Journal of Cleaner Production 177 (2018) 597–609

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Review

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

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ARTICLE INFO

Article history:
Available online 28 December 2017

Keywords:
Ammonia synthesis
Clean fuel and fertilizer
Low temperature and pressure synthesis
Sustainable ammonia production

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.

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https://doi.org/10.1016/j.jclepro.2017.12.229
0959-6526/

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

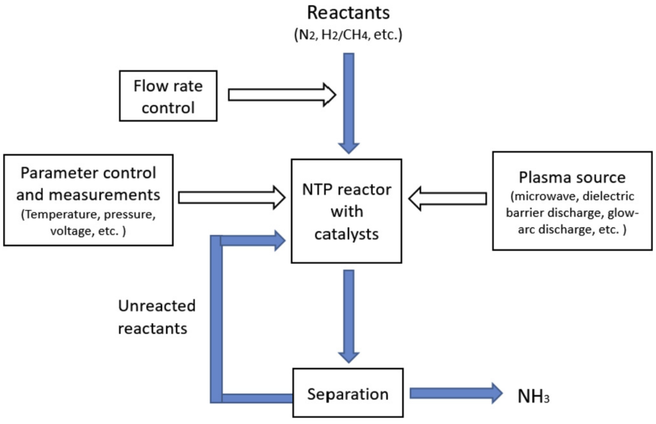

Fig. 1. A flow diagram of the non-thermal plasma ammonia synthesis process.