Review

# A review on the non-thermal plasma-assisted ammonia synthesis technologies

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## ABSTRACT

Ammonia has been intensively studied as a clean, sustainable fuel source and an efficient energy storage medium due to its effectiveness as a hydrogen carrier molecule. However, the current method of ammonia synthesis, known as the Haber-Bosch process, requires a large fossil fuel input, high temperatures and pressures, as well as a significant capital investment. These volatile conditions and high operating costs prevent decentralized and small-scale ammonia production at the level of small farms and local communities. This article provides systematic review of the plasma-assisted ammonia synthesis under low temperature and pressure conditions. Non-thermal plasma technology represents a promising alternative method of clean ammonia synthesis, as it circumvents the volatile operating conditions, fossil fuel use, and high capital costs of the Haber-Bosch process. This technology could be beneficial to the ammonia industry, through its potential to promote localized and environmentally friendly energy production and storage. The opportunities of the non-thermal plasma technology lie with providing an avenue towards a cleaner ammonia industry, including a renewable pathway that incorporates this technology with other renewable energy approaches. However, the two most critical challenges of this technology are the fixation of nitrogen gas and back reactions. To overcome these challenges, researchers could work to further develop catalysts with stronger plasma synergistic activities, and optimizing reactor designs for rapid separation of ammonia after being synthesized.

## Contents

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## 1. Introduction and history

Since the 1st half of the 20th century, the synthesis of ammonia was publicly recognized due to the efforts of Fritz Haber and Carl Bosch, two Nobel Prize recipients, who developed and industrialized the Haber-Bosch process for ammonia production. The Haber-Bosch process has shaped our world and resulted in humanity becoming heavily dependent on ammonia (Erisman et al., 2008). The most well-known applications of ammonia include fertilizer, explosives during the 1st world war, and pesticides, etc. (Galloway et al., 2008; Smil, 1997). In recent years, innovative applications of ammonia have been intensively studied, including refrigeration, fermentation, and energy carrier potential (Von Blottnitz and Curran, 2007). For example, ammonia has been investigated for its potential as an energy source for fuel cells (Cox and Treyer, 2015; Maffei et al., 2007), transportation (Miura and Tezuka, 2014), and other off-grid power applications (Davis et al., 2009). Due to its high hydrogen content, ammonia, as well as its derivative species like ammonia bromine , has been viewed as one of the most efficient and economical hydrogen carriers (Christensen et al., 2006; Cumaranatunge et al., 2007; Smythe and Gordon, 2010). In terms of energy content, ammonia has a heat of combustion of around 22 MJ/kg and a low heating value comparable to diesel fuels (Zamfirescu and Dincer, 2009). Furthermore, the high boiling point of ammonia makes it an ideal material for indirect hydrogen storage (Demirci and Miele, 2009; Lan et al., 2012). Most importantly, the complete combustion of ammonia is a sustainable process that does not emit any greenhouse gases. Therefore, ammonia, or ammonia bromide has also been introduced with petroleum-based fuels to vehicle engines for cleaner emissions (Stephens et al., 2007; Zamfirescu and Dincer, 2009).

Although the Haber-Bosch process is responsible for providing over 130 million tons of ammonia annually to support approximately 40% of the world's population, it is also responsible for up to 2% of the global energy consumption (Patil et al., 2016b). The reaction conditions of the Haber Bosch process lie in the range of 200–400 atm and 400–600 °C, respectively (Hargreaves, 2014). These intense temperature and pressure conditions are the main disadvantages of the Haber-Bosch process, as they prevent the possibility of lowering capital costs (Gilland, 2014; Razon, 2014). Additionally, the high pressure required for the traditional Haber-Bosch process is also a limiting factor in reducing the economies of scale of localized production facilities due to the high energy (and cost) requirements of compression (Razon, 2014). Life cycle assessment (LCA) results have shown that the ammonia generation pathways can greatly impact the for environmental performance of the ammonia-based power applications (Cox and Treyer, 2015). Therefore, researchers are seeking new methods of ammonia synthesis, which occur under more moderate conditions (Vojvodic et al., 2014; Zhang et al., 2012), require less carbon input (Gilbert et al., 2014), or can be powered by renewable energy sources (Bardi et al., 2013; Liu, 2014).

Since the start of late 1990s, many studies were carried out on non-thermal plasma (NTP) based processes for pollution control (Kim, 2004). Studies have shown that NTP is capable for the destruction and removal of sulfur dioxide (Ma et al., 2002), hydrogen sulfide (Ma et al., 2001), odors (Ruan et al., 1999), and other volatile organic compounds (Ruan et al., 1999, 2000). In recent years, the results from these studies have been applied to decompose pollutant gases from animal production to food processing facilities (Schiavon et al., 2015, 2017). Results show that NTP is more efficient and less energy intensive than most of the traditional gas treatment technologies (Stasiulaitiene et al., 2016). Ma et al. (2002) discovered that by injecting $SO_2$ into the odor stream passing through an NTP reactor, solid particles were produced at the exit of the reactor. These particles were then confirmed to be ammonia sulfate $((NH_4)_2SO_4)$. Researchers believed that $SO_2$ was ionized and reacted under the NTP conditions, resulting in $(NH4)_2SO_4$. These studies confirmed that NTP is capable of ionizing gaseous compounds and may lead to innovative methods of chemical synthesis reactions. Since then, NTP has been largely investigated in the fields of flow control in the past twenty years (Nie et al., 2013; Penetrante and Schultheis, 2013).

During this period, NTP was found to be a potential alternative to the high temperature and pressure method for the synthesis of many chemicals (Petitpas et al., 2007; Ruan et al., 2014), such as benzene and isooctane (Rahemi et al., 2013). Additionally the NTP-assisted nitrogen fixation method has been viewed as an attractive alternatives to the Haber-Bosch process (Patil et al., 2016a). In the early years of NTP nitrogen fixation, emphasis was placed on the synthesis of nitric oxide compounds instead of ammonia (Patil et al., 2016a). NOx synthesis was favored over ammonia production because it offered a thermodynamically favorable method of nitrogen fixation, requiring lower energy input (Patil et al., 2015; Wang et al., 2017).

A flow diagram of the NTP ammonia synthesis approach is shown in Fig. 1. This process relies on the plasma discharge to dissociate the reactants and form ammonia with the assistance of catalysts. Various sources such as microwave and dielectric barrier discharge can be used to generate the plasma required for the synthesis. Depending on the individual study, the products then go
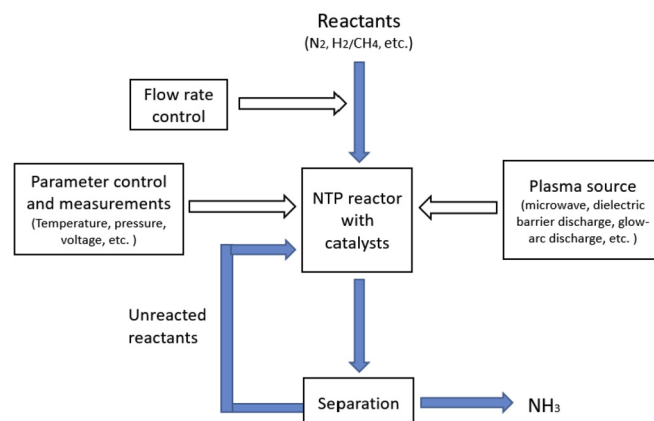
**Fig. 1.** A flow diagram of the non-thermal plasma ammonia synthesis process.

