Current Status of Non-Thermal Plasma (NTP) Ammonia Synthesis and Its Potential to Build a Sustainable Nitrogen Fixation Industry

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Abstract

Ammonia has far more sustainable applications than use as a fertilizer. For instance, ammonia's rich hydrogen content makes it ideal for use in chemical fuel cells, as a clean-burning transportation fuel, and many other off-grid power applications. Currently, large-scale ammonia synthesis is achieved via the Haber-Bosch process, a high temperature and high-pressure technique for nitrogen fixation. Unfortunately, the extreme conditions required for the Haber-Bosch method make the process inefficient, and demand that production be highly centralized. These intrinsic characteristics place significant limitations on the nitrogen fixation industries ability to explore alternative and sustainable uses for ammonia. Therefore, it is critical to introduce and develop a sustainable nitrogen fixation process that can be carried out at low temperature and pressure and can be decentralized. Non-thermal plasma (NTP) technology allows for the synthesis of ammonia at low temperature and pressure. Furthermore, it has been proposed that the moderate process conditions can potentially allow the wide distribution of ammonia and hydrogen production sites, which are powered by renewable energy. In this study, we present an overview of the technology, and some of the most recent development on the NTP ammonia synthesis from the interdisciplinary perspective. Analysis and recommendations will be made on the potential of changing the ammonia production industry using this technology, leading to further discussions on how a closer interdisciplinary collaboration could improve the current plasma-assisted ammonia production and contribute to a sustainable nitrogen fixation infrastructure.

Keywords: Non-thermal plasma, ammonia synthesis, nitrogen fixation, distributed production

Introduction

The agricultural industry's use of ammonia as a fertilizer is a well-known practice. Unfortunately, ammonia's potential as a renewable and environmentally friendly means of energy storage is not common knowledge. Specifically, ammonia is a simple and stable molecule whose complete combustion releases a significant amount of energy in a carbon-free and greenhouse gas-free process. While the ammonia's potential as a fuel source is intriguing, the application of this idea is inhibited by inefficiencies in the current method of industrial ammonia synthesis, the Haber-Bosch process. The Haber-Bosch process is a Nobel Prize winning chemical synthesis process, which relies on high temperature and high-pressure conditions (up to 400 atm and 600C) to synthesize ammonia. These extreme conditions require a significant amount of energy input (1-2% of the world's annual energy production) (Tanabe & Nishibayashi, 2013), which results in large greenhouse gas emissions. Furthermore, the extreme conditions demand that the process be highly centralized, which prevents small industries and farms from producing ammonia locally in an economically viable manner. As a result, farmers have to store large amounts of ammonia on site, much of which becomes waste and pollution. Additionally, the centralized production of ammonia requires additional energy input, as the nitrogen fertilizers are shipped to the end use site.

Therefore, researchers have been developing a method of ammonia synthesis, which occurs under low temperature and low-pressure conditions. In this manner, the process would circumvent many of the issues associated with the Haber-Bosch process. It is believed that non-thermal plasma (NTP) technology may provide a method of synthesizing ammonia under low temperature and low-pressure conditions. The term plasma describes a fully or partially ionized gas, rich in reactive chemical species, and represents the fourth fundamental state of matter. In general, NTP technology has low operational/maintenance costs, can operate under a broad range of pressures (vacuum, atmospheric, high pressure), and requires limited amounts of space. A recent study showed that non-thermal plasma was found to have the lowest theoretical energy requirement among the different ammonia production methods, such as the conventional Haber-Bosch process, thermal plasma, biological production, and Haber-Bosch with renewable hydrogen inputs (Cherkasov, Ibhadon, & Fitzpatrick, 2015). In this study, the current development on the NTP ammonia synthesis approach will be presented, along with an analysis of the future perspectives of how this approach should be incorporated into the distributed and sustainable ammonia production/nitrogen fixation infrastructure.

Plasma systems and catalysts

Figure 1 shows an illustrative diagram of how NTP-based ammonia synthesis works. The systems for the NTP ammonia synthesis approach generally consist two parts, the plasma generation system and the plasma reactor. Plasma is produced by ionizing gas under high intensity electric field or electromagnetic field (microwave) conditions. For plasma generated by electric field, the primary purpose of the plasma generation system is to provide a high frequency and high-voltage electrical signal to the plasma reactor. To convert the off-grid signal into what is required to form plasma, a step-up transformer is required to increase the voltage. An inverter is usually added prior to the transformer to provide a stable high frequency pulsed/continuous alternating

(AC)/direct (DC) current signal. Note that this setup only applies to the plasma generated by strong electric fields. Other types of plasma, for example microwave, uses electromagnetic waves to excite and ionize the gas, which requires different generating mechanisms.

