

Review

Recent Progress of Plasma-Assisted Nitrogen Fixation Research: A Review

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Received: 5 November 2018; Accepted: 30 November 2018; Published: 3 December 2018



Abstract: Nitrogen is an essential element to plants, animals, human beings and all the other living things on earth. Nitrogen fixation, which converts inert atmospheric nitrogen into ammonia or other valuable substances, is a very important part of the nitrogen cycle. The Haber-Bosch process plays the dominant role in the chemical nitrogen fixation as it produces a large amount of ammonia to meet the demand from the agriculture and chemical industries. However, due to the high energy consumption and related environmental concerns, increasing attention is being given to alternative (greener) nitrogen fixation processes. Among different approaches, plasma-assisted nitrogen fixation is one of the most promising methods since it has many advantages over others. These include operating at mild operation conditions, a green environmental profile and suitability for decentralized production. This review covers the research progress in the field of plasma-assisted nitrogen fixation achieved in the past five years. Both the production of NO_x and the synthesis of ammonia are included, and discussion on plasma reactors, operation parameters and plasma-catalysts are given. In addition, outlooks and suggestions for future research are also given.

Keywords: nitrogen fixation; plasma reactors; process intensification; novel reactors

1. Introduction

Nitrogen was discovered in the late 18th century by Daniel Rutherford, and it was called noxious air or azote, which means “no life” due to the asphyxiate property. However, nitrogen is a necessary component of many biomolecules, including amino acid, chlorophyll DNA, RNA and ATP. Nitrogen makes an indispensable contribution to protein synthesis, photosynthesis, determination of genetic characters and all the other important processes of life [1–3]. It is also essential to the production of many chemicals such as fertilizers, drugs, explosives or colourants, and it exists in various forms, including both organic and inorganic forms (such as ammonia, nitrate, amino acid, nuclear acid, etc.) that can be found in soils, rocks, oceans and living matters [4]. More than 99% of the global nitrogen is in the form of atmospheric N₂, which takes 78% of air [5]. However, N₂ is chemically inert and thus inaccessible for most of the organisms. Therefore, it has to be first converted into a reactive form (like ammonia or nitrates) in a process named nitrogen fixation. This process consists in breaking the strong triple bond of the N₂ and bonds the N atom to any other element like oxygen, hydrogen or carbon. This process completes the earth nitrogen cycle [4,6].

The estimated amount of global nitrogen fixation is around 413 Tg/y, which comes from both natural and anthropogenic ways [7,8]. The Biological nitrogen fixation (BNF) is the major source. However, the process is rather slow, thus not able to provide the fertilizing requirements to

support the growing population. The most widely used industrial nitrogen fixation process is the Haber-Bosch (H-B), which synthesizes ammonia via chemical reaction (of hydrogen and nitrogen) under high-temperature and high-pressure conditions with heterogeneous catalysts. Until 2010, more than 120 TonN/yr are fixed through this process [9], of which approximately 80% is subsequently used as fertilizer and the other 20% is used as feedstock for the synthesis of other N-containing chemicals [10,11]. The development of industrial nitrogen fixation has resulted in an exponential increase in global food production, able to meet the demand of the rapidly increasing population, as shown in Figure 1. According to the research done by Smil et al. and Erisman et al. [9,12,13], around 40% of the world population was making use of fertilizers by the end of the 20th century. This number increased to 48% by 2008, which indicates the enormous contribution made by the industrial nitrogen fixation. Furthermore, it has been predicted that the world's population will reach 8.6 billion in 2030 and further to 9.8 billion in 2050 [14]. Under this scenario, it becomes obvious that there will be an increasing demand for fertilizers, and thus further developments in industrial nitrogen fixation processes is of great importance.

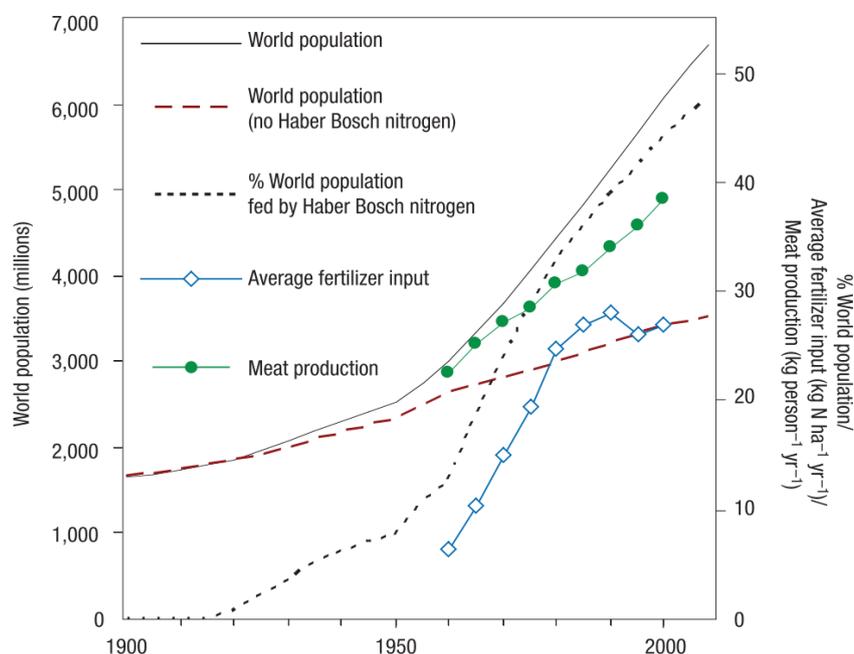


Figure 1. Human population growth with the increase of nitrogen usage from 1900 to 2008. Reprinted by permission from Springer Nature, Nature Geoscience, “How a century of ammonia synthesis changed the world”, Jan Willem Erisman et al. [9], [COPYRIGHT] (2018).

In history, many attempts have been made in order to artificially fix the nitrogen, including the Frank-Carlo process [15–17], the Birkland-Eyde (B-E) process [15,18–20] and the Haber-Bosch (H-B) process. Among them, the one invented by Fritz Haber and commercialized by Carl Bosch (the H-B process) has been widely recognized as one of the most important inventions of the 20th century [12]. Ammonia is synthesized by reacting N_2 and H_2 at high temperature (450–600 °C) and pressure (150–350 bar) in the presence of catalysts. Over the last 100 years, the H-B process has been fully optimized, with further developments in catalysts, replacing coal with natural gas as the feedstock, better heat integration, etc. As a result, energy consumption has been decreased to 0.48 MJ/mol ammonia produced [21,22]. Although the H-B process plays the dominating role in industrial nitrogen fixation, the process is highly energy intensive and associated with environmental concerns. In fact, about 1–2% of the total energy worldwide and 2% of the total natural gas are consumed by this process, which in turn is responsible for 300 million metric tons of CO_2 emissions [21,23,24]. Considering the fast-growing population and depletion of natural resources, it will be greatly

beneficial, both economically and environmentally, if the energy efficiency for nitrogen fixation can be improved. Therefore, continuous developments on sustainable methods for nitrogen fixation have been reported in the open literature, including efforts to improve the catalysts for the H-B process, the development of plasma-assisted nitrogen fixation processes, the study of biological nitrogen fixation and metallocomplex homogeneous catalysts. Reviews of the aforementioned green nitrogen fixation approaches along with a comparison between them have been given by Cherkasov and co-authors [22].

At its current state, the H-B process is very close to its theoretical limits of energy efficiency, and the most energy consuming part of the process is the generation of hydrogen. Therefore, the improvement of catalysts will not significantly increase the energy efficiency [25]. Water splitting using electricity has been suggested as a replacement of natural gas as the hydrogen source. However, this strategy is only of interest if renewable electricity is used, as the overall energy consumption will largely increase to circa 1.5 MJ/mol (three times higher than the H-B process [22]). This is associated with higher energy consumptions in hydrogen generation (360–480 kJ/mol [26]) compared to state of the art steam methane reforming.