through a separation process to collect the ammonia product and recycle the unreacted reactants. The first attempt at using NTP to synthesize ammonia was made at the end of the 1980s, where the authors tried to synthesize ammonia in high-frequency discharges (Sugiyama et al., 1986). Uyama et al. (1993) attempted the NTP synthesis of ammonia using microwave and radio frequency (RF) plasma. The process was operated at a pressure much lower than atmospheric pressure, approximately 700 Pa. After the concept of using plasma to synthesize ammonia was proved in these studies, researchers have started conducting more thorough investigations into the NTP-assisted ammonia synthesis process. Further research indicated that the non-equilibrium plasma, generated under non-thermal conditions, could dissociate diatomic nitrogen and hydrogen at atmospheric pressure with the assistance of select catalysts. The low operating pressure of NTP offers the opportunity to circumvent the compression processes by flowing hydrogen gas directly into the reactor from other renewable sources, such as gasification of biomass or electrolysis of water. Since pressurizing the system is not required, the NTP system can be operated continuously or incorporated directly into a syn-gas production stream. A recent study proposed that the moderate process conditions could potentially allow for the economically viable construction and operation of widely distributed NTP-based fertilizer production systems on farms and renewable hydrogen production sites (Ingels and Graves, 2015a, 2015b). A summative comparison between the NTP synthesis and the conventional Haber-Bosch process is shown in Table 1.

Along with the NTP methods, there are several recently developed synthesis approaches that could produce ammonia under low temperature and pressure, namely the biological and electrochemical cell synthesis. There have been review articles published regarding the biological (Hinnemann and Nørskov, 2006) and electro-chemical cell synthesis (Guo et al., 2017; Kyriakou et al., 2017) of ammonia. On the other hand, reviews that targets specifically on the plasma-assisted ammonia synthesis are sparsely developed. Thus the first goal of this paper is to provide a comprehensive review with an emphasis on the plasma-assisted ammonia synthesis. Overall, existing studies for the NTP synthesis of ammonia are focusing on the process and catalyst developments. In this paper, the three crucial factors to the successful development of non-thermal plasma ammonia synthesis technology were identified as: understanding of relevant reaction kinetics, reactor development, and catalyst development. The development of these aspects will significantly improve the energy efficiency and environmental sustainability of this technology. Additionally, this paper analyzes the effects of reactant type, composition, and feed rate on ammonia synthesis efficiency, reactant conversion. Most importantly, this paper recommended how the improvements of these factors could result in a cleaner ammonia production process. A cradle to factory gate life cycle assessment shows that nitrogen fixation by plasma can potentially reduce the global warming potential as compared to the conventional fixation pathways by 19%

(Anastasopoulou et al., 2016). However, the published life cycle assessment on nitrogen fixation technologies focuses primarily on the production of nitric acid using plasma. Therefore, another goal of this study is to fill in the knowledge gap between the published literature and a complete life cycle assessment that targets specifically on the NTP synthesis of ammonia. To achieve this, discussions and analysis needs to surpass the summarization of published literature on process developments. Therefore, this paper addresses the correlations between the state-of-art of this technology with cleaner productions and how its development could improve the sustainability in the ammonia production industry.

## 2. Method

### 2.1. General methodology

In order to effectively select the literature that could represent the current status and help identify the challenges and opportunities of the NTP technology, this paper incorporates a systematic and integrated literature review methodology adapted from Tranfield et al. (2003) and Whittemore and Knafl (2005). As indicated in Whittemore and Knafl (2005), the general steps of an integrated literature review are topic identification, literature search, data evaluation, data analysis and presentation, as indicated in Fig. 2.

### 2.2. Initial screening

During the literature search stage, the methodology from Tranfield et al., (2003) is implemented. The literature search method includes: the identification of literature, selection of literature, and literature quality assessment. First, approximately 300 pieces of literature were selected regarding the synthesis of ammonia via an intensive search from the research databases including: Elsevier, Web Of Science, and Wiley Online Library, etc. At this stage, the problems of the conventional ammonia synthesis, such as the high temperature/pressure, and the large consumption of fossil fuels, were identified. Second, qualities such as the validity, reliability, and trustworthiness of the studies are used to determine whether they should be analyzed after the initial literature screening (Elo et al., 2014). In this review, a high-quality study is identified by whether or not it has a detailed methodology, complete list of parameters, and a comprehensive and thorough discussion of the results, etc.

### 2.3. Categorization of literature

Third, the pieces of literature are categorized into different sections. Studies that involve the life cycle assessment and the environmental issues of the conventional ammonia production indicate the need of developing an alternative ammonia synthesis process. These studies also point out the necessity to improve the

**Table 1**
A summative comparison between the conventional Haber-Bosch and NTP ammonia synthesis.

|  | Advantages | Drawbacks |
|---|---|---|
| Conventional Haber-Bosch synthesis | Large scale available;<br>High production rate | Large energy input;<br>High temperature and pressure Requires fossil fuels;<br>Emission of green house gases;<br>Centralized production;<br>High capital cost |
| Non-thermal plasma synthesis | Clean, carbon-free production;<br>Low temperature and pressure;<br>Accessible to small-scale, on-site production; | Conversion and efficiency need to be improved;<br>Available only at small scale |
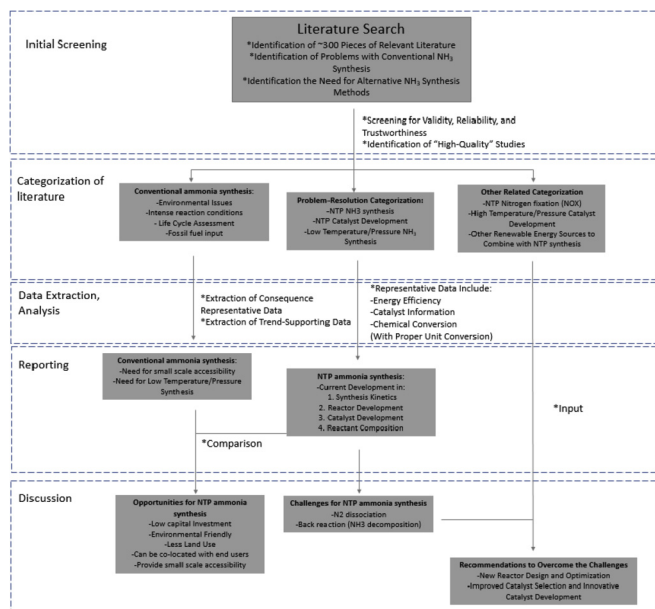
**Fig. 2.** A process flow diagram of the systematic and integrated literature review process used in this review.

accessibility of ammonia production to small industries and farms. Next, the studies about using NTP to synthesis ammonia under low temperature and pressure conditions are identified, which function as the building blocks (or "foundation") of this review paper. Finally, studies in the related area are selected to provide potential insight to resolve the challenges of the NTP ammonia synthesis. Examples of these studies include the plasma nitrogen fixation to produce nitric oxides and catalyst development of high temperature and pressure ammonia synthesis.

### 2.4. Data extraction, analysis, and reporting

For the literature included in this review, only the data that effectively represents the consequence of the study and addresses the trend of the studies is extracted, both qualitatively and quantitatively. The emphasis of data extraction also depends on the categorization of literature. Representative data such as the energy efficiency, catalyst information, and conversion are selected as analysis to the literature on NTP ammonia synthesis. During the data analysis stage, all the units of the synthesis efficiency and conversion rate are converted for comparison and analysis. During the reporting stage, two types of comparison are made, one between the conventional and NTP ammonia synthesis technologies, and the other within the NTP ammonia synthesis studies themselves. During the reporting phase, challenges of the NTP ammonia synthesis technology are discussed and the recommendations to overcome the challenges are proposed.