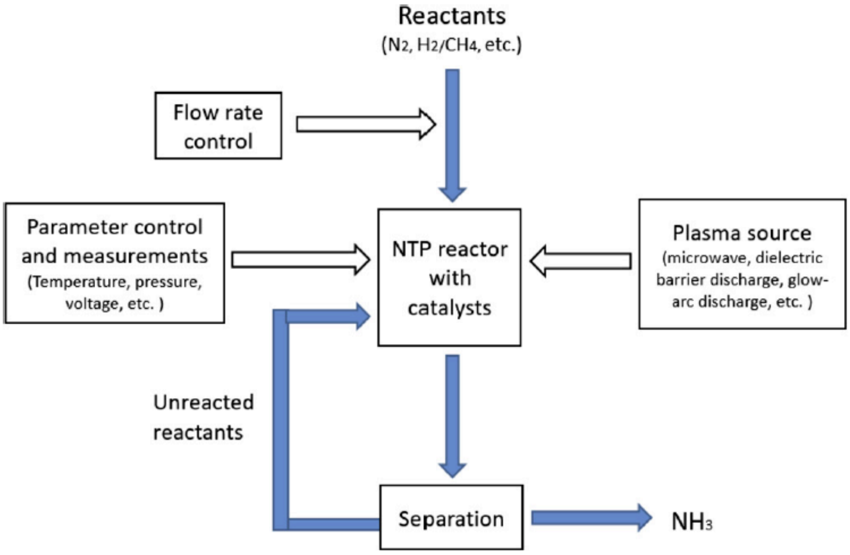

Figure 1 An illustrative flow diagram of the non-thermal plasma ammonia synthesis process. Re-printed from Peng, Chen, Schiappacasse et al. 2018 (Journal of Cleaner Production), with permission from Elsevier.

There are many types of plasma reactors that can be powered by the high intensity electric fields, including dielectric barrier discharge (DBD) plasma, gliding arc discharge plasma, corona discharge plasma, etc. The different types of plasma reactors and catalysts studied on/before 2018 for the NTP ammonia synthesis processes can be found in detail in the previous review articles (Hong, Prawer, & Murphy, 2017; Peng, Chen, Schiappacasse, et al., 2018). To summarize, the DBD plasma is the most commonly used discharge method, shown in Figure 2. Due to the fact that it has a dielectric barrier between the high voltage and ground electrodes, it can produce a uniform microfilament discharge and can be operated under atmospheric conditions with relatively small temperature rise.

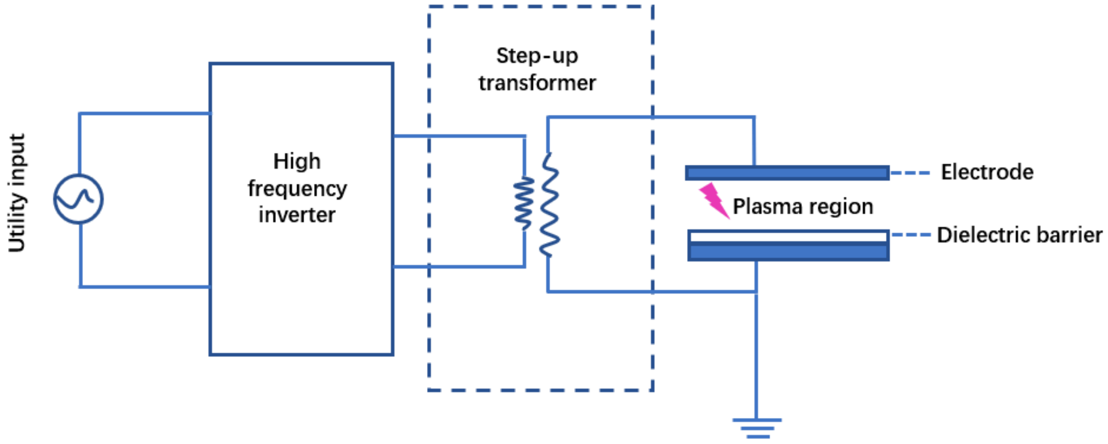

Figure 2. A simplified diagram of NTP systems, using dielectric barrier discharge as an example

