Islanded ammonia power systems: Technology review & conceptual process design

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ABSTRACT

Recent advances in technologies for the decentralized, islanded ammonia economy are reviewed, with an emphasis on feasibility for long-term practical implementation. The emphasis in this review is on storage systems in the size range of 1–10 MW. Alternatives for hydrogen production, nitrogen production, ammonia synthesis, ammonia separation, ammonia storage, and ammonia combustion are compared and evaluated. A conceptual process design, based on the optimization of temperature and pressure levels of existing and recently proposed technologies, is presented for an islanded ammonia energy system. This process design consists of wind turbines and solar panels for electricity generation, a battery for short-term energy storage, an electrolyzer for hydrogen production, a pressure swing adsorption unit for nitrogen production, a novel ruthenium-based catalyst for ammonia synthesis, a supported metal halide for ammonia separation and storage, and an ammonia fueled, proton-conducting solid oxide fuel cell for electricity generation. In a generic location in northern Europe, it is possible to operate the islanded energy system at a round-trip efficiency of 61% and at a cost of about 0.30–0.35 € kWh⁻¹.

1. Background

A fossil carbon-free, circular economy is required to decrease the greenhouse gases emissions [1]. This can be accomplished by renewable sources, such as wind power and solar power. However, these sources are intermittent and energy storage is required. Even though batteries can provide energy storage for up to a few days, large scale chemical energy storage is required to accommodate the storage for the remainder of the year. Currently, the world relies mostly on carbon-based chemicals for electricity production in the absence of renewable power, which is termed the carbon economy. A commonly suggested alternative to the carbon economy is the hydrogen economy, which can store renewable energy by the transformation of water (H₂O) to hydrogen (H₂) via electrolysis. However, storing and transporting hydrogen is difficult [2]. Therefore, the ammonia economy is proposed [2–5]. Ammonia (NH₃) is a carbon-free hydrogen carrier, which can mediate the hydrogen economy [1,4,6–8]. Thus, ammonia could become the chemical ‘to both feed and power the world’ [9]. Especially for long-term chemical energy storage (i.e., above 1 day), ammonia is more economically stored than hydrogen [10]. Among other chemical storage alternatives researched are methane [11] and methanol [12]. Various chemical storage alternatives are discussed in the supplementary information.

Ammonia can both be used to store energy in time (for islanded systems) and in space (transportation from places with abundant wind hours or solar hours to other places) [13]. Transportation costs are greatly reduced by adopting a decentralized, islanded energy economy [14]. Furthermore, political-economic factors influence energy prices less in a decentralized energy economy. With small-scale ammonia production gaining momentum in the upcoming decades [15], business models for the decentralized ammonia economy are currently under development [14].

Within this paper, current technological advances of the ammonia economy are reviewed, as well as their feasibility for long-term and practical application on a local scale. A process, based on the currently available literature is designed with the conceptual process design methodology published by Douglas [16]. Power-to-ammonia-to-power technologies within the range 1–10 MW are reviewed. The proposed solution constitutes of wind power and solar power, combined with a battery for short-term energy storage (up to 1 day) and a power-to-ammonia-to-power (P2A2P) process for long-term energy storage (above 1 day).
An islanded energy system is analyzed, in which all electricity is generated from intermittent, renewable sources. Various alternatives for renewable electricity generation are available, but in the current case only wind power and solar power are considered due to the location considered. In the case considered (Haaksbergen, a municipality in the Netherlands with over 24000 inhabitants and an electricity consumption of 1.1*10^8 MJ y^{-1}), wind power is mostly available in the winter months [17], while solar power is mostly available in the summer months. The power generated by wind power and solar power consumed directly is about 55%, whereas 45% must be stored for later use. The case is elaborated upon in the supplementary information. Nayak-Luke et al. [18] simulated similar scenarios for various locations in the United Kingdom. Power scheduling is elaborated upon by Allman et al. [19] and Nayak-Luke et al. [20].

### 1.1. Ammonia chemistry & thermodynamics

The synthesis of ammonia from nitrogen and hydrogen is an exothermic reaction, favored by low temperatures and high pressures [21,22]. Due to the limited activity of industrially used iron-based catalysts and the strong nitrogen-nitrogen bond of atmospheric nitrogen (N₂), industrial reactor conditions are typically 350–550 °C and 100–460 bar [21,23,24]. The equilibrium content of ammonia in a hydrogen-nitrogen mixture (H₂:N₂ = 3:1 M ratio) is shown in Fig. 1. From Fig. 1 it follows that in no case a near-complete conversion to ammonia is achievable under industrial conversion conditions. Thus, in commercial ammonia synthesis processes a significant recycle is required.

The overall reaction from water and air is given by, equations (3)-(1) with a minimum theoretical energy consumption of 20.3 GJ t⁻¹ ammonia (equivalent to 5.64 kWh kg⁻¹ ammonia) [21]. The total energy consumption of ammonia from steam methane reforming (SMR) is about 28.0–32.6 GJ t⁻¹ ammonia (equivalent to 7.78–9.06 kWh kg⁻¹ ammonia) [21,26]. If hydrogen can be produced at low overpotential, electrolysis-based ammonia can be produced with a lower specific energy demand than SMR-based ammonia (see Table 1). It should be noted that the energy in case of SMR-based ammonia is fully provided in the form of heat, whereas the energy in the case of electrolysis-based ammonia is mostly provided in the form of electricity [21].

1.5H₂O + 0.641(0.78N₂ + 0.21O₂ + 0.01Ar) → NH₃ + 0.885O₂
+ 0.0064Ar

(3-1)

Ammonia is thermally decomposed according to equations (3)-(2), an endothermic reaction favored by high temperatures and low pressures [27]. The energy requirement for producing 0.66 m³ (STP) nitrogen and 1.97 m³ (STP) hydrogen from 1 kg ammonia is 2.7 MJ (equivalent to 0.75 kWh kg⁻¹ ammonia, excluding preheating and evaporation) [27]. [21].

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**Fig. 1.** Ammonia equilibrium mole fraction (YNH₃) for various temperatures and pressures. (H₂:N₂ = 3:1, no inert). Data reproduced from Ref. [25].
2. Current developments in power-to-ammonia-to-power

Ammonia is currently widely researched as an energy vector [26,28–30]. Especially electrochemical ammonia synthesis has gained substantial attention in recent years [31]. Even though electrochemical ammonia synthesis can become a commercial technology after 2030 [32], improvement on the existing Haber-Bosch process are likely to be the near-term alternative for sustainable ammonia synthesis [29]. Recent developments in ammonia synthesis are scale-up for enhanced energy efficiency and scale-down for smaller investments, whereas medium-sized plants will be built less frequently in the upcoming decades [15]. Improvements on the existing Haber-Bosch process are the focus within this paper, with an emphasis on decentralization. Previously, Fuhrmann et al. [33], Bañares-Alcántara et al. [24], Ikäheimo et al. [13], and the ISPT (Institute for Sustainable Process Technology) [34] evaluated alternatives for renewable ammonia synthesis (and its combustion for electricity generation). For the ammonia-to-power part, both fuel cells and gas turbines have been evaluated within this paper. Valera-Medina et al. [35] and Yapıcıoğlu et al. [36] recently evaluated the alternatives for ammonia-to-power. Affi et al. [37], Lan et al. [38] and Siddiqui et al. [39] reviewed the alternatives for ammonia fed fuel cells. In the current paper, feasible alternatives are compared, but an extensive review on all possible technologies is not provided here. The selection of technologies presented here is based on the technology readiness level (TRL) as well as the technological progress made over the past decade. The technology readiness level is a measure of the maturity of a technology, where Level 1 represents the fundamental discovery of a principle and Level 9 an industrially applied technology. A schematic overview of the major components in a power-to-ammonia-to-power is shown in Fig. 2.