Plasma-assisted nitrogen fixation is one of the earliest attempts of industrial nitrogen fixation. The Birkland-Eyde (B-E) process uses an electrical arc discharge to generate thermal plasma at high temperature for the synthesis of nitric oxide [27,28]. Considering the environmental profile, plasma processes have a great advantage by directly using abundant material like air and water, without relying on expensive H_2 , and could be powered by electricity generated from renewable resources such as wind or solar energy. In addition, there are no greenhouse gas emissions and waste production, making the process environmentally friendly. On the other hand, the energy efficiency of thermal plasma cannot compete with the H-B process, as already reported in the literature, where it has been shown that the theoretical energy consumption of thermal plasma is 0.86 MJ/mol of NO, which can be achieved under hypothetical conditions of 20–30 bars, 3000–3500 K and 10^7 K/s cooling rate [29]. However, the use of non-thermal plasma has a theoretical limitation of energy consumption ~ 0.2 MJ/mol (for NO_x synthesis) [29,30], lower than the limits of H-B process, as shown in Figure 2. Besides, the non-thermal plasma process has many other technical advantages such as one-step synthesis, a fast reaction, instant control, and suitability for small-scale and decentralized production [31]. The development of plasma technology in the past decades greatly inspired the researches of nitrogen fixation and, as a result, an increasing number of research findings have been reported.

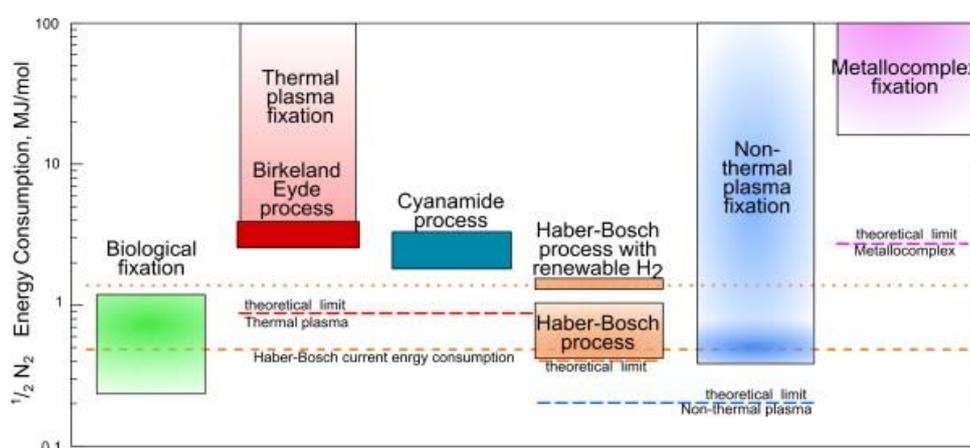


Figure 2. Energy consumption of different nitrogen fixation processes. Reprinted from Chemical Engineering and Processing, 90, N. Cherkasov et al., “A review of the existing and alternative methods for greener nitrogen fixation” [22,24–33], Copyright (2018) with permission from Elsevier B.V.

2. Brief Overview of Plasma Conversion Processes

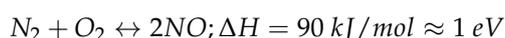
Plasma processes are among the oldest on earth (lightning) and are generated by the ionization of gases occurring when enough heat is supplied to the gas. Plasmas can be generated artificially by driving an electrical current through a gas, and it finds multiple applications. Plasma technology surrounds us, as it is widely used in surface cleaning and modification [32], cutting [32], coating [32] or in ozone generation. These applications are mature and commercialized. Besides, it has been proven that plasma technology has great potential in medical application [32], and “plasma medicine” may turn to large application and commercialization in near future.

However, nowadays there is an increased trend in finding new applications for plasma technology, in particular in the chemical sector for the conversion of different feedstocks into more valuable products. Production of NO_x from air, and direct conversion of N₂ and H₂ into NH₃ are among the most investigated processes using plasma reactors. However, other processes are also of interest and are here highlighted. Among the different processes, the reforming of CH₄ into syngas, and CO₂ decomposition are the ones with the highest interest nowadays. The effect of the operating conditions and reactor design in CO₂ conversion into CO has been recently reported by Mei et al. [33], indicating that developments in the design of a plasma reactor can result in important improvements in the overall energy efficiency. Other authors have recently reviewed the possibilities and challenges of the CO₂ conversion using plasma technology [34,35]. In this case, the conversion of CO₂ is not just limited to CO, but it can also be extended to CO₂ hydrogenation to syngas or CH₄, and also to dry reforming for H₂ production. The use of methane as feedstock is another research line of high interest, in which a plasma reactor can convert CH₄ into valuable products like syngas, H₂, methanol or acetylene in small-scale units [36], where the conventional technologies are not economically feasible. In this respect, many works have been recently published in the literature, with special emphasis on the reactor design and operating conditions in order to maximize the energy efficiency for the system [37–40]. In the different research topics, also the use of catalysts has been widely investigated [41,42], leading to the as known as plasma catalysis, which is currently another trend in the understanding of the reaction mechanism and all synergetic effects. A very detailed review on this topic has been recently published by Neyts and co-authors [43]. The research for the best reactor configuration, the type of plasma, operating conditions and integration of a catalyst are topics widely explored in the literature for several plasma conversions. In this review, all these topics are covered concerning plasma fixation as it will be presented in the coming sections.

3. NO_x Production

Plasma-assisted nitrogen fixation (in the form of NO_x) has many advantages, among which the possible use of air as feedstock, and the fact that NO_x can be used in many other applications. More importantly, non-thermal plasma for NO_x production has a lower limit of energy consumption than the H-B process. Till now, a large part of research efforts was focused on NO_x removal by plasma rather than the NO_x production process. However, there are still a lot of researches on NO_x synthesis reported during the last five years, including those targeting medical application and fertilizers production.

The overall reaction for NO_x production is shown below:



Generally, high temperature is favoured due to the endothermic nature and the high energy required for the dissociation of nitrogen molecules. In the case of the plasma process, reactive species such as atomic oxygen, vibrational excited nitrogen molecules generated from electron impact play important roles in the formation of NO. As suggested by R. Ingels and D.B Graves, the energy barrier for NO formation is about 20 GJ/tN if the kinetics are governed by excited states of N and O from non-thermal electron impact [44].

3.1. Type of Plasma and Reactors

In NO_x synthesis research, different plasmas have been used, and they could be classified into three different categories: thermal plasma, cold plasma and “warm” plasma. Most of the early researches reported the use of thermal plasmas, like the electric arc [45–47] or the spark discharge [48,49]. The electric arc plasma was used in the B-E process, in which 1% of nitric oxide was achieved, and subsequently used for the production of HNO₃ with an energy consumption of 3.4–4.1 MJ/mol [27,28]. In the case of thermal plasma, the limitation of theoretical energy consumption is high (see Figure 2). According to the thermodynamic calculation, a maximum NO concentration in an N₂-O₂ system in equilibrium at atmospheric pressure is 6.5% at 3500 K [50]. In order to obtain such concentrations in thermal plasma process, rapid cooling with a rate up to million K/s is required [51]. Therefore, the use of non-thermal plasmas is preferred as they can provide higher concentrations of NO_x due to their non-equilibrium behaviour. The production of NO in thermal plasmas involves both thermal Zeldovich mechanisms and electron-impact initiated reactions [52]. Vibrationally excited nitrogen molecules N₂^{*} are considered to be an important intermedia for NO production through electron-impact reaction, and formation of NO through N₂^{*} is an energy efficient route [53,54]. On the other hand, NO is the dominant product in most cases of thermal plasma, while the production of NO₂ and O₃ was suppressed partially due to the thermal effect.

