Invited Paper

SUSTAINABLE AMMONIA: A KEY TECHNOLOGICAL CHALLENGE FOR ASIA

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Abstract

Ammonia is one of the most important industrial chemicals in the world. The availability of an inexpensive and environmentally sustainable supply of ammonia which is an important ingredient in fertilizer is important for the security of the world food supply. Asia is one of the biggest consumers of ammonia. The Haber-Bosch process makes ammonia widely available now but it requires high temperatures and pressures, consumes large quantities of fossil fuels and releases large amounts of greenhouse gases. Sustainable ammonia is also important because it may make biomass-based alternatives to fossil fuels more practical. Possible alternatives under development are those that mimic the enzymatic processes that occur at mild conditions in nature and those that seek to obtain ammonia-based compounds from large-scale culture of microalgae and cyanobacteria. Many of the alternatives are still in the very early stages of development and researchers are urged to enter the field.

Keywords: Ammonia, Fertilizer, Food Security, Haber-Bosch, Microalgae, Nitrogen Fixation

Introduction

It is rather ironic that one of the most important chemicals to modern society remains to be one of its most obscure. Ammonia (NH_3) is so important that indeed one could say that half of the world's population would starve to death if, by some circumstance, its supply were suddenly cut off. Yet, many chemical engineers have to dig deep into their memories to recall how ammonia is manufactured. This article provides a short survey of the significance of this material to our society, why the present process for ammonia manufacture needs to be replaced and what alternatives can be explored to replace it. Key references are provided to give the interested reader a start in exploring this fascinating field.

The Significance of Ammonia

Why is ammonia so important? While 79% of the earth's atmosphere consists of nitrogen gas, the nitrogen atoms are so strongly bound together that nitrogen gas may be considered inert. For it to be available for conversion into more useful, it must be converted to more reactive forms. The nitrogen is then said to be "fixed" and the process is called nitrogen fixation. In current times, the most commonly available fixed form is ammonia.

Among the possible products from ammonia are explosives, plastics such as Nylon and Kevlar and a large number of pharmaceuticals. The most important use of ammonia, however, is in the production of agricultural fertilizer. Nitrogen is a vital component of all life. Proteins cannot be synthesized without nitrogen and plants obtain this from the soil. As food crops are grown and harvested, the nitrogen content of the soils are depleted and must be replenished. This can be done several ways. Natural means of replenishment include "biofixation" which take advantage of the ability of plants such as legumes to fix nitrogen from the air; atmospheric deposition via lightning and by recycling of waste products. However, it has been estimated of the global demand for fertilizer show that only about half has been provided by these sources and thus it may be concluded that the 50% of the world's protein requirements is dependent on the supply of synthetic fertilizer [1].

The global demand for ammonia is enormous. In 2010, the world supply capacity for the production was 130,978,000 tons (as N) and the world total consumption of ammonia as a primary fertilizer nutrient was 103,058,000 tons or about 79% [2]. Therefore, while other applications cannot be ignored, fertilizer is the major use for ammonia. Asia consumed the great bulk of this fertilizer (64,395,000 tons or 62.5%) [2]. The demand for fertilizer is expected to grow at a rate of 2.2% [3] – a rate faster than the world population growth rate of 1.1% [4]. It is not surprising that 68% of the increase in demand will be originating from Asia [2]. The combination of a rapidly increasing population and a burgeoning economy has led to "improved" diets, both in quantity and in the proportion of meat and dairy products. In spite of efforts to replace synthetic fertilizers with biomass based alternatives, it seems that the dependence of the world's food supply on synthetic fertilizer is not abating.

The Environmental Cost of Ammonia

Prior to the 19th century, fertilizer was not widely available. To restore fertility to agricultural soil, there were few alternatives: bat and bird droppings also known as guano and natural deposits in South America. Ancient farming practices also included the intercropping of legumes like peanuts and soybeans which have the ability to fix nitrogen from the air. These sources were extremely limited however and fixed nitrogen from the natural deposits in South America were so valuable that Chile and Bolivia fought a ruinous war for control of the deposits [5].

