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

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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_2 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 PNOCRA process (Plasma Nitrogen Oxidation and Catalytic Reduction to Ammonia), combining plasma-assisted nitrogen oxidation and Lean NO_x Trap technology, adopted from diesel engine exhaust gas aftertreatment. PNOCRA achieves an energy requirement of 4.6 MJ/mol NH_3, which is an over 4-fold energy reduction compared to the state-of-the-art plasma-enabled ammonia synthesis from N_2 and H_2 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.[1] The industrial production of ammonia via the Haber-Bosch process amounts to ca. 150 million tons annually. The Haber-Bosch (H-B) process operated with natural gas results in ca. 1.5 kg CO_2 production per 1 kg of NH_3.[2] Therefore, greener, more sustainable routes towards ammonia production are actively investigated.[3] The use of "green", "blue" or "turquoise" hydrogen in the H-B process is an option.[4,5] Alternatively, electrification of ammonia synthesis can be achieved with electrocatalysis[6] 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.[7] The vast interest in plasma is due to their unique properties. Plasma generates highly reactive species which facilitate N_2 fixation, can be operated under atmospheric pressure, and can be powered with renewable electricity, which makes it perfectly suited for decentralized and intermittent production.[8] The recent advances in employing plasma discharges for NH_3 production are related to direct plasma-driven reaction of N_2 with H_2[9], or even using H_2O instead of H_2.[10,11] Plasma-assisted (e.g. plasma-electrochemical [12] and, especially, plasma-catalytic [9,13]) 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_3 from N_2 and H_2 is thermodynamically favored. However, due to sluggish kinetics, large amounts of energy are required to activate the relatively inert N_2 molecule. Plasma could overcome this problem, because the applied electric energy mainly heats up the light electrons, which will activate the N_2 molecules by electron impact dissociation, ionization and excitation, creating N atoms, ions and excited species, which easily react into other compounds, such as NH_3. However, the current state-of-the-art of plasma-catalytic NH_3 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. NH_3 yields in excess of 10 % are accompanied by high energy consumptions exceeding 80 MJ/mol NH_3.[14] A plasma process with a relatively low energy consumption of 2 MJ/mol NH_3, being close to that of the H-B process, (0.52-0.81 MJ/mol[15–18]) yields a very diluted NH_3 product (<0.1 vol%).[19] The recovery of NH_3 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_3.[20]

A low ammonia concentration in the reactor outlet can increase dramatically the overall energy consumption of the ammonia synthesis process. Anastasopoulou *et al.*[21] quantified this energy penalty. For a mixture with 1 vol% NH_3, the energy needed for NH_3 separation from such a diluted gas mixture is in the range of the energy consumption of the H-B process (0.54 MJ/mol NH_3).[21]