### 3. Reaction principles and kinetics

Since the development of the ammonia production process, intensive investigations have been made to understand the kinetics of ammonia synthesis reactions. However, less effort has been demonstrated to study the kinetics of ammonia synthesis under NTP conditions, compared with the traditional Haber-Bosch process. The kinetics provides a foundation for manipulating and modeling the reaction to increase the rate, conversion, and efficiency of an ammonia synthesis reaction, and is also what guides

the design of the NTP reactors. Overall, the NTP has two major functions for the catalytic conversion of nitrogen and hydrogen to ammonia. First, it directly causes $N_2$ and $H_2$ to dissociate and form $NH_3$ with or without catalyst. Second, it provides the ionization energy necessary to produce electrons for the catalysis system to function (Neyts et al., 2015). Therefore, modeling of the synthetic process under NTP conditions will not only allow more efficient reaction, but will benefit significantly to the reactor and process design, which will further contribute to a cleaner production of ammonia using this technology. On a macroscopic level, the ammonia synthesis using N2 and H2 as the reactants are centered on equation (1), and its kinetics can be described via the following power equation (2) (Jennings, 2013).

$$N_2 \text{ (g)} + 3H_2 \text{ (g)} \leftrightarrow 2NH_3 \text{ (g)}; \Delta H = -92.44 \text{ kJ/mol} \quad (1)$$
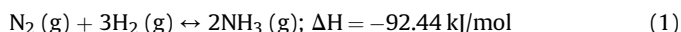
$$r = N_2^{\alpha} H_2^{\beta} \quad (2)$$

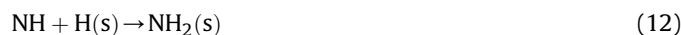The reported $\alpha$ and $\beta$ values for the power kinetic equation in the NTP ammonia synthesis were $\alpha = 0.77$ and $\beta = 1.16$ for a wool-like copper catalyst (Aihara et al., 2016). Comparing with the reported coefficients under high temperature and pressure conditions using transitional metal based catalysts (0.8–1.2 for $\alpha$ and 1.5 to 2.2 for $\beta$), the $\alpha$ and $\beta$ values from the NTP synthesis were lower, which corresponded to the slower synthesis rate of NTP over the high temperature and pressure process (Hagen et al., 2003). Furthermore, it was reasonable to propose that the kinetics of the NTP ammonia synthesis is limited more by the dissociation of $N_2$ than $H_2$ since the $\alpha$ value is lower than the $\beta$ value. However, due to the complex and non-equilibrium nature of the NTP, a more detailed kinetics analysis must be carried out to provide a better understanding of the intermediate species and chemical pathways in the NTP plasma synthesis (Hong et al., 2017).

Previous studies hypothesized that the synthesis of ammonia from nitrogen and hydrogen gas involved the following three mechanisms: decomposition, structural rearrangement, and fragment elimination (Penetrante et al., 1997; Van Durme et al., 2008). It has been widely understood that the first steps of plasma ammonia synthesis are the dissociation and ionization of the inlet nitrogen and hydrogen gases (Bai et al., 2003; Matsumoto, 1981). Furthermore, the formation of radical species by the elemental impacts in the plasma region is the essential step in the reaction (Mizushima et al., 2004). Previous studies proposed a detailed mechanism that can be described by the following reaction, with the dissociation of the injected $N_2$ gas being the rate-limiting step (Eliasson and Kogelschatz, 1991; Peng et al., 2016).

$$N_2 \rightarrow 2N^* \quad (3)$$

$$H_2 \rightarrow 2H^* \quad (4)$$

$$N^* + H^* \rightarrow NH \quad (5)$$

$$NH + H^* \rightarrow NH_2^* \quad (6)$$

$$NH_2^* + H^* \rightarrow NH_3 \quad (7)$$

Amongst the reactive plasma species shown above, it is believed that the NH radical is the precursor of $NH_3$ formation and its concentration has a strong effect on the ammonia synthesis rate (Uyama and Matsumoto, 1989). In a recent study performed by Hong et al. (2017), the authors analyzed the kinetics of the NTP ammonia synthesis by taking into account both electron and vibrational kinetics and surface reactions of the adsorbed species.

The authors confirmed that the reactions between radicals and vibrationally-excited molecules had a more significant affect on the reaction kinetics of ammonia synthesis than the ion-ion reactions. Additionally, the authors identified several other important factors in the NTP-mechanism including: electron excitation and vibrational excitation reactions in the gas phase, and surface adsorbed radicals (important in the later stages of forming NH₃). The general mechanisms described by equations (3)–(7) can then be broken down into more detailed gas-phase (Carrasco et al., 2011) and surface adsorption (Hong et al., 2017) reactions. Some examples of the reactions in the gas phase and surface adsorption phase are specified in equations (8) to (9) and (10) to (11), respectively. In these equations, surf stands for the catalyst adsorption surface; (s) stands for the surface-adsorbed species; and (υ) represents the vibrationally-excited molecules. Examples of the synergistic effect between the gas phase and the surface adsorbed species are represented by equations (12) and (13).

$$e + N_2 \rightarrow e + 2N \tag{8}$$

$$N + H_2(\upsilon) \rightarrow H + NH \tag{9}$$

$$N + surf \rightarrow N\,(s) \tag{10}$$

$$H + surf \rightarrow H\,(s) \tag{11}$$

$$NH + H(s) \rightarrow NH_2(s) \tag{12}$$

$$NH_2(s) + H(s) \rightarrow NH_3 \tag{13}$$

In the gas-phase, to weaken and break the triple bond of diatomic nitrogen, electrons must pass into the anti-bonding orbital of $N_2$ through the d orbital (Henrici-Olivé and Olive, 1969). The energy provided by the NTP could then break the weakened nitrogen triple bond (Peng et al., 2016). However, NTP alone could not provide sufficient energy for efficient nitrogen fixation. Based on the specific type of discharge, the energy provided by NTP ranges from 3 to 6eV, which is insufficient to ionize the Ru catalyst (ionization energy of 7.36eV) (Fridman and Kennedy, 2004; Kerpal et al., 2013). Therefore, whenever a ruthenium-based catalyst is selected as an ammonia synthesis catalyst without the presence of intense temperature and pressure, promoters must be present to facilitate the electron transfer and enhance the catalytic activity. For the surface adsorption reactions, they are the primary mechanism for $NH_3$ (or $NOx$) synthesis since the previously discussed gas-phase reactions are capable of providing the excited molecules necessary for surface reactions. Under the NTP discharge conditions, the nitrogen and hydrogen gas form N, H, and NHx radicals.

Within the discharge volume, these radicals will react with the surface of the catalysts via a direct adsorption process and stick to the surface of the catalysts (Carrasco et al., 2011). In the gas phase, the atomic nitrogen formed by the electron-excited diatomic $N_2$ reacts with the vibrationally-excited hydrogen molecules to form NH radicals. These NH radicals can then form $NH_3$ via reaction with the hydrogen atoms in the gas-phase or the ones adsorbed by the catalyst surface (Hong et al., 2017). This general mechanism agrees with the previously discussed importance of specific energy input and active surface area (i.e. specific energy input provides high-energy electrons and active surface area dictates surface reactions). In summary, it is the interactive reactions between these two phases that form the synergistic synthesis of $NH_3$ by non-thermal plasma (Neyts et al., 2015). Therefore, the development of the catalyst is crucial in two aspects, to promote the dissociation of diatomic nitrogen in the gas-phase and to facilitate the surface adsorption reactions.