Power-to-ammonia-to-power is currently going from merely academic research to pilot-scale plants. As of 2018, demonstration plants were opened in Japan and the United Kingdom, whereas the University of Minnesota operates its small-scale, wind-powered ammonia plant for five years already [40–43]. The NFUEL® units of Proton Ventures B.V. (mini ammonia plants) have industrial references in Argentina, China and Switzerland [44]. Furthermore, ammonia fueled SOFCs (solid oxide fuel cells) are currently tested in pilot plants by IHI cooperation (1 kW class power) [45].

2.1. Ammonia synthesis processes

Ammonia can be synthesized along various pathways, namely (1) thermochemical synthesis (the Haber-Bosch process), (2) electrochemical synthesis, (3) non-thermal plasmas, (4) dense metallic membranes and (5) solar thermochemical redox cycles [46]. The production of ammonia was published and patented by Haber and Le Rossignol in 1913 and 1916, which would be termed the Haber-Bosch process in the years to follow [47–49]. Ammonia has been synthesized for over 100 years by the Haber-Bosch process, starting from 1913 at BASF in Oppau, Ludwigshafen (Germany) [50,51]. A typical modern ammonia synthesis plant operates at around 400–450 °C and 100–150 bar [21]. The approximate energy demand of various ammonia production routes is listed in Table 1. The best SMR-based Haber-Bosch processes already outperform nitrogenase in nature. It should be noted that the energy

\[2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2\]  

(3-2)
consumption of the conventional, carbon-based Haber-Bosch processes is fully composed of heat, whereas electrolysis-based Haber-Bosch processes mostly require electricity input.

2.2. Decentralized production

Decentralizing ammonia synthesis is mainly conducted along two pathways, namely (1) using conventional high-pressure technology, and (2) using milder reaction and separation conditions with new technologies.

Conventional technology operating at high-pressure is currently the prevalent alternative. Literature data from Brown [54], Morgan et al. [56], Pfromm [57], and Palys et al. [58], as well as industrial data from the electrolysis-based ammonia synthesis systems of ThyssenKrupp [59,60], the NFUEL® units (Proton Ventures B.V.) [10,61] and the Morris Plant (University of Minnesota) [43] are compared, as shown in Fig. 3. The electrolyzer typically consumes 90–96% of the required energy input [44,56,57].

For large-scale electrolysis-based conventional Haber-Bosch plants down to the scale of the NFUEL® units, the energy consumption is nearly constant (about 9–11 kWh kg⁻¹ ammonia, see Fig. 3). However, upon further scale-down, heat transfer limitations become relevant for conventional high-pressure, electrolysis-based Haber-Bosch plants (see Fig. 3). This can be dealt with by designing the process for less severe process conditions (i.e., lower operating temperature and lower operating pressure than conventional Haber-Bosch plants). A solution proposed by Cussler et al. is a low-pressure ammonia synthesis process (at 10–30 bar) [63,64]. This technology, ammonia synthesis combined with an absorbent-enhanced process for ammonia removal, is elaborated upon in next section and section 2.6.

2.2.1. Synthesis pressure of small-scale ammonia synthesis plants

A small-scale, medium-pressure plant as investigated by Cussler et al. (production rate of 1.5 kg h⁻¹ ammonia, operating pressure 150 bar) uses 3.62 kWh kg⁻¹ ammonia for syngas feed compression and the ammonia synthesis loop (about 2.16 kWh kg⁻¹ ammonia for the synthesis loop and 1.46 kWh kg⁻¹ ammonia for the feed compression) [58]. These figures are similar to those of NFUEL® units (operating at 460 bar, as of 2010), for which 2 kWh kg⁻¹ ammonia is used for ammonia synthesis and 2 kWh kg⁻¹ is used for utilities (for instance the compressor and cooling fan) [65]. By increasing the pressure to above 300 bar, no refrigeration is required for ammonia separation (i.e., cooling water and cooling fans are sufficient, see Fig. 4). A benefit of small-scale operation is that high pressure equipment is more easily constructed than for large-scale operation.

As shown in Fig. 4, the separation efficiency of ammonia at a given temperature is a function of the ammonia partial pressure in the stream. Thus, upon operating at reduced pressures (< 100 bar), cooling to low temperatures (< 0 °C) is required when condensation is used for separation. However, a more complete separation of ammonia after the synthesis reactor may be attained by an affinity separation. In the small-scale, medium-pressure plant simulation of Cussler et al. the energy consumption for feed compression and the synthesis loop is decreased down to 0.7–3.1 kWh kg⁻¹ ammonia by utilizing supported metal halides for ammonia separation (in a low-pressure ammonia synthesis loop operating at 10–30 bar, see Table 2) [58,62]. The energy consumption of the feed compression is close to non-existent (0.017 kWh kg⁻¹ ammonia) [58]. This is the major driver to choose for an absorption-enhanced process, as compressors are major cost factors in chemical plants. A comparison of the electricity consumption and other characteristics of small-scale ammonia synthesis plants is listed in Table 2.

2.3. Hydrogen production

The usual source for zero-carbon hydrogen is water (i.e., by electrolysis), with a net reaction given by equations (3). The reaction is highly endothermic ($\Delta H^\circ = 571.8 \text{kJ mol}^{-1}$), giving it a high energy requirement.

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

(3-3)

Various alternatives for electrolysis are available. Some of these are already commercially available, such as alkaline electrolyzers and proton exchange membrane (PEM) electrolyzers. Other technologies are on the brink of commercialization (solid oxide electrolyzers), whereas other systems are currently in the research & development (such as anion exchange membrane (AEM) electrolyzers) [69]. In the current section, only (nearly) commercial technologies are considered (i.e., alkaline electrolysis, PEM electrolysis, and solid oxide electrolysis).

Electrolysis is achieved in an electrolysis cell composed of an electrolyte (the ionic conductor), active layers for redox reactions, and a current and material collector (the electronic conductor), which enables the electricity supply, as well as the supply and collection of reactants and products [70]. Next to the electrolysis cell, an electrolysis system consists of gas cooling, purification, compression, and storage [71]. Furthermore, the power from the power source needs to be conditioned for the electricity input system of the electrolyzer, and safety control systems are installed [72]. Pre-treatment is performed by either evaporation combined with mechanical vapor compression, reverse
osmosis, or electro dialysis [24,73]. In this case reverse osmosis is preferred (see section 2.3.1).

The main advantages and disadvantages of alkaline electrolysis, PEM electrolysis and solid oxide electrolysis systems are listed in Table 3. From this it follows that only alkaline electrolysers and PEM electrolysers are currently commercially available. Solid oxide electrolysers show great promise, but these are not yet commercially available (on the MW scale) [71,74].

A main consideration is the cost of the electrolyzer, as these typically make up for a major portion of the capital cost of electrolysis-based ammonia plants. In this regard, alkaline electrolysers are still preferable over PEM electrolysers, as the latter alternative is typically a few times as expensive as the former alternative. A combination of a battery for short-term storage with a conventional pressurized alkaline electrolyzer (operating at 3.8−4.4 kWh Nm−3 hydrogen [75] or 7.3−8.4 kWh kg−1 ammonia) for long-term storage is currently the most feasible available technology. A benefit of this is that day-night cycles can be accounted for by the battery function, which has a higher round-trip efficiency (about 80%) than chemical storage (20−40%). A pressurized electrolyzer is preferred, because this omits the requirement of pressurizing hydrogen for the ammonia synthesis loop. The Battolyser, technology developed by the Mulder et al. [76], combines an iron-nickel battery and an alkaline electrolyzer. Thus, this can reduce costs of the overall system. The capital cost of the Battolyser is projected to be 370 € kW−1 (purchased equipment cost) [52].

