

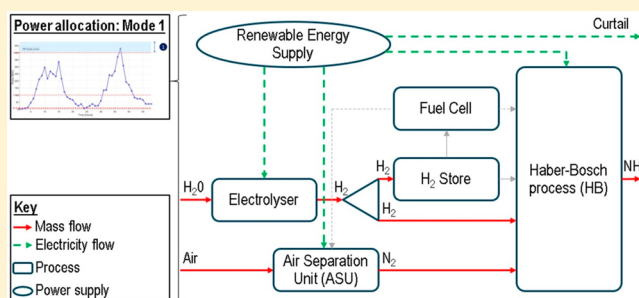
“Green” Ammonia: Impact of Renewable Energy Intermittency on Plant Sizing and Levelized Cost of Ammonia

Richard Nayak-Luke,[†] René Bañares-Alcántara,^{*,†} and Ian Wilkinson[‡]

[†]Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, United Kingdom

[‡]CT REE, Rutherford Appleton Laboratory, Siemens Corporate Technology, Oxford OX11 0QX, United Kingdom

ABSTRACT: Ammonia production currently contributes almost 11% of global industrial carbon dioxide emissions, or 1.3% of global emissions. In the context of global emission targets and growing demand, decarbonization of this process is highly desirable. We present a method to calculate a first estimate for the optimum size of an ammonia production plant (at the process level), the required renewable energy (RE) supply, and the levelized cost of ammonia (LCOA) for islanded operation with a hydrogen buffer. A model was developed to quantitatively identify the key variables that impact the LCOA (relative to a ± 10 GBP/tonne change in LCOA): levelized cost of electricity (± 0.89 GBP/MWh), electrolyzer capital expenditure (± 65 GBP/kW), minimum Haber–Bosch (HB) load ($\pm 12\%$ of rated power), maximum rate of HB load ramping, and RE supply mix. Using 2025/2030 estimates results in a LCOA of 588 GBP/tonne for Lerwick, Scotland. The application of the model will facilitate and improve the production of carbon-free ammonia in the future.



1. INTRODUCTION

Over the past decade, global carbon dioxide emissions have significantly increased at a rate of 2.4% per year.¹ These emissions are commonly attributed to four sectors: electricity, transport, heating, and industry. In recent years, there has been notable work to decarbonize all of these sectors. The most commonly overlooked of these sectors is industry, which currently accounts for 12% of global emissions.² Chemical production accounts for a substantial part of this and is predicted to contribute to 14% of total industrial emissions by 2050.³ The fossil fuel dependency of any given chemical process is determined by its fossil fuel requirements for energy, feedstock, or both. For effective interventions (technical, economic, social, and/or regulatory), those chemicals produced in significant quantities that also have a high dependency on fossil fuels (for both energy and feedstock) should be considered first, of which ammonia is a prominent example. Current global production of ammonia is ca. 200 Mtonne/year, and as 95% of its hydrogen feedstock is derived from fossil fuels, it accounts for 420 Mtonne/year of carbon dioxide emissions (1.3% of the global amount).^{1,3} Primarily driven by population growth, this is predicted to increase to ca. 270 Mtonne/year of ammonia by 2050.^{3,4} Currently about 85% of ammonia produced globally is used as fertilizer.⁵ However, in recent years ammonia has received increasing attention as a potential energy vector and direct fuel for use in the three other sectors (electricity, transport, and heating).

Cost-effective electrification of ammonia production is therefore an environmental imperative and a significantly disruptive business opportunity. In this paper we have

investigated using a Haber–Bosch (HB) process fed with hydrogen produced from the electrolysis of water and nitrogen from air separation.

Previous investigations of such an electrified ammonia production process can be divided into two main groups on the basis of their supply of electricity: a fully dependable supply (from dispatchable sources such as the grid) or renewable energy (RE) with a stabilizing energy supply. Investigation into production using dispatchable sources is more mature,⁶ with a notable recent example being the work of Wang et al.⁷ in 2017, whose modeling concluded that this production method could provide dispatchable electricity back to the grid at 0.18 GBP/kWh⁷ (the original value was 0.24 USD/kWh converted from USD using 1 USD:0.77 GBP⁸) and with a 72% round-trip electrical efficiency.⁷ For comparison, the levelized cost of electricity (LCOE) quoted by Wang et al. corresponds to a levelized cost of ammonia (LCOA) in the range of 547–905 GBP/tonne (assuming an ammonia-to-electricity efficiency of 60%). In contrast, Beerbühl et al. in 2014 considered a nonlinear load-dependency of specific electrolyzer electricity consumption (kWh/kg_{hydrogen}) that resulted in a LCOA of 449 GBP/tonne⁹ (original value 583 USD/tonne of ammonia). A practical demonstration of such a process is currently being considered by Nuon using three 437 MWe combined cycle gas turbines (MHPS 701F4) to generate electricity from the stored

Received: May 31, 2018

Revised: September 30, 2018

Accepted: October 8, 2018

Published: October 8, 2018

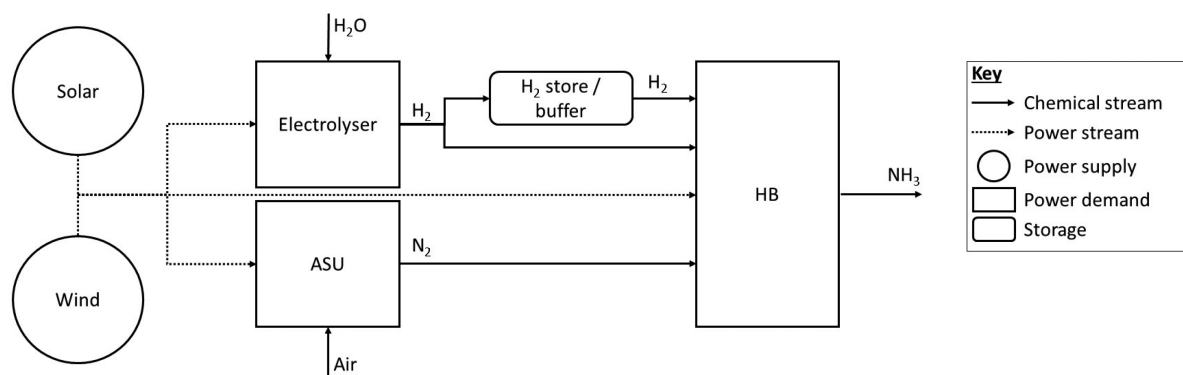


Figure 1. Simplified process block diagram of “green” ammonia production.

