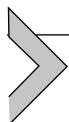


Alternative ammonia production processes and the use of renewables

Gal Hochman^a, Alan Goldman^b, Frank A. Felder^c

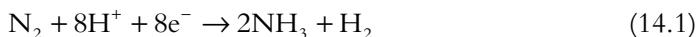
^aDepartment of Agriculture, Food & Resource Economics, Rutgers, The State University of New Jersey, New Brunswick, NJ, United States, ^bDepartment of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, New Brunswick, NJ, United States, ^cCenter for Energy, Economic & Environmental Policy, Edward J. Bloustein School of Planning and Public Policy, Rutgers, The State University of New Jersey, New Brunswick, NJ, United States



14.1 Introduction

In a single day, agriculture produces 19.5 million tons of cereals, roots, tubers, fruits, and vegetables. In a single day, crop production uses 300,000 tons of fertilizers. These amounts are used to feed 7 billion people today, and world population is expected to grow to 9.5 billion by the year 2050 [1]. Population growth is expected to result in agriculture needing to increase global production by 60%, while in developing countries it is likely to increase by 100% because of dietary changes attributed to income changes [2]. To meet this growing demand for food, yields should be maximized, where the intensification of land use for crop production will likely result in significant higher uses of nutrient inputs such as nitrogen.

Nitrogen is one of the essential nutrients for plant growth and usually a limiting nutrient in industrial-scale crop production. Nitrogen is taken up by plants in the form of ammonium compounds and various forms of nitrogen oxides. In nature, atmospheric nitrogen is converted (nitrogen fixation) into ammonium form by nitrogen-fixing bacteria associated with leguminous plants (Eq. 14.1).



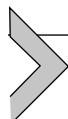
These forms of natural nitrogen cycles are susceptible to losses through leaching from soil to water or loss to the atmosphere; only about 30%–50% of applied nitrogen is taken up by the crop. Thus, naturally fixed nitrogen undermined by losses cannot support current levels of global food production. In fact, synthetic nitrogenous fertilizers fed nearly 45% of the world's population at 2011 [1]. As the world's population increases so will the requirement for nitrogenous fertilizers.

The gap between the requirement for naturally fixed nitrogen and agriculture requirement is filled by the Haber–Bosch (H–B) process which uses elemental nitrogen (N_2) and hydrogen (H_2) to synthesis ammonia (NH_3) (Eq. 14.2).



The Haber–Bosch process came into use around 1920. Its share in fertilizer production went from 20% in 1920 to almost 100% in 1990. Fertilizer synthesis using Haber–Bosch process led to multiple-fold increase in crop production in the 20th century. Without a synthetic source for ammonia, crop production would require significantly more land to compensate for the reduced productivity of the soil overtime [1]. However, the Haber–Bosch process is an energy-intensive polluting process; an unsustainable process that is generating about 2% of global greenhouse gas emissions [3]. However, is there a more sustainable alternative to that of ammonia production through Haber–Bosch?

In answering this question, first, the below section describes the current practice of ammonia production. The below sections, then, introduce two alternative processes to the Haber–Bosch and discuss the implications of adopting these technologies. Policy discussion and perspectives are offered in the below section.



14.2 Ammonia production via current practices

The Haber–Bosch is a two-step, energy-intensive process [4]. The first step includes hydrogen production, which then is followed by the Haber–Bosch process that combines the hydrogen with nitrogen (Eq. 14.2) to generate the ammonia (Fig. 14.1).

The hydrogen feed for Haber–Bosch can be produced via various methods, including natural gas reforming (and coal gasification) as well as electrolytic splitting of water (Fig. 14.1). However, natural gas reformation is currently most common [5]. So, any increase in ammonia production through Haber–Bosch means an increase in natural gas consumption and emission of natural gas pollutants to the environment.

The nitrogen feed used in the second step may be either produced as a coproduct of coal gasification and natural gas reforming or extracted from air using an air separation unit (ASU) [3]. The ASU uses a combination of compression, cooling, and expansion to separate the nitrogen, oxygen, and other compounds from the air.

Given the preferred hydrogen production methods (methane steam reforming), next energy is discussed, economic, and emissions implications of implementing these alternatives. To answer these questions, this paper builds on [6].

14.2.1 Energy requirements of Haber–Bosch based on natural gas

The overall energy requirement for ammonia production varies based on the choice of hydrogen and nitrogen production methods, where the Haber–Bosch technology is least energy-intensive among alternative fossil fuels when based on natural gas. Under the natural gas alternative, the net energy input of a typical modern natural-gas-based Haber–Bosch plant is 8.87 MWh/mt-NH₃ which is equivalent to 30.3 MBTU natural gas per mt-NH₃ [2,7].

