

‘Green’ ammonia Production: decarbonised commodity and energy vector

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Green ammonia production

Ammonia production currently accounts for over 1.8% of the world’s consumption of fossil fuels and consequently over 1% of carbon dioxide emissions [1]. The current production of ~180Mt/year is predicted to increase to ~270Mt/year by 2050 [1]; understandable given that over 80% of all ammonia produced is used for fertilisers. These predictions, combined with the requirement of net-zero carbon dioxide emissions for the 2°C scenario [2] mean that there is an environmental imperative to decarbonise industrial ammonia production methods. Currently, steam methane reforming or (to a lesser extent) coal gasification are used to provide the hydrogen component of the syngas. Three possible methods are currently being considered to de-carbonise the process namely: (i) conventional production with sequestration of the carbon dioxide, (ii) hydrogen production via electrification of water using renewable energies (wind, solar and tidal wave, etc) with adaptation of a small scale modified Haber-Bosch process as *eHB*, and (iii) development of alternative methods of production (i.e. electrochemical). While designing new ammonia plants with integrated carbon capture and storage (CCS) or retrofitting CCS to conventional plants does have notable potential, in this paper we will focus on the latter two other production methods mentioned above. The rationale for this is that, despite the fact that this method could play a part in production in the future, the cost of this method may be uncompetitive due to the dramatic falling cost of renewable energy.

Electrification of water using renewable energies in eHB process

The use of hydrogen gas from electrification (electrolysis of water using renewable energies) in *eHB* process for ammonia production contrasts with conventional large scale Haber-Bosch process utilizing natural gas/coal gasification as the former process gives zero carbon emission. However, adequate supply of dihydrogen from electrolysis may be challenging to couple with nitrogen to maintain high ammonia productivity. Generally, hydrogen pressure generated from electrolysis of water is relatively low (< 20 bar). The unfavourable kinetics at low pressure, combined with the strong thermodynamic barrier the nitrogen triple bond dissociation poses (94.1 kJ/mol) may limit the ammonia production rate. In the traditional industrial process, production volume and cost are highly dependent on natural gas availability. However, reducing the dynamic supply of H₂ for new

anticipated low pressure electrification process is likely to decentralize traditionally large integrated Haber-Bosch installations into small-scale islanded *eHB* units. The new process also requires a new catalyst to show significant catalytic activity at lower pressure to save the cost of investment and mitigate the safety risks. It is thus of great significance to dwindle the reaction pressure to reduce operational cost and energy requirements and achieve the *eHB* process.

Compared with the commercial Fe, Ru is a potential candidate for the *eHB* process as it is relatively active at low pressure. It is because Ru with higher electron density of d-orbitals can donate electrons into the anti-bonding orbital of adsorbed N₂, facilitating its dissociation and hence can work under a lower pressure. However, Ru based catalysts have found limited uses in conventional Haber-Bosch process because they are relatively more expensive and are easy to be poisoned by carbon deposition from CH₄ decomposition in syngas. In the *eHB* system with H₂ derived from water does not contain CH₄, so the poisoning effect can be well avoided, making Ru as a potential candidate for low pressure synthesis. On consideration of its high cost, it is also necessary to improve the activity of Ru based catalyst to operate the *eHB* process better. Cs–Ru based catalyst is currently used in low pressure Kellogg Advanced Ammonia Process (KAAP) [3]. Recently, there are some new promising Ru based systems [4,5] that have attracted great attention.

Direct electrochemical ammonia production

However, the high cost of H₂O electrolysis, coupled with the often low price of natural gas, make this *eHB* approach currently economically less attractive than the conventional Haber-Bosch synthesis. Electrochemical synthesis, in contrast, permits the direct reaction of N₂ with H₂O to form NH₃ at ambient pressure. In principle, the reaction can proceed under such conditions, as seen in biology. The challenge is to reduce the highly inert N₂ molecule in the presence of the more easily reduced species, H₂O, at industrially useful rates. Many cells have been proposed for carrying out the direct electrochemical NH₃ synthesis [6]. However, according to the targets for feasible industrial installations imposed by US Department of Energy's (DoE) REFUEL program (current density >300 mA cm⁻² and Current Efficiency >90%, which is equivalent to an effective rate of 9.3×10⁻⁷ mol cm⁻² s⁻¹), the vast majority of reports fall on or below 10⁻⁸ mol cm⁻² s⁻¹. This corresponds to a current density of around 3 mA cm⁻² at 100% current efficiency and is far short of the 300 mA cm⁻² at >90% current efficiency DoE target. This value may reflect the relatively low surface area electrodes used as compared to nanoparticle catalysts found in electrolyzers. This highlights the challenge of not just activating N₂ to make NH₃, but doing so selectively in the presence of more easily reduced species, such as H₂O. Recently, a novel hybrid cell to alleviate the problem has been reported [7]. This is achieved by combining both molten eutectics by separating N₂ reduction in LiCl/KCl from water splitting in NaOH/KOH with a bipolar Pd membrane. This allows H to be supplied from water