2.3.1. Water purification

Water can be purified by reverse osmosis, electro dialysis, and mechanical vapor compression [56]. Electrolysers generally have purification equipment based on reverse osmosis modules, as these are reliable and modular [56]. Alkaline electrolysers require a TDS of ≤ 10 ppm, whereas this is even more stringent for PEM electrolysers (≥ 2 ppm) [56,71,72]. As the system is circular, water with a low TDS value can be recycled from the ammonia-to-power part. Mixing fresh tap water with the recycled water results in low feed TDS values. The maximum TDS value from tap water is 500 ppm. Depending on the application the value of deionized water from reverse osmosis is 0.1−400 ppm [77]. Thus, it is possible to achieve 10 ppm (required for alkaline electrolysers) [71]. Reverse osmosis is not capable at producing the required water purity from sea water efficiently [56,73,78]. Thus, the application of reverse osmosis is limited to tap water and sea water is usually purified using evaporation combined with mechanical vapor compression.

The levelized cost of reverse osmosis are as low as 1 € t−1 ammonia (including maintenance and capital expense charges) [57,79]. The energy consumption is about 4.7 kWh t−1 ammonia (3 kWh t−1 water, 97% water utilization) [57]. The cost of the demi-water unit for a 1k NFUEL® unit of Proton Ventures B.V. costs about 50 k€ (purchased equipment cost) [80].

2.4. Nitrogen production

Various technologies may be employed for the production of purified nitrogen gas from air. Nitrogen is commercially separated from air by an air separation unit (cryogenic distillation), by pressure swing adsorption, by membrane permeation, or by hydrogen combustion [94]. Hydrogen combustion processes are not considered for the production of ammonia. Currently, cryogenic distillation is the prevalent technology in large-scale industry [94].

The nitrogen production should be able to follow the patterns of the hydrogen production to some extent. This can be achieved by (1) a fluctuating nitrogen production, or (2) by a storage tank that controls the release of purified nitrogen gas. In case of the first (i.e., fluctuating nitrogen production), pressure swing adsorption and membrane

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Table 2

| Alternative                        | Advantages                                      | Disadvantages                                      |
|-----------------------------------|-------------------------------------------------|----------------------------------------------------|
| High-pressure Haber-Bosch process | • Well-known technology                          | • Very high pressure and temperature               |
| 400-550°C [24]                    | • No sharp separation                            | • Operating safety                                 |
| 300-460 bar [24]                  | • No refrigeration                               | • High capital investment                          |
| Electricity consumption           | • Requires large scale                           |                                                    |
| 4.18 mol.% NH3 [66]               | • No sharp separation                            |                                                    |
| TRL 9                             | • High pressure and temperature                   |                                                    |
| Medium-pressure Haber-Bosch process| • Well-known technology                          |                                                    |
| 350-525°C [23]                    | • No sharp separation                            |                                                    |
| 100-200 bar [23]                  | • Requires large scale                           |                                                    |
| Electricity consumption           | • Operating safety                               |                                                    |
| 3.62 kWh kg−1 NH3 [58]            | • Efficient separation                           |                                                    |
| TRL 9                             | • Efficient separation                           |                                                    |
| Absorbent-enhanced Haber-Bosch process| • Relatively low pressure                      |                                                    |
| 370-400°C [58,67]                 | • Lower CapEx and OpEx                           |                                                    |
| 10-30 bar [58,67]                 | • Safer operation                               |                                                    |
| Electricity consumption           | • Efficient separation                           |                                                    |
| 0.7±3.1 kWh kg−1 NH3 [58,62]      | • Kinetics no longer rate limiting, recycle is rate limiting [66] | |
| TRL 4-5                           | • Operating safety                               |                                                    |

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![Ammonia vapor pressure as function of temperature.](image1)

![Ammonia fraction in gas phase as function of temperature.](image2)
Advantages and disadvantages of the alkaline, battolyser, PEM and solid oxide electrolysis systems. 1 Nm³ H₂ is equivalent to 0.090 kg H₂.

| Alternative | Advantages                                      | Disadvantages                                                                 |
|-------------|------------------------------------------------|-------------------------------------------------------------------------------|
| Alkaline    | • Mature technology [85]                        | • Low current densities (0.2-0.45 A cm⁻²) [69,81,82]                         |
|             | • Non-noble, abundant catalysts (Ni, Ni-Mo alloys) [74,81,83] | • Cross-over of gases [71,81]                                               |
|             | • Long term stability (60000-90000 h) [81,82]   | • High minimum load requirement (10-40%, although state of the art systems with 5% are available) [71,74,81] |
|             | • Low cost (current lowest: 450 € kW⁻¹) [75,86]  | • Slow dynamics (seconds scale) [71]                                         |
|             | • Stacks in MW range (up to 5.3 MW) [81,82,87]  | • Low operating pressures (nowadays high pressure systems of up to 30 bar are available) [74,82] |
| DC energy consumption | 2.4-6.6 kWh Nm⁻³ H₂ [69,82]                 | • Corrosive liquid electrolyte [71,81]                                      |
| Electrolyte | 20-40 wt% KOH [74,83]                           | • Complicated system design, especially when high purity is required [71]   |
| TRL 9       |                                                 | • (Most of the) disadvantages of alkaline electrolyzers                        |
|             |                                                 | • Low operating pressures (however, operation at pressures up to 30 bar (or above) is possible) |
| Battolyser  | • (Most of the) advantages of alkaline electrolyzers | • New technology (currently commercialized in Battolyser B.V.) [88]           |
| 30-60°C     | • Combined battery and electrolyzer [76]        | • High cost of components (capital cost 1860-2320 € kW⁻¹, possibly as low as 900 € kW⁻¹) [71,81,82,89] |
| 1-30 bar    | • Non-noble, abundant catalysts (Fe, Ni) [76]   | • Acidic corrosive environment [81]                                          |
| DC energy consumption | 4.4 kWh Nm⁻³ H₂ | • Low cost (about 370 € kW⁻¹) [52]                                            |
| Electrolyte | 21 wt% KOH [76]                                 | • Low stack lifetime (however, nowadays the warranted lifetime is equal to that of alkaline electrolyzers) [85] |
| TRL 4.5     |                                                 | • Stacks below MW range (however, nowadays 1.1 MW size available) [52]       |
| PEM         | • High current densities (0.6-2.0 A cm⁻²) [81,82]| • Use of scarce materials (Ir, Pd, Pt, Ru) [71,81]                           |
| 50-80°C     | • High voltage efficiency [81]                  | • High water purity requirement (≥ 1 μS cm⁻¹) [71,72]                       |
| 10-200 bar  | • Low minimum load requirement (0–10% or 5–10%) [81,82] | • High maintenance costs (≥ 1 € kW⁻¹) [71,72]                                |
| DC energy consumption | 4.2-6.6 kWh Nm⁻³ H₂ [69,82] | • High cost (current capital cost 2000 € kW⁻¹, potentially low cost due to low cost materials) [87] |
| Electrolyte | Nafion [74,81]                                  | • Low practical current densities (0.3–0.6 A cm⁻²) [71]                     |
| TRL 5-7     |                                                 | • New technology (not commercial yet) [71,74]                                |
| Solid oxide | • Potential low energy requirement for splitting water [87,90,91] | • Low stack lifetime (efficiency degradation 3–50% y⁻¹) [69,82]             |
| 650-1000°C  | • Reversible operation possible [93]            | • High temperature operation [85]                                           |
| 1-25 bar    | • Potential for using low cost materials (current materials are NIO/YSZ and La₀.₈Sr₀.₂MnO₃/YSZ) [90-92] | • High minimum load requirement (> 30%) [85]                                |
| DC energy consumption | > 3.7 (> 4.7) kWh Nm⁻³ H₂ [85] | • Slow dynamics (seconds scale) [85]                                       |
| Electrolyte | YSZ [90,91]                                    | • Stack sizes in kW range [69]                                               |
| Electrolyte | 3.7-9.9 kWh Nm⁻³ H₂ [69]                       | • Low operating pressures (oxygen removal down to 0.5 mol.%) [69,82]         |
| Electrolyte | TRL 3-5 [84]                                   | • (No pure oxygen product)                                                  |
| TRL 3-5     | • Potential high energy efficiency [69]         | • (No pure oxygen product)                                                  |
| Ammonia     | • High current efficiency degradation 0.5–2.5% y⁻¹ [69] | • (No pure oxygen product)                                                  |
| Cryogenic distillation | • High purity nitrogen production (up to 99.999 wt% purity) [12,94] | • Requires continuous operation (Load range 60–100%) [73]                   |
| Capacity range | 250-50000 Nm³ h⁻¹ [94]                       | • Slow dynamic response (order of hours) [73]                               |
| DC energy consumption | 0.11 kWh kg⁻¹ N₂ [78] | • Cryogenic conditions                                                        |
| Pressure swing adsorption | • (Pure oxygen product) | • Refrigeration compounds                                                     |
| Capacity range | 25-800 Nm³ h⁻¹ [94]                       | • Argon in oxygen product (up to 98 wt% purity oxygen) [94]                 |
| DC energy consumption | 0.22-0.31 kWh kg⁻¹ N₂ [95] | • Additional deoxo unit required                                              |
| TRL 9       | • Flexible operation (Load range 30–100%) [73,96] | • (No pure oxygen product)                                                  |
| Membrane permeation | • Ambient temperature [24,97] | • Nitrogen purity up to 99.8 wt% (however, oxygen can be as low as 0.01 wt%) [94] |
| Capacity range | 3-3000 Nm³ h⁻¹ [94]                       | • Argon in nitrogen product [94]                                             |
| DC energy consumption | 0.22-0.63 kWh kg⁻¹ [95] | • Additional deoxo unit required                                              |
| TRL 8-9     | • Flexible operation (Load range 30–100%) [73] | • Nitrogen purity up to 95 wt% (oxygen removal down to 0.5 mol.%) [94,95]    |