ammonia when required.¹⁰ Only a few investigations have considered using renewable energy (“green”) sources directly as part, or all, of their supply mix, principally due to the constraint of having to run the HB at steady state using intermittent RE sources. On the other hand, the RE option has two important advantages over the dispatchable power supply option: it eliminates overall carbon dioxide emissions,¹¹ and it has the potential to be economically viable sooner.¹² The four most important studies involving RE have each dealt with the intermittency differently, thereby resulting in a significant variation of LCOA estimates (GBP/tonne of ammonia): Morgan,¹³ 447–942 (original value 580–1224 USD/tonne of ammonia); Beerbühl et al.,¹⁴ 264–528 (The original values considered in the analysis were 300–600 EUR converted from EUR using 1 EUR:0.88 GBP⁸); Bañares-Alcántara et al.,¹² 504–609 (original value 655–791 USD/tonne of ammonia); and Tună et al.,¹⁵ 524–1771 (original value 680–2300 USD/tonne of ammonia). One important difference among the analyses is how they managed the RE intermittency. To stabilize the supply, Morgan and Tună et al. used dispatchable sources such as the grid or biomass, whereas Beerbühl et al. and Bañares-Alcántara et al. assumed islanded systems that had hydrogen and ammonia “buffers”, respectively, a “buffer” being the intentional overproduction (regions 1 and 2 in Figure 2) and storage of a specified chemical so that it can be drawn from, as either feedstock and/or an energy source, in times of low power supply (regions 3–5 in Figure 2). The range of LCOA estimates within each of the papers is due to technological, energy source, and cost parameter variations. While some key variables (particularly production cost) could be deduced from previous results, none, barring Beerbühl et al., has explicitly identified them or investigated the LCOA’s sensitivity to them. This, therefore, leaves some specific gaps in knowledge: How should one size an ammonia plant (at the process level) with a hydrogen buffer for islanded operation to minimize LCOA? What is the impact of optimizing the plant and RE supply in combination? Finally, what are the key variables that impact LCOA and the LCOA’s sensitivity to them?

In this paper we identify, and subsequently quantify, the key variables for the case of islanded electrified ammonia production processes. To achieve this, we first modeled the process in MATLAB based on a HB synthesis process with a hydrogen buffer (as defined by Beerbühl et al.⁹). However, the work presented here expands on Beerbühl et al.’s work⁹ by identifying (for a different location) the LCOA’s sensitivity to an additional cost variable (electrolyzer CAPEX as well as LCOE) and process variables in combination. This model,

when provided with RE supply profiles, calculates the RE supply mix and plant size (at the process level) that decreases the LCOA. It achieves this by individually considering each specified combination of plant size and RE mix, calculating their resulting LCOA, and identifying the lowest. This approach was favored over formal optimization methods because one of the objectives was to understand the impact that individual variables have on the LCOA. Perturbation analysis was considered but was found to be viable only for the impact of cost variables. Use of Lagrange multipliers was also attempted but was found unpractical due to discontinuities in the results surface (due to certain combinations of RE supply and production process sizing being unviable) and, more importantly, because the model adapts to any change by resizing the plant and RE supply (thereby not giving the independent impact of one variable on LCOA that we require). When used with process variables, the individual changes impact the optimum plant size and power supply, and therefore, the resulting LCOA values are not directly comparable. In this investigation we have chosen not to prescribe the use of the ammonia (either as a commodity or an electrical energy storage vector) after its production. Potential synergies that could be realized through process integration,⁷ such as heat integration or recovery of feedstock, have therefore not been taken into account, resulting in potentially conservative LCOA estimates. To enable identification of the key variables that impact LCOA and their sensitivity, the model was provided with Met Office data of solar irradiation and wind speeds¹⁶ for Lerwick, Scotland (2000–2016). The resulting model provides a tool for industry and academia that fulfills the vision expressed in a recent IEA study, namely, the development of “detailed, specific studies with hourly output of solar and wind [to] optimise the respective capacities of solar, wind and electrolyzers, the design of the NH₃ plant, and the means to prevent undesirable disruptions in the synthesis loop”.¹⁷ The sensitivity analyses have quantified the improvements that need to be made to the process and the LCOE required for “green” ammonia to be economically viable.

This paper is organized as follows: section 2 outlines the modeling assumptions and the methodology in detail. Section 3 describes the sensitivity analysis calculations that were performed using the model. Section 4 presents and evaluates the results from the sensitivity analysis. Section 5 outlines ongoing work and potential future investigations. Section 6 concludes the paper by highlighting the key findings.

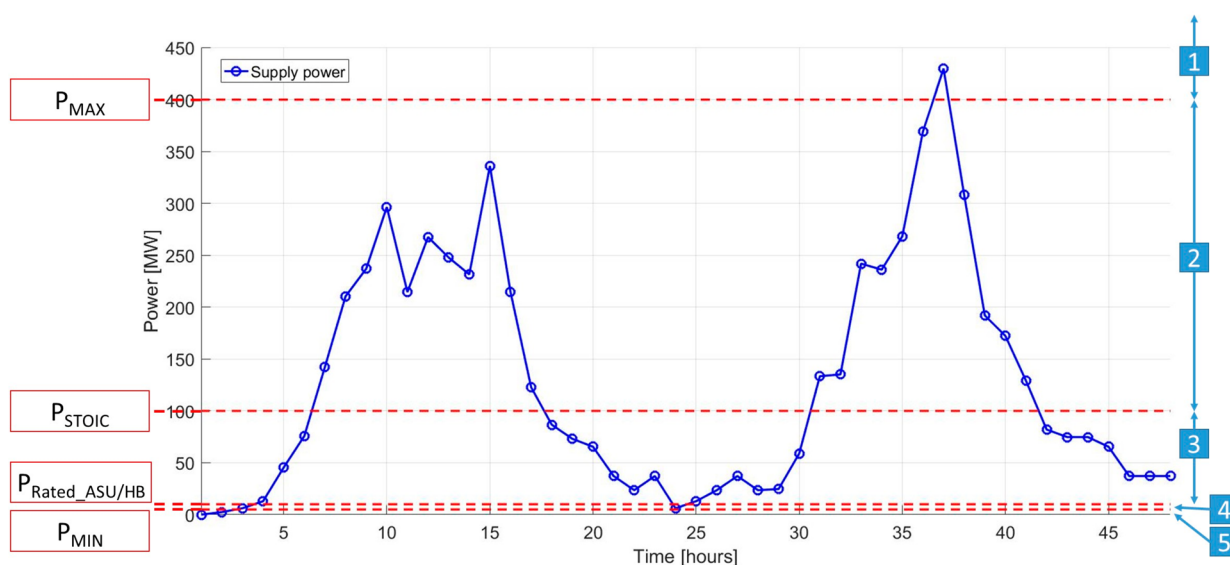


Figure 2. Power allocation to electrolyzer and ASU/HB processes.

2. METHODS (MODELING METHODOLOGY)

2.1. Overview of the Model. The model that we have constructed for this investigation was written in MATLAB to enable the high-level analysis required. The model, when provided with RE supply profiles, outputs the optimum size of the electrolyzer, air separation unit (ASU), HB process, and hydrogen storage (see Figure 1). Optimization of additional variables such as the RE mix and HB operating variables (maximum rate of load ramping and minimum process load) is also possible. The model has been designed to operate using RE supply data with 30 min or hourly resolution due to the nature of electrical settlement periods in the UK (and therefore the data resolution most commonly available from the Met Office¹⁶). This, therefore, limits the accuracy of the final results unless subminute variations are taken into account using dynamic modeling. The ASU and HB processes are lumped together (ASU/HB) for power allocation to simplify the problem; see Figure 3. This has been deemed acceptable at present due to the small demand for power and capital expenditure (CAPEX) of the ASU relative to the HB process, particularly in relation to the electrolyzer.