without a spontaneous reaction with N^{3-} , thus preventing an increase in required cell voltage. In both hydroxide and chloride electrolytes there is evidence that rates can be enhanced by varying the catalyst material. Overall, there are some promising approaches particularly using molten eutectics with rates and/or current efficiencies approaching the DoE targets. This success has led to an increasing amount of research over the last couple of years and more developments can be expected.

Techno-economic evaluations

Previous investigations into the electrification of hydrogen production have resulted in a range of LCOA estimates depending on their mode of operation. These investigations can be separated into three groups defined by their energy supply: solely grid supply (Wang et al. (713-1178 USD/t) and Beerbühl et al. (520 EUR/t) using wholesale market electricity), semi-islanded, i.e. supported by either the grid or another dispatchable source (Morgan (580-1124 GBP/t) and Tuna et al. (680-2300 GBP/t) using grid supply and biomass in semi-islanded operation), or islanded operation, i.e. uses a ‘buffer’ to maintain system stability (Bañares-Alcántara (665 GBP/t) and Beerbühl et al. using ammonia and hydrogen buffers, respectively [8]). As outlined by Philibert at the IEA, “*ammonia production in large-scale plants based on electrolysis of water can compete with ammonia production based on natural gas, in areas with world-best combined solar and wind resources*” [9].

The use of renewable power sources to electrify the production process in islanded operation brings its own problems. The intermittency of the power supply (specific to the location of interest) requires careful consideration during planning of the plant design and its subsequent operation. If this is not taken into account undesirable disruptions in the synthesis loop are likely to occur [9] which would increase operational cost and the predicted LCOA.

We have recently identified that five key variables have significant impact on the estimated LCOA for islanded production. Aside from the location, two cost and three process variables were found to have the most impact (calculated relative to a ± 10 GBP/Tonne change in LCOA): levelised cost of electricity (± 0.89 GBP/MWh), electrolyser capital expenditure (± 65 GBP/kW), minimum Haber-Bosch (HB) process load ($\pm 12\%$ of rated power), maximum rate of HB process load ramping and renewable energy supply mix.

While production of ‘green’ ammonia as a commodity will be economically viable long before it is as an energy vector (unless there are significant incentives for long term duration energy storage services), it appears to have significant potential for seasonal electricity storage. As the penetration of intermittent renewable power sources increases so does the requirement for network flexibility to facilitate their integration. There are multiple methods (such as demand side management, curtailment and energy storage) to provide this flexibility, but realistically a combination of all of them will be

most economical for most networks at high renewable energy (RE) penetration. Pumped hydroelectric is widely considered to the ‘gold standard’ and clearly dominant electrical energy storage method employed to date. This however ignores that the majority of networks still store virtually all of their energy as unburnt fossil fuel stocks. Take the storage capacities in the UK in 2016 for example: Batteries (lithium-ion, lead acid, lithium phosphate) 0.0234 GWh, Pumped hydroelectric 27.6 GWh, Coal 29,900 GWh , Natural gas 47,100 GWh. While simply looking at the energy capacity of stored energy is certainly not the whole picture (appreciation of dispatchable power and understanding of the network balancing methods are essential) this does highlight the dependence that we have on fossil fuels at present. The increasing RE penetration is therefore a compounding problem: it increases the need for network flexibility, while cutting existing network flexibility based on fossil fuel stocks (that we depend on for medium to seasonal balancing). The impact of this has been seen in multiple networks around the world (e.g. UK and Germany) where an increased need for frequency stabilisation and a fall in storage costs has led to significant integration of battery storage (predominantly lithium ion). With ever increasing renewable penetration, even with careful selection of RE supply, more and longer duration electrical storage is likely to be needed (see Figure 1).

