> A plasma process with a relatively low energy consumption of 2 MJ/mol NH<sub>3</sub>, being close to that of the Haber-Bosch process, (0.52-0.81 MJ/mol<sup>[15-18]</sup>) yields a very diluted NH<sub>3</sub> product (<0.1 vol%).<sup>[19]</sup> The recovery of NH<sub>3</sub> from such a diluted product mixture would be very challenging and highly energy intensive. The lowest reported energy cost with a reasonable yield (1.4 %) is 18.6 MJ/mol NH<sub>3</sub>.<sup>[20]</sup> A low ammonia concentration in the reactor outlet can increase dramatically the overall energy consumption of the ammonia synthesis process. Anastasopoulou *et al.*<sup>[21]</sup> quantified this energy penalty. For a mixture with 1 vol% NH<sub>3</sub>, the energy needed for NH<sub>3</sub> separation from such a diluted gas mixture is in the range of the energy consumption of the Haber-Bosch process (0.54 MJ/mol NH<sub>3</sub>).<sup>[21]</sup>

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**Figure 1:** PNO CRA process, with its two phases: Phase 1: Plasma-assisted  $N_2$ -oxidation, followed by  $NO_x$  adsorption on a Lean  $NO_x$  trap (LNT); Phase 2: Catalytic operation of the LNT to reduce the adsorbed  $NO_x$  with  $H_2$  to  $NH_3$  and followed by  $NH_3$  extraction with water. Temperatures: Red = 1100 °C, Orange = 175 °C and Blue = 40 °C.

The high energy demand of plasma-driven  $NH_3$  synthesis in its current state calls for an alternative approach.

In this work, we propose the PNO CRA process (Plasma Nitrogen Oxidation and Catalytic Reduction to Ammonia): a novel process, combining plasma with engine exhaust gas after-treatment technologies to overcome the inefficiency of plasma processes for ammonia synthesis. Plasma is suited very well for oxidation reactions, rather than chemical reduction. Therefore, in the proposed process,  $N_2$  is first oxidized to  $NO_x$ , and reduced subsequently to  $NH_3$  using concepts from the automotive industry where ammonia is synthesized aboard of vehicles for abating  $NO_x$  emissions from exhaust gases. The operation of PNO CRA is simulated, based on previously published experimental data on fertilizer production with the old plasma process from the early 20<sup>th</sup> century (Birkeland-Eyde process<sup>[22]</sup>) and of Lean  $NO_x$  Traps from literature.<sup>[23]</sup>

## Results and Discussion

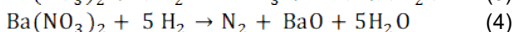
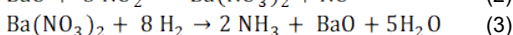
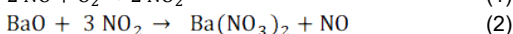
The first commercially successful approach to plasma-driven oxidation of  $N_2$  to  $NO$  for the production of nitrogen-based fertilizers was the Birkeland-Eyde process.<sup>[22,24]</sup> An electric arc was formed between two coaxial electrodes, consisting of water-cooled copper tubes, and powered by a high voltage (5 kV) alternating current at mains frequency (50 Hz). The arc was spread into a disc of a few cm thick and about 1.8 m in diameter, through a strong static magnetic field ( $\sim 0.45$  T  $cm^2$ ) generated by an electromagnet placed at right angles to the electrodes. Air was driven past both sides of the disc. The gas stream leaving the refractive reactor at about 1100 °C contained between 1 and 2%

of  $NO$ .<sup>[25]</sup> The exhaust gas was allowed to pass through waste-heat boilers for the generation of steam used to operate turbo-generators for the (re)production of electrical energy. In the next step, oxidation of  $NO$  to form  $NO_2$  took place in a very large oxidation chamber at a slow rate. The oxide leaving the economizers at about 200 °C was further cooled to 50 °C in cooling towers, because the absorption rate increases with decreasing temperature. The gas was brought in intimate contact with water, and nitric acid ( $HNO_3$ ) was formed through the reaction  $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$ . One-third of the  $NO_2$  reacting with water reverts to  $NO$  which had to be re-oxidized. Therefore, oxidation and re-oxidation of the liberated gas took place until it was completely absorbed. The resulting product contained about 30% concentrated nitric acid.<sup>[26]</sup> The energy consumption of the Birkeland-Eyde process was about 2.4 MJ/mol  $NO$ .<sup>[27]</sup>