The ability to fix nitrogen from the air was therefore a much most sought after objective. Before the 1920's, there were two commonly used processes for manufacturing ammonia: the electric arc process and the calcium cyanamide process [6]. Both of these processes were so energy-intensive however that widespread availability was still out of reach. In the early 20th century, Fritz Haber discovered the process that enabled the large-scale manufacture of ammonia. Haber and many chemists of his time realized that the synthesis of ammonia can proceed via the reversible reaction $N_2 + 3H_2 = 2NH_3$. However, there is a contradictory effect of temperature on the reaction. Because the reaction is exothermic, removal of heat drives the equilibrium forward. However, when this is done, the reaction temperature is lowered and the rate of reaction is inhibited. Haber discovered that with the appropriate catalyst and a recycle stream, an acceptable yield can be achieved at an operating temperature of about 400-600 ^{o}C. Despite the high operating temperature and the fact that equilibrium also dictates that the reaction be done at high pressures, the Haber-Bosch process (which came to be called the Haber-Bosch process after Karl Bosch successfully scaled it up) became the dominant source of fixed nitrogen in the world. With this achievement, inexpensive fertilizer became available for the entire. The process has been so successful that the reaction section has remained essentially unchanged since the early 20th century [6].

Indeed, it is difficult to arrive at a better process than one wherein one of the major raw materials is free. The Haber-Bosch process was a truly wonderful invention which has led to it being called the most important invention of the 20th century[7]. Modern times however have changed the criteria by which success is judged. Much like Freon and DDT, which were initially regarded as among the best inventions of mankind, the changing standards of the times have forced a reassessment of the cost and benefit equation. When the Haber-Bosch process was developed, fossil fuels were cheap and in seemingly limitless supply and this is one of the chief requirements of the Haber-Bosch process. The fossil fuel is needed to produce hydrogen, the other reactant. While hydrogen can be made via electrolysis or via the partial oxidation of heavy fuel oils, the most commonly used process is the steam reforming of natural gas [8]. Steam reforming obtains hydrogen from methane via the overall reaction $CH_4 + 2H_2O = CO_2 + 4H_2$. The overall reaction is endothermic and the reaction equilibrium requires that the reaction also be conducted at high temperatures. Overall, therefore, the methane steam reforming process consumes large amounts of energy and fossil fuels.

Note also that the steam reforming reaction produces a large amount of CO_2. If this fact is coupled with the need for high temperatures and pressures for both the ammonia synthesis reaction and the methane steam reforming, it is not surprising that the energy demand and the global warming impact of ammonia production is enormous. The ecoinvent® database states that the production of 1000 kg of liquid ammonia consumes 41,000 MJ of nonrenewable energy and releases the equivalent of 1,920 kg of CO_2. The estimated production of ammonia in 2010 was 157,300,000 tons [9]. Thus, ammonia production in that period may be estimated to have consumed about 6.4×10^{12} MJ of nonrenewable energy and released the equivalent of 3.0×10^{11} kg of CO_2 in global warming potential. The demand for fertilizer is so large that it is estimated that 3-5% of the world's natural gas is consumed to produce ammonia [10].

The Synergy between Ammonia and the Energy Problem

The importance of ammonia is not limited to its current use as fertilizer and as an important chemical feedstock. Producing ammonia sustainably may make some proposed solutions to the energy problem more viable.

As fossil fuels get depleted and fuel prices rise, the search for alternative fuels for transportation has been on the mind of every chemical engineer. One of the possible sources of fuel is from biomass. Obtaining the fuels from traditional crops such as sugarcane, soy oil, palm oil and coconut oil is already done in many countries. However, in most cases, while there are environmental benefits derived from their use, the fuel from such sources are more expensive than their equivalents derived from petroleum. What's more, legitimate concerns have been raised that the demand for these feedstocks, commonly used for food, may drive up food prices [11].