permeation offer the highest flexibility (see Table 4). A significant drawback of membrane permeation is the low attainable nitrogen purity at low energy consumption (up to 95 wt% nitrogen purity), which makes this alternative unfeasible when other options are available [94].

As nitrogen is produced from air, oxygen containing compounds can be present in the purified nitrogen stream. Therefore, a deoxo unit for deep oxygen removal is often installed as a last step in the nitrogen production stage as a safety measure. If oxygen containing compounds are not removed, these can build up in the ammonia synthesis loop. Oxygen containing compounds can poison ammonia synthesis catalysts, as discussed in section 2.5.1.

Sánchez et al. reviewed the cost of nitrogen production recently [98]. For small-scale systems (< 1 MW scale), membrane permeation is the preferred alternative, while pressure swing adsorption is preferred at intermediate scales (1–100 MW) [98]. At large scales (> 100 MW), cryogenic distillation is preferred [98]. Concluding, the pressure swing adsorption unit is the preferred alternative for nitrogen production at
the scale considered, because of its flexible operation, (near) ambient temperature operation and low cost. The hydrogen and nitrogen production can be streamlined, and these can be operated at similar temperatures and pressures. The energy consumption for nitrogen production is about 0.32 kWh kg⁻¹ nitrogen or 0.25 kWh kg⁻¹ ammonia (see Table 4) [95]. The energy consumption depends on the required nitrogen purity. A major portion of the energy consumption is required for the feed air compression (about 0.18 kWh kg⁻¹ ammonia).

2.5. Ammonia synthesis catalyst

Various catalytic systems have been researched for ammonia synthesis. Among these, iron-based catalysts and ruthenium-based catalysts are the prevalent alternatives in heterogeneous catalysis. Industrially, iron-based catalysts are used in ammonia synthesis for over a century [27]. However, academic research focuses more on ruthenium-based catalysts, because these catalysts are more active at lower temperature (and consequently lower pressure can be applied) and at high ammonia conversion levels [21,99]. Both iron-based catalysts and ruthenium-based catalysts were extensively discussed by Liu [21]. Bi-metallic catalysts have also been researched, but these have not found any industrial application so far [99]. A drawback is the high temperature nitrification process, which makes the production of catalysts with high surface areas difficult for bi-metallic catalysts [100].

The activities of various catalysts at low temperature and low pressure are listed in Table 5. For comparison, the reaction rate of industrial catalysts at industrial conditions (i.e., ≥ 400 °C and ≥ 100 bar) is typically ≥ 100 mmol ammonia h⁻¹ g⁻¹, based on the kinetic rate expression of Sehested et al. [101]. Ru/Ba-Ca(NH₂)₂ is the most active catalyst in the low temperature regime. Other catalysts, such as Ru/ C12A7:ε and Cs-Ru/SrZrO₃ only exhibit similar activities when electric fields are employed [102,103] or when the temperature is increased [104]. The use of an electric field amounts to an additional energy consumption of 2–5 kWh kg⁻¹ ammonia.

Ru/Ba-Ca(NH₂)₂ offers a solution to suppress hydrogen poisoning, as barium acts as an efficient electronic promoter, which forms a shell around ruthenium nanoparticles [105]. In this manner the nitrogen dissociation is accelerated in such a manner, that the hydrogenation is the rate limiting step rather than the nitrogen dissociation for the Ru/ Ba-Ca(NH₂)₂ catalytic system [105]. In conventional catalysis (both iron-based and ruthenium-based), nitrogen dissociation is the rate limiting step [21]. As hydrogenation is the rate limiting step for Ru/Ba-Ca(NH₂)₂, hydrogen poisoning is less apparent due to fast consecutive reactions with adsorbed nitrogen.

Conventional iron-based catalysts show a more or less linear increase in activity upon increase in temperature (range 250–400 °C) [21,105]. Conventional ruthenium-based catalysts are typically more active than iron-based catalysts in the range 375–450 °C [21,105]. However, conventional ruthenium-based catalysts experience severe hydrogen poisoning below 320 °C [105]. Ru/Ba-Ca(NH₂)₂ is the preferred catalyst for low temperature operation, having both little hydrogen poisoning and a high surface area (100 m² g⁻¹) [105]. By using Ru/Ba-Ca(NH₂)₂ rather than the conventional iron-based and ruthenium-based catalysts, the temperature can be decreased by about 100 °C to achieve the same activity [105]. The Tokyo Institute of Technology have teamed up with Ajinomoto and other companies for the commercialization of the technology [106]. Tsubame BHB aims to have the catalyst operational in an ammonia test facility by 2021 [106].

The choice for the catalytic system mostly depends on the reaction product separation and the operating pressure. For small-scale processes with intermittent operation, low temperature (275–300 °C) and consequently low pressure operation (5–30 bar) is preferable over high temperature (375–550 °C) and consequently high pressure operation (100–450 bar) due to increased heat losses to the environment upon scale-down [58]. Furthermore, it is desirable to have a small temperature swing between the ammonia synthesis reactor and the ammonia separation step during intermittent operation to keep the synthesis loop operating in a stable manner.