The catalyst used for the NTP ammonia synthesis is critical to the system. As summarized in Hong, Prawer, & Murphy (2017) and Peng, Chen, Schiappacasse et al. (2018), many types of catalyst, for example ruthenium-based, nickel-based, iron-based, and Mg-based catalysts have been explored (Hong, Prawer, et al., 2017; Peng, Chen, Schiappacasse, et al., 2018). The catalysts are placed in the plasma discharge region and can be used directly or supported on other metal oxide frameworks such as MgO (Peng et al., 2016) and Al_2O_3 (Hong et al., 2016; Xie et al., 2016). Also, it was found that the performance of the process can be enhanced by depositing the catalyst onto mesoporous supporting materials that have larger surface area, and adding promoters to facilitate the catalytic synthesis (Peng et al., 2017). Most recently, it was found that supporting nickel onto the Metal organic frameworks (MOF) can enhance the NTP ammonia synthesis yields and energy efficiency compared with traditional nickel catalysts (Shah, Wu, Lucero, Carreon, & Carreon, 2018). For details of how the reactant interacts with the catalysts on the molecular level, Hong et al. 2017 provided an up-to-date review on the kinetic modeling of the NTP ammonia approach, and pointed out that the catalytic functions of the catalysts are mainly to absorb the dissociated nitrogen/hydrogen molecules to form reactive sites on the catalyst surface. Also, under atmospheric and non-thermal conditions, the radicals and vibrationally-excited molecules are the determining reactive species instead of the ions (Hong, Pancheshnyi, et al., 2017).

Hydrogen sources for NTP ammonia synthesis

The hydrogen sources for the NTP ammonia synthesis are critical to the overall process efficiency. Compared to nitrogen, which can be made directly from air via various separation methods, hydrogen is much harder to produce. Therefore, the hydrogen source can significantly effect the capital cost and overall energy consumption of the system. Needless to say, the most common hydrogen source used in the NTP ammonia synthesis is from hydrogen gas, which can be produced from electrolysis of water or steam methane reforming. The NTP-based ammonia synthesis approaches that use hydrogen gas are straightforward, feeding both nitrogen and hydrogen gases to the plasma reactor, which is performed by most of the aforementioned studies. Again, the main purpose of using plasma to synthesis ammonia is that under plasma environments, the hydrogen and nitrogen gases can be ionized into reactive species. Therefore, the goal of producing the hydrogen source for the NTP ammonia synthesis process is to generate hydrogen radicals rather than hydrogen gas. In other words, the hydrogen source of the NTP ammonia synthesis does not have to be hydrogen gas. Researchers have successfully generated ammonia using plasma-ionized nitrogen, from alternative hydrogen sources such as methane and water. Similar to ammonia, methane is a hydrogen-rich molecule and is a relatively reactive gas. A study that used methane and non-thermal plasma to produce ammonia achieved good results, with a peak CH_4 conversion of around 60% and the highest concentration of 7000 ppm (Bai, Zhang, Bai, Bai, & Gao, 2008).

Water is also another common hydrogen source and could be considered as a reactant for the NTP ammonia synthesis or nitrogen fixation approach. The idea of using water as the reactant for the NTP process is plausible for several reasons. First, at the current stage, the ammonia synthesis rate for the NTP process is low, and water could help capture the produced ammonia to prevent it from being decomposed in the plasma region. Second, with water being used as the hydrogen source, the intermediate step of electrolyzing water to produce hydrogen gas could be eliminated. There have been several studies that used water to produce ammonia under NTP conditions, since this idea was first introduced by Kubota et al. 2010, who used water and a plasma jet to synthesis ammonia in its liquid cation form (Kubota, Koga, Ohno, & Hara, 2010). The follow up studies performed recently by Haruyama et al. 2016 and Sakakura et al. 2018 utilized the excitation effect of UV light on water to produce more reactive hydrogen species to enhance this process (Haruyama et al., 2016; Sakakura et al., 2018). In their processes, the plasma was generated outside of the water-UV reactor, and Peng et al. 2018 took a further step of generating the plasma directly above the water surface and also studied the temperature effect for the N_2-H_2O plasma nitrogen fixation (Peng, Chen, Addy, et al., 2018).

The two alternative hydrogen sources, methane and water, have their own advantages. As discussed in our previous review, methane can be produced via waste streams by processes such as anaerobic digestion, which increases the overall sustainability of the NTP ammonia synthesis approach (Peng, Chen, Schiappacasse, et al., 2018). As for N_2-H_2O plasma ammonia synthesis, aqueous NO_3- and NO_2- are also the main products. Therefore, the liquid products of this process may be used directly as fertilizers for hydroponic and irrigation systems. In this case, the nitrogen source for the plants/crops could come from the NTP N_2-H_2O synthesis, with the addition of other nutrients to generate liquid fertilizers directly. Since this process does not require high temperature/pressure, it could be possibly made into a mobile on-site and on-demand liquid fertilizer generation system for the farmers.