2.2. Assumptions in the Model. As part of the methodology we have made some assumptions to simplify the calculations: (1) the operation is assumed to be year round (justified by the impact that operational hours have on LCOA shown by ISPT¹⁸), (2) the electrolyzer can ramp instantaneously (0–100% load, justified by hourly resolution of the power data used and that Siemens' SILYZER 300 has the ability to ramp at 10% rated power per second¹⁹), (3) the stored hydrogen can be consumed ("cannibalized") as input to a PEM fuel cell (with 50% efficiency²⁰) to meet a power deficit [this will be explained in detail as part of the power allocation algorithm (section 2.3.3), but this cannibalization to maintain ammonia synthesis is a costly method that would only be favored in islanded systems with neither grid connection nor alternative dispatchable power sources], (4) the electrical energy consumption for production of hydrogen (53.4 kWh/kg²¹), nitrogen (0.119 kWh/kg¹²), and ammonia (0.600 kWh/kg²² i.e., high-temperature synthesis) is constant, regardless of process load factor, and (5) currently, the model is only looking at the impact of RE intermittency on the process, so

steady-state operation is assumed for each time period of operation (dependent on granularity of data).

The last assumption is justified by the fact that they provide more conservative LCOA estimates than reality: the electrolyzer CAPEX is a dominant variable in the determination of the LCOA, and given that efficiency nonlinearly increases at lower loads (i.e., the energy required per kg of hydrogen produced decreases from 4.40 kWh/m³ toward the thermodynamic minimum of 3.54 kWh/m³),^{9,23,24} by assuming constant electricity consumption per unit mass of hydrogen we have overscaled the size of the electrolyzer required in practice. Revision of these, and their impact on the sensitivity results, forms a key part of future work described in section 5.

2.3. Detailed Description of the Model. The methodology is largely dependent on the allocation of available RE power to the electrolyzer and ASU/HB units, and is split into seven steps.

2.3.1. Step 1: Specification of Problem in the Control Panel. The user defines the type of analysis to be conducted (single or multivariable analysis), ammonia process assumptions (including those outlined in section 2.2), time period of interest, size of the average RE supply, LCOE of individual RE sources, and the HB process specifications of maximum ramping rate and minimum power (P_{MIN} in Figure 1). This assumes that other necessary variables (e.g., CAPEX and OPEX of each process per kW rated power) have already been provided to the model for the location of interest.

2.3.2. Step 2: RE Supply Power Formulation. The data sets that this model is currently designed to work with cover long time periods (greater than a year) with a temporal resolution of 30 min or greater. The model loads the RE data sets and aligns the incident solar radiation and wind speed data with a time vector, linearly interpolating for short gaps in data (smaller than two consecutive hours) and converting the wind speed to power (as explained in section 3). The aligned solar and wind power profiles are then scaled using the RE mix and size specified by the user in the control panel.

2.3.3. Step 3: Power Allocation. The power allocation to the electrolyzer and ASU/HB units is determined on the basis of which region the plant is operating in for that given period. Figure 2 only presents the supply power data for Lerwick,

Table 1. Power Allocation to Electrolyzer and ASU/HB

| Operating region | | Operation | Electrolyser (Elec) | ASU/HB | Graphically |
|------------------|-------------------------------------|--|-----------------------------------|--|-------------|
| 1 | $P > P_{MAX}$ | Curtail excess supply & store excess H_2 | Rated power (P_{Rated_Elec}) | Rated power ($P_{Rated_ASU/HB}$) | |
| 2 | $P_{MAX} > P > P_{STOIC}$ | Store excess H_2 | $P_{Rated_Elec} - (P_{MAX} - P)$ | $P_{Rated_ASU/HB}$ | |
| 3 | $P_{STOIC} > P > P_{Rated_ASU/HB}$ | H_2 from storage for feedstock | $P_{Rated_Elec} - (P_{MAX} - P)$ | $P_{Rated_ASU/HB}$ | |
| 4 | $P_{Rated_ASU/HB} > P > P_{MIN}$ | H_2 from storage for feedstock and energy* | 0 | $P_{Rated_ASU/HB} - (P_{ASU/HB} - P)$ | |
| 5 | $P_{MIN} > P$ | H_2 from storage for feedstock and energy | 0 | P_{MIN} | |

*Only if the maximum ramping rate limit is applied.

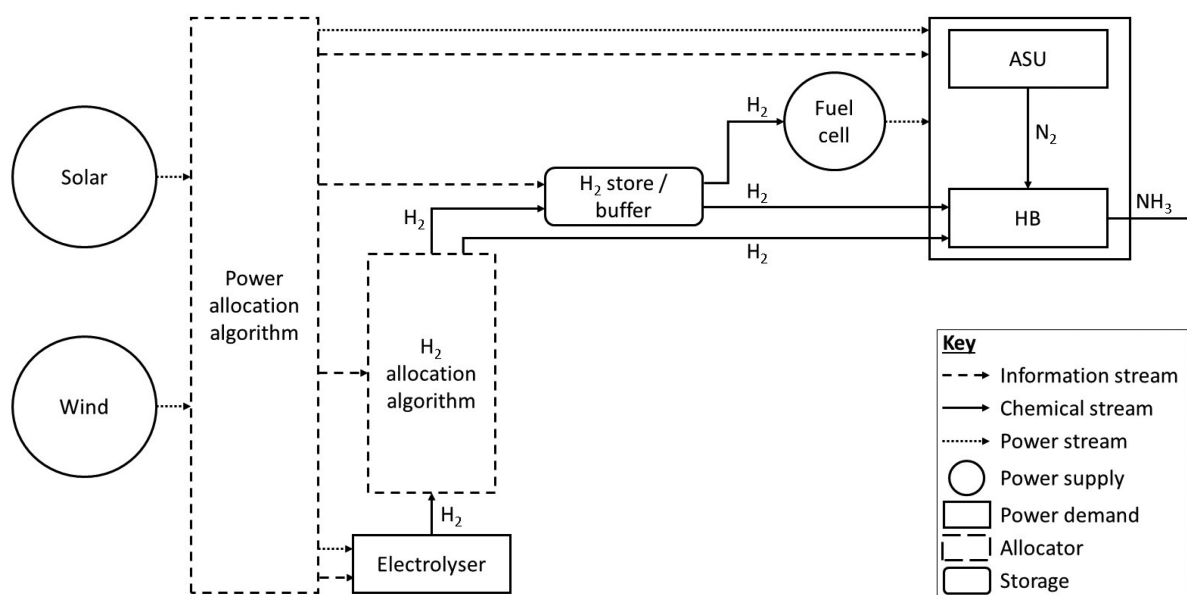


Figure 3. Process block diagram including power, chemical, and information flows.

Scotland, over a 48 h period. However, the supply power profile is highly dependent on time, location, and RE supply. The operating regions are defined on the basis of two core principles: the electrolyzer manages all RE supply variations above the rated power of the ASU/HB block ($P_{Rated_ASU/HB}$) and the power allocated to the ASU/HB is never allowed to drop below 20% of its rated power ($P_{MIN} = 0.2P_{Rated_ASU/HB}$), in line with the most optimistic literature.²⁵ This therefore results in five operating regions, defined by four power boundaries specific to the size of the plant under consideration (Figure 2): (1) maximum power demand (P_{MAX}) as the sum of the electrolyzer and ASU/HB rated power ($P_{MAX} = P_{Rated_Elec} + P_{Rated_ASU/HB}$), (2) stoichiometric power demand (P_{STOIC}) when the amount of hydrogen produced is equal to the amount required for the ASU/HB to run at the rated power, (3) ASU/HB rated power ($P_{Rated_ASU/HB}$), and (4) minimum power demand (P_{MIN}).