Cold plasma refers to non-thermal plasma operated at a temperature which is close to room temperature. This type of plasma has a lower energy density than thermal plasma, and ozone is normally produced, which can oxidize NO to NO₂ [55,56]. Till now, high energy efficiencies have not been reported in the literature, and several researchers doubt the suitability of this strategy for NO production [57]. However, the cold gas temperature of this type of plasma enables the delivery of produced reactive nitrogen species to sensitive material, providing opportunities for applications such as wound disinfection and skin treatment [58–60].

Warm plasmas, which include both thermal and non-thermal plasma conditions, have been used for nitrogen fixation, and progress regarding energy efficiency and product selectivity has been recently reported in the literature. Among the different reactor configurations, the gliding arc is the one that has been considered to be the most efficient and promising discharge type for gas conversion [61–64]. In particular, the use of this reactor type has also been extended to other systems like CO₂ conversion and CH₄ reforming [62,65,66]. The schematic diagram of a typical gliding arc reactor is shown in Figure 3. The arc, initially formed at the narrowest gap between electrodes, moves along the horn-shape electrode by the gas flowing towards the wider end of the gap until it extinguishes. After that, a new cycle starts with the arc formation at the narrowest gap again. The production of NO_x has been reported in several previous works [67–69], and more detailed studies with special interest in energy efficiency, yield and reaction mechanisms were done recently. Wang et al. [53] investigated the NO_x synthesis in a pulsed power gliding arc discharge through chemical kinetic modelling, and their results showed that the vibrational excited N₂ can help overcome the energy barrier of the non-thermal Zeldovich mechanism $O + N_2(v) \rightarrow NO + N$, providing an energy efficient way to produce NO. The gliding arc reactor works in non-equilibrium conditions (maximum temperature of 1500 K), thus achieving much higher yields of NO when compared with the thermal process. Patil et al. [70] used a milliscale gliding arc reactor in their experimental study. Such milliscale configuration could reduce the volume of the gas that bypasses the arc, thus improving the contact between reactive species and gas molecules with a consequent increase in NO_x production. The highest concentration of NO achieved in this study is close to 1%, with an energy efficiency of 10 kWh/kg of NO_x. In a follow-up study [71], the NO_x concentration was increased up to 1.4%, which is a promising concentration for container-size fertilizer production plant.

A different strategy is to produce liquid fertilizers, where water can be used in a gliding arc reactor and the nitrogen is fixed as NO₂⁻ and NO₃⁻. This configuration was developed by Mizukoshi et al. [72], where a stable plasma was generated in this system.

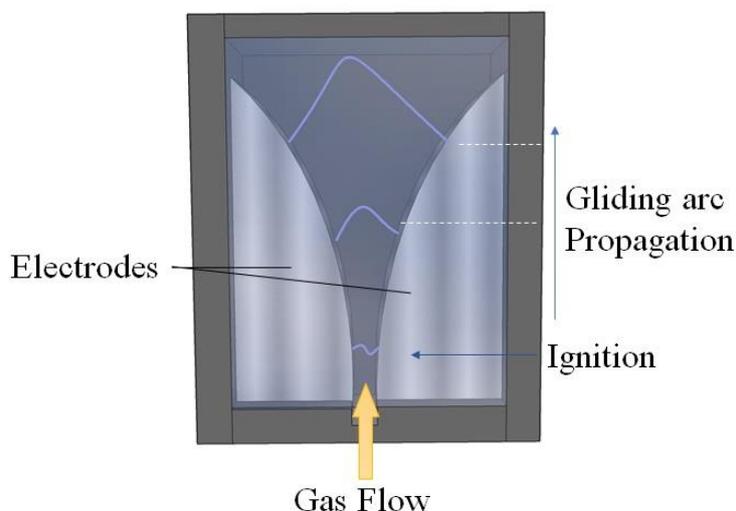


Figure 3. Schematic diagram of a typical gliding arc discharge.

Another type of warm plasma, the so-named transient spark discharge, was used by Janda et al. [73] for NO_x production. The transient spark discharge starts from a streamer phase, which is considered as non-thermal plasma and is subsequently transformed into short spark current pulses which generate thermal plasma [74,75]. Due to the self-pulsing feature, thermalization of the plasma can be avoided. However, a high electron density (as high as 10^{17} cm^{-3}) can be achieved during the spark phase, leading to high chemical activity comparable with a nanosecond pulsed spark discharge [76]. In their research, the energy consumption for NO_x production is 8.6 MJ/mol, and the excited nitrogen molecules N_2^* were observed in both the streamer and the spark phases. In another research conducted by Pavlovich et al. [52], a spark-glow discharge reactor was developed and the plasma discharge generated could have spark phase (thermal plasma) and glow phase (non-thermal plasma) in one cycle. By fine-tuning the voltage waveforms, the percentage of glow phase could be controlled. From their research, it was concluded that an increase in the percentage of the glow phase resulted in higher concentrations of NO_2 . The spark phase, which has a very high electron density and energy, generates more NO , while the glow phase promotes the NO oxidation to NO_2 . It should be noted that in the case of discharge types such as the transient spark, the plasma volume is generally limited, as a result, the production of NO_x is also limited. This could be considered for further research on optimization or up-scaling.

Non-thermal plasma reactors were mostly used to produce reactive nitrogen species and reactive oxygen species for biomedical application, meaning that the energy efficiency was not the main target, but just the production of NO_x in therapeutic levels. DBD (dielectric barrier discharge) reactors have also been used in NO_x synthesis, as they provide the possibility to enhance the energy efficiency and product selectivity by combining the plasma with a catalyst. However, few investigations have been reported with this reactor type. As one of the most explored plasma reactors for biomedical application, plasma jet has been investigated regarding the NO production not only directly from the gas phase, but also biological NO or intracellular NO generation following the plasma delivery [77]. Other types of plasmas and reactors like the DC corona or microwave plasma have also been reported recently, and an overview has been listed in Table 1.

Table 1. Plasma/reactor types used in recently reported researches of NO_x production.

Plasma/Reactor	Reactants Tested	Main Product	Reference
Spark-like	air, water	NO, NO ₂ , HNO ₃ , N ₂ O ₄	[52]
AC (alternating current) barrier corona with Magnetic field	air	NO, NO ₂ , O ₃	[78]
Microwave plasma	N ₂ , O ₂	NO, NO ₂	[79]
Transient spark	air	NO, NO ₂	[73]
DBD (dielectric barrier discharge)	air	NO, NO ₂ , O ₃	[80]
DBD	N ₂ , O ₂ , NO, H ₂ O	NO, NO ₂ , N ₂ O, N ₂ O ₅ , HNO ₂ , HNO ₃	[81]
DBD	N ₂ , O ₂	NO, NO ₂	[82]
Gliding arc	N ₂ , O ₂	NO, NO ₂	[53]
Gliding arc with flow system	water, air	NO ₂ ⁻ , NO ₃ ⁻ , OH	[72]
Sliding discharge	air	NO, NO ₂ , O ₃	[83]
Milliscale gliding arc	air, N ₂ , O ₂ with Ar addition	NO, NO ₂	[71]
Milliscale gliding arc	N ₂ , O ₂	NO, NO ₂	[70]
Pulsed arc discharge	air, N ₂ , O ₂	NO, NO ₂ , O ₃	
Spark discharge Gliding arc Transferred arc	air, water	NO, NO ₂ ⁻ and NO ₃ ⁻	[84]
Pulsed discharge DC (direct current) corona DBD off gas	N ₂ , O ₂ , Ar	H ₂ O ₂ , NO ₂ ⁻ , NO ₃ ⁻	[85]
DBD	N ₂ , O ₂	NO, N ₂ O ₅	[86]
DBD	air	NO, NO ₂	[87]
DC plasma jet	air	NO, NO ₂ , O ₃	[88]
Micro DBD Microwave plasma torch	air, Ar, N ₂	NO	[89]
Spray-type jet	N ₂ , H ₂ O	NO ₂ ⁻ , NO ₃ ⁻ , NH ₄ ⁻	[90]
Array type DBD	air	N ₂ O, O ₃ , HNO ₃ , and N ₂ O ₅	[91]
Spark discharge	air	NO, NO ₂ , O ₃	[92]
Plasma Jet	Ar, air	NO, NO ₂	[93]
AC corona	air	NO, NO ₂ , O ₃	[94]
Microwave plasma torch	N ₂ , O ₂	NO	[95]
Needle-type plasma jet	Ar + 2% air	NO	[96]