## 4. Reactor development

As mentioned in section 1, one of the advantages of the NTP synthesis of ammonia is that it could be operated under low temperature and pressure. The proper reactor design could significantly improve the efficiency of the ammonia production system and lead to a higher production to energy input ratio, which further represents a cleaner production of ammonia. Previous studies have explored a wide array of NTP reactors as means of ammonia synthesis. When the technology first started to emerge, Uyama et al. (1993). attempted the NTP synthesis of ammonia using micro-wave and RF plasma. These processes were achieved at approximately 700 Pa, much lower than atmospheric pressure. Due to the vacuum condition required in these studies, the experiments were carried out in batch reactors. To eliminate the vacuum requirements and operate the system in a continuous fashion, the studies published in recent years have been largely focused on the synthesis of ammonia using dielectric barrier discharge (DBD) plasma except those conducted by Nakajima and Sekiguchi (2008).

Fig. 3 shows a schematic diagram of a typical DBD plasma reactor, also known as a silent discharge reactor. The structure of the DBD reactor is composed of two electrodes and a dielectric barrier. As shown in the figure below, the dielectric barrier is placed between the high voltage electrode and the ground electrode. For DBD to occur, a strong electric field is required. The distance between the electrodes and the applied voltage dictate the strength of the electric field. The optimum voltage frequency to generate DBD is between 1 kHz and 10 MHz (Kogelschatz, 2003).

The discharge occurs and the plasma is generated in the small gap between the two electrodes. Among the plasma treatment
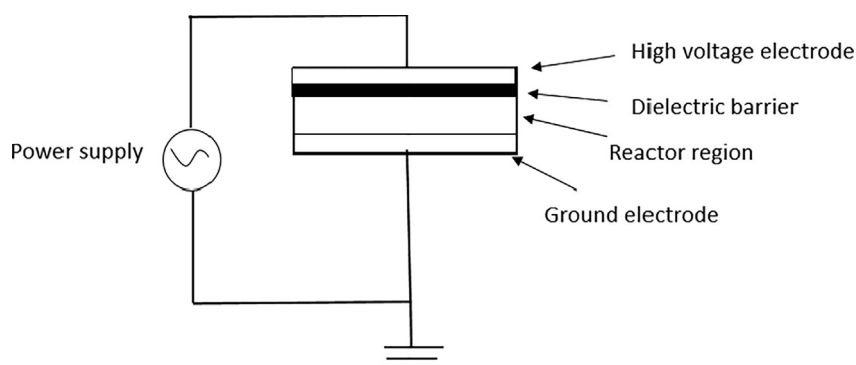


**Fig. 3.** A schematic diagram of Dielectric Barrier Discharge plasma generation.

technologies, DBD plasma offers the advantages of a low operational/maintenance cost (Conrads and Schmidt, 2000; Liu et al., 2006), and has the broadest range of operational pressures, ranging from 5 to $10^5$ Pa (Schütze et al., 1998; Wang et al., 2011). For example, a recent comparison between DBD plasma and microwave-induced argon plasma showed that DBD plasma generates higher electron density and atomic oxygen concentration with less temperature increase (Florian et al., 2015).

By using DBD plasma, most studies on NTP ammonia synthesis after the 20th century were able to achieve continuous operation under atmospheric pressure. Bai et al. (2000) used a planner structured DBD reactor to synthesize ammonia. The study at atmospheric pressure enhanced the conversion of ammonia and most importantly, greatly shortened the gas residence time from the scale of hours to the scale of milliseconds. The authors further made an improvement to the planner structured system by reducing the discharge gap to the level of $10^{-1}$ mm (Bai et al., 2008). In two more recent studies, Gómez et al. (2015, 2016) introduced a ferroelectric packed bed reactor for the NTP synthesis of ammonia. The reactor consisted of two circular plain electrodes with catalysts packed between them. The authors pointed out that by using this design; the effect of the electrode gap or the size and shape of the inner-electrode could be investigated more flexibly than the planner or tubular electrodes. The results from this study showed a conversion of nitrogen to ammonia at approximately 8%. On the other hand, the optimum synthesis efficiency obtained in this study is around 0.8 g/kwh, which is lower than using a tubular-shaped NTP reactor with 1.5 mm of discharge gap (Peng et al., 2016). Note that in this study, the ferroelectric material acts both as the catalyst and electrode. This idea is later implemented in a more recent study that uses a wool-like copper wires as both the catalyst and electrode in a tubular NTP reactor (Aihara et al., 2016). Since the current $N_2$ conversion of the continuous NTP ammonia synthesis is low (less than 10% of $N_2$ conversion), Peng et al. (2016) introduced an absorbing and recycling stream into the NTP system that could separate the product ammonia and recycle the unreacted $N_2$ and $H_2$ gases. Due to the low conversion rate of most NTP ammonia synthesis technologies, a method of recycling the gas streams could contribute to material saving and lowering the capital cost of this technology, which further promotes the clean production of ammonia.

Another significant part of the reactor development was the selection and design of the electrical discharge systems and operating conditions. Proper matching between the electrical discharge power supply and the reactor was essential to reduce the energy input of the system by lowering the specific energy input to reach the same plasma intensity. For the electrical discharge conditions, the alternate current (AC) and direct current (DC) discharges have been used for the NTP synthesis of ammonia. In general, AC was used more commonly for DBD plasma, as DC cannot pass the insulated dielectric layer (Kogelschatz, 2003). However, it was worthwhile to point out that the studies carried out by Bai et al. (2003, 2008) used DC as their power supply. Table 2 further illustrated AC power's superiority to DC power as the greatest energy efficiencies and conversions were achieved by studies carried out using AC power as opposed to DC power. Previous research indicated that the current of the DC DBD plasma spikes when the voltage reached a certain value, usually 5 kV–8 kV, depending on the specific dielectric layer (Ishida et al., 2011). The dramatic increase in the operating current led to a much greater energy consumption. For this reason, the NTP ammonia synthesis studies that used AC power were conducted at higher voltages than their DC counterparts. Besides the energy efficiency, the different voltage ranges used in NTP studies are also associated with the plasma intensity, electron density, and ionization potentials (Keller et al.,

2012). For DBD plasmas, the main collision of the ionized gas is with neutrals (Paliwoda, 2016). The collision intensity and frequency of the plasma was closely related to the electron temperature, which was proportional with the driving voltage (Naz et al., 2012). Research also showed that for AC power at higher frequencies (over 10 kHz), the $N_2$ breakdown voltage and the power consumed per cycle of the DBD plasma was significantly lower than at low frequency regions (less than 100 Hz) (Khatun et al., 2010). The plasma intensity was directly related to the effects of the feeding gas compositions in the DBD ammonia synthesis reactor as well, which would be discussed in detail in Section 6.

## 5. Catalyst development

Catalyst development is another critical factor to improve the NTP ammonia synthesis process and achieve a cleaner production. To facilitate the NTP ammonia synthesis reaction and enhance its efficiency, various efforts have been made to the catalyst development for this technology. The first catalysts used to synthesize ammonia under plasma conditions were iron and molybdenum wires (Tanaka et al., 1994; Uyama et al., 1993). Other studies have examined the performance of catalysts loaded on metal oxide supports, $Al_2O_3$ (Mizushima et al., 2004) and MgO (Bai et al., 2000, 2003), in non-thermal plasma reactors for ammonia synthesis. Table 3 summarizes the catalyst used for the NTP synthesis and their maximum energy efficiency or conversion rate reached. It can be seen from the table that there are several key factors for the catalyst selection of the NTP synthesis of ammonia.

