PROCEEDINGS OF THE 32nd European Symposium on Computer Aided Process Engineering (ESCAPE32), June 12-15, 2022, Toulouse, France
L. Montastruc, S. Negny (Editors)

http://dx.doi.org/10.1016/B978-0-323-95879-0.50039-4

Sustainable Ammonia Production via Electrolysis and Haber-Bosch Process

Gbemisola Ojo,[a]Kyle Camarda[a]

[a]*University of Kansas, Lawrence, KS 66047, United State*

Abstract

The production of ammonia accounts for nearly 2% of global carbon emissions (Palys et al. 2018) and therefore finding ways to make ammonia using renewable energy sources is paramount. The current mechanism for NH_3 production is dominated by the Haber-Bosch process, in which the hydrogen is produced from a water-gas shift reaction (Martín, 2016). Rather than obtaining this hydrogen from fossil fuels, this project employs electrolysis, driven by a solar plant coupled with battery storage. In this work, a dynamic simulation of a chemical process plant for the synthesis of the production of ammonia electrolysis is simulated using Aspen Hysys. Since renewable sources of energy are naturally variable, the plant's dynamic performance over varying electricity availability is also investigated. Case studies are used to demonstrate the feasibility of the plant as well as to explore the maximum and minimum battery capacities required.

Results show production profiles utilizing variable energy availability while avoiding shutdowns and minimizing battery charging cycles. The results also demonstrate the feasibility of completely sustainable ammonia production. This study produced 60.25 tons/day of ammonia using 8 tons/day of hydrogen at a current density range of 43 – 90 A/cm^2. The minimum battery capacity required is 56.25 MW.

Keywords: Electrolysis, Ammonia, Battery, Renewable, Solar Energy.

1. Introduction

Ammonia (NH3) is the second most produced chemical in the world. Traditionally, hydrogen is produced from methane steam reforming, while nitrogen is separated from the air. This project utilizes Aspen Hysys to simulate a dynamic model of an ammonia production plant that utilizes sustainable hydrogen production. Nitrogen is obtained from an air separation unit using a pressure swing adsorption technique. Hydrogen is produced via water electrolysis at moderate pressure and temperature conditions to ensure overall energy usage is reduced and high purity of hydrogen is obtained.

While renewable energy is crucial to handling global warming, a major challenge is intermittency. In this work, rechargeable lithium-ion batteries are implemented to allow continuous production of ammonia. The specific objectives of this study are (1) to simulate a dynamic model for hydrogen production, nitrogen separation, and ammonia synthesis (2) to integrate the process with a solar energy and battery source, (3) to test and analyze the effects of varying process parameters (4) to perform an assessment of the system to determine battery charging and discharging schedules.

2. Background

2.1. Hydrogen Production

Several production methodologies for hydrogen production can be considered in the context of ammonia production, including Alkaline Water Electrolysis (AWE), Proton Exchange Membrane Electrolysis (PEM), and Solid-Oxide Water Electrolysis (SOWE). These methods are differentiated by two major parameters: pH, and temperature. The criteria used to decide the most effective technique is based on the temperature range, the electrolytes and durability of the system. AWE was chosen because of its low capital cost, low corrosivity, high durability, and thermodynamic stability. Based on these factors, the AWE process was chosen for this project. The simulation for the proposed AWE was completed using Aspen Custom modeler.

2.2. Nitrogen Separation

A renewable-resourced ammonia production facility should obtain the required nitrogen directly from the air. Three methods of air separation were considered for this project: cryogenic distillation, pressure swing adsorption, and membrane separation. Although cryogenic distillation is the most common process employed in industry, it requires large energy input. While membranes offer a low-energy solution for air separation, the current production of membranes does not provide sufficient selectivity for practical use. PSA, on the other hand, provides a trade-off between practically and energy consumption. Furthermore, high-quality adsorbents for oxygen already are in industrial practice. PSA was not modelled in this work, it is recommended for future work.

3. Process Description

A dynamic process is simulated which integrates a Haber-Bosch reactor with water electrolysis for hydrogen production. It utilizes a solar plant as the main source of energy with lithium-ion batteries to buffer the power availability. The process model was developed using Aspen Hysys and Aspen Custom Modeler. An overall schematic of this process is shown in Figure 1.

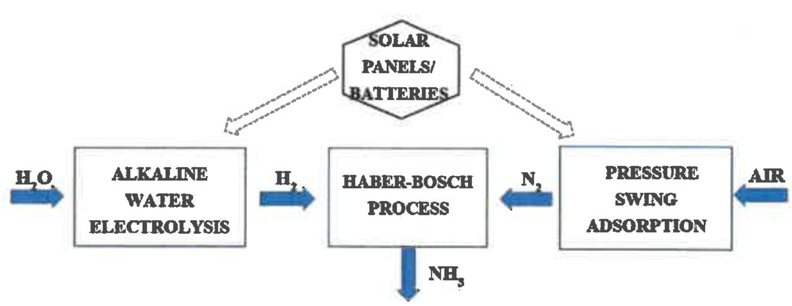

Figure 1: Overall schematic for ammonia production

3.1. Hydrogen Production Section

Alkaline water electrolysis is a process by which water is decomposed into hydrogen and oxygen in an electrolytic cell. Water is fed to the cell, which includes a porous nickel electrode and a diaphragm. Figure 2 shows the anode circulation loop, which produces oxygen while the cathode circulation loop produces hydrogen for the Haber-Bosch process. This affects a direct separation between the hydrogen and oxygen produced. The AWE was simulated using a custom unit operation created in this work.