In operating region 1, the excess supply power ($P - P_{MAX}$) is curtailed, and the excess hydrogen produced (due to $P_{MAX} - P_{STOIC}$) is stored. In operating region 2, there is no energy to curtail, but there is still excess hydrogen (due to $P - P_{STOIC}$) that needs to be stored. In region 3, there is not enough RE

supply power to operate the electrolyzer stoichiometrically (the power allocated to the electrolyzer produces a mass of hydrogen below the amount required for the rate of ammonia production), and this shortfall in hydrogen feedstock to the HB is drawn from the hydrogen storage. Only when there is no power allocated to the electrolyzer (operating regions 4 and 5, i.e., when $P < P_{Rated_ASU/HB}$) does the ASU/HB block manage the supply intermittency by running at partial load. In operating regions 4 and 5, all supply power is allocated to the ASU/HB and hydrogen is drawn from storage not only for feedstock but also as feed to the fuel cell to meet the power supply deficit. In Table 1 (columns 3–5), the allocated power to each process, dependent on the operating region, is specified. This information is presented graphically (not to scale) with the gray box representing the rated power of the process and the blue fill its allocated power. The black dashed line shows how the power allocation to that process varies within that operating region.

The outputs of this power allocation algorithm are 2-fold: process-specific power supply profiles for the electrolyzer and the ASU/HB per unit time over the time period, and the power supply profile required from the hydrogen fuel cell. The

Table 2. Indices and the Characteristic Size Used When Calculating Process CAPEX^a

| process | characteristic size | cost constant (<i>K</i>) | index (<i>n</i>) | source |
|---------------------|---|----------------------------|--------------------|--|
| electrolyzer | rated power ($P_{\text{Rated_Elec}}$) (kW) | 880 | 1 | ISPT ¹⁸ |
| | mean kg/day of hydrogen produced | (1) | (0.6–0.7) | (for <1000 kg/day plants use NREL ²⁹) |
| air separation unit | mean tonne/day of ammonia produced | 9.2×10^5 | 0.49 | fitted to day from Morgan ¹³ |
| Haber–Bosch process | mean tonne/day of ammonia produced | 3.4×10^6 | 0.50 | Aspen Economic Evaluator ³⁰ and Sinnott ²⁶ |

^aThe electrolyzer's CAPEX function was set to a linear function because the rated power of the electrolyzers considered was large (>100 MW).

combination of these outputs enables the next step of the calculation: the determination of the chemicals' mass flows (shown in Figure 3) including those to and from hydrogen storage.

2.3.4. Step 4: Power to Chemical Conversion. Having allocated the power to the processes over the time period, we now have a power profile for each of the processes (electrolyzer, ASU, and HB). Using simple energy balances (as outlined in section 2.2), with constant specific electricity consumption for all of the processes for a given time period (i.e., no load-dependency, unlike ref 14), the model can calculate the mass of hydrogen, nitrogen, and ammonia produced per unit time

2.3.5. Step 5: Evaluation of viability. The model now has the mass of chemicals produced per unit time across the time period. This, therefore, enables it to determine if the plant sizing is viable. It achieves this by considering if enough hydrogen has been stored while operating in regions 1 and 2 to enable operation while in regions 3–5. If this is the case, then the operation of the plant over that time period is viable and the size of the required hydrogen storage is calculated. If the plant is not viable, it is no longer considered (i.e., not costed) and the next larger plant size is assessed.

2.3.6. Step 6: Costing. The CAPEX of the electrolyzer, ASU, and HB is calculated using the factorial method shown in eq 1, where *K* is a cost constant and *S* is the characteristic size parameter, both specific to a given type of process.²⁶ Values of the cost constants and indices used for each of the processes are shown in Table 2. CAPEX of the hydrogen fuel cell and hydrogen storage is calculated linearly using 739 GBP/kW rated power²⁷ (original value 47 966 USD/50 kW stack) and 31.53 GBP/m³.²²

To enable identification of the key variables' individual impact on the LCOA, the time value of money is assumed as constant. This assumption was required to ensure that the LCOA's notable sensitivity to discount rate, interest rate, and inflation did not distort the results. The equipment is assumed to depreciate linearly over the 20 year plant lifetime. The operational expenditure (OPEX) of each component, including maintenance and catalyst replacement but not electrical demand (which is taken into account separately), has been taken as 5% of the CAPEX per annum²⁸ for each individual process (HB, ASU, electrolyzer, hydrogen fuel cell, and hydrogen storage), regardless of location.

$$\text{CAPEX} = KS^n \quad (1)$$

2.3.7. Step 7: Determining the optimum. The model can identify the lowest achievable LCOA (Figure 6) from the viable plants identified (that do not require HB shut down) and subsequently costed and output the process sizes, RE supply mix, and other related results. This model therefore enables us to enter RE supply data (which is dependent on geographical location) and calculate an initial LCOA estimate with its corresponding RE supply mix and plant size (at the

process level). Developing on these simulation results, the impact that any variable of interest has on the LCOA can be quickly identified by plotting the LCOA's dependency on that variable.

3. CALCULATION

To achieve our aim of identifying the key variables that impact LCOA and the LCOA's sensitivity to them, the model was run with (2000–2016) Met Office wind and solar MIDAS data, which have a resolution of 1 h.¹⁶ The use of historical data, instead of an artificial statistical data set, and its long time coverage enabled the model to provide more realistic results.

We decided to perform our investigation using data for Lerwick, Shetland Islands, Scotland, for two reasons: plentiful wind and solar power (therefore enabling high electrolyzer utilization rate³) and a predicted increase of otherwise curtailed RE in the regional network. To elaborate on the second rationale, the UK's original 2050 greenhouse gas emissions target (to reduce emissions by 80% of 1990 levels³¹) requires significant RE integration.³² However, while Shetland does have significant wind resources, it has no grid connection to the UK mainland. With one method of network flexibility unavailable (i.e., interconnection) Shetland is highly dependent on others such as curtailment of RE. Even with grid connection, as shown by the EU-funded BIG HIT project in Shapinsay and Orkney,³³ such RE integration has the potential to require significant energy curtailment unless alternative network flexibility is provided.³⁴

To facilitate the comparison of different cases, we decided to constrain the supply power to an average of 100 MW rather than fix the plant production rate (in tonne of ammonia per day); the simulation then finds the best plant size (from those trialed) that minimizes the LCOA. For Lerwick, the LCOE from renewables was taken from historic data as 67 and 80 GBP/MWh for wind^{35,36} and solar photovoltaic (PV)³⁶ sources, respectively. One should note that this is a conservative estimate due to the recent dramatic and continued falling cost of renewable power. The wind speed provided in the MIDAS data (at a height of 10 m) was first converted to a hub height of 80 m using eq 2 (the nomenclature can be found in the Abbreviations section) and then converted to power using the power profile of the Vestas V90 3.0 MW turbine with an air density of 1.225 kg/m³.³⁷ The cut-in and cut-out speeds were taken as 4 and 25 m/s, respectively. The global irradiance (with units of kW/m²) was used for solar power. A solar efficiency factor was not applied, because the subsequent scaling of the power profile within the model required to meet a defined RE mix made it irrelevant (if it is assumed to be independent of power per unit area).