The first factor is the presence of catalyst. Although many would believe that catalyst is a critical factor in the NTP synthesis of ammonia, there are three studies that successfully generated ammonia without the presence of any catalyst. For the first study without catalyst, Nakajima and Sekiguchi (2008) relied on using the quenching gas including Ar and He. This study was able to generate ammonia at an energy efficiency of 0.78 g/kWh (best reported value). The authors also stated the importance of using quenching gas to improve the synthesis of ammonia. For the second study, Bai et al. (2008) successfully synthesized ammonia at a relatively high conversion rate (9% H2 equivalent) using $CH_4$ and $N_2$. For these two studies, the reactant species and reactant composition played another key role and the details of the gas compositions will be discussed in the later section. For the third study without catalyst, the authors used a liquid solution containing water and ethanol to immediately absorb the ammonia after reaction in the plasma jet and achieved a relatively comparable energy efficiency (1.16 g/kWh) (Kubota et al., 2010). It has been understood that the decomposition of ammonia, which is very likely to happen under NTP conditions, is one of the limiting factors of the NTP synthesis (Lu et al., 2014; Peng et al., 2017). Therefore, by injecting the reactant and product mixture right into the solution immediately after the reduction, the authors were able to separate and collect ammonia and prevent it from decomposing. If this idea is adopted in future studies with more effective catalysts, it is reasonable to achieve a breakthrough on the synthesis efficiency.

The second factor is the type of catalysts. So far, for all the studies of plasma synthesis of ammonia, metallic catalysts have been used except several studies that did not introduce any catalyst. The metallic catalyst can be divided into several types as well. The first is a mono catalyst system, where only one type of metal is used, which in these cases are MgO (Bai et al., 2000, 2003), Cu wires (Aihara et al., 2016; Tanaka et al., 1994), and Lead zironate titanate (Gómez-Ramírez et al., 2015, 2016). Among the studies that used mono catalysts, the copper wires with wool-like shape presented the greatest energy efficiency (Aihara et al., 2016). Note that in this study, the copper wools act not only as the catalyst, but an electrode

**Table 2**
A summary of the reactor development for NTP ammonia synthesis.

| Plasma type | Plasma parameter | Pressure | Temperature | Reactor time | Greatest reported energy efficiency | Greatest Conversion | Comments | Reference |
|---|---|---|---|---|---|---|---|---|
| Glow discharge | DC, 6 mA | 5-10 torr | Room temperature[a] | Batch | N/A | 77.4% for MgO & CaO; no ammonia detected for $Al_2O_3$, $WO_3$, and $SiO_2$-$Al_2O_3$ | Batch process, 30 min | (Sugiyama et al., 1986) |
| Microwave plasma | 13.56 MHz−2540 MHz, 150 W | 5 Torr | 600-700 K | Batch | 0.078 g/kWh[b] | N/A | Batch process. 2 hrs | (Tanaka et al., 1994; Uyama et al., 1993) |
| DBD discharge | DC, 140 kV/cm, 1 μs pulse width, 5000 Hz | 750 Torr | Room temperature[a] | Continuous | N/A | 0.5% | Continuous process, residence time 1.90s | (Bai et al., 2000) |
| DBD discharge | DC, 80 μs pulse width, 1800V−2150 V, 10 kHz | 750 Torr | 78 to 155 C | Continuous | 1.83 g/kWh | N/A | Continuous process, residence time 0.20s | (Bai et al., 2003) |
| DBD discharge | AC, 2.5−4.5 kV, 21.5 kHz | 750 Torr | Room temperature[a] | Continuous | 0.34 g/kWh[b] (5.5E-9 mol/J) | 2.3% | Continuous process, residence time 0.95s−3.82s | (Mizushima et al., 2004) |
| DBD discharge | DC, 240 W, 10 kHz; the pulse width, 40 μs | 750 Torr | 293 K−473 K | Continuous | N/A | 9.1% | Continuous process, residence time 1.6 s | (Bai et al., 2008) |
| Microwave plasma | 2.45 GHz, 1.3 kW | 750 Torr | 790 K−1240 K | Continuous | 0.78 g/kWh[b] | 2.5E-2% | Continuous process, residence time 0.0065s−0.27s | (Nakajima and Sekiguchi, 2008) |
| DBD plasma jet | DC pulse,16 kHz, 300 W | 750 Torr | Room temperature[a] | Simi-continuous (ammonia absorbed after production) | 1.16 g/kWh[b] | 1.7E-6% at 45 min[b] | Semi-continuous absorption process, Residence time 45 min | (Kubota et al., 2010) |
| DBD discharge | AC, 1 kHz, 11−13 kV | 750 Torr | 450 K−1750 K | Continuous | N/A | 4.2% | Continuous process, residence time 27s | (Hong et al., 2014) |
| DBD discharge | AC, 0−7.5 kV, | 750 Torr | 323 K | Continuous | 0.9 g/kWh | 2.7% | Continuous process, residence time 8.8−17.5s | (Gómez-Ramírez et al., 2015) |
| DBD discharge | AC, 8−16 kHz, 5−10 kV | 750 Torr | Room temperature[a] | Continuous | 1 g/kWh | N/A | Continuous process, residence time 0.024s−0.38s | (Peng et al., 2016) |
| DBD discharge | AC, 50 kHz, 5 kV | 750 Torr | Room temperature[a] | Continuous | 3.3 g/kWh (H2:N2 = 0.5:1) | 3.5% (H2:N2 = 3:1) | Continuous process, residence time 9.7s | (Aihara et al., 2016) |
| DBD discharge | AC, 500−5000 Hz, 2.5−5.5 kV, | 750 Torr | 333 K | Continuous | 0.7 g/kWh | 7% | Continuous process, residence time 9−121s | (Gómez-Ramírez et al., 2016) |
| DBD discharge | AC, 500 and 1 kHz, 12−17.5 kV | 750 Torr | 387 K | Continuous | 0.16 g/kWh | 2.3% | Continuous process, residence time 50s | (Hong et al., 2016) |
| DBD discharge | AC, 7−14 kV, 11 to 14.5 kHZ | 750 Torr | Room temperature | Continuous | 0.68 g/kWh | N/A | Continuous process, residence time | (Xie et al., 2016) |
| DBD discharge | AC, 20 kV, 20 kHz | 750 Torr | 413 K | Continuous | N/A | 12% | Continuous process, residence time 4 min | (Akay and Zhang, 2017) |
| DBD discharge | AC, 5 kV, 50 kHz | 750 Torr | Room temperature | Continuous | N/A | N/A | Continuous process, residence time 9.7 s, | (Iwamoto et al., 2017) |
| DBD discharge | AC, 20−26 kHz, 5−10 kV | 750 Torr | Room temperature | Continuous | 1.7 g/kWh | N/A | Continuous process, residence time 0.024s−0.38s | (Peng et al., 2017) |

[a] Only the gas temperature before the plasma treatment is reported.
[b] Unit conversion is required from the original result to g/kWh.