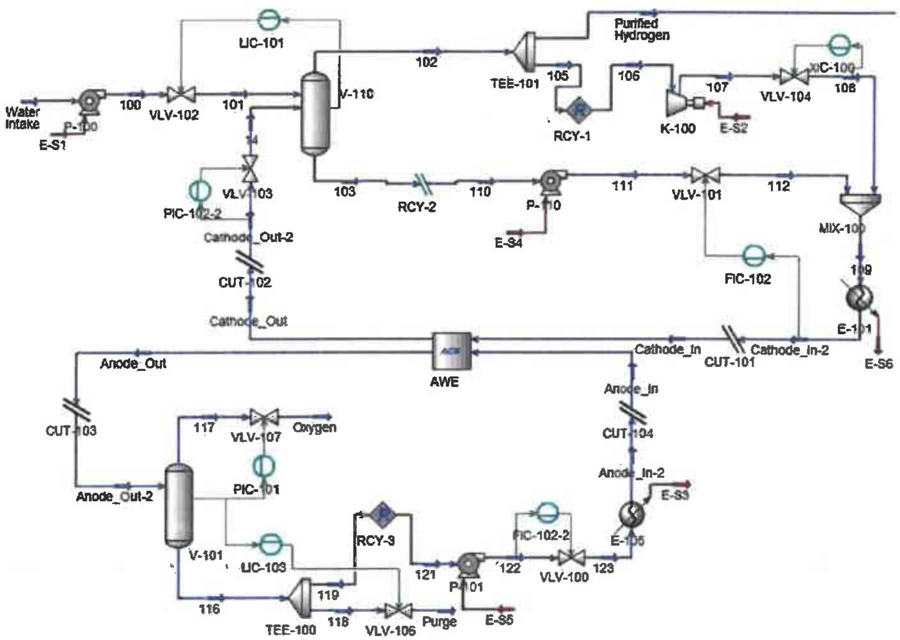

Figure 2: Alkaline Water Electrolysis showing anode and cathode circulation

3.2. Ammonia Production System

As discussed earlier, the Haber Bosch process is operated in a plug flow reactor temperature of 580 K and 150 bar. Heat integration is applied to recover excess energy from the product. Unreacted nitrogen and hydrogen are recycled to reduce energy usage.

3.3. Energy Specification

Upon the implementation of the above process model, a dynamic simulation was completed for three different case studies to demonstrate the energy requirements of the system. The objective of these case studies is to show the dynamic profile of the plant given various weather and location scenarios. The case studies are also used to understand the battery capacity required for the plant.

The storage energy system is an essential part of most off-grid renewable energy systems. Batteries are employed to store the surplus power produced from solar power allowing them to serve the load demand while balancing the hybrid system's fluctuations. The model used in this paper estimates the state of charge of the battery storage following the methods by Guezgouz et al. (2019).

4. Results and Discussions

The case studies shown describe the relationship between power availability and ammonia production level. Knowing that water electrolysis dominates the power consumption operation of this plant, it is important to understand the power requirement of the alkaline water electrolysis based on the overall ammonia produced. The study uses a minimum and maximum current density specification to control the amount of hydrogen produced. This controls the overall ammonia production rate. The maximum and minimum current density is identified by using the specific requirements of AWE, at a limiting temperature of 90° C. Current density is directly properly proportional to temperature of the electrolytic cell. At current density ranging from 0.2 A/cm^2 to 0.3 A/cm^2, temperature ranges from 66 ° C – 90 ° C respectively.

The dynamic behavior of the integrated process was modeled using Aspen Hysys. In the system, controllers are placed in strategic places to stabilize the open loop response of the system as the current density of the process is changed. The controllers in the AWE will be tunned electrolysis to decrease the settling time and overshoot by tuning the control parameters. Dynamic studies will be continued to determine optimal operating conditions and charging/discharging schedules

For each case, the electrolyzer inlet temperature is set to 25 °C, while the inlet temperature of the for the Haber-Bosch PFR is set to 257 °C. This gives a 92% conversion rate of hydrogen to ammonia.

Case study one shows a startup for this process leading to full-capacity operation. The plant then runs at a constant density of 0.3 A/cm^2. Figure 3 describes the dynamic profile of the plant. It can be observed that at a constant density of 0.3 A/cm^2, the maximum amount of ammonia produced is 27.45 tons/day, which corresponds to a small industrial facility. The energy requirement is estimated to be 5.54e +04 kW per day. This case study serves as a base case to compare with real-word scenario.