3.2. Operation Parameters

In order to control the NO_x synthesis, the operating conditions are key factors that determine the NO_x concentrations, NO₂/NO ratios and overall energy efficiency. Regarding the operating conditions, they can be divided into two different sets: (1) electrical parameters and discharge regimes, and (2) process parameters.

Electrical parameters and discharge regimes are directly associated with the energy input and the density of electrons produced, which have an influence on the temperature and determine the reaction mechanism. In research carried out by Pekárek [78], who used a corona-like DBD reactor combined with magnetic field to generate nitrogen oxides, the production of NO₂ increased with an increase in the applied voltage from 5800 V to 7400 V, while NO was not observed.

The study of transient spark discharge by Janda et al. [73] showed that the total NO_x generation is not affected by a change in frequency, although the NO₂/NO ratio is actually decreased with an increase in frequency. This is caused by the change in the discharge properties, which are directly related to the NO₂/NO synthesis mechanism in both the streamer and the spark phases of the discharge. Han et al. [80] also investigated the effect of frequency on the NO_x production in DBD plasmas in air.

Experiments were carried out at different frequencies in the ranges of 5–10 kHz and 40–65 kHz and the frequency was considered as the main factor affecting the concentration of NO_x and the energy yield. At a fixed power of 73 W, the concentration of NO was 1051.7 mg/m³ and 135 mg/m³ at 10 kHz and 50 kHz respectively. The optimal frequency within the tested range was 7 kHz, and the energy efficiency was 20.5 mg/m³·W. Patil et al. [70] investigated the electrical and process parameters of the milli-scale gliding arc discharge for NO_x production. Different frequencies, pulse widths and amplitudes were tested in their experiments. The author stated that the increase in those parameters resulted in an increase in the specific energy input of the plasma, so that more energetic electrons and ions will be produced to facilitate the synthesis of NO_x . Moreover, discharge regimes could be altered when changing the frequency. At a frequency of 8 kHz, the reactor was operated in a static arc regime, which has a lower efficiency than the gliding arc regime operated at 7 kHz and 9 kHz.

Process parameters such as gas composition, flow rate and temperature, are also of great importance in NO_x production, and in many works, their influence has been investigated. For instance, the effect of flow rate and oxygen content on the NO_x synthesis by microwave plasma was reported by Lee et al. [79]. In particular, a decrease in the inlet flow rate from 45 slpm to 25 slpm and an increase in O_2 content from 1% to 3%, resulted in a remarkable increase in the NO_x concentration from 1612 ppm to 9380 ppm. The NO_2/NO ratio also increased (from 4.3% to 14.8%) with the increase in flow rate. Na et al. [95] used a microwave plasma torch to generate NO, and different N_2 (5–30 slpm) and O_2 (0–250 sccm) flow rates were tested. It was observed that lower N_2 flow rates and higher oxygen content resulted in a higher NO concentration. In the research of Hao et al. [88], the highest NO concentrations were also achieved at the lower flow rates (maximum 1000 ppm at 0.5 slm). However, the highest production rate (0.98 $\mu\text{mol/s}$) was achieved around 4 slpm, which is in the middle of the tested flow rate range.

A detailed experimental investigation on the process parameters in gliding arc discharge reactors was performed by Patil et al. [71]. In their study, oxygen contents around 35–48% were found to be optimal for NO_x production, and the NO selectivity decreased linearly with the increase in O_2 content until the O_2 content reached 48%. Further increase in O_2 content did not have an obvious effect on the NO selectivity. In this work, it was also observed that the NO selectivity decreased with the increase in the feed flow rate. In particular, it was measured that a decrease in the flow rate resulted in an increase in the specific energy input and residence time of the reactant, thus leading to a higher conversion of NO to NO_2 . Moreover, the highest NO_x concentration of 1.4% was achieved at the lowest flow rate of 0.5 L/min.

The temperature also has an influence on the NO_x production as reported by Malik et al. [83], who studied the temperature effect on NO_x production by pulsed sliding discharge. In their experiments, the electrode/dielectric surface in contact with the plasma was heated from 20 °C to 420 °C, and it was observed that the production of ozone and NO_2 were diminished while NO production became dominant at higher temperatures. It was also observed that the energy per pulse under the same peak voltage was increased. Ozone could be destroyed at high temperatures, and the conversion of NO to NO_2 was suppressed. At 420 °C, the NO_2/NO ratio was decreased to 0.25 and NO was produced with an energy consumption of 24–67 MJ/mol. An opposite tendency was claimed by Li et al. [94], who observed that the NO_2/NO ratio slight increased from 0.67 at 273 K to 0.80 at 373 K in their study using a corona discharge. It should be noted that the gas temperature varies largely for different types of plasma, reactors and operation parameters, so the temperature effect should be considered along with other factors but not separately. Also, extra heating or cooling will increase the energy cost of NO_x production and capital costs of the process.

3.3. Plasma-Catalysis for NO_x Production

Although plasma-catalysis has been intensively investigated in recent years, very few works have been reported in the field of NO_x production. Among these works, Cavadias and Amouroux used WO_3 as catalysts, and the nitrogen fixation rate achieved was 19%, which is much higher than using

plasma alone under low pressure (8%) [97]. Their research was carried out at atmospheric conditions using a fluidized bed reactor with $\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst [98]. Mutel et al. used MoO_3 as catalysts in their experiments and the energy consumption achieved was 28 MJ/kg of NO , which was 78% higher compared with a plasma jet arc generator [99]. Sun et al. investigated the catalytic activity of Cu-ZSM-5 and Na-ZSM-5 in a pellet filled DBD reactor. Significantly higher NO_x yields were observed in the case of Cu-ZSM-5 over Na-ZSM-5 at 350 °C [100].

A recent study by Patil et al. investigated the effect of support materials on the synthesis of NO_x in a DBD reactor [82]. Among all the tested supports ($\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$, MgO , TiO_2 , BaTiO_3 and quartz wool), $\gamma\text{-Al}_2\text{O}_3$, with the smallest particle size, showed the best performance on NO_x concentration and energy consumption. The authors believe that the formation of filamentary discharges is highly related to the NO_x production. It is also suggested that a good catalyst support should have a high surface area. Several metal oxides were loaded on the support and tested in the plasma-assisted NO_x synthesis. In particular, the 5% $\text{WO}_3/\gamma\text{-Al}_2\text{O}_3$ gave the highest concentration of NO_x , which is 10% higher than with $\gamma\text{-Al}_2\text{O}_3$ solely. Although there was an increase in NO_x concentration, the selectivity towards NO decreased, and this was associated to oxidation reactions on the catalyst surface with the oxygen species.