$$U_1 = U_2 \left(\frac{\ln \frac{H_1}{z}}{\ln \frac{H_2}{z}} \right) \quad (2)$$

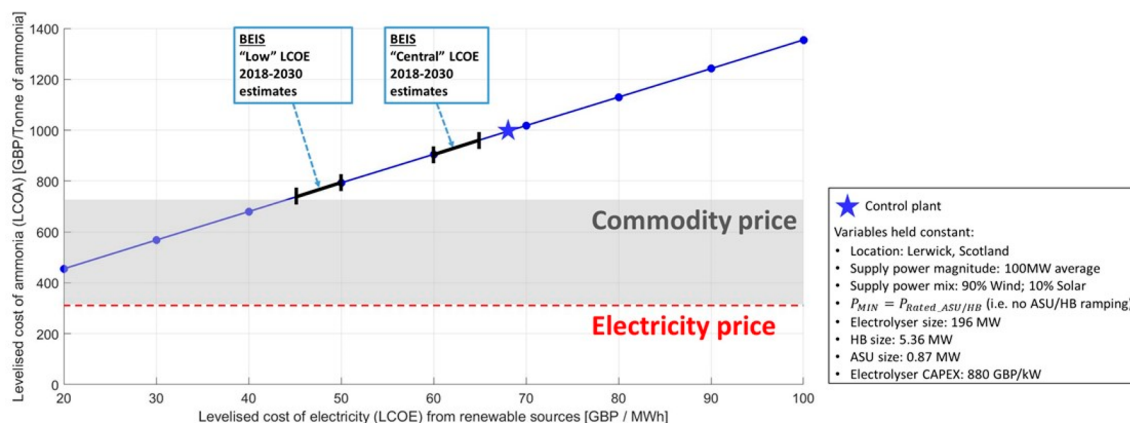


Figure 4. LCOA sensitivity to LCOE [i.e., ignoring other variables, how low does LCOE have to drop before “green” ammonia production is competitive against conventional steam methane reforming (SMR) production?].

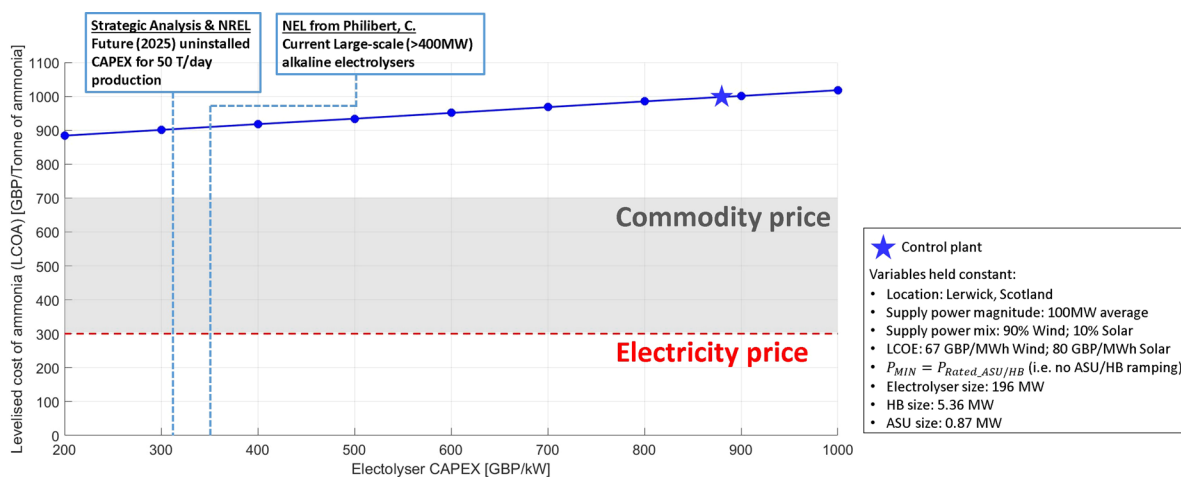


Figure 5. LCOA sensitivity to electrolyzer CAPEX per kW rated power.^{17,40}

The identification of the key variables that determine the LCOA value was achieved by performing sensitivity analyses on numerous variables, prioritized when possible (if they were cost of production variables), by their fraction of total production cost. Having identified five key variables (discussed further in section 4) that notably impact LCOA, we performed more detailed sensitivity analyses. These analyses were performed differently, depending on the type of variable that they were considering. Analysis of production cost variables held the size of the plant (all component processes) constant and changed linearly the value of that variable to consider its impact on LCOA. However, analysis of production process variables allowed the size of the plant (each component process individually) to change. This allows the model to find a better plant sizing (and its corresponding RE supply mix) if one is available, thereby providing not only an impact on LCOA but also individual process sizing.

4. RESULTS: SENSITIVITY TO KEY VARIABLES

From the definition of LCOA (eq 3), the five key variables identified in having the most significant impact on LCOA can be separated into two groups: (a) production cost variables (those that dominate OPEX and CAPEX values), i.e., levelised cost of electricity (LCOE) and electrolyzer CAPEX per kW of rated power, and (b) production process variables (those that influence the mass of ammonia produced), i.e., RE sources

ratio (dependent on RE supply profiles, i.e. geographical location), ASU/HB process minimum power consumption (P_{MIN}), and ASU/HB process maximum ramping rate (maximum difference in power for contiguous intervals).

$$\text{LCOA (GBP/tonne)} = \frac{\text{cost of production (GBP)}}{\text{mass of ammonia produced (tonne)}} \quad (3)$$

The production cost variables, as shown in Figures 4 and 5, can be seen to have significant impact on the LCOA: a change in LCOE of ± 0.89 GBP/MWh results in a change of ± 10 GBP/tonne NH_3 . In turn, a change in the electrolyzer CAPEX per kW rated power of ± 65 GBP/kW has the same effect on the LCOA, i.e., ± 10 GBP/tonne NH_3 . The significance of these variables is widely acknowledged but has only been previously quantified by Beerbühl et al. (using a dispatchable electrical supply)⁹ and by the Institute for Sustainable Process Technology (ISPT),¹⁸ respectively. The results presented here corroborate Beerbühl et al.'s result of ± 0.97 GBP/MWh resulting in ± 10 GBP/tonne NH_3 ⁹ and correlate well with ISPT's finding that a significant reduction in electrolyzer CAPEX (to 300 GBP/kW) is needed to make the process economically viable.¹⁸ As a consequence of the LCOA's sensitivity to the electrolyzer's rated power it was found that the size of hydrogen storage should be calculated as required