Energy efficiencies

The reported energy efficiency for the NTP ammonia synthesis ranges widely from 0.025 g/kWh (Matsumoto, 1998) to 25-36 g/kWh (H.-H. Kim, Teramoto, Ogata, Takagi, & Nanba, 2016; H. H. Kim, Teramoto, Ogata, Takagi, & Nanba, 2017), and even over two orders of magnitude difference for the studies published on/after 2010. The conversion ranges from 0.00025% (Nakajima & Sekiguchi, 2008) to 19% (Shah, Wang, Bogaerts, & Carreon, 2018). It was found in several studies (Gómez-Ramírez, Montoro-Damas, Cotrino, Lambert, & González-Elipe, 2017; Peng et al., 2017) that higher flow rates of nitrogen and hydrogen gas lead to greater energy efficiency. An explanation for this is that under the same conversion rate, increasing the reactant feed rate leads to increased product. Therefore, it is recommended that plasma-assisted ammonia synthesis processes be operated at their greatest gas flow capabilities to achieve higher energy efficiencies. Furthermore, increasing turbulence is beneficial to the system as well. If the plasma synthesis process is operated in the laminar region, the concentration profile of the reactive plasma species in the gas steam will not be as uniform as those operated under turbulent conditions.

It is notable that the energy efficiencies reported in almost all previous studies were calculated differently. Until now, there have been many different attempts at measuring and calculating the energy efficiencies of the plasma ammonia synthesis process. Such examples include the efficiencies that were calculated by the dissipated power measured at the plasma region, the input power to the plasma system, and the total input power to the entire process, etc. The large range in the energy efficiencies may also depend on how the same power value is measured and calculated. The common methods used for plasma power measurement are the Lissajous method, current & voltage-based method, and the input power method. The first two methods aim to determine the energy efficiency at the plasma region, whereas the third tries to calculate the utility power input to the plasma generating system. To use the Lissajous method, a small capacitor is introduced into the circuit and is connected in series with the plasma reactor. The voltage difference between the capacitor is then measured to plot the Lissajous curve for calculating the dissipated power within the plasma reactor. For the current & voltage-based method, the in-line current at the plasma reactor is directly measured using a current probe. As the high voltage line will significantly interfere, or likely break the current measuring device, this approach has been performed in-line between the plasma reactor and the ground, rather than from the transformer to the reactor (Ni et al., 2013). In other scenarios, the current could also be measured on the primary side of the high voltage transformer where the inverter sends in high-frequency signals to the transformer, and then determine the current on the reactor side using the coil ratio/turns ratio of the transformer. For the same location, there are also different ways to measure the current, such as the Rogowski coil (magnetic), the shunt resistor method (direct measurement), RDS (on) sensing method (transistor), etc. In our previous publication, the magnetic sensing method was selected because compared to the other methods, it is flexible, and more importantly, non-intrusive (does not introduce additional resistor to the circuit, which will cause power/current loss). However, this method might be influenced by the phase shift between the voltage and current since DBD plasma is a combination of a resistive and inductive circuit. The different methods and/or locations used to measure the current and power could introduce a one to over two orders of magnitude difference between the measured power and the real input power to the system, which could contribute to the wide range of energy efficiencies in the published literature. To resolve this issue, unification of the methods used to measure/calculate energy efficiency is recommended. Specifically, the authors recommend that the total energy input to the entire NTP system should be used in the future studies to avoid any discrepancies caused by methods, locations, and other factors (heat generation, recycle, vacuum pump for some processes) that might contribute to the different power measurements. Furthermore, it is the overall energy efficiency of the whole system per mole of products that should be considered for any scale up analysis.

The future of NTP: Building a sustainable nitrogen fixation industry

Using NTP to synthesize ammonia is a siginificant step toward improving the broader issues of the nitrogen fixation industry. In addition to ammonia, nitrogen compounds such as nitrate/nitrite could also be produced by NTP in aqueous environments. Shown below are the different stages required for the development of the NTP nitrogen fixation process, including ammonia, nitrate, and nitrite synthesis. The primary potential advantage of this technology is the non-centralized, local production of ammonia, produced on an as-needed basis. For example, farmers could produce nitrogen-based fertilizer on-site using renewable energy sources, thus preventing waste/pollution and reducing greenhouse gas emissions. However, greater interdisciplinary efforts are required for this technology to become commercialized. Until present day (2019), development of NTP technology has been limited to small-scale research explorations. As this innovative process moves forward, more efforts to understand and plan the future of the NTP nitrogen fixation technology will likely be made from the policy makers and end-users. For the end-users, such as local nitrogen fertilizer producers and farmers, the power source and product composition of the plasma nitrogen fixation process are important considerations. The relative concentrations of the ammonia, nitrate, and nitrite may determine how this process will utilized. For example, the composition of the different nitrogen fixation products will determine the types of plants/crops that can utilize the corresponding nitrogen source. Lastly, the feasibility of using renewable energy source to power the NTP nitrogen fixation system is crucial for the policy makers and end-users to see the potential of this technology.