2.5.1. Poisoning

Iron-based catalysts have been the preferred alternative for conventional SMR-based ammonia synthesis plants, in which methane is present in the ammonia synthesis loop, while oxygen-containing compounds are completely removed [27]. Carbon poisoning is not significant for industrial iron-based catalysts [21]. Carbon is a poison for ruthenium-based catalysts [21]. Decomposition of methane is an inhibitor of using ruthenium-based catalysts in conventional Haber-Bosch plants [111]. In case hydrogen is produced via electrolysis rather than via steam methane reforming, oxygen compounds may be present in the synthesis loop rather than carbon compounds. Industrial iron-based catalysts are poisoned by oxygen [21]. On the other hand, ruthenium-based catalysts are less poisoned by oxygen [105]. All in all, iron-based catalysts are suitable for streams containing carbon impurities, whereas ruthenium-based catalysts are suitable for streams containing oxygen impurities, which is the situation in this case study.

2.6. Ammonia separation & storage

Conventionally, ammonia is separated by phase separation of liquid ammonia from gaseous nitrogen and hydrogen by cooling. As shown in Fig. 4, the condensation fraction of ammonia highly depends on the synthesis pressure. Recent developments in affinity separation by absorption in metal halides have made sharp separation at high temperatures feasible (at > 100 °C and 5–30 bar) [57,68]. This makes low-pressure ammonia synthesis feasible. Both temperature swing absorption and pressure swing absorption systems were proposed. Although the latter shows promise with up to 32 wt% ammonia reversibly stored at room temperature in CaCl₂.Br₃.67 [112], no stable systems with near-term relevance for practical application have been reported so far. Therefore, temperature swing absorption is discussed in section 2.6.1.

Beach et al. [113,114] have developed a zeolite as adsorbent for ammonia separation, at low conversions (down to 1 mol.% ammonia) for their fast-ramping reactor concept. Commercial molecular sieves (4A, 5A, and 13X) are used for the sharp removal ammonia [115]. The adsorbents can take up 9 wt% ammonia [113]. Zeolites can separate ammonia at low temperatures (20–100 °C). The ammonia is desorbed at elevated temperatures (> 200 °C) [116,117]. After desorption from the zeolite, the ammonia is liquefied [113,114].

A wide range of solid and fluid materials have been proposed for ammonia separation, such as activated carbon, covalent organic frameworks, deep eutectic solvents, ionic liquids, metal organic frameworks, oxides, and porous organic polymers [115,116,118–123]. However, these materials are either still in the proof of concept phase or

| Catalyst | TRL | tₜₕₜ (mmol g⁻¹ h⁻¹) | NH₃ yield (%) | Stability |
|----------|-----|---------------------|--------------|-----------|
| Ru(10%)/Ba-Ca (NH₂)₂ | 3 | 23.3 [105] | 3.16 [105] | +/0 [105,107] |
| Industrial Fe catalyst | 9 | 5.4 [105] | 0.74 [105] | +/0 [21,122,108] |
| Ru(10%)/Cs/MgO | 6–7 | 0.6 [105] | 0.08 [105] | 0 [27] |
| Ru(20%)/C12A7:ε | 4–6 | 0.76 [105] | 0.10 [105] | 0 [109] |
| Cs/Ru/SrZrO₃ | 3 | – | – | – [103,110] |
insufficient ammonia separation capacities have been obtained. The relevant ammonia separation technologies are compared in Table 6. Among the non-conventional technologies, absorption of ammonia in metal halides is currently most technologically advanced. Absorption-based ammonia separation by supported metals is capable of intermittent operation, whereas condensation must be operated continuously. Thus, absorption of ammonia in metal halides is the preferred alternative. The absorption bed is regenerated when sufficient ammonia is absorbed.

2.6.1. Absorption-based ammonia separation by metal halides

The fundamentals of absorption-based ammonia separation can be understood by the atomic structure of ammonia. The hydrogen atoms are not equally distributed around the nitrogen atom (as is the case for the hydrogen atoms around the carbon atom in methane). Therefore, ammonia is a polar molecule with a negative dipole at the nitrogen atom, and with positive dipoles near the hydrogen atoms.

The ammonia capturing effect in metal halides can be understood from the polarity of the ammonia molecule. Metal halides are composed of metals (such as Sr$^{2+}$, Mg$^{2+}$ and Ca$^{2+}$) and halides (such as Cl$^{-}$ and Br$^{-}$). Therefore, the polar properties of ammonia can be employed by the metal halide. The negative dipole of the ammonia molecule is located towards the metal ion, whereas the positive dipoles are located towards the halide ion, thereby forming ammine complexes. Depending on the combination of metal, halide and temperature, the coordination number is determined (i.e., the number of ammonia molecules captured per metal halide unit structure)\[125,126\]. The affinity for ammonia separation in various metal halides can be derived from electro-negativities of cations and anions\[127\].

Silica (gel) supported calcium chloride (CaCl$_2$/SiO$_2$) is currently the preferred alternative among the chlorides and bromides for scale-up\[125\]. Its absorption capacity is lower than that of other alternatives (MgCl$_2$, MgBr$_2$ and CaBr$_2$), but the low cost of CaCl$_2$ and the high stability are reasons to choose for CaCl$_2$. Among experimented supports (alumina, kaolinite, diatomaceous earth, silica and zeolite), only silica and zeolite are effective supports\[125\]. Zeolite has a higher capacity than silica at high temperatures (i.e., at > 200 °C)\[125\]. However, the higher absorption capacity of zeolite does not outweigh the additional costs\[125\]. The reversible absorption capacity of ammonia on CaCl$_2$ supported on silica is about 70 mg$_{\text{NH}_3}$/g$_{\text{CaCl}_2}$/SiO$_2$ at 150 °C and 4 bar operating pressure\[125\].

2.6.2. Storage

Ammonia is conventionally stored in liquid form\[25\]. The methods for liquid ammonia storage are listed in Table 7. The main factor determining the type of storage is the required storage capacity. At large capacities, low-temperature liquid storage is economically feasible, whereas at the smallest capacities, non-refrigerated pressure storage is most feasible\[22\]. There is a growing trend towards the use of pressurized storage\[25\]. A significant drawback of conventional storage methods is high ammonia vapor pressure of 7 bar at ambient conditions (see Fig. 4).

Another option for ammonia storage is the use of an absorbent as storage material. This adds inherent safety to the system, because ammonia can only be desorbed upon heating or pressure decrease. Metal halides are proposed for ammonia storage\[4,126,128,129\]. About 5–10 wt% ammonia can be stored on CaCl$_2$/SiO$_2$ (40 wt% CaCl$_2$ and 60 wt% SiO$_2$)\[125\].

Energy is released upon combustion of ammonia for electricity generation (see section 2.7). This heat can be used for the regeneration of the absorbent bed (i.e., the CaCl$_2$/SiO$_2$). A synergy between ammonia separation and storage can be achieved by integrating the process steps into a single process step\[129\]. This saves on energy consumption, as the ammonia storage system can be integrated with the ammonia combustion step.

The most practical configuration of this storage alternative is having a storage with many cylinders of about 0.5–1.0 m diameter and a few meters in height. After desorbing modus at 350 °C, the cylinders are cooled with nitrogen flow from the pressure swing adsorption unit.

2.7. Ammonia-to-power

Power generation from ammonia was systematically studied by Tanner in the 1940s for the first time, even though the first known use of ammonia for power generation in vehicles was in 1933\[28,130\]. Power generation from ammonia can be performed directly or indirectly\[131\]. In the latter case, ammonia is first cracked into nitrogen and hydrogen. At least 14% of ammonia is lost in the cracking process for heating purposes\[27\]. Therefore, direct ammonia combustion is preferred over an intermediate cracking step. In case of direct ammonia fuel cells, ammonia is first decomposed into nitrogen and hydrogen within the fuel cell (over the anode), after which the hydrogen is combusted. Key advantages and disadvantages of various alternatives for electricity generation from ammonia are listed in Table 8. Two main alternatives are available for power generation, namely gas turbines and fuel cells. It should be noted that the efficiency estimates in Table 8 represent the electrical efficiency. This is an important distinction from the total energy efficiency, which includes useful heat generation.