Attention has shifted therefore to nontraditional crops including terrestrial plants like jatropha and even aquatic and marine species like seaweed and microalgae. Jatropha was first promoted as a non-edible alternative to traditional vegetable oils because it is known to grow in poor soils [12]. On the other hand, microalgae were proposed because they offer a much higher biomass yield per hectare than terrestrial plants [13]. Even these however have had problems with sustainability. Jatropha has, so far, not lived up to its promise and remains controversial [14]. On the other hand, the microalgae were found to consume large amounts of energy for production because the ponds and photobioreactors needed for their culture require continuous input of energy and even more energy is needed for their harvest and conversion to fuels (see, for example, [15]). It must be noted however that there is still disagreement on this finding [16]. The expected prices from these sources are also much higher than the petroleum products [17].

When these systems are analyzed for important contributors to their environmental and economic cost, there is a very common conclusion. The analyses almost all show that one of the most significant inputs to biomass-based fuel systems is the nitrogen-based fertilizer (see, for example, [18], [19]). This is true both for terrestrial and aquatic systems but much more so for the latter. Fresh water-based systems in particular are always in need of fertilizer because fresh water has no naturally occurring nutrients, unlike soil. It makes sense that the nitrogen fertilizer bears so much of the overall environmental cost of a biomass-based system because its present mode of production consumes so much energy and releases great amounts of greenhouse gases. It is clear that a more sustainable source of fixed nitrogen could make biomass-based systems more practical.

Alternatives to the Haber-Bosch Process

While the Haber-Bosch process has been around for nearly a century and the potassium-promoted iron catalyst is still the most dominant catalyst used in industry [8], research into its exact mechanism continues [20]. Ruthenium-based catalysts have been developed and great strides have been made in reducing the energy usage and greenhouse gas emissions of the Haber-Bosch process through process integration, the fundamental constraints on the system will always remain the same: high temperature and pressure and a relatively pure source of hydrogen [21]. It is time to explore other approaches to obtaining nitrogen on a large scale and there are two approaches that have gotten some attention.

The first involves the observation that, in the living world, the fixation of nitrogen by cynabacteria or blue-green algae occurs under room temperature and atmospheric pressure by using the nitrogenase enzyme. The overall reaction is

$$N_2 + 8H^+ + 8e^- + 16\ MgATP \rightarrow 2NH_3 + H_2 + 16MgADP + 16Pi$$

where Pi means that an inorganic phosphate is generated. It can be seen that the overall reaction is extremely endergonic. For every 2 equivalents of ammonia, 16 equivalents of adenosine triphosphate (ATP) are hydrolyzed to adenosine diphosphate (ADP). The reaction has the added side benefit of producing hydrogen gas. The reaction is catalyzed by a nitrogenase enzyme which consist of two component proteins, an iron(Fe) protein and a molybdenum (MoFe) protein. The (MoFe) protein contains two iron-molybdenum cofactors (FeMoco) which are the active portions of the enzyme for nitrogen fixation. Research has focused on emulating the action of the FeMoCo cofactor in reducing nitrogen gas to ammonia. The progress in these efforts has been reviewed very thoroughly recently [22]. Two approaches involving transition metal complexes have been proposed initially by Schrock [23, 24] and Chatt [25]. However, the ligands and catalysts in these systems are protonated and consumed in acidic environments, so further progress must be made in developing more durable versions of these catalysts [26]. Other chemical approaches include converting nitrogen gas to silylamine ($N(SiNa_3)_3$ or $N(SiLi_3)_3$) which can then be converted by hydrolysis to ammonia [27, 28].