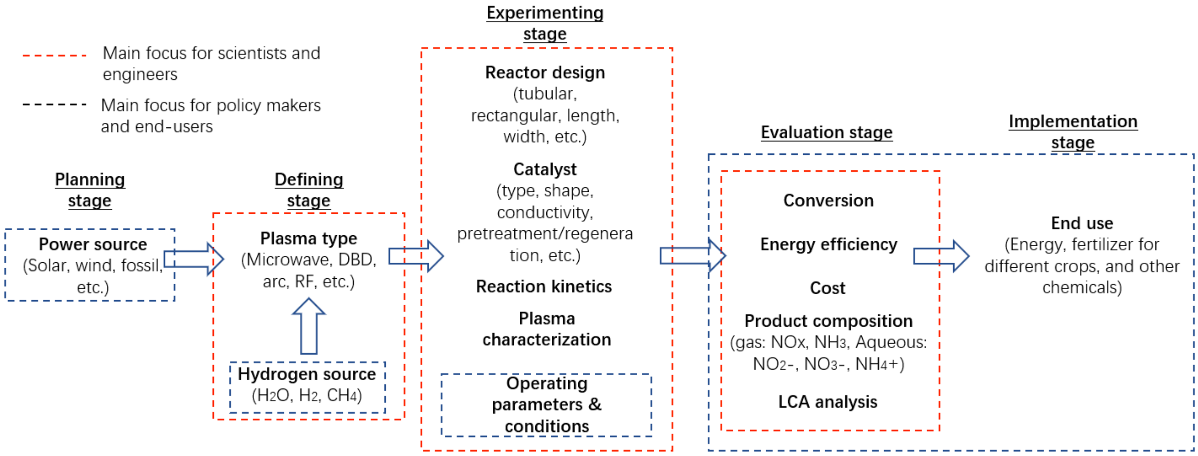

Figure 3 Process flow diagram of the interdisciplinary development for NTP nitrogen fixation

More interdisciplinary collaborations are required to improve the science and engineering aspects of the NTP nitrogen fixation technology. For example, chemical engineers are interested in the catalytic kinetics, physicists have the strength of characterizing and modeling the plasma behaviors, and electrical engineers may be able to develop more efficient high-voltage and high-frequency generators. Furthermore, agricultural/biological engineers may contribute by investigating the environmental impacts and overall efficiencies of a field-ready system. It was shown by a recent LCA analysis that under many operating scenarios, the greatest energy consuming process within the NTP system was the conversion of electrical energy to plasma (Anastasopoulou, Butala, Lang, Hessel, & Wang, 2016). It was recently reported by Wang et al. 2017 that the plasma discharge power occupies only up to 35% to 56% of the total energy input to the plasma generating system (Wang et al., 2017). Therefore, inputs from the electrical perspective are highly beneficial for the current stage of this technology to provide a new direction of increasing the energy efficiency of the NTP ammonia synthesis process by optimizing the plasma generating system. For example, minimizing power transistor switching losses, increasing control effectiveness of the NTP ammonia synthesis system could reduce the current between the inverter and the transformer and increase the dissipated plasma energy efficiency at the plasma region (Peng et al., 2019). Also, Kim et al. reported that that by switching from AC to DC power supply could increase the nitrogen fixation energy efficiency by 3 to 4 times (H. H. Kim et al., 2017). Therefore, with more electronic improvements added to the reactor/catalyst/kinetics development, it is promising that the energy efficiency of the NTP nitrogen fixation can be further enhanced.

Conclusions and future perspectives

In conclusion, NTP can potentially benefit from improvements in reactor configuration and catalyst development. Scientific investigations into each of these areas have helped the NTP technology approach commercial viability. The hydrogen source of the NTP ammonia synthesis process determines whether the end products are ammonia gas or aqueous ammonium with other nitrogen compounds, which further decides the end use of the process. Although the studies of the NTP ammonia synthesis are relatively small in scale and the energy efficiency still needs to be improved by at least one order of magnitude for this technology to be compatible with the Haber-Bosch process, it has the potential of being directly applied by farmers. To build a more sustainable nitrogen fixation infrastructure in the future, the NTP technology could be incorporated onto a mobile, on-site, on-demand system that can generate nitrogen fertilizer as needed for the end users.

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