Besides the electric arc-based Birkeland-Eyde process, other concepts have been investigated for the formation of  $NO_x$  from air, e.g. radio-frequency discharge<sup>[28]</sup>, DC plasma jet<sup>[29]</sup>, lasers<sup>[30]</sup>, glow discharge<sup>[31]</sup>, dielectric barrier discharge<sup>[32]</sup>, gliding arc discharge<sup>[33–36]</sup>, and microwave discharge<sup>[37–40]</sup>. The energy consumption varies a lot among the different plasma types, i.e. from 0.3 up to 1600 MJ/mol  $NO_x$ . The lowest energy cost (0.3 MJ/mol  $NO_x$ ) was reported for low pressure microwave plasma with magnetic field (so-called electron cyclotron resonance).<sup>[39]</sup> However, this low value for energy cost only accounts for the plasma power and not for the energy-intensive process of reactor cooling. Among the atmospheric pressure plasma reactors, gliding arc plasmas have shown the most promising results, up to 2 %  $NO_x$  yield and down to 2.8 MJ/mol energy consumption<sup>[33–36]</sup>.

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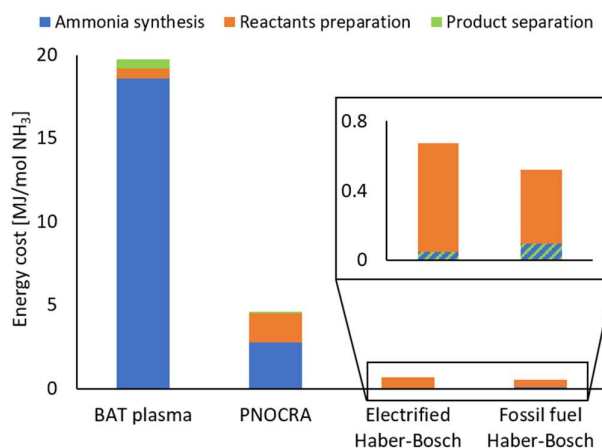
Converting NO<sub>x</sub> selectively to NH<sub>3</sub> can be done conveniently with a hydrogenation catalyst. The problem to be dealt with here is the presence of large quantities of unreacted oxygen from air leaving the plasma reactor. Separation of NO<sub>x</sub> and O<sub>2</sub> is needed to save hydrogen in the hydrogenation step. The automotive industry has dealt with a similar problem, namely the reduction of NO<sub>x</sub> to nitrogen in the exhaust of lean burn engines operating with excess air. The so-called "Lean NO<sub>x</sub> Trap" has a dual function and is operated in a cyclic mode. It has the ability to selectively adsorb NO<sub>x</sub> from a gas mixture in presence of O<sub>2</sub>, and to reduce this adsorbed NO<sub>x</sub> to N<sub>2</sub> catalytically under reducing conditions in the second phase of the cycle. Such a catalyst typically consists of barium oxide on γ-alumina washcoat, supporting finely dispersed platinum. It is mounted on a cordierite honeycomb monolith to minimize pressure resistance<sup>[41]</sup>. There the aim is to reduce NO<sub>x</sub> to N<sub>2</sub> rather than NH<sub>3</sub> in the present case, but that is a matter of the selectivity of the hydrogenation catalyst. The desired reactions are given in Eqs. 1-4.



Some Lean NO<sub>x</sub> traps produce NH<sub>3</sub> as main product. Clayton *et al.*<sup>[23]</sup> studied three samples of Pt/BaO/Al<sub>2</sub>O<sub>3</sub> catalyst, with a different degree of Pt dispersion. They reported the highest selectivity of 87 % towards NH<sub>3</sub> for the lowest Pt dispersion. Other publications also reported a selectivity towards NH<sub>3</sub> of 75 % and higher for a variety of Pt/BaO/Al<sub>2</sub>O<sub>3</sub> catalysts<sup>[42-44]</sup>.