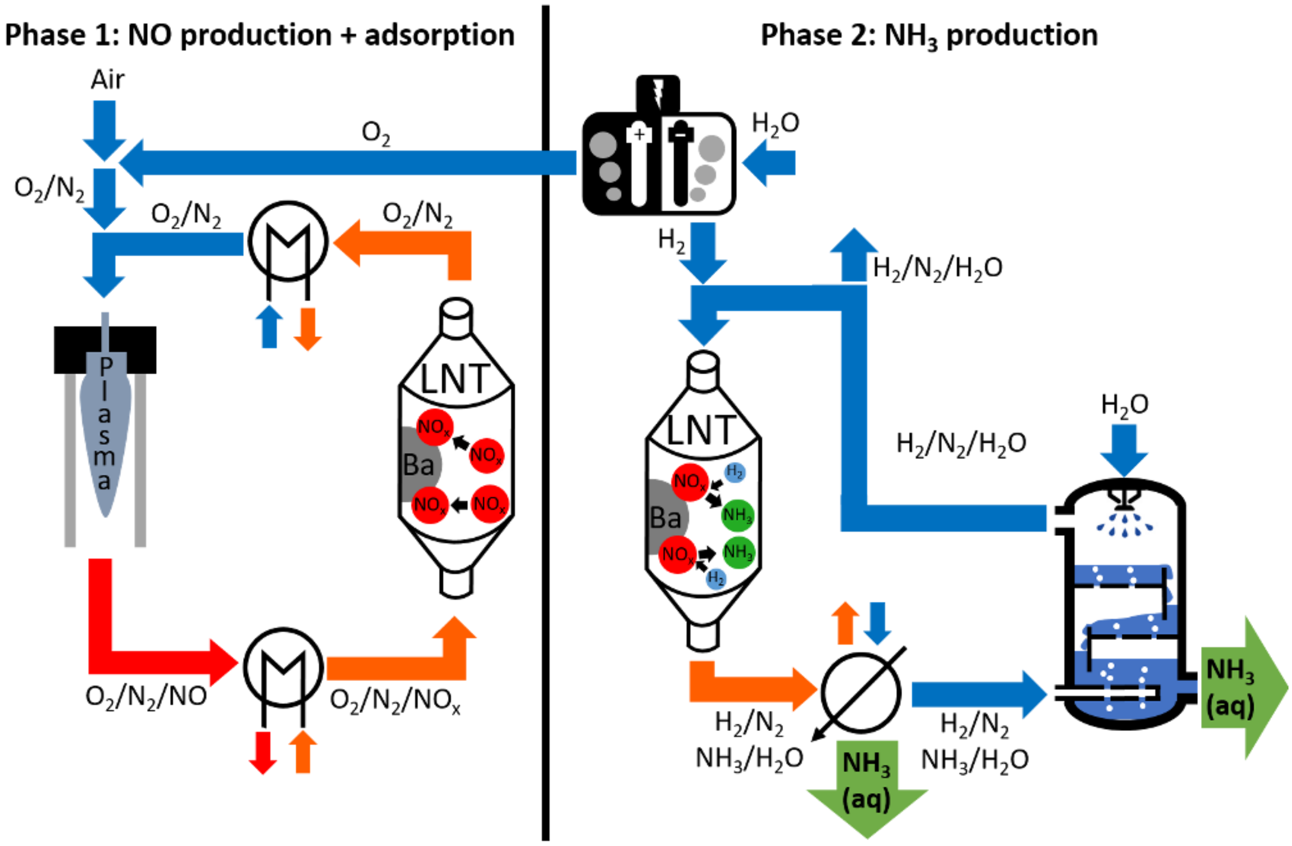

Figure 1: PNOCRA process, with its two phases: Phase 1: Plasma-assisted N_2-oxidation, followed by NO_x adsorption on a Lean NO_x trap (LNT); Phase 2: Catalytic operation of the LNT to reduce the adsorbed NO_x with H_2 to NH_3 and followed by NH_3 extraction with water. Temperatures: Red = 800-1100 °C, 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 PNOCRA 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 PNOCRA is simulated, based on previously published experimental data on fertilizer production with the old plasma process from the early 20th century (Birkeland-Eyde process[22]) and of Lean NO_x Traps.[23]

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.[22,24] 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 (~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.[25] 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.[26] The energy consumption of the Birkeland-Eyde process was about 2.4 MJ/mol NO.[27]

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[28], DC plasma jet[29], lasers[30], glow discharge[31], dielectric barrier discharge[32], gliding arc discharge[33–36], and microwave discharge[37–40]. 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).[39] 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[33–36].

Converting NO_x selectively to NH_3 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_x and O_2 is needed to save hydrogen in the hydrogenation step. The automotive industry has dealt with a similar problem, namely the reduction of NO_x to nitrogen in the exhaust of lean burn engines operating with excess air. The so-called “Lean NO_x Trap” has a dual function and is operated in a cyclic mode. It has the ability to selectively adsorb NO_x from a gas mixture in presence of O_2, and to reduce this adsorbed NO_x to N_2 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[41]. There the aim is to reduce NO_x to N_2 rather than NH_3 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.

$$2\,NO + O_2 \rightarrow 2\,NO_2 \quad (1)$$
$$BaO + 3\,NO_2 \rightarrow Ba(NO_3)_2 + NO \quad (2)$$
$$Ba(NO_3)_2 + 8\,H_2 \rightarrow 2\,NH_3 + BaO + 5H_2O \quad (3)$$
$$Ba(NO_3)_2 + 5\,H_2 \rightarrow N_2 + BaO + 5H_2O \quad (4)$$

Some Lean NO_x traps produce NH_3 as main product. Clayton *et al.*[23] studied three samples of $Pt/BaO/Al_2O_3$ catalyst, with a different degree of Pt dispersion. They reported the highest selectivity of 87 % towards NH_3 for the lowest Pt dispersion. Other publications also reported a selectivity towards NH_3 of 75 % and higher for a variety of $Pt/BaO/Al_2O_3$ catalysts[42–44].