14.2.2 Economics of the Haber–Bosch process

Following [6] while assuming plant capacity of 2200 mt-NH₃ per day, the construction cost for a natural-gas-based Haber–Bosch production facility is \$404,000 per mt-NH₃/

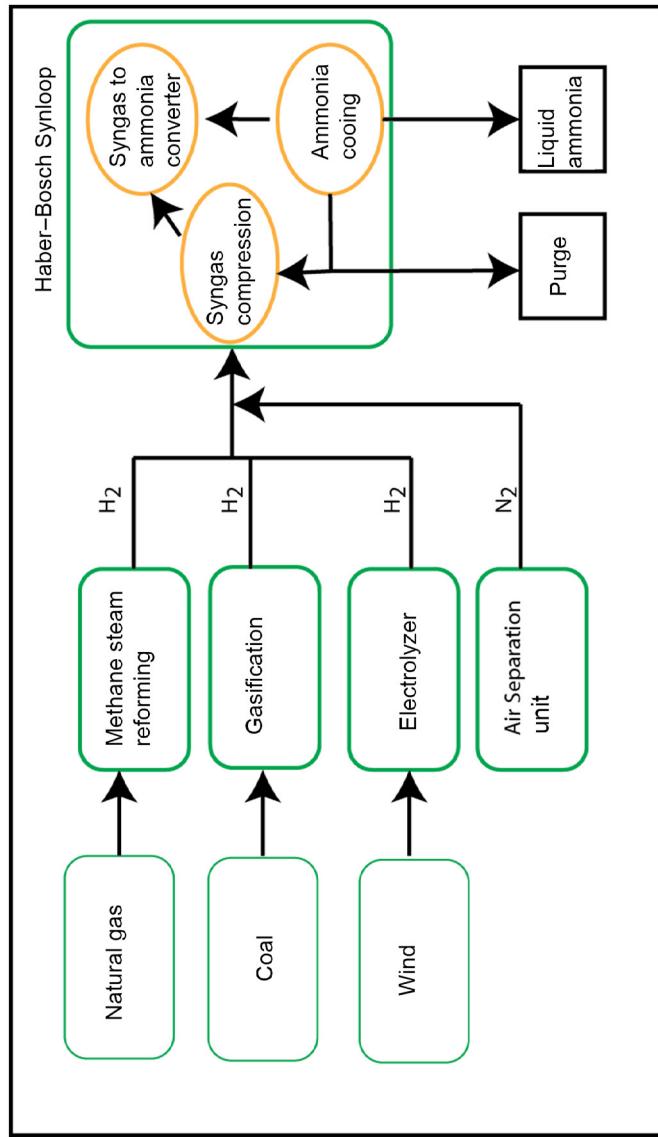


Fig. 14.1 Ammonia process based on Haber-Bosch synthesis using different energy sources.

day capacity. Of this, \$235,000 per mt-NH₃/day capacity is the cost of the Haber–Bosch process and the ASU without the gas turbine. The cost of the Haber–Bosch process alone is \$134,000 per mt-NH₃/day capacity. Based on the value of 30.3 MBTU natural gas per mt-NH₃, and using the average Henry Hub natural gas price of \$3.08/MBTU for January 2017 through December 2018, (with annual averages of \$2.99 and \$3.17 respectively) [8] the cost for the natural gas required by a plant of the type considered is \$93 per mt-NH₃ produced.

Using the above construction costs, the capital cost is estimated. The assumptions made in the U.S. Department of Energy H2A Distributed Hydrogen Production Model (Version 3) [9] are assumed and consider a capital cost of 5.00% per year (corresponding to an interest rate of 4.00% per year repaid over 40 years). At this rate the construction cost of \$404,000 per mt-NH₃/day capacity corresponds to \$20,200/year per mt-NH₃/day capacity, corresponding to \$55/mt-NH₃. To approximate operation and maintenance (O&M) costs, the employment values reported for the recently built Yara/BASF ammonia plant (2018 start-up) in Freeport, TX, with a capacity of 2055 mt-NH₃/day with 35 full-time employees are used [10]. The DOE H2A estimates of salary, administrative costs, and insurance costs, are used to obtain yearly expenses of \$16.6 million, or \$22/mt-NH₃ [11].

The estimated capital and O&M costs, \$55/mt-NH₃ and \$22/mt-NH₃ respectively, combined with the estimated cost of natural gas noted above (\$93/mt-NH₃) contribute \$170/mt-NH₃ to the production cost of ammonia for large plants (Table 14.1). Smaller plants, ranging from 90 mt-NH₃/day to 550 mt-NH₃/day capacity, incur substantially greater per-ton capital and operating costs from [6], with examples shown in Table 14.1.

14.2.3 CO₂ emissions from a Haber–Bosch plant

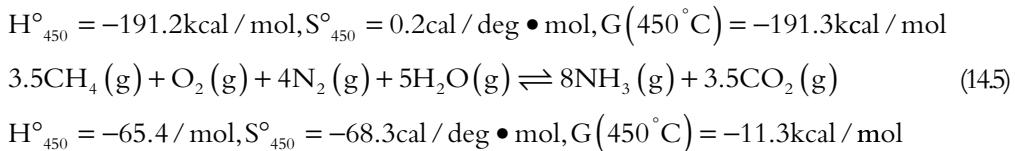
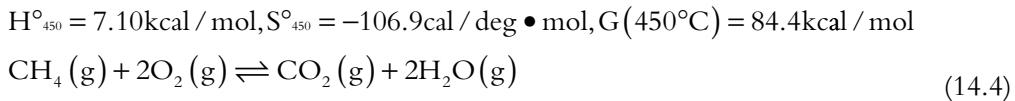
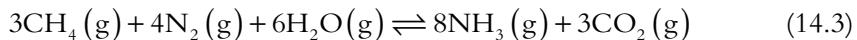
A minimum of 0.97 mt-CO₂ emissions per mt-NH₃ produced is required to provide the necessary hydrogen from the steam reforming of gas (or from direct reaction of gas with N₂), based only on consideration of the stoichiometry of (Eq. 14.3) (3.0 mol CH₄

Table 14.1 Estimated costs of ammonia production (\$/mt-NH₃) via Haber–Bosch, by natural-gas-based Haber–Bosch plants of varying capacity (based on a cost of \$3.08/MBTU natural gas).