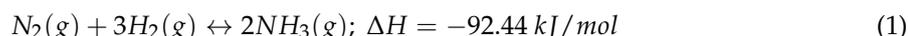
4. Ammonia Synthesis

Ammonia is the second largest chemical synthesis in the world today, and 90% of this chemical is produced by the H-B process [101]. The research on ammonia synthesis is always of great importance, not only because of the wide application of ammonia, but also the great scientific value. Started in the 1970s, the interest in ammonia synthesis using plasma technology has been increased [102–105] and, in particular, great efforts have been made in terms of plasma reactor design, catalysts development and the study of the reaction mechanism.

4.1. Reactants and Composition

4.1.1. Direct Synthesis of Ammonia from N_2 and H_2

Till now, most of the reported research used N_2 and H_2 to directly synthesize ammonia. Those researches are mainly focused on the plasma reactions without considering the source of hydrogen. In general, the reaction (1) is favored at low temperatures due to its exothermic nature, however, high energy input is required for the N_2 dissociation.



The main reaction mechanism in the plasma-assisted process has been shown in reactions (2)–(8). Initially, N_2 and H_2 are dissociated, the dissociation of N_2 is normally considered as the rate-limiting step due to its high dissociation energy (9.8 eV) [106,107].



The dissociation reactions are followed by the formation of NH radicals, which are considered as the most important intermedia [106–108]. Then NH_3 can be produced through stepwise addition reactions with H and H_2 .





In addition to the more general reactions, Akay et al. [109] presented the reaction mechanism including gas phase and surface reactions. The catalytic surface can adsorb N and H, forming NH and further react with H or H₂ in either gas phase or adsorbed phase on the surface.

The feed gas ratio (N₂/H₂) is an important factor that could influence the production of ammonia. Gómez-Ramírez et al. [110] found that the best energy efficiency was achieved with the feed gas ratio equal or close to the stoichiometric ratio. This conclusion is in line with many previously reported researches [110–114]. On the other hand, other studies have shown that a higher N₂/H₂ is favoured for the ammonia production [107,112,115–119]. A plausible explanation for this difference was given by Peng et al. [120], who believes that the average electron density and temperature is higher in a high hydrogen content environment with less intensive discharges (low voltage and frequency), promoting the formation of NH radicals, hence resulting in high ammonia productions. In the case of more intensive plasma discharges, which have higher electron energies, a nitrogen-rich environment is beneficial for generating more active nitrogen species that react with hydrogen, so that more ammonia can be produced. In their experimental study [107], plasma discharge with 7 kV and 10 kHz was used to produce ammonia under different feed gas ratios, and values of around 0.5 g NH₃/kWh were achieved with the stoichiometric ratio, while more than 0.8 g NH₃/kWh was achieved at N₂/H₂ = 3:1.

The residence time also plays an important role to achieve optimal results. As it was concluded in the research carried out by Peng et al. [107], the energy efficiency was increased with an increase in the flow rate from 0–5 L/min, and similar results were found elsewhere [121]. Gómez-Ramírez et al. [110] also observed this trend along with a decrease in N₂ conversion. The main reason was related to a lower extent of ammonia decomposition by plasma at high flow rates due to shorter residence times.

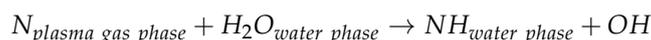
The addition of noble gases to N₂-H₂ plasmas could also influence the production of ammonia. Hong et al. [122] investigated this effect by adding argon in a pack-bed DBD reactor. More precisely, they added 10 sccm of Ar to the feed gas stream consisting of 30 sccm of N₂ and 30 sccm of H₂. They observed an increase in the discharge power, uniformity and gas temperature, and those factors lead to higher ammonia production rates. The optical emission spectra also indicated an increase in N⁺, which is possibly a result of the reaction between Ar⁺ and N₂. The authors stated that noble gases can be seen as an additional source of N atoms that contribute to the increase in NH₃ production [123]. De Castro et al. investigated the effect of helium addition in their research with DC glow discharge plasma [124,125]. Ammonia production was enhanced by 45% with 8% helium addition. According to their study, surface modification of the tungsten wall caused by helium addition is the key factor which enhanced the N–H recombination. Besides, the authors suggested that helium addition causes the increase in electron temperature and the change of the mass spectrometry measurements, which might also contribute to the increase of the measured value of ammonia.

4.1.2. Plasma-Assisted Ammonia Synthesis with H₂O

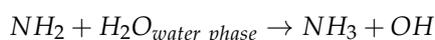
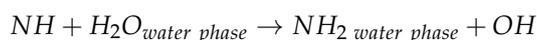
Besides H₂, H₂O can also be used along with N₂ for ammonia synthesis in plasma reactors. The role of H₂O is to provide hydrogen through its dissociation by the plasma. Xie et al. [115] investigated the production of ammonia with N₂ and H₂O in gas phase by using a DBD reactor packed with Ru/Al₂O₃ catalyst. The best energy efficiency of ammonia production was 18 mg/kWh, achieved with 0.14% H₂O content. However, a much higher energy efficiency (640 mg/kWh) was achieved by using H₂ + N₂ as reactants. This was attributed to an easier dissociation of H₂. In the case of using a ternary mixture of N₂, H₂, and H₂O, it was found that the addition of 0.14% H₂O promotes the ammonia production, especially when H₂ concentration was lower than 10%. It should be noted that the existence of gas phase H₂O has an influence on the electrical characteristics and the reactive species generated, which could further influence the ammonia production. The electron affinities of H₂O can cause a decrease in electron density in plasma, and an increase in the inception voltage for plasma generation [126].

H₂O can also be introduced into the reactor in liquid form to produce ammonia through plasma-liquid interaction. Despite strong hydrogen bond on the surface of water, some hydrogen bonding is lost [127], providing hydrogen species for ammonia synthesis. Haruyama et al. [128] used plasma in combination with (ultraviolet) UV radiation to produce ammonia in air/N₂ + liquid water environment, as shown in Figure 4. UV radiation was used to enhance the hydrogen extraction by plasma-liquid interaction, which was considered as the rate-limiting step. The formation of ammonia was suggested as:

Extraction of H to form NH on the surface:



Reduction of NH to NH₃ in liquid phase:



In a follow-up study [129], pre-exposure to UV radiation before plasma + UV treatment resulted in a higher ammonia concentration. The authors suggested that the way to increase ammonia production is to increase the number of activated nitrogen molecules in plasma and hydrogen atoms in the liquid phase.

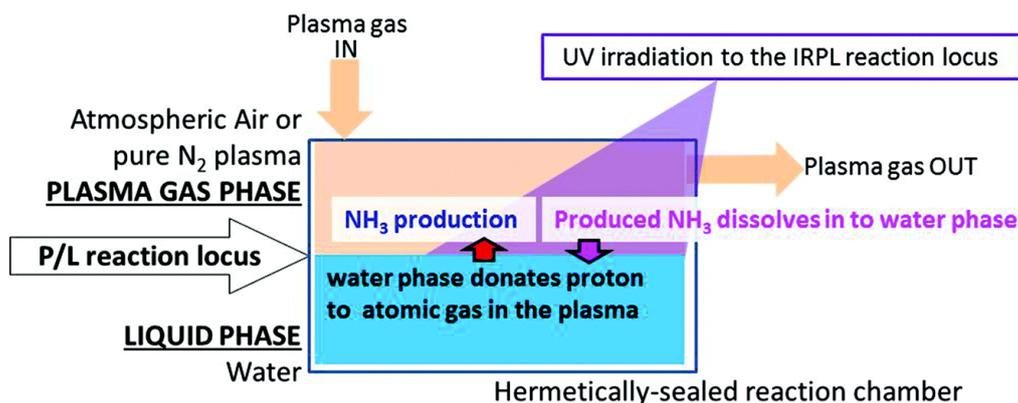


Figure 4. Plasma-liquid interfacial reaction locus with ultraviolet (UV) radiation for ammonia synthesis. Reprinted from “Non-catalyzed one-step synthesis of ammonia from atmospheric air and water”, Haruyama et al. in Green Chemistry issue 16, 2016 [128], Published by The Royal Society of Chemistry.