**Table 3**
A summary of the catalyst development for NTP ammonia synthesis.

| Catalyst type | Catalyst | Catalyst shape | Reference |
|---|---|---|---|
| Mono catalyst | MgO & CaO $Al_2O_3$; $WO_3$, and $SiO_2$-$Al_2O_3$ | Disks | (Sugiyama et al., 1986) |
| Mono catalyst | Iron and molybdenum | Wires | (Tanaka et al., 1994; Uyama et al., 1993) |
| Mono catalyst | MgO | Powders | (Bai et al., 2000) |
| Mono catalyst | MgO | Powders | (Bai et al., 2003) |
| Catalyst-support | Ru/Alumina | Powders | (Mizushima et al., 2004) |
| N/A | No catalyst | N/A | (Bai et al., 2008) |
| N/A | No catalyst | N/A | (Nakajima and Sekiguchi, 2008) |
| N/A | No catalyst | N/A | (Kubota et al., 2010) |
| Mono catalyst | MgO and glass spheres | Pallets | (Hong et al., 2014) |
| Mono catalyst | Lead zirconate titanate, $BaTiO_3$ | Pellets | (Gómez-Ramírez et al., 2015) |
| Catalyst-support with promoters | Ru on MgO | Powders | (Peng et al., 2016) |
| Electrode catalyst | Copper | Small wool-like wires | (Aihara et al., 2016) |
| Mono catalyst | Lead zirconate titanate (pallets) | Pallets | (Gómez-Ramírez et al., 2016) |
| Catalyst-support | Nanodiamonds and diamond-like carbon coated $Al_2O_3$ | Sphere powders | (Hong et al., 2016) |
| Catalyst-support | Ru on $Al_2O_3$ | Powders | (Xie et al., 2016) |
| Catalyst-support | Ni on microporous silica | Pallets | (Akay and Zhang, 2017) |
| Mono catalyst | Au, Pt, Pd, Ag, or Cu | Small wool-like wires | (Iwamoto et al., 2017) |
| Catalyst-support with promoters | Ru on Si-MCM-41 | Powder | (Peng et al., 2017) |

of the NTP discharge system as well. The authors further performed a comparison analysis between different wool-like metallic catalysts including Au, Pt, Pd, etc. This study shows that for wool-like metallic catalysts, Au has the highest activity (Iwamoto et al., 2017). The second type is the catalyst-support system, which coat catalyst (ruthenium and carbon) on to supporting materials including MgO and $Al_2O_3$ (Hong et al., 2016; Mizushima et al., 2004; Xie et al., 2016). Another study performed by (Akay and Zhang, 2017) uses microporous silica to support nickel catalyst to enhance the surface area. Although studies have shown that the catalyst-support system performs better (in terms of energy efficiency) than the support alone, its performance is still not as good as the third catalytic type, which is the catalyst-support and promoter system. For this catalytic system, promoters are used to enhance the synthesis efficiency and conversion rate (Peng et al., 2017). The promoters used in these studies are alkaline metals, typically Cs, Ba, and K. Studies have shown that these promoters are able to increase the catalytic activity of the catalytic system by effectively decreasing the energy barrier for the dissociation of $N_2$, and facilitate the destabilization of the NHx species in equations generated during the plasma synthesis of $NH_3$ (Aika, 2017; Ma et al., 2017). Attaching promoters such as Cs and Ba to Ru can enhance the catalytic conversion process. Since Cs can easily be ionized, it can pass electrons onto Ru and nitrogen, which will aid the dissociation of nitrogen gas (Iwamoto et al., 2007). The high applied frequency and the metallic cation promoters added could enhance the electron transfer within the catalyst systems to aid the dissociation and ionization of nitrogen, which requires the highest ionization potential among the reactions shown in Section 3 (Bai et al., 2003; Larichev, 2010). The fact that the Ru catalysts with Cs promoters has much higher dissociative catalytic activity on $N_2$ than catalysts without promoters was proved by a study that used an isotropic analysis on the kinetic of the ammonia synthesis (Hinrichsen et al., 1997). A relatively more recent kinetic study pointed out that in this catalyst-promoter ammonia synthesis system, the cesium and barium each acted as an electronic promoter and andstructural promoter that controls the concentration of active sites (Szmigiel et al., 2002).

The third factor is the shape and structure of the catalyst. As discussed in the previous section, the reactors used in the plasma synthesis of ammonia were mostly fixed-bed reactors with gas-phase reactions. Therefore, the shape and structure of the catalyst were crucial as they could influence the flow channels, reaction time, surface area, number of active sites, etc., which were all critical parameters for the plasma synthesis of ammonia. More specifically for DBD plasmas, shielding effects and discharge with between the catalyst and electrodes should also be taken into consideration. From Table 3, it can be seen that the shape of the catalyst used in the earlier studies were powders, wires, and pellets. Prior to 2014, the study on NTP synthesis of ammonia mainly used powder and wire catalysts. Pellet-shaped catalyst were introduced and used in most studies after 2014. As Kim et al. (2016) mentioned, powder catalysts were not suitable for plasma process because they tend to spread under plasma conditions. According to other literature, the spreading of the powdered catalyst could be due to the charging and static electricity during the plasma treatment (Mazumder et al., 2006). In the later study carried out by Aihara et al. (2016), the authors claimed that the wool-like copper catalyst could increase the surface area of the electrode, allowing for more discharge, and enabling more effective ammonia synthesis over the electrode discharge.

## 6. Reactant type, composition, and feed rate

### 6.1. The effect of $N_2$ and $H_2$ composition and feed rate

From Table 2, it can be seen that the studies with the highest conversion rates do not correlate with the highest energy efficiencies. Several studies demonstrated that the greatest ammonia synthesis occurs with a feed-gas composition equal to (Bai et al., 2003; Gómez-Ramírez et al., 2016), or nearly equal to (Gómez-Ramírez et al., 2015; Mizushima et al., 2004), the stoichiometric ratio in equation (1). The increased hydrogen content promoted an increase in both electron density and temperature, which led to a positive shift in the mean electron energy distribution. This shift favored the formation of the NH species in equations (3)–(7). For these studies, the plasma discharge conditions were relatively less intense with lower voltages and frequencies (below 5 kHz and 500 kV/m). However, there are several studies that reported increased ammonia synthesis results under high $N_2$ compositions (Aihara et al., 2016; Bai et al., 2000; Hong et al., 2016; Nakajima and Sekiguchi, 2008; Peng et al., 2016). For these studies, the gas-phase discharge conditions are relatively high, above 500 kV/m and 10 kHz. According to the recent kinetic modeling study, the effects

of the N2 and H2 composition on the continuous NTP synthesis of ammonia depend on several factors, including the electron temperature and density (Hong et al., 2017). It is mentioned in this study that $N_2$ compositions higher than the stoichiometric value in equation (1) were favored under high-density plasma conditions with high-energy electrons, which agreed with previous findings (Peng et al., 2016). The same trend was observed in the study using thermal plasma to synthesize ammonia as well (Van Helden et al., 2007).

The second factor affected by the reactant feed rate was the residence time. Residence time also had a significant impact on ammonia synthesis, especially for the continuous NTP packed-bed reactors. From Table 2, it could be observed that the range of residence time in the NTP ammonia synthesis studies varied from the scale of milliseconds to a minute. The study from Gómez-Ramírez et al. (2015) indicated that longer residence time would result in less ammonia production. This concept is supported by several other studies that specifically explored the dissociation of ammonia under plasma conditions (Lu et al., 2014; Wang et al., 2013). These studies revealed that non-thermal plasma could also promote the decomposition of ammonia back to hydrogen and nitrogen gas, especially with the presence of iron-based catalysts (Wang et al., 2013). Therefore, decreasing the residence time of the feed-gas within the NTP region helped prevent efficiency diminishing back reactions, such as ammonia decomposition.