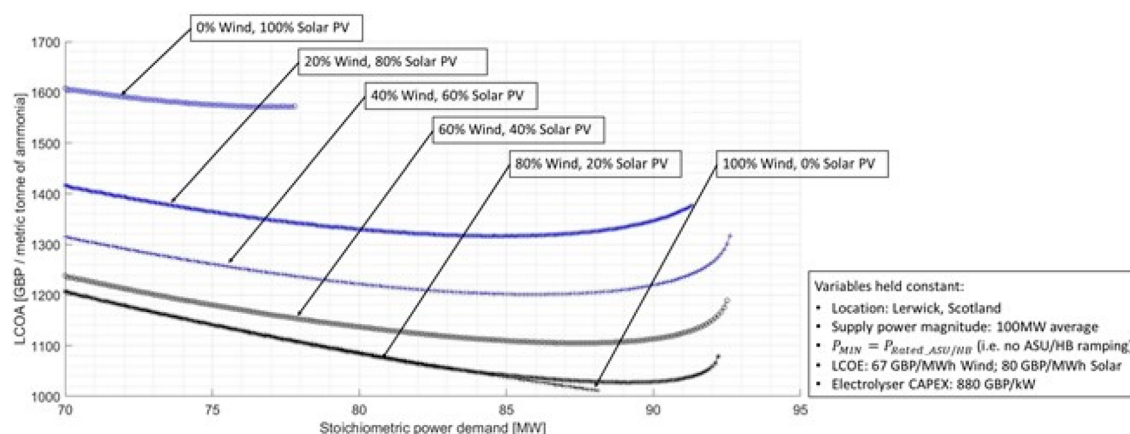


Figure 6. LCOA sensitivity to the RE sources ratio and the identification of the optimum process for 100 MW average supply power.

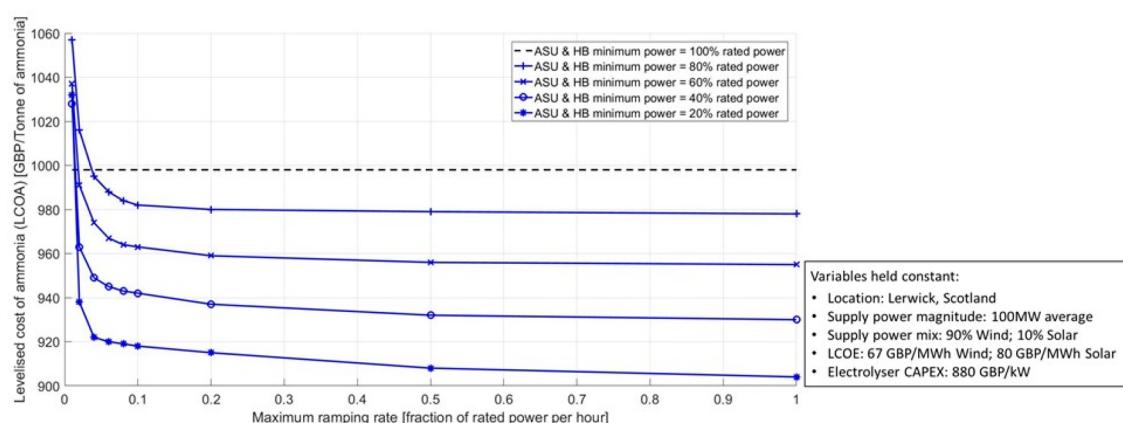


Figure 7. LCOA sensitivity to ASU and HB process minimum power and maximum ramping rate.

rather than predefined (thereby requiring an increase in the electrolyzer's rated power for the plant to viably operate). We have benchmarked our analysis against the two major potential uses of the ammonia product: as a commodity (showing the range of global ammonia prices 2012–2015³⁸) and for seasonal spikes in the UK wholesale electricity price (prices of 0.12 GBP/kWh with a 50% ammonia-to-electricity efficiency). While commanding the highest price, and therefore likely to be the first economically viable use, we have not benchmarked against the use of ammonia for transport fuel/fuel additives in this paper due to the comparably high barriers to large-scale market entry (despite the potential of hydrogen and the recent success of AdBlue, a urea-based diesel exhaust fluid used to reduce NO_x emissions from diesel engines,³⁹ for which ammonia is a raw material). To provide industrial context to these findings, we have also entered estimates and tender submissions to Figures 4 and 5: in Figure 4 we have plotted the BEIS's "central" and "low" UK power cost estimates for 2018–2030,³⁶ and in Figure 5 we have plotted NEL's current estimate for alkaline electrolyzers (greater than 400 MW rated power)¹⁷ and Strategic Analysis Inc. and NREL's large-scale prediction for 2025 (original value 400 USD/kW).⁴⁰ It should be noted that, given the significant drop of RE cost in recent years [down to 18.6 GBP/MWh (original value 24.2 USD/MWh) strike price for solar PV in Abu Dhabi⁴¹], LCOA estimates for certain locations with significant RE resources³ could already be below the upper limit of commodity prices. While plant production capacity does vary

significantly for the plants considered (P_{STOIC} can be seen in Figure 6), the control plant in Figures 4 and 5 has an output of 83 220 tonne_{NH₃}/year.

In contrast, the process variables (shown in Figures 6 and 7) have been largely ignored to date and their impact had not been quantified previously. Figure 6 shows that RE supply mix and plant size must be determined in combination rather than optimized independently: the wrong RE mix or plant size could independently result in higher LCOAs. The increase of stoichiometric power demand shown in this figure is predominantly due to an increase in rated power of the electrolyzer, but it is also due to the size of the HB, ASU, fuel cell and hydrogen storage capacity and other free variables. Figure 7 shows the benefits of a flexible HB process but also the limitations that the process must be able to operate within, i.e., ramping faster than 1% of rated power/hour, to enable these benefits to be realized. As shown, should the ramping limitation be slower than 1% rated power/hour, it would not be beneficial to allow ASU/HB ramping at all. The higher than base case (i.e., no ramping) LCOA in these instances is due to a large oversizing of the electrolyzer to manage an increased hydrogen demand, specifically the additional hydrogen that is "cannibalized" for power when operating in region 4 (see Figure 2 and Table 1). The ramping bottleneck within the process would most likely be the catalyst if the output ramping is too fast (temperature and pressure would be held constant). If this is the case, this result provides a technical

requirement for future catalyst development for use in an electrified ammonia production process.

5. FUTURE WORK

Future research building on the model and solutions presented here can be split into two areas: consideration of other locations (within the UK and in other locations with favorable RE resources) in combination with semi-islanded production and further developing the model to improve the reliability of predictions and calculation efficiency.

To gain a better understanding of where to locate a “green” ammonia plant, we have already considered two other locations in the UK (Camborne in Cornwall and Holbeach in Lincolnshire), but are aiming to consider up to 20 locations in the UK and others of particular interest around the world.³ Semi-islanded operation would result in a less intermittent power supply and therefore has the potential to reduce substantially the size of the required electrolyzer.

Improvement of the model so that its predictions are more reliable requires additional quantitative information on how the load factor affects electricity consumption for the processes and integration of the model with a dynamic process analysis tool to provide an end-to-end solution (i.e., where to locate, how large each of the processes should be, and the predicted LCOA). The importance of these variables was first recognized by Beerbühl¹⁴ and Weiss et al.,⁴² respectively.

Improving calculation efficiency (from the 0.01–0.02 s per simulation at the moment), most likely through the use of formal optimization methods and the use of the storage duration index (SDI)^{43,44} to predict the optimal RE supply mix, will enable additional variables to be considered automatically. The additional variables of interest, specifically the plant lifetime, discount rate, interest rate, inflation, and location specific OPEX and CAPEX, will be investigated in combination with those identified in this paper. To ensure that these additional analyses will be relevant, OPEX and CAPEX cost functions and relevant benchmarks (such as the market price and the cost of alternative methods of production, e.g., based on steam methane reforming) will be updated.