The coupling of plasma and Lean NO<sub>x</sub> Trap units and the organization of the two-phase PNO CRA process is illustrated in Figure 1. In Phase 1, an O<sub>2</sub>/N<sub>2</sub> gas mixture such as air is supplied to the plasma reactor operated at 1100 °C, where it is partly converted to NO. At this temperature NO is the thermodynamically favored NO<sub>x</sub> compound, while upon cooling part of it may be oxidized to the more stable NO<sub>2</sub>. The gas exiting the plasma reactor is sent through a heat exchanger, where it is cooled to 175 °C, a temperature suited for NO<sub>x</sub> adsorption, as well as for subsequent NH<sub>3</sub> synthesis on the Pt/BaO/Al<sub>2</sub>O<sub>3</sub> Lean NO<sub>x</sub> Trap (Eq. 3).<sup>[45]</sup> At this reduced temperature, part of the NO reacts spontaneously to NO<sub>2</sub>, forming an NO<sub>x</sub> mixture (NO+NO<sub>2</sub>), both compounds of which being adsorbed. At the end of Phase 1, the Lean NO<sub>x</sub> Trap is saturated with NO<sub>x</sub>. A Lean NO<sub>x</sub> Trap very efficiently adsorbs NO<sub>x</sub> from the gas stream resulting in negligibly low residual NO<sub>x</sub> concentrations.<sup>[41,46]</sup> During Phase 2, the Lean NO<sub>x</sub> Trap is fed with H<sub>2</sub> to perform the reduction of the trapped NO<sub>x</sub> to NH<sub>3</sub> (Eq. 3). This H<sub>2</sub> can be produced via electrolysis of water with renewable electricity. The oxygen produced in the electrolysis unit serves as feed for the plasma reactor to enhance the O<sub>2</sub> content of intake air. The original Birkeland-Eyde process simply used air as feed for the plasma reactor, but previous research showed an increased O<sub>2</sub> concentration can increase the NO<sub>x</sub> yield of the reactor.<sup>[35,36]</sup>

The reaction products are cooled to 40 °C to enable the extraction of ammonia with liquid water. This can be done effectively in a spray column or a multistage scrubber column. Recycling of gases from the Lean NO<sub>x</sub> trap is foreseen to maximize the use of H<sub>2</sub>. In this way the H<sub>2</sub> concentration on the Lean NO<sub>x</sub> Trap during regeneration can be kept high, and above 50 mol% at the inlet of the Lean NO<sub>x</sub> trap to facilitate the reduction of the stored NO<sub>x</sub>.



**Figure 1:** Energy consumption of the current Best Available Technology (BAT) for plasma-catalytic NH<sub>3</sub> production,<sup>[19]</sup> the PNO CRA process, the electrified Haber-Bosch process with H<sub>2</sub> production through electrolysis<sup>[9]</sup> and the natural based Haber-Bosch process with H<sub>2</sub> production through Steam Methane Reforming<sup>[15]</sup>.

Part of the gas stream is purged to avoid build-up of inert N<sub>2</sub> in the process loop, formed in the Lean NO<sub>x</sub> Trap through Eq. 4.

In automotive industry, a Lean NO<sub>x</sub> Trap is typically operated in cycles with a 60 s lean phase (Phase 1) and a 10 s rich phase (Phase 2)<sup>[23,44]</sup>. It is however inconvenient to restart the plasma reactor and electrolyzer so frequently. This problem can be addressed by installing several Lean NO<sub>x</sub> Traps in parallel. For instance, seven units in total, with six operating in Phase 1 and one operating in Phase 2, a continuous operation is ensured by switching an NO<sub>x</sub>-saturated Lean NO<sub>x</sub> Trap to Phase 2 every 10 s. The process variables and the energy consumption of PNO CRA were estimated, based on the performance of the original Birkeland-Eyde process<sup>[22]</sup> and available literature on Lean NO<sub>x</sub> Trap technology.<sup>[23,41,43,46]</sup> Details of the methodology are provided in the Supporting Information.