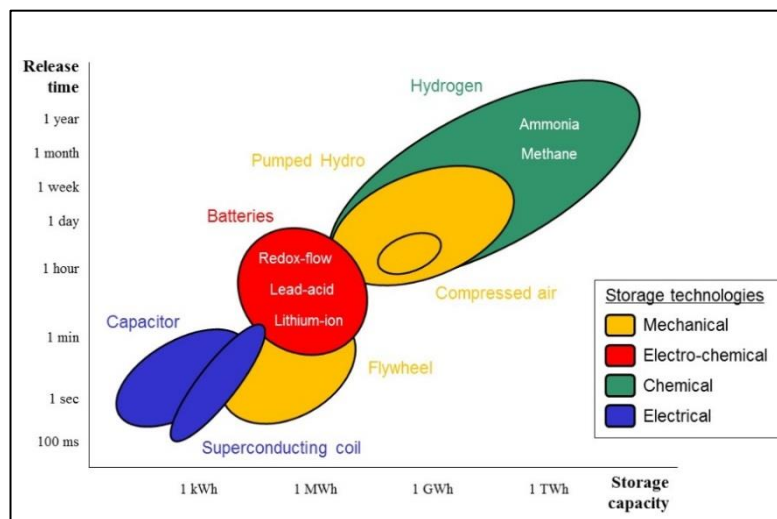


Figure 1: Energy storage technologies. Adapted from Hydrogenius Technologies [10].

While hydrogen has significant potential for filling this storage gap, enthusiasm has unquestionably decreased from the ‘hydrogen economy’ heights. Two of the main reasons for this were the infrastructure required for its implementation, and the technical requirements for storage. ‘Chemical storage’ of hydrogen has been of particular interest in recent years. Ammonia has significant potential due to its favourable chemical and technical characteristics. Not to avoid the obvious: ammonia, unlike many other options such as methane and methanol, is carbon free. It has a good energy density (LHV of 18.6 MJ/kg), is easy to store (boiling point of -33°C at 1atm), stability (can be stored without notable energy loss) and is relatively safe (i.e. non-explosive and easily detectable). Ammonia is

already produced in large quantities and therefore there is already significant infrastructure for its manufacture, transportation and storage. However, if it is also to be used as a 'green' energy storage vector, then this production would have to significantly increase: if all current ammonia production was converted to electricity (assuming 50% conversion efficiency) it could independently meet average global electricity demand for ~7 days.

In conclusion, the development of 'green' ammonia production methods is an environmental imperative as one of the measures to reach net-zero carbon dioxide emissions. There are promising new multiple ammonia production methods outlined above that can work well under mild conditions. As the cost of RE is rapidly decreasing, the use of ammonia should constitute a great potential, given its favourable technical and chemical characteristics, to at least partially substitute fossil fuels as a seasonal electrical storage method. This offers an exciting potential for ammonia to be used to store energy with better energy density factors than liquid hydrogen. An established logistics chain for worldwide trading and transportation of ammonia already exists. Compressed ammonia is a current solution for ammonia storage and transportation, but for longer term applications as ammonia is toxic and corrosive, new storage and transport systems for decarbonised commodity and energy vector should continuously be developed.

References

1. Philibert, C. *Renewables crossing boundaries: ammonia et al.* in *NH3 Event*. 2017. Rotterdam.
2. Millar, R., et al., *The cumulative carbon budget and its implications*. Oxford Review of Economic Policy, 2016. **32**(2): p. 323-342.
3. Aika, K., Takano, T. & Murata, S. *Preparation and characterization of chlorine-free ruthenium catalysts and the promoter effect in ammonia synthesis: 3. A magnesia-supported ruthenium catalyst*. J. Catal. 1992. **136**, 126–140.
4. Kitano, M. et al. *Ammonia synthesis using a stable electride as an electron donor and reversible hydrogen store*. Nature Chem. 2012. **4**, 934–940.
5. Sato K. et al. *A low-crystalline ruthenium nano-layer supported on praseodymium oxide as an active catalyst for ammonia synthesis*. Chem. Sci. 2017. **8**, 674–679.
6. Kyriakou V, Garagounis I, Vasileiou E, et al. *Progress in the Electrochemical Synthesis of Ammonia*. Catal Today 2017. **286**, 2–13.
7. Ito Y, Nishikiori T, Tsujimura H. *Advances toward industrialization of novel molten salt electrochemical processes*. Faraday Discuss 2016. **190**, 307–326.
8. Bañares-Alcántara, R., et al., *Analysis of islanded ammonia-based energy storage systems*. 2015, University of Oxford: Oxford, UK. p. 158.
9. Philibert, C. *Producing ammonia and fertilizers: new opportunities from renewables*. 2017.
10. Olson, N. "NH3 - The World's Optimal Energy Solution", presentation at the NH3 event 2017, Rotterdam, 2017, May 18-19.

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