	Haber–Bosch plant size (mt-NH ₃ /day)		
	Large Haber–Bosch (ca. 2000 mt/day)	Medium Haber–Bosch (545 mt/day)	Small Haber–Bosch (91 mt/day)
Natural gas	\$93	\$93	\$93
Capital	\$55	\$88	\$113
O&M	\$22	\$62	\$133
Total	\$170	\$243	\$339

Source [6].

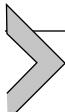
per mol NH_3). Since (Eq. 14.3) and methane steam reforming are both endothermic, additional combustion of methane is required, thus increasing the minimum CO_2 emissions from a natural-gas-based Haber–Bosch plant.



Since Eq. (14.3) is only modestly endergonic, while methane combustion (Eq. 14.4) is highly exergonic, only a small amount of methane for combustion is thermodynamically required to drive the reaction of Eq. (14.2). (With 0.42 mol CH_4 combusted per 3.0 mol CH_4 required for hydrogen, as per Eq. (14.3), $\text{G}(450^\circ\text{C}) = 0$). Thus (Eq. 14.5), in which 0.5 mol methane is combusted per 3 mol methane used as a hydrogen source is highly exothermic and significantly exergonic. This is used as the approximate theoretical lower limit of CO_2 production required for a methane-based Haber–Bosch process, 3.5 mol CO_2 per 8 mol NH_3 , or 1.13 kg- CO_2 /kg- NH_3 . In practice, various analyses of Haber–Bosch plants conclude that CO_2 emissions range from 1.33 mt to 1.69 mt per mt- NH_3 produced [12,13]. (Note that these estimates do not include methane leakages, which may significantly increase greenhouse gas emissions from Haber–Bosch.)

Similar to the analysis above [9], suggesting a ratio of 1.33 ton of CO_2 per 1 ton of anhydrous NH_3 with 99.9% purity. Other factors used in Morgan include air emissions caused during steam reforming include NO_x , SO_2 , CO , amines, and particulates. During the Haber–Bosch process, some methane left from the steam-reforming process is released to the atmosphere, which can also cause some amount of ammonia to be released as well. There are also emissions of water pollutants in the form of methanol, liquid ammonia, and other organics [14].

This creates a need for an alternative method of hydrogen production and better management of agroecosystem to reduce nitrogen losses. Electrolysis of water [15] and direct electrochemical nitrogen reduction (ENR) [6] are potential methods of hydrogen synthesis, which can use renewable sources of electricity thus significantly reducing the environmental cost of ammonia production. The distributed sources of renewable electricity like biomass, wind, and solar energy in rural areas can be coupled with the alternative forms of hydrogen synthesis and can further reduce the cost of transportation to agricultural regions.

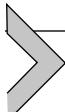


14.3 Haber–Bosch using electrochemical H₂ production (E/H–B)

Our starting point for the electrochemical H₂ process is the U.S. Department of Energy H2A Distributed Hydrogen Production Model (Version 3), specifically the modeling of a process for the production of hydrogen from the electrolysis of water using grid-based electricity [8]. The system on which this paper focuses is a standalone grid-powered PEM electrolyzer system with a hydrogen capacity of 50,000 kg (50 mt) H₂/day (corresponding to 282 mt-NH₃/day). Our baseline model is the generic model, which uses process water and grid electricity. Costs are in 2017 US dollars.

More specifically, the energy of H₂ is 143 MJ/kg or 39.7 kWh/kg. The energy efficiency of electrochemical H₂ production can be as high as ca. 80% corresponding to 49.6 kWh required per kg-H₂. For a reference point, at a price of \$0.05/kWh (\$50/MWh) this corresponds to a cost for electrical power of \$2480/mt-H₂. Assuming 100% efficiency for the Haber–Bosch reaction (Eq. 14.2) (0.178 mt-H₂/mt-NH₃) this corresponds to \$441/mt-NH₃ for the H₂ feed (Table 14.2).

In the analysis, and similar to the Haber–Bosch process, assume that the electrolysis-based ammonia plant operates 330 days, or 7920 operating hours, per year. Then, while the Haber–Bosch through natural gas consumes 8.86 MWh per metric tons of NH₃ (in the above section), the electrolysis consumes 11.60 MWh per metric tons of NH₃; energy use is 29% higher under the electrolysis process than the natural gas reforming process.



14.4 Direct electrochemical nitrogen reduction

The process of ENR process involves oxidation of water at the anode to yield O₂ and H⁺, and reduction of N₂ at the anode, and protonation to yield ammonia (Eq. 14.6) (Fig. 14.2).