4.1.3. Other Reactants

In the open literature, the research into ammonia synthesis in plasma reactors has been extended with investigations using different reactants. In early years, Oumghar and Lergand et al. [130–132] carried out experiments using CH₄ as H₂ source. Ammonia was produced along with other carbon-based products including C₂H₂, C₂H₄, C₂H₆ and HCN. Horvath et al. [133] investigated the plasma generated in N₂ and CH₄ mixture in a pack-bed DBD plasma, although very small amounts of ammonia were observed. Bai et al. [134] also used CH₄ and N₂ as reactants and published their research in 2008. By using a microgap DBD reactor without catalysts, ammonia was successfully produced in the order of 8000 ppm, and also other products were produced such as hydrogen, with a yield of 9.1% (v/v). CH₄ is the major constituent of natural gas, thus the direct use of CH₄ for plasma-assisted ammonia synthesis could bring many benefits. Among them, the step of hydrogen production is no longer needed, hence simplifying the process. As CH₄ is a greenhouse gas which also comes from the waste treatment industry, the utilisation of CH₄ could improve the sustainability of the industry [120,135].

Besides direct synthesis in plasma/plasma-catalysis reactions, ammonia can also be synthesized indirectly. Zen et al. [136] have proposed a method of such indirect synthesis by using Mg_3N_2 as the solid-state ammonia carrier. In their research, MgO was exposed to DBD plasma in N_2 at atmospheric pressure to produce Mg_3N_2 through nitridation. Then NH_3 can be produced by Mg_3N_2 reacting with H_2O at room temperature. After the reaction, MgO can be regenerated by heating the $\text{Mg}(\text{OH})_2$, as shown in Figure 5. This indirect method does not cause the decomposition of NH_3 in plasma and does not require hydrogen as feedstock. However, only a maximum 93 mg/kWh efficiency for Mg_3N_2 can be reached, and extra energy is needed for the regeneration of MgO , leading to a lower efficiency for ammonia production. Therefore, further research is needed to dramatically improve the energy efficiency, especially for the plasma nitridation of MgO .

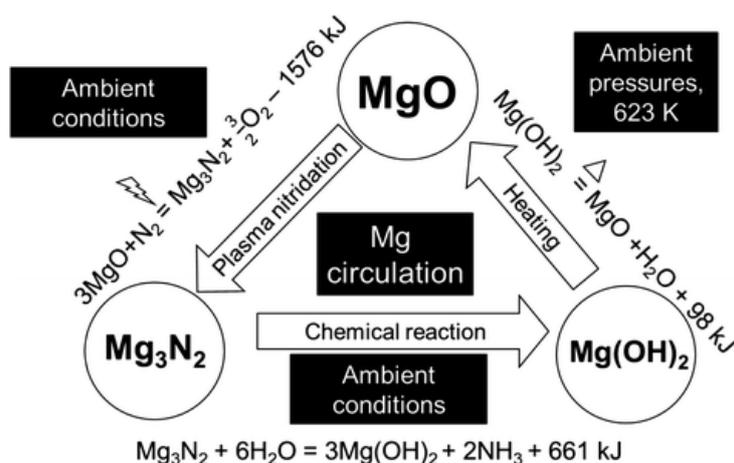


Figure 5. Plasma-assisted indirect synthesis of ammonia by using magnesium compounds. Reprinted by permission from Springer Nature, Plasma Chemistry and Plasma Processing, “Indirect Synthesis System for Ammonia from Nitrogen and Water Using Nonthermal Plasma Under Ambient Conditions”, Zen et al., [136], [COPYRIGHT] (2018).

4.2. Plasma/Reactor Types and Electrode Configurations

The adopted reactor configuration and the plasma characteristics can have a large influence on the reaction mechanism, resulting in different ammonia production efficiencies. This effect was summarized by Hong et al. [137], who gave an overview of the reported researches of ammonia synthesis by different types of plasma and categorized them into three groups: thermal plasma, low-pressure non-thermal plasma and atmospheric pressure non-thermal plasma. Due to the high processing temperature, thermal plasma is not considered to be the ideal plasma type for ammonia synthesis. Low-pressure non-thermal plasma, which has a low density of excited species and requires vacuum condition for plasma generation, does not normally have a high ammonia production rate. On the other hand, atmospheric non-thermal plasma is considered to have great potential in ammonia production. The high density of neutral radicals and excited molecules can be generated in atmospheric non-thermal plasma to facilitate the reactions on the catalysts surface, therefore high ammonia production rates can be achieved.

Despite few studies in low-pressure glow discharge plasma [124,125,138], atmospheric DBD plasma was used in most of the recent works. DBD is favoured over other configurations as it provides many advantages such as high density of energetic electrons, low processing temperature, continuous process, easy to integrate with catalysts and low cost for operation and maintenance [139–145]. The configuration of a DBD reactor normally consists of two electrodes and a dielectric material between them. Bai et al. [113] used a micro gap DBD reactor with a discharge gap of 0.47 mm, and a thin $\alpha\text{-Al}_2\text{O}_3$ layer was used as the dielectric material. In that research, ammonia was produced with a concentration of 12,500 ppm at an energy efficiency of 1.53–1.83 g/kWh. Mizushima et al. [114]

designed a DBD reactor with the tubular membrane-like catalyst (Ru/alumina catalysts). These authors claimed that the existence of catalysts in this design does not have an obvious influence on the discharge current and power consumption. In recent studies, pack-bed cylindrical DBD reactors were the most popular design, and a typical design of such reactor is shown in Figure 6. Akay and Zhang et al. [109] used such a reactor for ammonia synthesis, where supported microporous catalysts were packed in the discharge gap. Moreover, the authors investigated different electrode configurations in their study, and the results showed that the energy consumption of a single dielectric barrier reactor (which covers the stressed electrode) with and without catalysts are 81 MJ/mol and 112 MJ/mol correspondingly. The numbers are lower than in the case of double dielectric barrier reactor (both electrodes covered by dielectric layers), which are 143 MJ/mol without catalysts and 132 MJ/mol with catalysts.

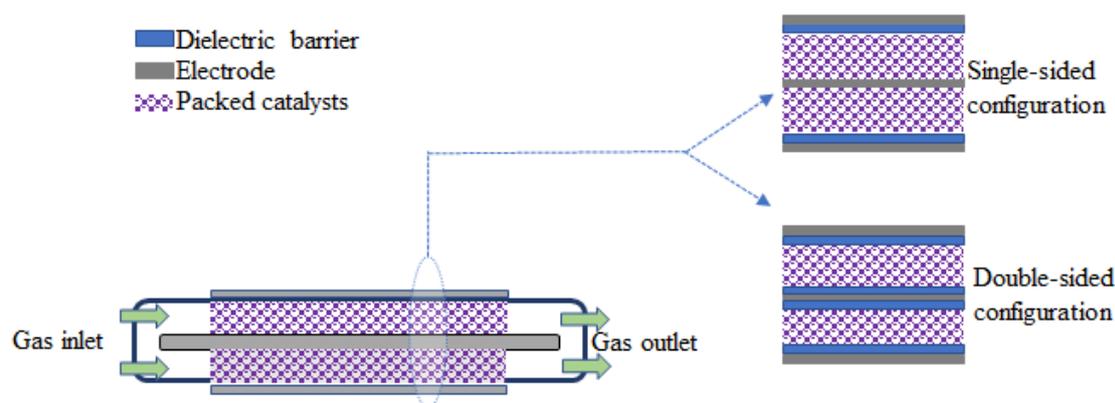


Figure 6. Packed-bed cylindrical dielectric barrier discharge (DBD) reactor.