### 6.2. Reactants other than $N_2$ and $H_2$

Similar to the conventional Haber-Bosch process, most of the NTP ammonia synthesis studies used $N_2$ and $H_2$ gas as the reactants. However, there are two exceptions. Overall, the attempts of investigating in reactants other than $N_2$ and $H_2$ is to explore the possibilities of improving the efficiency for the NTP ammonia synthesis approach and enhance its environmental sustainability. However, there is one study that has the potential of leading to a promising alternative to combine the NTP process with other waste treatment technologies for a cleaner production of ammonia. The study carried out by Bai et al. (2008) used $CH_4$ and $N_2$ as feed gas for NTP ammonia synthesis. Although there were no catalysts used in this study, the authors managed to produce ammonia with a maximum conversion of 0.8%. The authors did not report the synthesis efficiency data. But it is notable that in this study, many $C_xH_y$ species were formed during the reaction from the dissociation of $CH_4$, such as $C_2H_6$, $C_2H_4$, $C_3H_8$, etc. Although this study is only at preliminary stage, its results provide a potential alternative for the clean production of ammonia. As $CH_4$ is a greenhouse gas emission during anaerobic digestions used at many waste water treatment facilities (Ma et al., 2015), its use for synthesizing ammonia could significantly improve the sustainability of the waste treatment industry. The second study used N2 gas with water and ethanol solution. Note that in this study, the water and ethanol solution used act not only as the reactants, but also absorbents for the synthesized ammonia. Therefore, the ammonia produced in this study was in the form of aqueous $NH_4^+$. Like the previous study that used $N_2$ and $CH_4$ as the reactants, this study also led to the formation of side products, which were aqueous $NO_2^-$ and $NO_3^-$.

Although $N_2$ and $H_2$ were used as the reactants, the two studies carried out by Nakajima and Sekiguchi (2008) and Hong et al. (2014) incorporated the idea of introducing a "quenching gas" into the system. The authors suggested that due to the exothermic nature of ammonia synthesis, the injection of a quenching gas could effectively lower the temperature of the reactor, which could further enhance the ammonia synthesis by preventing the decomposition of ammonia. Therefore, an increase in ammonia production was observed in this study. As a result, another study by

Hong et al. (2014) managed to achieve a 4.2% conversion to ammonia, which is one of the highest conversions yet reported amongst NTP ammonia synthesis studies. With the exception of the three studies just discussed, a review of literature demonstrated an almost unanimous use of $N_2$ and $H_2$ as reactant feedstock. However, despite the continuity in choice of feedstock, these studies exhibited remarkably different results when testing gas feed rates. Of note, an additional study that utilized expanding thermal plasma (ETP) in the synthesis of ammonia from $N_2$ and $H_2$ also confirmed the positive effects of introducing Ar as a quenching gas (Van Helden et al., 2007).

## 7. Challenges and opportunities

### 7.1. Challenges

Based on the relevant studies discussed in the previous sections, the main challenges of the NTP synthesis of ammonia are two-fold. The first challenge is the nitrogen fixation. The energy required to break the nitrogen triple bond is approximately 945 kJ/mol (9.79 eV), which is the largest activation energy required in both conventional and NTP ammonia synthesis (Misra et al., 2016). The specific energy plays a critical role in facilitating the reaction to synthesize ammonia. Unfortunately, the effects of increased specific energy input are a bit of a double-edged sword with regards to ammonia synthesis. Increased specific energy input leads to an increase in the number of high-energy electrons and important reaction intermediates (such as NH*), which are reportedly responsible for both the product formation and undesired back reactions (the decomposition of the product) (Van Helden et al., 2007). This leads to the second challenge of the NTP ammonia synthesis, which is the immediate dissociation of ammonia after it is produced. The decomposition effect of NTP on ammonia was first revealed by studies related to air pollution and off-gas treatment (Oda, 2003; Urashima and Chang, 2000). Wang et al. (2013) demonstrated that NTP could decompose ammonia with the assistance of Fe catalysts and avoid nitrogen poisoning during the process. Furthermore, other studies also indicate that transitional metals including Fe, Co, Cu and Ni demonstrated relatively high activities during plasma-assisted ammonia decomposition (Ji et al., 2013; Wang et al., 2015). Therefore, to minimize the dissociation of ammonia during its plasma-assisted synthesis process, it is encouraged that transition metals should be avoided for the catalyst selection.

### 7.2. Opportunities

This section is a discussion of the opportunities to overcome several of the major difficulties in developing an efficient method NTP ammonia synthesis, as well as future opportunities in the application of this technology as a competitive and environmentally friendly alternative to the traditional method of ammonia synthesis. Since NTP ammonia synthesis is still considered a cutting-edge research topic, it is very possible that the opportunities for breakthroughs could be inspired from the most recent and innovative ammonia synthesis studies under intense conditions. Some studies that synthesize ammonia under high temperature and pressures have been depositing ruthenium onto carbon nanotubes, or innovative structures to enhance the catalytic binding efficiencies (Wu et al., 2003). Another creative catalyst structure that could potentially benefit NTP ammonia synthesis is the use of electrode support within the catalyst matrix. Several studies, although performed under high temperature and pressure, used a new catalyst structure that loads ruthenium onto a new electrode support $12CaO \cdot 7Al_2O_3$ to prepare a unique catalytic structure of Ru/

C12A7:e⁻ (Kanbara et al., 2015; Kitano et al., 2012, 2015). The three studies pointed out that the stable electrode material could perform both as an electron donor and as a reversible hydrogen storage site, while simultaneously enhancing ammonia synthesis by shifting the rate limiting reaction from nitrogen dissociation to hydrogen bonding. With regards to the previously discussed reactor development, the rapid absorption of ammonia after its synthesis is critical to prevent back reactions. A recent study pointed out a potential opportunity to overcome this obstacle, showing that the introduction of lewis acidic and redox-active sites to porous sorbents could enhance the ammonia absorption (Tan et al., 2015), which could be another worthwhile topic of investigation related to NTP ammonia synthesis. Since ammonia can be easily decomposed by NTP, it is greatly beneficial if ammonia can be absorbed and removed from the plasma discharge region immediately after it is synthesized. In this way, this technology can be significantly more environmental sustainable due to the large increase in conversion and efficiency.

Despite the current challenges, NTP is still considered a promising technology for the future of ammonia production. The largest opportunity of this technology is the elimination of fossil fuels from the ammonia synthesis process. Due to its "green" nature, this technology is recognized as one potential method of realizing sustainable agriculture (Pfromm, 2017). further pointed out that it could act as an essential part of the wind-to-ammonia concept, where the hydrogen from renewable sources can be fed the NTP reactor to sustainably generate ammonia to be used as a fertilizer and clean fuel (Peng et al., 2016; Tallaksen et al., 2015). The new version of this renewable concept with the implementation of NTP ammonia synthesis technology is demonstrated in Fig. 4. On farm sites or renewable energy plants, energy sources such as wind, solar or hydro can be used to provide energy for the electrolysis of water, which would provide the hydrogen gas required for ammonia synthesis. The hydrogen gas, or other hydrogen-rich gases such as methane, can also be converted from biomass agricultural waste through gasification or anaerobic digestion. Lastly, the NTP plasma synthesis can be powered by the renewable energy technologies as well. This renewable energy solution provides a promising alternative for farm sites and small industries to become accessible to sustainable energy and ammonia fertilizer via a renewable

pathway. Furthermore, this pathway has promising opportunities due to the fact that it fully utilizes the advantages of the NTP ammonia synthesis such as less land use, low capital cost, and less intense reaction conditions, and incorporates these advantages with other renewable technology processes. Due to ammonia's excellent performance as an energy carrier and storage material, one of the advantages of using wind energy to power the NTP ammonia synthesis is that the ammonia could be considered as an excellent off-peak energy storage material (Matzen et al., 2015). Furthermore, the combination of using wind and electrolysis with the NTP ammonia synthesis will reduce fuel transportation costs and enable the synthesis fuel and fertilizers on site. For small industries and local farms, this is critical since the distributed energy and fertilizer synthesis will free them from market price fluctuations (Morgan et al., 2014). Additionally, using gasification to convert biomass into hydrogen gas can utilize the waste produced by farms and generate sustainable fuel and energy (Lozano and Lozano, 2017). However, the main challenges for the wind and biomass gasification technologies are their inconsistency (Karltorp, 2016). For wind energy, the power produced for the plasma is highly dependent on the wind resource at the specific time frame. On the other hand, the large variance of the biomass would result in the change of syngas components from the gasification process (Sansaniwal et al., 2017). Therefore, the hydrogen separation process needs to be adjusted according to the syngas composition, which would introduce additional undesired cost.