The simulation suggested an NH<sub>3</sub> concentration of 6.3 mol% at the gas inlet of the extraction column is realistic. At a temperature of 40 °C, this limits the maximum achievable concentration of NH<sub>3</sub> in the liquid outlet to 3.3 mol%, estimated using Henry's law.<sup>[47]</sup> To ensure a sufficient driving force for NH<sub>3</sub> to move to the liquid phase, the concentration at the liquid outlet was set at 3 mol% or 1.67 mol/L. As NH<sub>3</sub> is a weak base, the pH increases from 7 at the liquid inlet to 11.6 at the liquid outlet.

If desired, pure ammonia can be obtained in a distillation step downstream. A 10-stage distillation column functioning at atmospheric pressure was designed in *Aspen Plus V11*. The condenser of the distillation column consumes 0.13 MJ/mol NH<sub>3</sub> of cooling energy, supplied at -33 °C. The reboiler consumes 0.2 MJ/mol NH<sub>3</sub> of heat, supplied at 99 °C. This heat can easily be supplied by one of the heat exchangers present in the PNO CRA process. A detailed description of the column and its operation parameters is provided in the Supporting Information. PNO CRA contains essentially three energy-consuming unit-operations: (i) the plasma reactor, (ii) the electrolyzer for reactant production (H<sub>2</sub> and O<sub>2</sub>), and (iii) the NH<sub>3</sub> extraction step followed by distillation to produce pure NH<sub>3</sub>. The contribution of the different unit operations is visualized in Figure 2. The plasma reactor is responsible for the major part of the energy cost (60 %), followed by the electrolyzer (37 %), while the separation of the NH<sub>3</sub> only takes up a small part of the energy consumption (3 %).

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The total energy consumption of PNO CRA is estimated at 4.61 MJ/mol NH<sub>3</sub>.

The current BAT (Best Available Technology) for plasma-catalytic NH<sub>3</sub> synthesis from H<sub>2</sub> and N<sub>2</sub> has an energy cost of 18.6 MJ/mol NH<sub>3</sub> and a yield of 1.4 %.<sup>[20]</sup> Adding the energy consumption of reactants production (0.51 MJ/mol NH<sub>3</sub>) and product separation (0.54 MJ/mol NH<sub>3</sub>) results in a total energy consumption of 19.65 MJ/mol NH<sub>3</sub> as shown in Figure 2.<sup>[21]</sup> The energy consumption of PNO CRA is an over 4-fold reduction, compared to the current BAT for plasma-based NH<sub>3</sub> synthesis.

Provided the selectivity of the Lean NO<sub>x</sub> Trap catalyst for ammonia, that according to literature was considered to be 87 %<sup>[23]</sup>, can be enhanced, and the Birkeland-Eyde plasma reactor, which design dates from 1906, is optimized, the overall energy requirements of PNO CRA can be reduced even further.

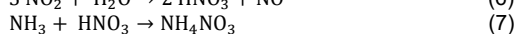
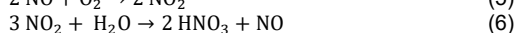
The quantity of Lean NO<sub>x</sub> Trap-catalyst required for PNO CRA seems realistic. Forzatti *et al.* reported an NO<sub>x</sub> storage capacity of 345 μmol/g at 150 °C for a Pt/BaO/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>[43]</sup> Implemented in PNO CRA, this corresponds to 59 g catalyst for an NH<sub>3</sub> production of 1 mol/h, or a WHSV (Weight Hourly Space Velocity) of 0.29, which is realistic for a heterogeneous catalytic process.