The addition of Ar was investigated by Aihara and Iwamoto et al. [116], who used a wool-like copper electrode as shown in Figure 7 and obtained a maximum ammonia yield of 3.5% and a maximum energy efficiency of 3.30 g/kWh. The catalytic effect of the electrode material has been considered as a major reason for this result, and this effect changes with the deposition of copper on the reactor wall. In a follow-up study [146], the authors tested twelve different electrodes and the results showed that Au has the highest catalytic activity.

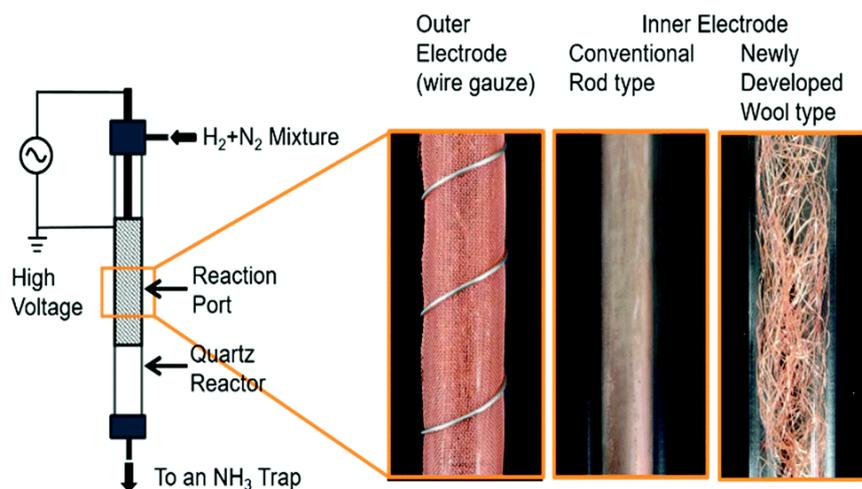


Figure 7. DBD reactor with wool-like electrode. Reprinted from “Remarkable catalysis of a wool-like copper electrode for NH₃ synthesis from N₂ and H₂ in non-thermal atmospheric plasma”, Aihara et al. [116], in Chemical Communications, 2016, with permission from Royal Society of Chemistry.

Planar DBD reactors have also been proposed for ammonia synthesis [117]. This type of reactor provides higher flexibility for the investigation of reactor parameters such as discharge gap size. Gómez-Ramírez et al. [112] used a planar DBD reactor packed with ferroelectric material to study the effect of varying the discharge gap. The energy efficiencies measured in the case of the 3 mm gap and 10 mm gap were 0.45 and 0.55 g NH₃/kWh respectively. However, the conversion of N₂ showed a reverse tendency (2.7% for the 3 mm gap and 1.8% for 10 mm gap). In the literature there are other types of electrode configurations, such as the needle array DBD [142,147]. However, until now there is not a solid conclusion on the reactor design for the plasma-assisted ammonia synthesis process, and thus further research in combination of catalyst development and scale-up attempts is needed.

4.3. Catalysts Selection

In a plasma-catalysts system, the catalytic surface reaction is determined by both, the reactive species generated from the plasma and the chemical and physical properties of the catalyst. The characteristics of the plasma can be influenced by the catalysts, while catalysts properties can also be altered by plasma discharges. Until now, the mechanism of plasma-catalysis is not fully understood, and the researches on plasma catalysis are mainly based on the knowledge of thermal catalyst and the trial-and-error experiment method. The development of catalysts is equally important as the development of reactor and plasma systems. In general, three factors need to be considered when selecting a proper catalyst for plasma-assisted ammonia synthesis: (1) material of catalysts, (2) support and promoter, and (3) structure and shape. In many early researches, the catalytic effect of many materials on plasma-assisted ammonia synthesis has been reported [104,105,148,149]. Catalysts used in recent researches are listed in Table 2. A study by Gómez-Ramírez et al. [110,112] used ferroelectric material (BaTiO₃ and Lead zirconate titanate) to enhance the performance of a DBD reactor for ammonia synthesis. A maximum conversion of 7% was achieved in their study. They suggested that the enhancement by the ferroelectric material is attributed to two main reasons: (1) effect on the discharge behavior, which resulted in a higher electron density, and (2) the catalytic effect of the ferroelectric material surface.

Table 2. Catalysts used for ammonia synthesis by plasma-assisted process. Adapted with permission from (Plasma Catalysis as an Alternative Route for Ammonia Production: Status, Mechanisms, and Prospects for Progress, Hong et al, ACS Sustainable Chemistry & Engineering [135]). Copyright (2018) American Chemical Society.

Catalysts	Support	Promoter	Shape	Reference
BaTiO ₃ , PZT	-	-	Pellets	[110,112]
MgO	-	-	Pellets	[122]
Cu	-	-	Wool-like	[116]
Au, Pt, Pd, Ag, or Cu	-	-	Wool-like	[146]
Ru	Al ₂ O ₃	-	Powder	[115]
Ru	MgO, CNT	Cs, K, Ba	Powder	[107]
Ru	γ-Al ₂ O ₃	Mg, Cs, K	Pellet	[150]
NDs, and DLC	α-Al ₂ O ₃	-	Sphere	[118]
Ni	SiO ₂	-	Pellets	[109]
Ru	Si-MCM-41	Cs, Ba	powder	[121]

Due to the good performance in conventional ammonia synthesis process, Ru based catalysts have been selected as the reference in plasma-assisted process [101,115,121,150]. However, the ionization energy of Ru is 7.36 eV, and it might be difficult to be ionized by atmospheric DBD plasma. Therefore, a promoter such as Cs, which are easy to be ionized, was used to provide electrons to Ru for better

catalytic activity [107,151,152]. Kim et al. [150] investigated the effect of promoters in their research, and the measured yields towards ammonia follow the trend of Mg > K > Cs > no promoter. In another research, Peng et al. [107] investigated the synergy between catalysts, supports and promoters. In their study, experiments were performed in four cases: supported catalyst with promoter Cs-Ru/MgO, without promoter Ru/MgO, only the support MgO, and plasma alone. A reproduction of their results is presented in Figure 8. Similar yields were achieved in the case of MgO and Ru/MgO, but an obvious enhancement was achieved when using a promoter. The authors suggested that the existence of MgO may enhance the surface discharge, which dissociates N₂ and H₂, hence increasing the ammonia production. This suggestion is in line with other investigations [104,117,122]. In this case, it is worth remarking that the presence of Cs greatly promoted the catalytic effect, doubling the ammonia yield. In this research, carbon nanotubes (CNT), active carbon (mesoporous) and MCM-41 were also used as support material in order to compare their effect. From the results it was concluded that with CNT the best efficiency of 2.2 g/kWh was achieved. On the other hand, when using MCM-41 as support, an efficiency of 1.7 g/kWh was achieved [121].