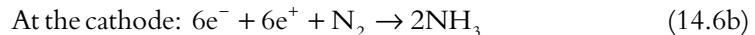
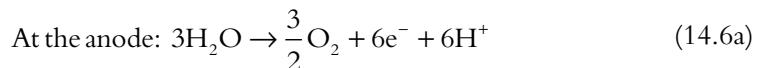


Table 14.2 Estimated costs of ammonia production (\$/mt-NH₃) via E/H–B, based on H2A model, PEM electrolyzer system with capacity 50 mt-H₂/day, with accompanying Haber–Bosch plants of varying capacity, at a fixed benchmark electric power cost of \$50/MWh.

Haber–Bosch plant size (mt-NH₃/day)

Large Haber–Bosch (2000 mt/day)	Medium Haber–Bosch (545 mt/day)	Small Haber–Bosch (91 mt/day)
\$627	\$669	\$725

Source [6].

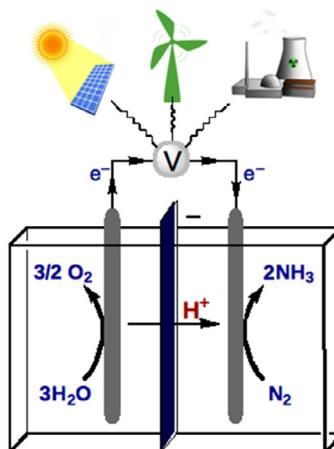
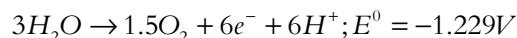


Fig. 14.2 Electrochemical approach to sustainable dinitrogen fixation.

The electrochemical potentials of these processes are as follows:



The purely theoretical (thermodynamic) energy requirement for ENR obtained from these values is 5.37 kWh per kg NH_3 produced. By comparison, to produce H_2 needed for E/H-B, the anodic reaction (H_2O oxidation) is the same while the cathodic reaction (reduction of H^+) has a (defined) potential of 0.0 V. The corresponding thermodynamic energy requirement is about 8% greater, at 5.80 kWh/kg. These values of course only represent purely theoretical lower limits of the energy requirements.

Unlike the Haber–Bosch process as currently implemented, ENR or E/H-B would not necessarily involve the use of fossil fuel as a source of hydrogen and commensurate emission of CO_2 . Thus, both avoid the production of CO_2 (assuming that carbon-free energy, e.g., wind, solar, or nuclear are used) as well as many of the other gases currently emitted in the course of ammonia production. ENR, however, unlike E/H-B, obviates the need for the highly energy- and capital-intensive Haber–Bosch process. Moreover, the ENR process would have the flexibility to exploit intermittent supplies of renewable electricity to produce NH_3 , without the need to store hydrogen. The ENR process thus benefits from the use of electricity during periods of low demand at a much lower energy and capital cost than does E/H-B.

The efficiency of an electrochemical synthesis like ENR is determined by the overpotential required to generate NH_3 (i.e., the operating voltage that is beyond the thermodynamic potential) and the Faradaic efficiency (the fraction of the current that leads to product according to the desired reaction). The values of these parameters are the main determinant of cost, and therefore economic viability, for ENR process. For example [6],

it showed that assuming an aspirational 95% Faradaic efficiency, 0.60 V overpotential, and \$50 per MWh, yields energy cost per mt-NH₃ of \$432. However, if the Faradaic efficiency is changed to 60% (as opposed to 95%) then the energy cost per mt-NH₃ is \$690; reducing the Faradaic efficiency by 37% resulted in energy cost increasing by 60%.

When assessing the economic viability of the ENR plant, the levelized cost of NH₃ was used, that is, a measure of the lifetime costs of the project divided by total ammonia produced during that same period was used. The above assumptions then suggest a cost of \$508 per metric ton of NH₃, where Table 14.3 shows the breakdown of the various cost factors with the feedstock (energy cost) being 85% of the cost per kg of NH₃.

Building on [6], parameters determining the cost of electrochemical direct nitrogen reduction were identified and linked these parameters to electricity prices. To establish the economic viability of intermittent production of ammonia, the year 2015 was analyzed for electricity price data taken from the Electric Reliability Council of Texas (ERCOT) region in the United States. ERCOT manages the flow of electricity in most of Texas and performs financial settlement for the competitive wholesale bulk-power market and administers retail switching [16]. The ERCOT price data used below are hourly data. Because the ERCOT price is the wholesale price, the following assumptions were needed to calculate the industrial price. Specifically, assume that the difference between industrial and wholesale prices is fixed and therefore the difference between the industrial and wholesale prices equals the difference between the average annual industrial price and the average wholesale price. EIA annual industrial electricity price data [17], together with ERCOT prices, were used to calculate this difference [18].

Given the industrial price calculated, the estimated number of hours that ammonia plants would operate throughout the year was calculated, where the data suggests electricity prices fluctuate significantly over time, within a day, over a week, and across seasons. In the simulation, assume future prices of electricity can be set a day in advance and that the plant management can decide whether the plant should operate during a given hour. The hourly price density graphs of the ERCOT wholesale prices show that the density peak occurs sufficiently below the price ceiling of \$0.04 per kWh for the fall and winter seasons, while it covers a significant portion of the peak in the spring and summer seasons. The density for the various hours' and seasons' wholesale prices per MWh are depicted in Fig. 14.3. The analysis shows the frequency where wholesale

Table 14.3 The baseline specific item cost calculations.