Another constraint on the system is intermittent operation, which requires a fast switch on and off capability within the minutes range. At large scale power generation, a combined cycle gas turbine is the most electrically efficient power generation method. However, as system sizes decrease, heat losses increase. At small scale, fuel cells are generally the preferred alternative. So far, no ammonia-fueled systems are industrially employed. However, ammonia fueled SOFCs (solid oxide fuel cells) are currently tested in pilots by IHI cooperation (1 kW class power)\[45\], and ammonia fueled gas turbines are currently tested in pilots in the United Kingdom\[42\].

| Table 6 |
| --- |
| Comparison of reaction product separation technologies. |

| Condensation |  
| --- |
| Separation temperature | 20 °C to 30 °C\[124\] |
| TRL | 9 |
| Advantages | Well-known technology |
| Disadvantages | Large temperature swing in process (~20 °C to 250–400 °C, see Fig. 4) |
| High heat exchange and refrigeration costs |
| High pressure (100–460 bar)\[23,80\] |
| Not capable of intermittent operation |
| No sharp separation |
| Lab-scale/pilot plant scale\[63,64,67,68\] |
| Absorption material required |
| Temperature swing for regeneration (to 300–400 °C)\[64\] |
| Lab-scale/pilot plant scale\[114\] |
| Adsorbent material required |

| Absorption (metal halides) |  
| --- |
| Separation temperature | 150–250 °C\[58,125\] |
| TRL | 4–5 |
| Advantages | Small temperature swing in process (150–250 °C to 250–400 °C) |
| Low pressure (5–30 bar) |
| Capable of intermittent operation |
| Sharp separation |
| Disadvantages | Large temperature swing in process (~20 °C to 250–400 °C, see Fig. 4) |
| High heat exchange and refrigeration costs |
| High pressure (100–460 bar)\[23,80\] |
| Not capable of intermittent operation |
| No sharp separation |
| Lab-scale/pilot plant scale\[63,64,67,68\] |
| Absorption material required |
| Temperature swing for regeneration (to 300–400 °C)\[64\] |
| Lab-scale/pilot plant scale\[114\] |
| Adsorbent material required |

| Adsorption (zeolites) |  
| --- |
| Separation temperature | 20–100 °C\[115,116,119\] |
| TRL | 4 |
| Advantages | Separation at low conversions (1 mol.% ammonia) |
| Low pressure (5–30 bar) |
| Capable of intermittent operation |
| Sharp separation |
| Disadvantages | Large temperature swing in process (~20 °C to 250–400 °C, see Fig. 4) |
| High heat exchange and refrigeration costs |
| High pressure (100–460 bar)\[23,80\] |
| Not capable of intermittent operation |
| No sharp separation |
| Lab-scale/pilot plant scale\[63,64,67,68\] |
| Absorption material required |
| Temperature swing for regeneration (to 300–400 °C)\[64\] |
| Lab-scale/pilot plant scale\[114\] |
| Adsorbent material required |
2.7.1. Solid oxide fuel cells

Solid oxide fuel cells (SOFCs) are the preferred alternative for electricity generation from ammonia in the 1–10 MW range. As compared to gas turbines, solid oxide fuel cells have a higher electrical efficiency at the required scale (1–10 MW). Furthermore, solid oxide fuel cells offer a higher electrical efficiency than low-temperature fuel cells when operating each with air. Both the SOFC-O and SOFC-H type fuel cells are available [37,39].

In a SOFC system, ammonia is cracked to hydrogen and nitrogen at the anode side of the fuel cell. The subsequent reaction depends on the type of SOFC used. The SOFC-O types are oxygen anion conducting electrolyte-based solid oxide fuel cells and SOFC-H are proton conducting electrolyte-based solid oxide fuel cells [39]. The SOFC-H is also termed a protonic ceramic fuel cell (PCFC).

In the SOFC-O type, the anode serves for both ammonia decomposition and electro-oxidation of hydrogen [132]. A drawback of this is the formation of NOx due to the presence of both nitrogen gas at high temperature combined with oxygen anions. Upon decomposition of ammonia over the Ni cathode, nitrogen gas dilutes the hydrogen gas, thereby reducing the reversible cell potential [37]. The highest peak power densities obtained so far are for SOFC-O systems (1190 mW cm\(^{-2}\) at 650 °C) [133].

In the SOFC-H type, ammonia decomposition occurs at the anode side, and the protons subsequently pass through the electrolyte, to react with oxygen gas at the cathode side [37]. No NOx is formed in case of the SOFC-H type, because the oxidation occurs at the cathode side, rather than the anode side [37]. The theoretical efficiency of the SOFC-H type is higher than that of the SOFC-O type [134]. This is partially due to the lack of hydrogen dilution of SOFC-H type, as protons pass through the electrolyte [37]. However, the highest peak power density obtained so far is 390 mW cm\(^{-2}\) at 750 °C [135], which is lower than power densities reported for SOFC-O systems.

A major drawback for SOFC-O systems is the formation of water vapor on the anode side. In case of SOFC-H systems, the anode side only consists of ammonia, nitrogen and hydrogen, making it possible to use this off-gas for desorption of the ammonia from the storage. Another benefit of SOFC-H types is the requirement for conducting the small protons rather than the larger oxygen ions, making operation of the former feasible at lower temperatures [136]. Proton-conducting membranes (such as BZYC) are stable against water and carbon dioxide, making operation in air feasible [136,137]. Eguchi et al. operate their SOFC system at an efficiency of 55%(LHV) [138]. Thus, assuming a

Table 8
Comparison of ammonia-to-power alternatives for a 1–10 MW system.

| Alternative | Advantages | Disadvantages |
|-------------|------------|---------------|
| Alkaline fuel cells | - Pure oxygen feed required [139] | - High operation temperature (700–775 °C) [138,144] |
| 20°C [139] | - Low lifetime (target 1 yr) [143] | - Minimum load of 7% required [144] |
| (< 100°C [140,141]) | - Reactivity of electrolyte [142] | - Brittle ceramic components [142] |
| Electrical efficiency | - Large temperature swing between ammonia decomposition and fuel cell | - Slow cold start-up [142] |
| 60-65%(LHV) (Pure oxygen) [140,141] | Ammonia fuel specific: | Ammonia fuel specific: |
| Electrolyte | - No sufficiently efficient system known (in research) | - Not commercial (demonstration stage) [147] |
| NaOH/KOH [142] | Cannot be fed with ammonia due to acidic environment of PEM fuel cells | Minimum load of 10% required to suppress NOx emissions [155] |
| TRL 8–9 (H2-based), 1–3 (NH3-based) [38] | Hydrogen fuel specific: | Slow start-up (hours range) |
| PEM fuel cells | - Large temperature swing between ammonia decomposition and fuel cell | Low electrical efficiency |
| 60-80°C [139] | | High pressure operation (> 5 bar) [146] |
| (< 120°C [140,141]) | | Ammonia fuel specific: |
| Electrical efficiency | - Operation with air [139] | - Low laminar burning velocity [156-158] |
| 40-55%(LHV) [140,141] | - Operation near room temperature (20°C) [139] | Increased NOx formation [159] |
| Electrolyte | - Fast start-up [139] | High ignition temperature required |
| Naflon [142] | - High electrical efficiency [140,141] | Slow burning speed (5 times smaller than methane) [153] |
| TRL 8–9 (H2-based), N/A (NH3-based) [38] | | Low flame stability |
| Solid oxide fuel cells | - Operation with air [139,144] | Increased oxygen content required |
| 700-775°C [138,144] | - Fast hot start-up (130 s) [138] | Not commercial |
| (500-1000°C [139,141]) | - High efficiency (> 50%(LHV) in commercial application) [144] | |
| Electrical efficiency | - Commercially available (hydrogen-based systems) [144] | |
| > 50%(LHV) [138,144,145] | - Near ambient pressure operation [146] | |
| TRL 8–9 (H2-based), 4 (NH3-based) | - Operation with (oxygen-enriched) air [150] | |
| Gas turbines | - Conventional combustion equipment [151] | |
| 900-1100°C [146] | - Demonstration stage with near-term use-case [152-154] | |
| Electrical efficiency | | |
| 25-30%(LHV) [148,149] | | |
| TRL 4–7 (H2-based), 4–6 (NH3-based) | | |