The coupling of plasma and Lean NO_x Trap units and the organization of the two-phase PNOCRA process is illustrated in Figure 1. In Phase 1, an O_2/N_2 gas mixture such as air is supplied to the plasma reactor operated at 800-1100 °C, where it is partly converted to NO. At this temperature NO is the thermodynamically favored NO_x compound. The gas exiting the plasma reactor is sent through a heat exchanger, where it is cooled to 175 °C, a temperature suited for NO_x adsorption as well as for subsequent NH_3 synthesis on the $Pt/BaO/Al_2O_3$ Lean NO_x Trap (Eq. 3).[45] At this reduced temperature, part of the NO reacts spontaneously to NO_2, forming an NO_x mixture ($NO+NO_2$). At the end of Phase 1, the Lean NO_x Trap is saturated with NO_x. A Lean NO_x Trap very efficiently adsorbs NO_x from the gas stream resulting in negligibly low residual NO_x concentrations.[41,46] During Phase 2, the Lean NO_x Trap is fed with H_2 to perform the reduction of the trapped NO_x to NH_3 (Eq. 3). This H_2 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_2 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_2 concentration can increase the NO_x yield of the reactor.[35,36]

The reaction products are cooled to 40 °C to enable the extraction of ammonia with liquid water. This can be done effectively in a spay column or a multistage scrubber column. Recycling of gases from the Lean NO_x trap is foreseen to maximize the use of H_2. In this way the H_2 concentration on the Lean NO_x Trap during regeneration can be kept high, and above 50 mol% at the inlet of the Lean NO_x trap to facilitate the reduction of the stored NO_x.

Part of the gas stream is purged to avoid build-up of inert N_2 in the process loop, formed in the Lean NO_x Trap through Eq. 4.

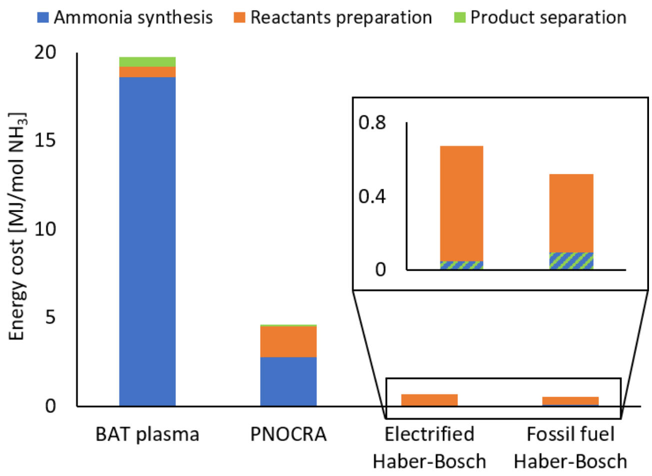

Figure 1: Energy consumption of the current Best Available Technology (BAT) for plasma-catalytic NH_3 production,[19] the PNOCRA process, the electrified Haber-Bosch process with H_2 production through electrolysis[5] and the natural based Haber-Bosch process with H_2 production through Steam Methane Reforming[15].

In automotive industry, a Lean NO_x Trap is typically operated in cycles with a 60 s lean phase (Phase 1) and a 10 s rich phase (Phase 2)[23,44]. It is however inconvenient to restart the plasma reactor and electrolyzer so frequently. This problem can be addressed by installing several Lean NO_x 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_x-saturated Lean NO_x Trap to Phase 2 every 10 s. The process variables and the energy consumption of PNOCRA were estimated, based on the performance of the original Birkeland-Eyde process[22] and available literature on Lean NO_x Trap technology.[23,41,43,46] Details of the methodology are provided in the Supporting Information.

The simulation suggested an NH_3 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_3 in the liquid outlet to 3.3 mol%, calculated by Henry's law[47]. To ensure a sufficient driving force for NH_3 to move to the liquid phase, the concentration at the liquid outlet was set at 3 mol% or 1.67 mol/L. As NH_3 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_3 of cooling energy, supplied at -33 °C. The reboiler consumes 0.2 MJ/mol NH_3 of heat, supplied at 99 °C. This heat can easily be supplied by one of the heat exchangers present in the PNOCRA process. A detailed description of the column and its operation parameters is provided in the Supporting Information.