Cost component	Cost contribution (\$/kg of NH ₃)	Percentage of NH ₃ cost (%)
Capital costs	\$0.035	6.9
Fixed O&M	\$0.041	8.1
Feedstock costs	\$0.432	85.0
Total	\$0.508	

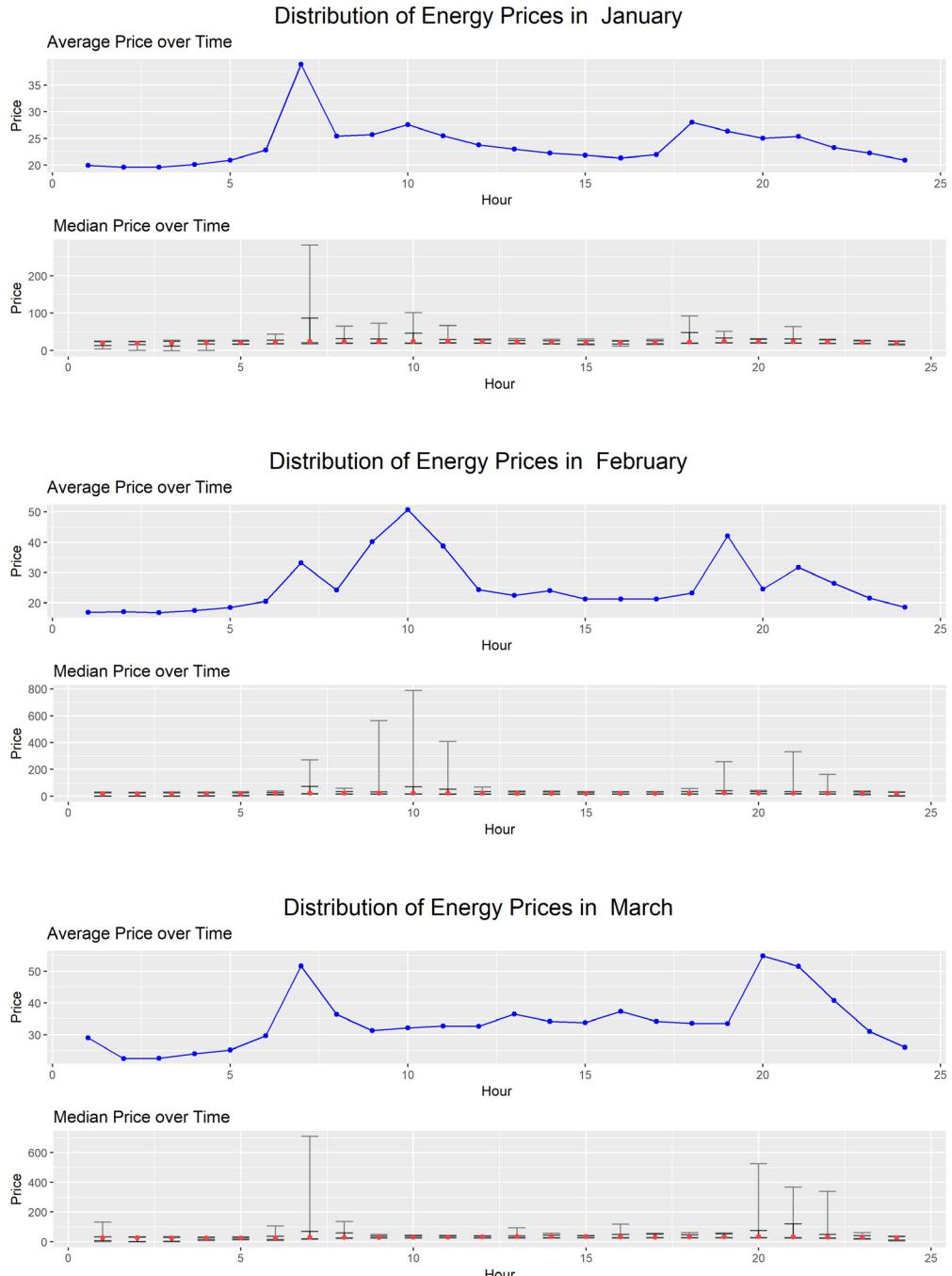
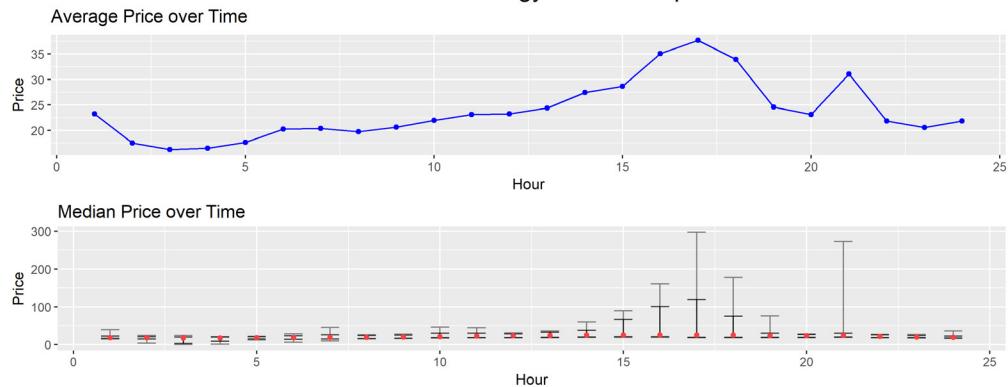
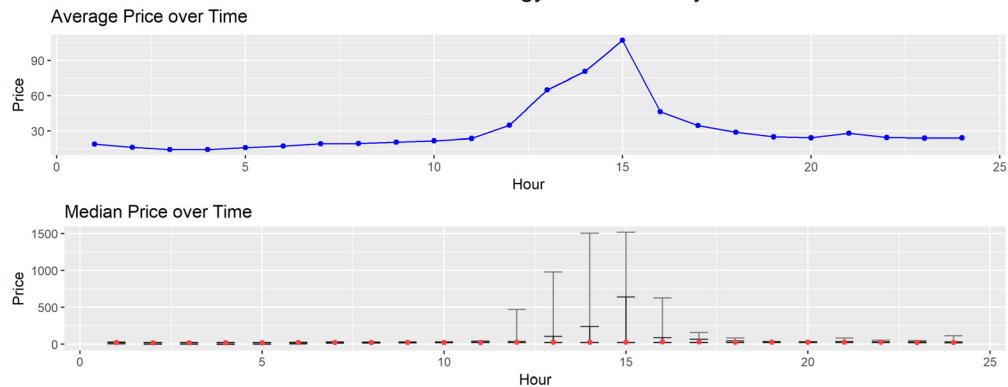