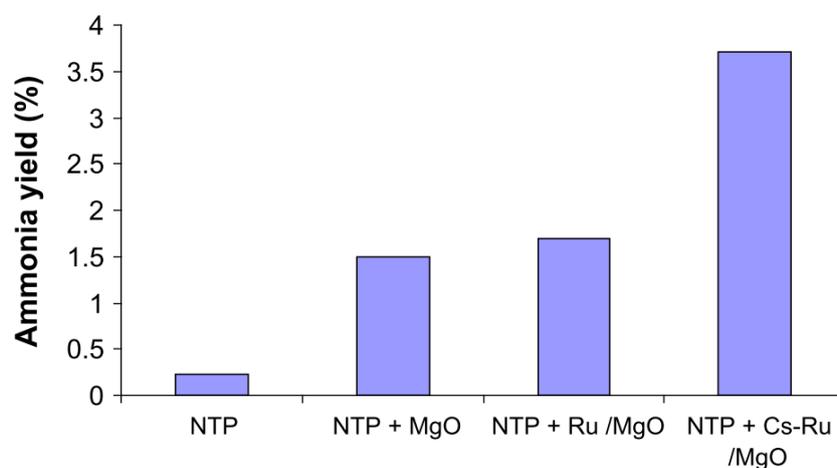


Figure 8. Ammonia synthesis by non-thermal plasma alone, and with different packings ($V_{N_2}:V_{H_2} = 3:1$, N₂ and H₂ total flow rate 60 mL/min, voltage 5000 V, frequency 8000 Hz). Reprinted by permission from Springer Nature, Plasma Chemistry and Plasma Processing, “Atmospheric Pressure Ammonia Synthesis Using Non-Thermal Plasma Assisted Catalysis”, Peng et al. [107], [COPYRIGHT] (2018).

The size and structure are always key factors for selecting a proper catalyst, especially in the case of packed-bed DBD reactors. Catalysts in powder form have been used in early researches. However, they were not very ideal comparing with pellet form as the charging and static effect caused by the plasma was leading to the spread of powder catalyst [120,153]. Pellet form catalysts are favoured as they give better yields, and have higher chemical stability and mechanical resistance [154]. Parameters such as residence time, surface area and active sites are strongly affected by the size and structure of the catalysts.

The size and structure of the catalyst also influenced the plasma discharge characteristics [155–157]. It has been confirmed that the discharge characteristics (such as uniformity, power) can be altered differently by packing catalysts with a different physical property [158–162]. As described in [43], the main effect of catalysts on plasma is the enhancement of the local electric field near the catalyst surface, causing the modification of electron energy distribution, and consequently influencing the reactive species generated by the plasma. The enhancement of the local electric field is brought by the curvature of catalysts, which is determined by the catalyst size and structure. Catalysts with sharp edges produce high local electric fields, leading to the generation of energetic electrons [158], resulting in improved conversions as reported in the literature [163,164]. The pellet size determines the void space, which is related to the local electric field and the residence time of the reactant [165]. It should be noted that the optimal pellet size may vary, regarding different discharge gaps. Therefore, the void

fraction or discharge gap/pellet size ratio can be used as a better indicator [158]. Besides, the size effect of packed catalysts/packing material also depends on other parameters such as input power [166] and the dielectric constant [167].

5. Conclusion and Outlook

Nitrogen fixation is one of the most important processes to all life forms on earth. Today, industrial nitrogen fixation is dominated by the Haber-Bosch process, which consumes 1% of the world's total energy production and is associated with environmental concerns such as CO₂ emissions. During the past decade, research has been focused on the development of alternative methods for green nitrogen fixation. Non-thermal plasma has been considered as one of the most promising alternatives to the conventional H-B process, and the development of plasma technology has brought new opportunities to fix nitrogen at low temperatures and atmospheric pressure with high energy efficiency and a green environmental profile.

The research on the plasma-assisted nitrogen fixation in the last five years has been reviewed in this work. In particular, the research in this field has focused on two targeted products, NO_x and ammonia. In the case of NO_x production, non-thermal plasma has a lower theoretical limitation of energy consumption (0.2 MJ/mol) than the H-B process. The activation of N₂ via vibrational excited N₂^{*} produced by electron impact is considered an energy efficient way to overcome the high activation barrier of dinitrogen reactions. Thermal plasma, such as arc and spark, have been studied intensively in the past, while "warm" plasma, like the gliding arc discharge, has recently received a lot of attention due to its high energy efficiency. The operation parameters such as frequency or gas composition have a great influence on the NO_x production rate, NO₂/NO ratio and energy consumption. In the case of ammonia synthesis, a plasma reactor in combination with catalysts has been intensively investigated. DBD packed catalyst reactors are the preferred reactor configuration. The effect of the catalysts has been tested including mono catalysts, supported catalysts and catalysts with promoters. Besides, attempts have been made in the literature in order to use feedstocks that reduce the energy impact of H₂ production upstream. In particular, the feasibility of using H₂O, CH₄ and indirect routes have been proposed.

However, the plasma-assisted nitrogen fixation process is still not comparable with the H-B process, which has been improved over 100 years, especially when considering the energy consumption and product yield. As suggested by Patil et al. [20], the aim of future research should target energy consumption below 33–35 GJ/TonN and production concentration above 15%. To reach this goal, further investigation on plasma reactor along with plasma-catalysis interaction is needed. Similar with the H-B process, the selection of catalysts is the key in plasma-catalysis for nitrogen fixation, and a large amount of work on catalysts screening is needed in future research. Besides, pulsed energization has proven to be beneficial to many plasma processes [150,168–170]. Using high frequency, nanosecond pulsing for plasma generation could potentially optimize the energy efficiency and yield of the plasma-assisted nitrogen fixation process. As suggested by Anastasopoulou et al. [171], there are three critical aspects for the energy performance of the plasma-assisted nitrogen fixation process: integration of renewable energy, power supply system and reactor and the process design for industrial scale. Current research has been just focused on the reactor itself, and limited research has been carried out concerning topics like product separation, absorption or the overall process design. As mentioned by Peng et al. [120], the back reaction of ammonia synthesis by plasma is a major hurdle that needs to be overcome. To avoid this problem, the strategy would consist of the immediate absorption of the produced ammonia and its removal from the plasma region. On the other hand, due to the low conversion of current technology, separation of the product and recycling the unreacted gas save material and reduce capital costs. In addition, developing large-scale plasma processes is also a great challenge. Owing to the complex nature of the plasma, a very limited knowledge for the scaling up of a plasma-assisted nitrogen fixation process has been acquired so far. However, valuable experience

could be learnt from the industrialized plasma process such as the ozone production process in which numbering-up approaches have been used [172,173].

On the other hand, the technology for renewable energy production has rapidly advanced during the past decades. Integration with renewable energy could greatly compensate for the high energy demand of the plasma process and provide a sustainable solution to the environmental concerns of industrial nitrogen fixation. Renewable energy sources such as wind and solar could generate electricity to power the plasma plant, and it could also be used to produce hydrogen for ammonia synthesis. Furthermore, the small-scale character of plasma-assisted nitrogen fixation process fits perfectly in the concept of decentralized production. Container/modular size plants could be developed for the small-scale production of NO_x or ammonia for application such as fertilizers and fuels. This will largely reduce the cost and product lost during transportation, enable on-site production and provide flexibility to meet the varying demand. Despite the progress made during the past decades and the growing attention attracted, there is still a long way for plasma-assisted nitrogen fixation technology before it can compete with the H-B process in industrial scale. However, it can be predicted that small-scale application under certain conditions could be realized in the near future. As suggested by Pfromm [25], emerging markets with currently low NH₃ capacity but a fast-growing population are ideal targets for the research of alternatives to the H-B process. For example, the access to fertilizers is stranded in Africa, but the ever-fast growing population brings a significant demand. Instead of large-scale industrial fertilizer production, plasma-assisted process with the decentralized concept can better meet the requirements of low capital cost, scale-down economics and utilization of rich renewable resources distributed in local areas. In addition to the development of the technology, evaluation study on the techno-economic feasibility and sustainability of the plasma-assisted nitrogen fixation process should also be conducted in parallel [171,174,175]. This will provide guidance to further improve the process performance towards practical applications.

Author Contributions: F.G., S.L. and J.M. conceived the review structure; S.L. and J.M. wrote the paper; All authors corrected the review.

Conflicts of Interest: The authors declare no conflict of interest.

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