In terms of energy conversion, NTP is a technology that could theoretically fix nitrogen more efficiently than the conventional thermal fixation methods (Patil et al., 2016b). Cherkasov et al. (2015) reported that NTP nitrogen fixation has a theoretical efficiency floor of 0.2 MJ/mol, which is more efficient than the Haber-Bosch method of 0.48 MJ/mol. Additionally, Azizov et al. (1980) allegedly reported an energy consumption of 0.29 MJ/mol through the oxidation of diatomic Nitrogen in a microwave-induced plasma generator. Other factors that make NTP one of the most attractive alternatives to the Haber-Bosch method are the low land requirement and mobile capability. Being able to produce ammonia in a continuous manner at a scale accessible to the small industries and local farms, the NTP ammonia synthesis is well suitable for the world's trend of distributed and renewable energy production (Ingels and Graves, 2015a, 2015b).

As mentioned in Section 1, the two other relatively new technologies that synthesize ammonia under low temperature and pressure conditions are the biological and electro-chemical synthesis. Among the three processes, NTP is reported to have greater future improvement prospects of a variety of N-fixation methods such as Haber-Bosch and biological synthesis (Cherkasov et al., 2015). The biological ammonia synthesis utilizes nitrogenase enzyme in microorganisms to fix the nitrogen from nitrogen gas or nitrate/nitrite solutions and convert them into ammonia (Hinnemann and Nørskov, 2006). For this technology, the growth media provides the energy sources of the microorganisms. Therefore, electricity, or other energy input is not required. However, the drawbacks of this technology are that the system could only be operated in the liquid phase with slow production rates, and produces byproducts such as nitrate and nitrite species. Furthermore, like other biological conversion processes, the improvements of this technology rely heavily on the engineering of complex enzymes, which is a more challenging obstacle compared with the development of inorganic catalysts. Instability in the market of enzyme producers and lack of fixed cost is also a large hindrance to expanding enzyme-based technologies. For the electro-chemical synthesis approach, it uses electrolytes to facilitate hydrogen transfer between the reactants and produce ammonia (Kyriakou et al., 2017). The largest advantage of this technology is that it
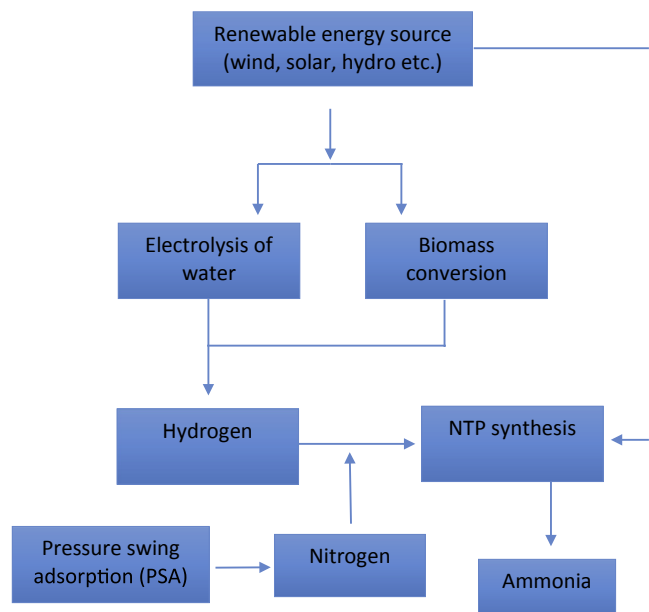


**Fig. 4.** An illustrative diagram of the renewable-to-ammonia approach.

can be operated with both liquid and gas reactants. However, the major limitation of this technology is the high cost for the coated mesoporous electrolytes (Montoya et al., 2015). Furthermore, the production rate and the efficiency of this technology could only be enhanced via the development of new electrolytes and coated catalysts, which restricts its room for improvements. On the other hand, the wide selection of plasma discharge types offers more opportunities for the NTP synthesis of ammonia. According to the plasma type, the operational pressure could be from vacuum to atmospheric pressure. Furthermore, the different discharge type, as listed in Table 2, has different discharge principles and leads to a larger room of improvement for this technology beyond the catalyst development.

## 8. Conclusions and remarks

In conclusion, the NTP synthesis of ammonia is a potential alternative technology to the Haber-Bosch ammonia synthesis process that could lead to a cleaner ammonia production. It is a promising technology and is suitable for the distributed hydrogen energy production and storage. This emerging technology has been realized at the bench scale and is currently been optimized by various efforts. In summary, the current development of this technology is mainly focused on the kinetic study, reactor/catalyst development, and reactant composition studies.

For the kinetics studies, most of the efforts have been made trying to identify the rate-limiting step of the plasma ammonia synthesis and classify the complex plasma reactions. For reactor development, reactors from rectangular, ferroelectric, to tubular DBD discharge reactors, etc. have been explored. System parameters such as discharge conditions and residence time are the crucial factors to develop and design efficient reactors for this technology and realize the cleaner production of ammonia with less energy input. For catalyst development, non-catalyst, mono catalyst, catalyst-support, and catalyst-support with promoters were investigated. During the investigation of the reactant composition, the effects of changing the $N_2$ to $H_2$ ratio were studied. However, several preliminary studies revealed the possibility of using $CH_4$ or a liquid-gas reaction to synthesis ammonia under NTP conditions. These studies provided a potential avenue of combining the NTP technology with other waste treatment processes for a cleaner and more environmental sustainable ammonia production industry.

From the results obtained from the literature, the main barriers faced by this technology were identified as the fixation of nitrogen gas and prevention of unwanted back reactions (ammonia decomposition). To overcome these obstacles, reactors with instantaneous product absorption and separation are recommended, along with catalysts of stronger plasma synergistic activities. Furthermore, the development of a catalyst with higher activities and introduction of a fast-separation reactor, using solid or liquid sorbents, could potentially solve the challenges and ensure the competitiveness of the technology. Despite these challenges, NTP's remarkably low theoretical energy floor provides an enticing opportunity for future use in industrial process. Its other advantages, such as low capital cost, less land use, small scale accessibility, offer this technology many opportunities to reshape the ammonia production industry towards a greener and cleaner process.

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## Appendix: Nomenclature

*Nomenclature*

$\alpha$: and $\beta$ Coefficients for the power kinetic equation
*r*: Rate constant
*X*($\upsilon$): Vibrationally-excited X
*Surf*: Catalyst surface
*e*: Electron
$X^*$: X radicals
*X* (*s*): Surface-adsorbed X