PNOCRA contains essentially three energy-consuming unit-operations: (i) the plasma reactor, (ii) the electrolyzer for reactant production (H_2 and O_2), and (iii) the NH_3 extraction step followed by distillation to produce pure NH_3. 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_3 only takes up a small part of the energy consumption (3 %). The total energy consumption of PNOCRA is estimated at 4.61 MJ/mol NH_3.

The current BAT (Best Available Technology) for plasma-catalytic NH_3 synthesis from H_2 and N_2 has an energy cost of 18.6 MJ/mol NH_3 and a yield of 1.4 %.[20] Adding the energy consumption of reactants production (0.51 MJ/mol NH_3) and product separation (0.54 MJ/mol NH_3) results in a total energy consumption of 19.65 MJ/mol NH_3 as shown in Figure 2.[21] The energy consumption of PNOCRA is an over 4-fold reduction, compared to the current BAT for plasma-based NH_3 synthesis.

Provided the selectivity of the Lean NO_x Trap catalyst for ammonia, that according to literature was considered to be 87 %[23], can be enhanced, and the Birkeland-Eyde plasma reactor, which design dates from 1906, is optimized, the overall energy requirements of PNOCRA can be reduced even further.

The quantity of Lean NO_x Trap-catalyst required for PNOCRA seems realistic. Forzatti *et al.* reported an NO_x storage capacity of 345 µmol/g at 150 °C for a $Pt/BaO/Al_2O_3$ catalyst.[43] Implemented in PNOCRA, this corresponds to 59 g catalyst for an NH_3 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 PNOCRA is still about 4.5 times higher than for the electrified H-B process (0.70 MJ/mol[5]) where H_2 is produced through H_2O electrolysis, and up to 9 times higher than the traditional fossil fuel-based H-B process (0.52-0.81 MJ/mol[15–18]) where H_2 is produced through steam methane reforming. However, the H-B process is only cost-efficient at a very large scale. Most H-B plants produce 300,000 to 600,000 ton/year, with some even up to 1,000,000 ton/year.[48] PNOCRA 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.[49]

A nitrogen oxidation plasma reactor can operate at feed gas flow rates starting from 10 L/min[36], a Lean NO_x Trap can be scaled to virtually any size and the equipment for ammonia extraction can handle flow rates starting from a few L/min[50]. PNOCRA therefore enables decentralized NH_3 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 PNOCRA process employs both nitrogen oxidation to NO_x and reduction to NH_3, it is particularly well suited for decentralized fertilizer production. While around 80 % of the globally produced NH_3 is used for the production of N-fertilizers, only 3 % is used directly as fertilizer[51]. One of the most common fertilizers is ammonium nitrate (NH_4NO_3), accounting for 43 % of N-fertilizers[52]. Besides using NO_x from the plasma reactor for ammonia synthesis as described above, NO_x can also be used to react with O_2 (Eq.5) and H_2O (Eq. 6) to form an aqueous solution of nitric acid, just like in the original Birkeland-Eyde process[22]. When this solution is used for the extraction of NH_3 in Phase 2 (Figure 1), ammonium nitrate is formed (Eq. 7).

$$2\,NO + O_2 \rightarrow 2\,NO_2 \quad (5)$$

$$3\,NO_2 + H_2O \rightarrow 2\,HNO_3 + NO \quad (6)$$

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \quad (7)$$

NO_x plasma reactors for decentralized ammonium nitrate production by reacting the NO_x with ammonium present in manure to decrease the use of fossil fuel based N-fertilizer already today are an economically viable option.[53] Similarly, the PNOCRA process could contribute to replacing fossil fuel based N-fertilizers in an economic way.

PNOCRA 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 H-B processes for centralized ammonia production. PNOCRA is one of these new pieces of the CO_2-neutrality puzzle.

Conclusion

To summarize, we propose the PNOCRA process for small scale green ammonia production. PNOCRA has no intrinsic CO_2 footprint and runs on air, water and renewable electricity. It is a new, energy-efficient route towards plasma-driven NH_3 synthesis involving plasma oxidation of N_2 and catalytic conversion of temporarily stored NO_x to NH_3 in a Lean NO_x Trap in a two-phase cyclic process. The energy performance of PNOCRA is significantly better than for the previously reported plasma-based NH_3 production, directly from N_2 and H_2. 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_x Trap • Nitrogen fixation • Plasma chemistry

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