Fig. 14.3 Distribution of wholesale electricity prices at ERCOT. The figure shows the distribution of wholesale electricity prices for each month. The first graph shows the average hourly price while the second shows the median price, with error bars for the 1st to 99th percentile and the 5th–95th percentile. All prices are USD per MWh. ERCOT, Electric Reliability Council of Texas.

Distribution of Energy Prices in April



Distribution of Energy Prices in May



Distribution of Energy Prices in June

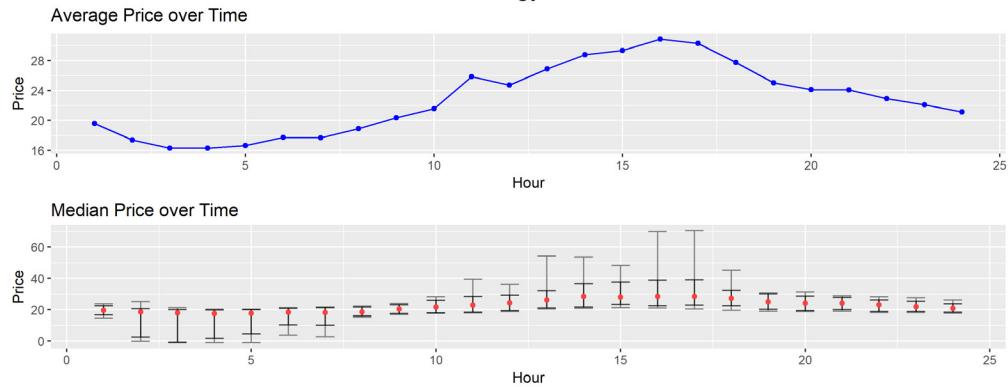
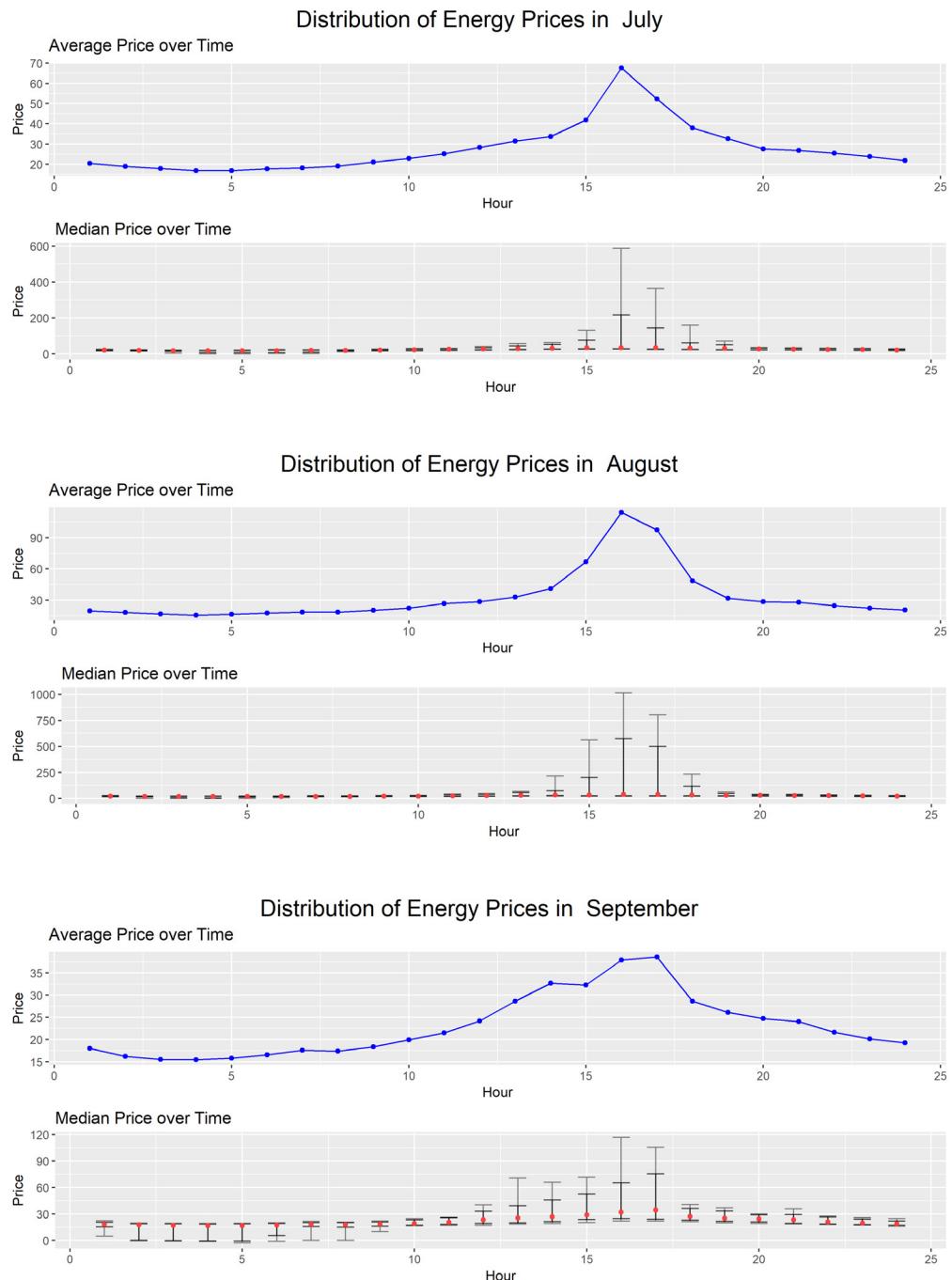