6. CONCLUSIONS

The outline of a model implemented in MATLAB has been presented which, for a given location, will design a “green” ammonia plant with the optimum size (at the process level), RE mix, and operation schedule. In response to a recent IEA challenge,¹⁷ this model makes possible detailed plant design in combination with RE supply sizing for any given location and facilitates further optimization (through dynamic analysis) by providing a good initial solution. Beyond the purely academic study, this model has substantial value as an “applied” research tool that can be used by industry to identify promising site locations and facilitate the scale-up of the “green” ammonia production process from demonstration (e.g., the Siemens’ 30 kW plant at Harwell) to pilot plant (ca. 20 MW). As shown below, the model has enabled us to identify the five most significant variables for the production of “green” ammonia and to investigate the LCOA’s sensitivity to each of these. In practice, a combination of these improvements in a suitable geographical location (i.e., with favorable supply profiles) has the potential to become the first economically viable decarbonized process substitute to conventional ammonia production.

The five most significant variables include production cost variables, i.e., (1) levelized cost of electricity (LCOE), where a change of ± 0.89 GBP/MWh results in ± 10 GBP/tonne NH_3 , and (2) electrolyzer CAPEX per kW rated power, where a change of ± 65 GBP/kW results in ± 10 GBP/tonne NH_3 , and production process variables, i.e., (3) RE sources ratio, which results in significant impact to the LCOA and the optimum plant size, (4) ASU/HB process minimum power (P_{MIN}), where a change of $\pm 12\%$ of rated power results in ± 10 GBP/tonne NH_3 , and (5) ASU/HB process maximum ramping rate, where the LCOA is relatively insensitive to faster than 4% rated power/hour.

A combination of predicted 2025/2030 estimates for these variables [an LCOE of 45.7 GBP/MWh³⁶ (solar PV = 52 GBP/MWh and wind PV = 45 GBP/MWh with a 90% wind and 10% solar renewable power supply), electrolyzer CAPEX of 308 GBP/kW⁴⁰ (original value 400 USD/kW), $P_{\text{MIN}} = 20\%$ rated power, and a maximum ramping rate of 6%] results in a LCOA estimate of 588 GBP/tonne NH_3 . These estimates can be seen as conservative in that they have also not taken into account the impact that future carbon pricing. “Green” ammonia production from RE therefore has the potential in the near future to be economically competitive with conventional methods, thereby reducing the 1.3% of global carbon dioxide emissions currently attributable to ammonia production.

AUTHOR INFORMATION

Corresponding Author

*E-mail: rene.banares@eng.ox.ac.uk.

ORCID

Richard Nayak-Luke: 0000-0002-6872-5820

René Bañares-Alcántara: 0000-0002-7859-6102

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

MATLAB, Aspen Plus, and Aspen Economic Evaluator were used under academic licenses. This work has been supported by an EPSRC-Siemens Industrial CASE Studentship.

ABBREVIATIONS

- ASU = air separation unit
- CAPEX = capital expenditure
- CO_2 = carbon dioxide
- GBP = Great Britain pound
- H = height
- HB = Haber–Bosch process
- ISPT = Institute for Sustainable Process Technology
- $\text{kWh/kg}_{\text{hydrogen}}$ = electrical energy consumption per kilogram of hydrogen produced
- K = cost constant
- LCOA = levelized cost of ammonia (GBP/tonne of ammonia)
- LCOE = levelized cost of electricity (GBP/MWh)
- MWe = megawatt electric
- n = costing index
- NH_3 = ammonia
- OPEX = operational expenditure
- P = supply power for a given time interval

$P_{\text{ASU/HB}}$ = power demand of the combined ASU and Haber–Bosch processes, also the power demand below which the electrolyzer is turned off

P_{MAX} = maximum power demand

P_{MIN} = minimum power demand required (ASU and HB processes running at minimum load)

P_{R} = rated power of a process (electrolyzer, air separation unit, or Haber–Bosch process)

P_{STOIC} = Power demand for stoichiometric production (amount of hydrogen produced is stoichiometric with the amount of nitrogen produced and the amount of ammonia produced)

PEM = proton exchange membrane

RE = renewable energy

S = characteristic size parameter

SDI = storage duration index

SMR = steam methane reforming

U = velocity

USD = United States dollar

z = roughness level (taken as 0.03, i.e., open ground)