Table 7
Characteristics of ammonia storage methods. Data reproduced from Refs. [22,25,67,125].

| Type | TRL | Typical pressure (bar) | Design temperature (°C) | t ammonia per t steel | Capacity (t\(_{\text{Btu}}\)) | Refrigeration compressor |
|------|-----|-----------------------|-------------------------|---------------------|--------------------------|-------------------------|
| Non-refrigerated storage | 9 | 16–18 | 20–25 | 2.8–6.5 | < 270 or < 1500 | None |
| Semi-refrigerated storage | 9 | 3–5 | Ca. 0 | 10 | 450–2700 | Single stage |
| Low-temperature storage | 9 | 1.1–1.2 | – 33 | 41–45 | 4500–45000 (< 50000) | Two stage |
| Absorption-based storage | 3–4 | 1–30 | 20–250 | – | – | None |
3. Process proposal for power-to-ammonia-to-power storage system

Process alternatives were discussed previously, from which a conceptual process design is constructed and the process was modelled in Aspen Plus. The Aspen Plus model is elaborated upon in the supplementary information. An index flowsheet of the major components in the power-to-ammonia-to-power storage system is shown in Fig. 5. Technology pushes within the process design are the development of new materials (the battolyser for a combined battery function and hydrogen generation, the Ru/Ba-Ca(NH2)2 catalyst for ammonia synthesis at relatively low temperature, and the CaCl2/SiO2 absorbent for ammonia separation and storage), enabling the decentralized production of ammonia from renewables at a relatively low temperature and pressure (275 °C, 8 bar) [58,76,105,125]. By combining emerging technologies, the hydrogen production, nitrogen production and ammonia synthesis loop operate at the same pressure (8 bar), thereby simplifying the process and allowing for intermittent operation. Furthermore, the development of ammonia-fueled solid oxide fuel cells (SOFCs) enables direct electricity generation from ammonia, rather than from a cracked hydrogen and nitrogen feed stream [138,160]. This simplifies the process design significantly (no ammonia cracker is required), and temperature swings within the process are decreased. The synergistic effects are discussed in the supplementary information.

The ammonia stored in the CaCl2/SiO2 is released by heating the absorbent with the heat produced by the SOFC (see section 3.1), giving an electrical round-trip efficiency of about 33% for P2A2P (power-to-ammonia-to-power). For comparison, the electrical round-trip efficiency of a battery is about 80% [76]. The resulting round-trip efficiencies of the case study (Haaksbergen) are listed in Table 9. About 55% of the electricity is provided by wind and solar power directly, 16% by the battery function of the battolyser (efficiency 80%) and 29% by the power-to-ammonia-to-power process (efficiency 33%, see section 3.1 and the supplementary information). The overall efficiency of the system becomes 61%. More details on the Haaksbergen case can be found in the supplementary information.

3.1. Energy consumption of power-to-ammonia-to-power

In order to understand how much energy is consumed during full load ammonia synthesis, the energy consumption of the subsystems is quantified. This serves as an indication on the round-trip efficiency after power generation. An increased energy consumption of 15% is assumed during low load operation [161].

The estimated energy consumption of the power-to-ammonia plant is listed in Table 10. As inefficiencies are taken into account in most units, a reasonably accurate energy consumption is provided. The calculated energy consumption of 8.7–10.3 kWh kg⁻¹ ammonia is comparable to that of a large-scale Haber-Bosch process with a low temperature PEM electrolyzer (8.6–9.5 kWh kg⁻¹ ammonia, see Table 1). The variation in energy consumption is due to the desorption energy of ammonia, which can be heat integrated with the SOFC, thereby resulting in a power-to-ammonia energy consumption of 8.7 kWh kg⁻¹ ammonia. The high value (10.3 kWh kg⁻¹ ammonia) represents the case in which heat must be provided externally. The SOFC is assumed to have an energy efficiency of 55%(LHV), as discussed in section 2.7. The heat from the SOFC is used for the desorption (1.6 kWh kg⁻¹ ammonia). This results in a round-trip efficiency of 33% for power-to-ammonia-to-power.

All in all, small-scale ammonia synthesis can be close to or as energy efficient as large-scale ammonia synthesis, when assuming the heat of the SOFC can be used for desorption of ammonia from the absorbent. However, this requires the synthesis loop to be operated at a lower temperature and consequently a lower pressure to prevent heat losses associated with small-scale operation. It should be noted that conventional SMR-based ammonia synthesis plants require mostly heat input, whereas the small-scale ammonia synthesis plants discussed here are electrolysis-based. As a reference, the energy consumption of the most efficient, large-scale ammonia plants based on steam methane reforming (SMR) is 7.78 kWh kg⁻¹ ammonia [54].

3.2. Dynamic operation

The electricity source for the ammonia synthesis plant is variable due to the intermittency of power from wind turbines and solar panels. Therefore, the process must be capable of following this intermittent input electricity. Compressors typically have a load range of 55–115% [24]. Thus, it is desirable to minimize the use of compression within the process design, especially in the feed compression. As discussed

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Fig. 5. Index flowsheet of major components for power-to-ammonia-to-power. Electricity and heat streams are indicated by dotted lines, while material streams are indicated by full lines.

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previously, the use of compressors has been minimized by operating the hydrogen production, nitrogen production and ammonia synthesis loop at the same pressure (8 bar).

Various control strategies can be employed for load variation, namely (1) pressure variation, (2) loop parallelization, and (3) inert variation [162]. In case of pressure variation, the loop pressure is adapted to the load by regulating the duty of the recycle compressor. Pressure variation following load variation is not feasible due to fatigue stress occurring in processing equipment [162]. Loop parallelization can be employed by opening or closing parts of the equipment, thereby increasing or decreasing the ammonia production capacity. A drawback of this is the requirement for an advanced control system, as well as a high capital cost for equipment [162]. Load variation by inert variation is the most feasible alternative. Ammonia licensor Casale S.A. has patented this control strategy for load variation [161].

Inert variation is regulated by purge control. By decreasing the purge fraction, the inert fraction within the process is increased and the single pass conversion is decreased. The increased inert fraction can be accomplished by (1) increasing the argon fraction, and (2) increasing the nitrogen fraction. Although the latter is a reactant, it retards the reaction rate upon decreasing the H₂:N₂ ratio to below 1:1. As nitrogen production by pressure swing adsorption can only be ramped down to 30% load [73], changing the H₂:N₂ ratio is the primary strategy for dynamic operation. Upon increasing the inert fraction (for operating at 10% load), the specific energy consumption for ammonia synthesis is claimed to increase by only 10–15% as compared to full load operation [161]. This load variation is dynamically possible in the hour range [162].

3.3. Comparison to other systems

The conceptual process design developed in this paper utilizes various novel technologies, thereby allowing for operation at a single pressure level and a synthesis temperature of 275 °C. The significance of these technological developments is discussed in the current paragraph by comparing the proposed process design to various alternative process designs. However, before performing this analysis, hydrogen and ammonia as energy vectors are compared.