Fig. 14.3 (continued)

**Fig. 14.3 (continued)**

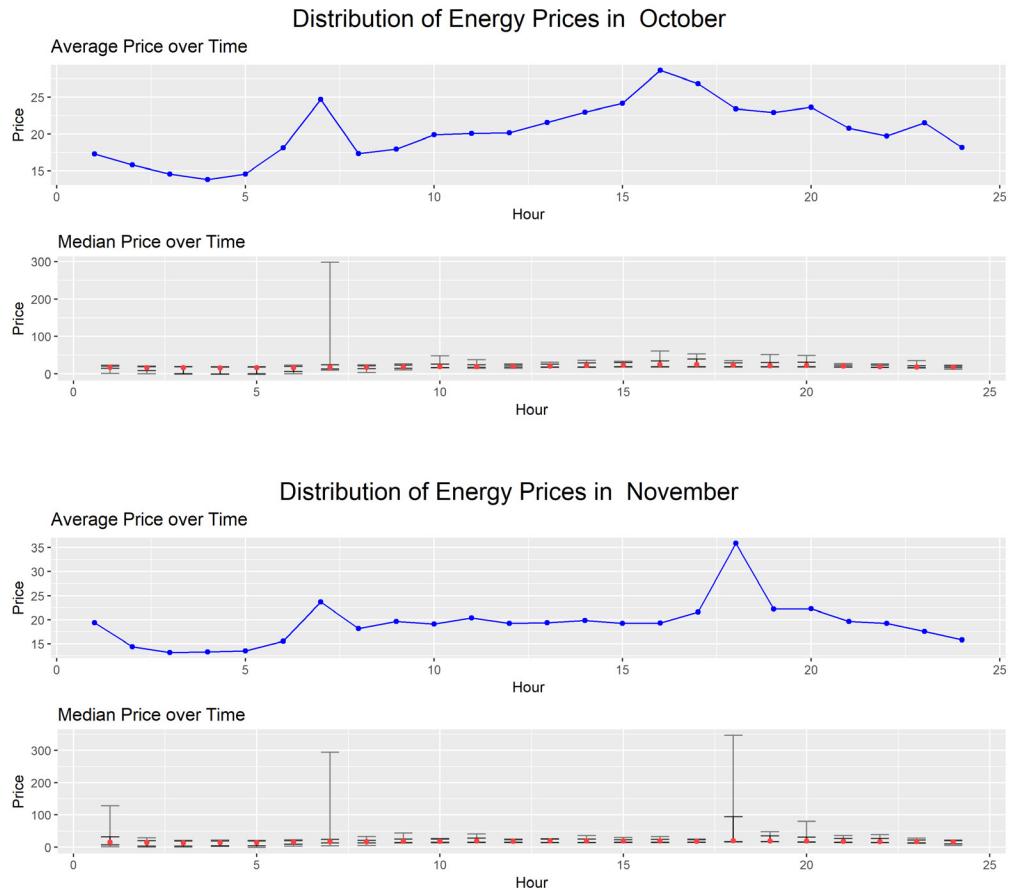


Fig. 14.3 (continued)

ERCOT prices are above the price of \$40 per MWh—that price at which it is not economical to produce ammonia. This analysis is done for the four seasons. For all the seasons, most of the time, the wholesale prices are below the price ceiling. The analysis shows that, ex-post, the number of working hours per year in which the price is below \$40 per MWh is around 6500 out of 8760 hours in a year. Hence, the analysis suggests that an ammonia plant utilizing ENR technologies can operate about 74% of the year if the price the ammonia plant faces is the ERCOT wholesale price.