REFERENCES

- (1) *Key World Energy Statistics*; International Energy Agency: Paris, 2007.
- (2) *Recent Trends in the OECD: Energy and CO₂ Emissions*; International Energy Agency: Paris, 2016.
- (3) Philibert, C. Renewables crossing boundaries: ammonia et al. Presented at NH₃ Event, Rotterdam, Netherlands, May 18–19, 2017.
- (4) *World fertilizer trends and outlook to 2020*; Food and Agriculture Organization of the United Nations: Rome, 2017.
- (5) Buckley, G. NH₃ Transportation Challenges and a Solution—Distributed Production. Presented at NH₃ Fuel Conference, San Antonio, TX, Sept 30–Oct 3, 2012.
- (6) Grundt, T.; Christiansen, K. Hydrogen by Water Electrolysis as Basis for Small Scale Ammonia Production. A Comparison with Hydrocarbon Based Technologies. *Int. J. Hydrogen Energy* **1982**, *7* (3), 247–257.
- (7) Wang, G.; Mitsos, A.; Marquardt, W. Conceptual Design of Ammonia-Based Energy Storage System: System Design and Time-Invariant Performance. *AIChE J.* **2017**, *63* (5), 1620–1637.
- (8) Bank of England. Statistical Interactive Database: Daily Spot Exchange Rates against Sterling. [Online] <http://www.bankofengland.co.uk/boeapps/iadb/Rates.asp> (accessed Jul 18, 2017).
- (9) Beerbühl, S.; Kolbe, B.; Roosen, C.; Schultmann, F. Synthesis of Ammonia from Intermittently Generated Hydrogen. *Chem. Ing. Tech.* **2014**, *86* (5), 649–657.
- (10) Laagland, G. Carbon Neutral Fuels To Enable the Energy Transition. Presented at NH₃ Event, Rotterdam, Netherlands, May 18–19, 2017.
- (11) Tallaksen, J.; Bauer, F.; Hultberg, C.; Reese, M.; Ahlgren, S. Nitrogen Fertilizers Manufactured Using Wind Power: Greenhouse Gas and Energy Balance of Community-Scale Ammonia Production. *J. Cleaner Prod.* **2015**, *107*, 626–635.
- (12) Bañares-Alcántara, R.; Dericks, G., III; Fiaschetti, M.; Grünwald, P.; Lopez, J. M.; Yang, A.; Ye, L.; Zhao, S. *Analysis of Islanded Ammonia-Based Energy Storage Systems*; Technical Report, University of Oxford: Oxford, UK, September 2015.
- (13) Morgan, E. R. Techno-Economic Feasibility Study of Ammonia Plants Powered by Offshore Wind. Ph.D. Thesis, University of Massachusetts Amherst, February 2013.
- (14) Schulte Beerbühl, S.; Fröhling, M.; Schultmann, F. Combined Scheduling and Capacity Planning of Electricity-Based Ammonia Production to Integrate Renewable Energies. *European Journal of Operational Research* **2015**, *241* (3), 851–862.
- (15) Tunå, P.; Hultberg, C.; Ahlgren, S. Techno-Economic Assessment of Nonfossil Ammonia Production. *Environ. Prog. Sustainable Energy* **2014**, *33* (4), 1290–1297.
- (16) Met Office Integrated Data Archive System (MIDAS) Land and Marine Surface Stations Data (1853–Current). <http://catalogue.ceda.ac.uk/uuid/220a65615218d5c9cc9e4785a3234bd0> (accessed Jul 18, 2017).
- (17) Philibert, C. Producing Ammonia and Fertilizers: New Opportunities from Renewables. [Online] 2017, https://www.iea.org/media/news/2017/Fertilizer_manufacturing_Renewables_01102017.pdf (accessed Jul 18, 2017).
- (18) ISPT. Power to Ammonia: Feasibility Study for the Value Chains and Business Cases to Produce CO₂-Free Ammonia Suitable for Various Market Applications. [Online] 2017, www.ispt.eu/media/ISPT-P2A-Final-Report.pdf (accessed Jul 18, 2017).
- (19) Siemens AG. Silyzer 300: The Next Paradigm of PEM Electrolysis. [Online] 2018, PDL-D-T10120-00-74000, https://www.siemens.com/content/dam/webassetpool/mam/tag-siemens-com/smdb/corporate-core/sustainable_energy/hydrogensolutions/brosch%C3%BCren/ct-ree-18-047-db-silyzer-300-db-de-en-rz.pdf (accessed Aug 30, 2018).
- (20) United States Department of Energy. Fuel Cells. [Online] 2015. https://www.energy.gov/sites/prod/files/2015/11/f27/fcto_fuel_cells_fact_sheet.pdf (accessed Nov 25, 2015).
- (21) NREL. Technology Brief: Analysis of Current-Day Commercial Electrolyzers. [Online] 2004, NREL/FS-560-36705, <https://www.nrel.gov/docs/fy04osti/36705.pdf> (accessed Aug 30, 2018).
- (22) Hughes, T. *Internal Report for a Project Proposal: Green NH₃ for a Post Fossil Economy*; Siemens AG: Oxford, UK, 2013.
- (23) LeRoy, R. L.; Bowen, C. T.; LeRoy, D. J. The Thermodynamics of Aqueous Water Electrolysis. *J. Electrochem. Soc.* **1980**, *127* (9), 1954–1962.
- (24) Hamann, C. H.; Hamnett, A.; Vielstich, W. *Electrochemistry*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2007.
- (25) Ostuni, R.; Zardi, F. Method for Load Regulation of an Ammonia Plant. U.S. Patent US 9463983 B2, Nov 2, 2011.
- (26) Sinnott, R. K. *Chemical Engineering Design: Chemical Engineering*, 4th ed; Elsevier Science: Oxford, UK, 2005; Vol. 6, pp 243–283.
- (27) Battelle Memorial Institute. *Manufacturing Cost Analysis of 100 and 250 kW Fuel Cell Systems for Primary Power and Combined Heat and Power Applications*; Technical Report for United States Department of Energy, Golden, CO, Jan 2016.
- (28) Wilkinson, I. Siemens Corporate Technology, CT REE, Rutherford Appleton Laboratory, Oxford, UK. Personal communication, 2016.
- (29) NREL. *Current (2009) State-of-the-Art Hydrogen Production Cost Estimate Using Water Electrolysis*; Technical Report (Independent Review) for United States Department of Energy Hydrogen Program, Golden, CO, Sep 2009.
- (30) *Aspen Economic Evaluation*, Version 9; Aspen Technology, Inc.: Bedford, MA, 2017.
- (31) *United Kingdom Climate Change Act 2008*, Chapter 27, 2008.
- (32) Committee on Climate Change (CCC). The 2050 Target—Achieving an 80% reduction including emissions from international aviation and shipping. [Online] 2012, https://www.theccc.org.uk/wp-content/uploads/2012/04/CCC_IAS_Tech-Rep_2050Target_Interactive.pdf (accessed Jul 18, 2017).
- (33) Hyde, K. BIG HIT: Europe's Largest Integrated Hydrogen System. Presented at Hannover Messe, Hannover, Germany, Apr 24–28, 2017.
- (34) Denholm, P.; Ela, E.; Kirby, B.; Milligan, M. *The Role of Energy Storage with Renewable Energy Generation*; Technical Report for United States Department of Energy, Golden, CO, 2010.
- (35) McClatchey, J. Hydrogen—Key to enabling the replacement of oil, gas and coal by renewables? Presented at Scotland's Hydrogen Future Conference, Edinburgh, UK, Sept 15–16, 2015.
- (36) UK Department for Business, Energy & Industrial Strategy. Electricity Generation Costs (November 2016). [Online] <https://assets.publishing.service.gov.uk/government/uploads/system/>

uploads/attachment_data/file/566567/BEIS_Electricity_Generation_Cost_Report.pdf (accessed Jul 18, 2017).

(37) Vestas Wind Systems A/S. General Specification V90 - 3.0MW 60 Hz Variable Speed Turbine. [Online] http://www.gov.pe.ca/photos/sites/envergfor/file/950010R1_V90-GeneralSpecification.pdf (accessed Jul 18, 2017).

(38) Jones, A. Ammonia Prices in the International Market Inch Up. *Market Realist* [Online] <https://marketrealist.com/2016/04/ammonia-prices-international-market-inch/> (accessed Jul 18, 2017).

(39) Barnett, C. AdBlue revolution. *Commercial Motor* **2015**, 224 (5652), 40–41.

(40) Colella, W. G.; James, B. D.; Moton, J. M. Techno-economic analysis of PEM electrolysis for hydrogen production. Presented at Electrolytic Hydrogen Production Workshop, Golden, CO, Feb 27, 2014.

(41) Potheary, S. World record low price entered for solar plant in Abu Dhabi. *PV Mag.* [Online] https://www.pv-magazine.com/2016/09/19/breaking-world-record-low-price-entered-for-solar-plant-in-abu-dhabi_100026145/#ixzz4KhtPrL8x (accessed Jul 18, 2017).

(42) Weiss, R.; Savolainen, J.; Tähtinen, M.; Sihvonen, T.; Bennani, Y.; Hans, V.; Vrijenhoef, H. Operational Optimization and Simulation of Power-to-Ammonia (P2A) Process. Presented at NH3 Event, Rotterdam, Netherlands, May 18–19, 2017.

(43) Nayak-Luke, R. M.; Bañares-Alcántara, R.; Collier, S. Quantifying the Need for Electrical Energy Storage Using the Storage Duration Index (SDI). Presented at UK Energy Storage Conference, Newcastle, UK, Mar 20–22, 2018.

(44) Nayak-Luke, R. M.; Bañares-Alcántara, R. Quantifying the Relationship Between Renewable Energy Sources and Electrical Energy Storage Requirements. Presented at the Offshore Energy and Storage Symposium, Valletta, Malta, Jul 13–15, 2016.