The chemical approaches seem to be very promising and they may indeed hold the key to a sustainable source of fixed nitrogen. There are other approaches that propose, instead of mimicking the processes that are used by living things, actually use the living things themselves. Three distinctively different approaches have been proposed. Liao and co-workers [29, 30] propose the general concept of using simultaneously harvesting the lipids and proteins from a microalgal culture to simultaneously generate fuel and fertilizer for the microalgal culture but do not specify the means by which this is achieved. Wang and Brown [31] obtained aromatics by the catalytic pyrolysis of the microalgae Chlorella vulgaris and also obtained NH_3 and HCN which could presumably also be captured and purified. By using the data from Gonzalez et al. [32], Razon[33] reported the life-cycle assessment the renewable energy usage and global warming potential of a process to culture the cyanobacterium Anabaena sp. ATCC 33047 and convert the resulting biomass and exopolysaccharides to biogas. In this process, the biogas residue could be treated using the ANASTRIP ® process to obtain ammonium sulfate [34]. The process is shown in Figure 1. While the process still has to be executed in reality, large savings in nonrenewable energy use and greenhouse gas emissions may be expected. This is largely because the process has two major products: biogas and ammonium sulfate and also because the chosen microorganism produces biomass and excretes exopolysaccharides.

The advantage of these biomass-based processes is that the technology for them is already available. However, they share the disadvantages of other biomass-based systems. That is, large quantities of land and water will be required; although, it must be noted microalgal systems will not require arable land and marine organisms will not require fresh water. Proper evaluation of environmental and economic costs must be conducted.

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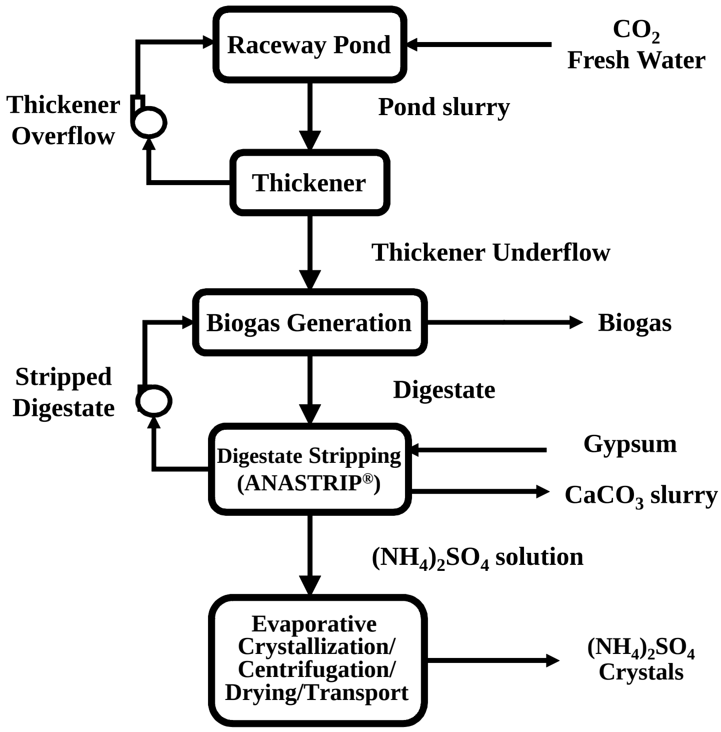

ATCC 33047 (adapted from [33])

Figure1**.** Process flow diagram for production of ammonium sulfate from Anabaena sp

Conclusion

It would be an understatement to say that the security of the global food supply is a major issue. In addition to the food security issue, however, a sustainable supply of ammonia would have a large impact also on the energy problem by improving the practicability of biomass-based processes to replace petroleum. It could make biomass-based systems that were once considered to be impractical to be practical. So, the availability of sustainable ammonia impacts three very important global issues: food security, climate change and energy.

As the largest and fastest-growing consumer of ammonia, Asia has a considerable stake in ensuring that sustainable supplies are available. Researchers in chemical engineering are encouraged to participate in finding and developing solutions to this important, challenging and intellectually interesting problem.

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