However, industrial facilities usually do not have the capacity to utilize high voltage and thus require a supply of low voltage. An ammonia plant can invest in an off-grid solar/wind farm [19], but it might also elect to purchase low-voltage electricity from the grid. When looking at the industrial price, the distribution of the price in the Texas

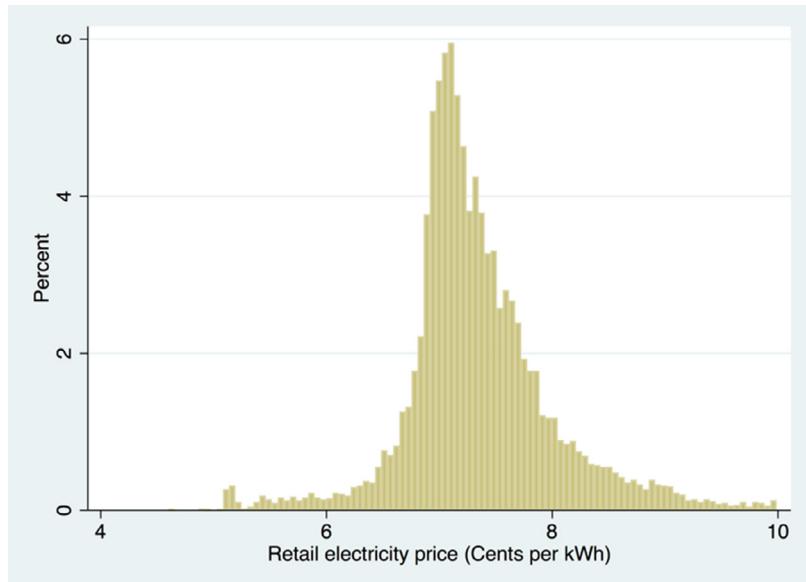
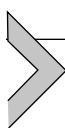


Fig. 14.4 The distribution of industrial retail electricity prices in the ERCOT region. *ERCOT*, Electric Reliability Council of Texas.

ERCOT Houston node region is depicted in Fig. 14.4. The mean calculated industrial price is \$76.5 per MWh (Fig. 14.4), with a standard deviation of 2.95. With high overpotential values and low Faradaic efficiency, production of NH_3 using ENR would be challenging when the plant connects to the grid. However, with low overpotential and high Faradaic efficiency, the ammonia plant can become competitive with the existing technologies over large portions of the 24-h cycle.

Although high fixed costs describe the Haber–Bosch process, if the ENR plants are relatively efficient then these plants will probably connect to the grid and compete with the existing incumbent Haber–Bosch plants. However, if the electrochemical direct nitrogen reduction plant is not sufficiently efficient, then the plant may elect to make a larger upfront investment and connect to an off-grid solar/wind farm, paying larger upfront costs but lower marginal costs. Recall that the Haber–Bosch process does require very large upfront investments, but its operations and maintenance costs are relatively cheap because of the low natural gas prices.



14.5 Conclusions and perspectives

The goal of this chapter is to break down the ENR cost structure, separate out the different system components, and shed new light on the futuristic supply structures of ammonia. The analysis evaluated how improvements resulted in lower electricity

feedstock costs and assessed the sensitivity of the ENR process to the assumptions on the Faradaic efficiency, overpotential, and electricity prices.

The chapter compared the outcome of the ENR process through its cost, energy use, and emissions to those generated by the Haber–Bosch and the E\H–B processes. It showed that the cost of electricity is determined via overall energy efficiency (i.e., Faradaic efficiency and overpotential) and the cost of MWh. Our results show that key to the success of this technology are improvements in efficiency and energy use. The comparison with the other processes highlights the importance of electricity costs. The analysis implies that the ENR process is much more flexible than the Haber–Bosch, and that its resource adequacy and usage may result in cleaner and more sustainable production processes, compared to other existing options.

This work depicts a futuristic production structures of nitrogen to ammonia, suggesting a supply chain alternative to the existing ammonia industry that may use solar or wind energy to supply electricity off the grid and work well with intermittency and renewable energy systems introduced. The ENR technology can be utilized to shift electric load, which increases the reliability of the supply of electricity, reduces the generation, and transmission capacity needed when electricity load peaks, and increases the electric power system's ability to handle intermittent resources such as wind and solar. Although the current state of ENR technology is far from economically viable, this work suggests that the development of an efficient ENR technology is an objective with tremendous potential.

Acknowledgement

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- [18] Capacity costs are not introduced, since the ERCOT region does not have capacity costs.
- [19] Note that a 10 MW solar farm costs around 25 million USD and uses about 50 acres of land (recall that under our aspirational scenario -0.95 V overpotential and 95% Faradaic efficiency—energy input under the ENR process is 8.70 MWh per metric ton of NH₃). <http://innovativesolarfarms.com/solar-farm-cost-per-acre/>. [Accessed October 2018].