Despite this significant reduction of energy need of this plasma-driven ammonia synthesis process, the energy need of PNO CRA is still about 4.5 times higher than for the electrified Haber-Bosch process (0.70 MJ/mol<sup>[51]</sup>) where H<sub>2</sub> is produced through H<sub>2</sub>O electrolysis, and up to 9 times higher than the traditional fossil fuel-based Haber-Bosch process (0.52-0.81 MJ/mol<sup>[15-18]</sup>) where H<sub>2</sub> is produced through steam methane reforming. However, the Haber-Bosch process is only cost-efficient at a very large scale. Most Haber-Bosch plants produce 300,000 to 600,000 ton/year, with some even up to 1,000,000 ton/year.<sup>[48]</sup> PNO CRA is scalable and very well suited for a decentralized small to medium scale ammonia production, e.g. close to farms, eliminating transport costs for fertilizers.<sup>[49]</sup>

A nitrogen oxidation plasma reactor can operate at feed gas flow rates starting from 10 L/min<sup>[36]</sup>, a Lean NO<sub>x</sub> Trap can be scaled to virtually any size and the equipment for ammonia extraction can handle flow rates starting from a few L/min<sup>[50]</sup>. PNO CRA therefore enables decentralized NH<sub>3</sub> production starting at a scale below 1 ton/year.

Furthermore, the two heat exchangers (Figure 1, Phase 1) and the condenser (Figure 1, Phase 2) allow the recovery of a large part of the invested energy as heat, e.g. for the heating of greenhouses.

Because the PNO CRA process employs both nitrogen oxidation to NO<sub>x</sub> and reduction to NH<sub>3</sub>, it is particularly well suited for decentralized ammonium nitrate fertilizer production. While around 80 % of the globally produced NH<sub>3</sub> is used for the production of N-fertilizers, only 3 % is used directly as fertilizer.<sup>[51]</sup> One of the most common fertilizers is ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), accounting for 43 % of N-fertilizers<sup>[52]</sup>. Besides using NO<sub>x</sub> from the plasma reactor for ammonia synthesis as described above, NO<sub>x</sub> can also be used to react with O<sub>2</sub> (Eq.5) and H<sub>2</sub>O (Eq. 6) to form an aqueous solution of nitric acid, just like in the original Birkeland-Eyde process<sup>[22]</sup>. When this solution is used for the extraction of NH<sub>3</sub> in Phase 2 (Figure 1), ammonium nitrate is formed (Eq. 7).



The use of NO<sub>x</sub> plasma reactors for decentralized ammonium nitrate production by reacting the NO<sub>x</sub> with ammonium present in manure to decrease the use of fossil fuel based N-fertilizer is already documented as an economically viable option.<sup>[53]</sup> Similarly, the PNO CRA process could contribute to replacing fossil fuel based N-fertilizers in an economic way.

PNO CRA is a disruptive alternative technology to the fossil-fuel based Haber-Bosch process, and its implementation would go along with industrial and market transformation. Likely one technology currently cannot be disruptive enough. Thus, the integration of a combination of innovative concepts, each with their own strengths and weaknesses is required to complement electrified Haber-Bosch processes for centralized ammonia production. PNO CRA is one of these new pieces of the CO<sub>2</sub>-neutrality puzzle.

## Conclusion

To summarize, we propose the PNO CRA process for small scale green ammonia production. PNO CRA has no intrinsic CO<sub>2</sub> footprint and runs on air, water and renewable electricity. It is a new, energy-efficient route towards plasma-driven NH<sub>3</sub> synthesis involving plasma oxidation of N<sub>2</sub> and catalytic conversion of temporarily stored NO<sub>x</sub> to NH<sub>3</sub> in a Lean NO<sub>x</sub> Trap in a two-phase cyclic process. The energy performance of PNO CRA is significantly better than for the previously reported plasma-based NH<sub>3</sub> production, directly from N<sub>2</sub> and H<sub>2</sub>. The new process is attractive especially for small and medium-scale decentralized ammonia synthesis and offers unique opportunities for decentralized production of ammonium nitrate fertilizers.

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**Keywords:** Green ammonia • Haber-Bosch • Lean NO<sub>x</sub> Trap • Nitrogen fixation • Plasma chemistry

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