When comparing hydrogen and ammonia, the combined production & storage cost are important. The estimated production costs of hydrogen and ammonia (in terms of hydrogen) and their storage cost are listed in Table 11, based on an estimate by Vrijenhoef. From this it follows that the total cost for hydrogen as a chemical storage medium increases significantly with storage duration. On the other hand, the total cost of ammonia as a chemical storage medium is fairly constant. For one day storage, hydrogen and ammonia are similar in terms of costs. However, for long-term storage, ammonia is the preferred alternative in terms of production and storage costs. Short-term energy storage (i.e., for about 1 day) can already be accounted for by batteries, which have a higher round-trip efficiency than chemical storage alternatives.

In the process design a combination of short-term storage and long-term storage is proposed with a battery and a power-to-ammonia-to-power process. The Battolyser was proposed within the process, because the combination of the battery functionality and electrolyzer functionality can decrease costs. However, the Battolyser is not the best electrolyzer available (about 4.4 kWh Nm⁻³ hydrogen). A case without a battery functionality, but with the best electrolysis efficiency available (about 3.8 kWh Nm⁻³ hydrogen) is compared to the proposed

## Table 9
Fractions of various electricity inputs and outputs, and efficiencies.

| System                                           | Efficiency (%)<sub>i,el</sub> | Total output (x10⁷ kWh y⁻¹) | Fraction of total output (%) | Total input electricity (x10⁷ kWh y⁻¹) | Fraction of total input (%) |
|--------------------------------------------------|--------------------------------|-----------------------------|-----------------------------|---------------------------------------|-----------------------------|
| Wind turbines and solar panels                   | N/A                            | 1.68                        | 55                          | 1.68                                  | 34                          |
| Battery function (≤ 1 day)                       | 80                             | 0.49                        | 16                          | 0.61                                  | 12                          |
| Chemical storage (≥ 7 days)                      | 33                             | 0.89                        | 29                          | 2.69                                  | 54                          |
| Total                                            | 61                             | 3.06                        | 100                         | 4.98                                  | 100                         |

## Table 10
Electricity consumption of power-to-ammonia plant. Electricity consumption for storage and controls are not taken into account.

| Unit | Energy consumption (kWh kg⁻¹ NH₃) | Fraction (%) | Note                                                                 |
|------|----------------------------------|--------------|----------------------------------------------------------------------|
| Hydrogen production                  | 8.36          | 81–96         | See section 2.3                                                      |
| Nitrogen production                  | 0.250         | 2.4–2.9       | See section 2.4                                                      |
| Synthesis loop                       | 0.1–1.7       | 0.9–16        | Recycle compression from Aspen Plus simulation. Cooling data reproduced from Ref. [58]. Desorption data was estimated. |
| Cooling                             | 0.062         |              |                                                                      |
| Desorption                          | 0–1.6         |              |                                                                      |
| Total                               | 8.7–10.3      | 100           | 154–183% of theoretical minimum (5.64 kWh kg⁻¹ ammonia)              |

## Table 11
Estimated costs of hydrogen and ammonia as an energy vector. Reproduced from Ref. [163].

|              | Hydrogen (€ kg⁻¹H₂) | Ammonia (€ kg⁻¹H₂) |
|--------------|---------------------|-------------------|
| Production   | 2.70                | 3.40              |
| Storage period |                    |                   |
| 1 day        | 0.71                | 0.03              |
| 15 days      | 1.78                | 0.05              |
| 182 days     | 13.48               | 0.49              |

## Table 12
Comparison of the proposed process design (base case) to alternative process designs.

| System                      | Relative energy input | Overall system efficiency (%) |
|-----------------------------|-----------------------|-------------------------------|
| Base case                   | 1.00                  | 61                            |
| Best electrolyzer without battery | 1.07                 | 57                            |
| Best electrolyzer with battery | 0.93                 | 66                            |
| Conventional electrolysis-based Haber-Bosch process | 1.08-1.14 | 53-56 |
| Less efficient ammonia-to-power system | 1.20-1.45 | 42-51 |

The increased inert fraction can be
process design. The system with the best electricity system gives a power-to-ammonia-to-power efficiency of 38%. However, due to omission of a battery function, the total energy input is increased to 5.4*10^7 kWh y^-1, which is an increase of 7% compared to the proposed process design. As the overall system scales with the total energy input, the cost of electricity is also expected to be 7% higher for the system with the best available electricity and without a battery functionality.

If a battery functionality is added to the best available electrolysis system, the total energy input becomes 4.7*10^7 kWh y^-1, which is 7% lower than the process proposed within this paper. The overall efficiency of such an islanded system is 66%. It should be noted that the cost of batteries is significant and the best available electrolyzers are more expensive than the Battolyser. Thus, the cost of such a system will be similar to that of the proposed process design. However, it cannot be concluded that the development of a combination of a battery function and electrolysis function is not the bottleneck for islanded ammonia energy systems.

A synergy in the proposed process design is the heat integration of the heat-to-ammonia and ammonia-to-power part by utilizing the heat losses of the SOFC-H for the desorption of ammonia from the supported metal halide. This decreases the energy consumption of the total energy input from 10.3 kWh kg^-1 ammonia to 8.7 kWh kg^-1 ammonia. When using a conventional electrolysis-based Haber-Bosch process at the given scale, the energy input is about 10–11 kWh kg^-1 (see Fig. 3). With a SOFC-H operating at 55%(LHV) efficiency, the power-to-ammonia-to-power efficiency becomes 26–28%, as compared to the 33% for the process designed in this paper. With the electricity distribution in Table 9, this leads to an overall efficiency of 53–56%, as compared to 61% for the process designed in this paper. Whereas the total energy input is 5.0*10^7 kWh y^-1 for the process designed in this paper, it becomes 5.4–5.7*10^7 kWh y^-1 for a conventional electrolysis-based Haber-Bosch process (i.e., a 8–14% increase).

Ammonia-fueled SOFC-H systems are currently researched at the academic level and these systems are not commercially available yet. In case small-scale gas turbines or hydrogen-fed fuel cells are used instead, the systems operate less efficiently (at about 30–40%(LHV), see Table 8). This leads to power-to-ammonia-to-power efficiencies of 18–24%. The effect of the efficiency of the ammonia-to-power part is profound. The total energy input becomes 6.0–7.3*10^7 kWh y^-1, which is about 20–31% higher than for the process designed in this paper. All in all, the efficiency of the ammonia-to-power is most important for the overall system efficiency, as follows from Table 12. The synergy of the fuel cell and the absorbent is of significance as well. The choice of the electrolysis system and the use of a battery is of lesser significance. In a generic location in northern Europe, the estimated cost of such an islanded energy system is about 0.30–0.35 € kWh^-1.

4. Conclusion

Current technological developments for islanded energy storage systems were reviewed, based on ammonia as a long-term chemical energy storage medium. Current technological developments discussed in this paper may make ammonia synthesis at temperatures of 275°C and pressures of 8 bar feasible. These operating conditions are significantly milder than the operating conditions of the current benchmark of 375–450°C and 100–450 bar.

The electricity consumption of the proposed power-to-ammonia process is about 8.7–10.3 kWh kg^-1 ammonia. When ammonia fueled, hydrogen conducting solid oxide fuel cells (SOFC-H) are developed at the required scale, power can be generated from ammonia at a high efficiency (50–60%(LHV)) at 700–775°C. With the development of the innovative electrolysis systems such as the Battolyser, which is a combination of an electrolyzer and a battery, part of the electricity can be stored at a round-trip efficiency of 80%, increasing the overall storage efficiency. The overall efficiency of the islanded system is 61%. The estimated cost of such an islanded energy system is about 0.30–0.35 € kWh^-1, which includes wind turbines, solar panels, a battery, and a power-to-ammonia-to-power storage system.

Declarations of interest

None.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rser.2019.109399.

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