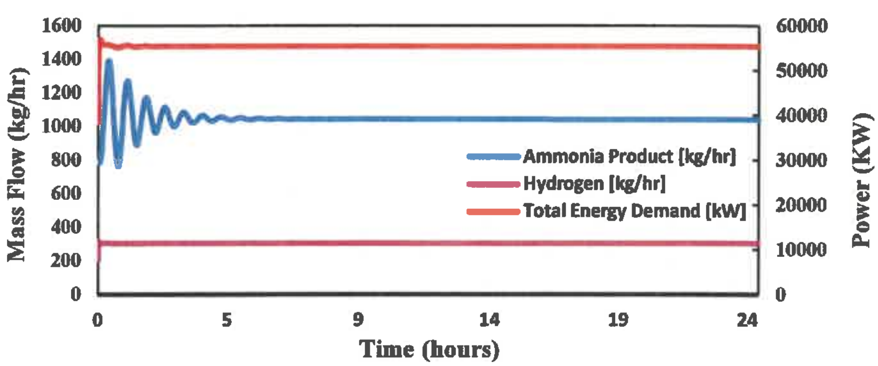

Figure 3: Ammonia production profile for case study one

Case study two assumes construction at a location closer to the equator, where there is approximately 12 hours of daylight. The current density at high solar hours is assumed to be 0.3 A/cm^2 which gives an ammonia production rate of 27.84 tons/day, as seen in the previous case study. This production rate decreases to 19 tons/day at a lower current density of 0.2 A/cm^2 when power is obtained from batteries. The excess energy produced from the solar panel at peak hours is transferred into batteries for use during the night. A total of 600 solar modules are utilized for functionality of the plant. Figure 4 shows the response to the change in current density of the overall ammonia production.

The dynamic profile also illustrates a second order response to the change in current density.

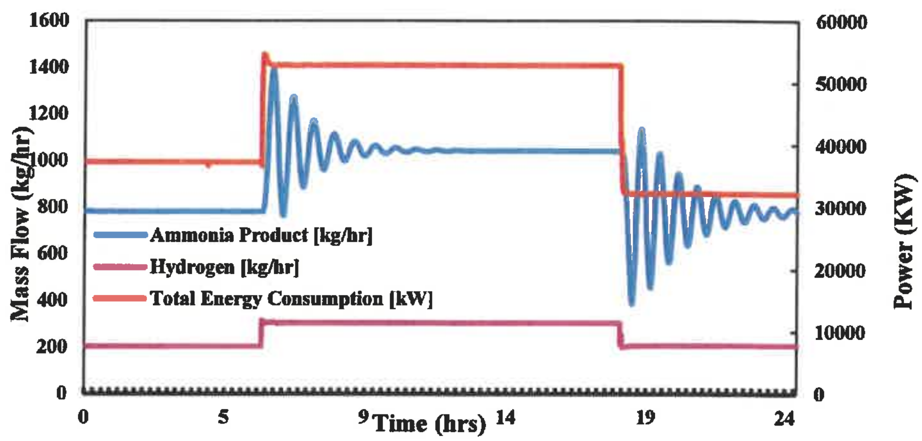

Figure 4: Ammonia production profile for case study two

Case study three involves a location further away from the equator, where there is lower amount of sunlight. The plant runs at 0.2 A/cm^2 for 16 hours at night while it runs at a higher current density 0.3 A/cm^2 for 8 hours. From the result shown in Figure 5, it can be inferred that there is an 60% increase in battery required to make the same amount of ammonia. excess energy supplied during the data is stored because it is needed to power the plant at night.

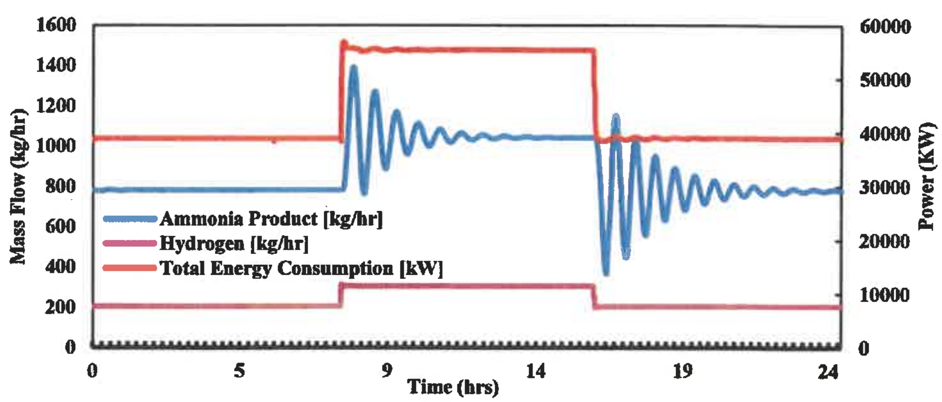

Figure 5: Ammonia production profile for case study two

5. Conclusions and Future Work

In this project, the feasibility of a 100% renewable energy chemical production plant to produce ammonia was considered. Due to the intermittency of renewable energy sources, the dynamic production profile was considered, to size the energy storage requirements. Water alkaline electrolysis and pressure swing absorption were applied to produce hydrogen and separate nitrogen respectively. The resulting profiles show the feasibility of a full-scale ammonia plant utilizing 100% renewable energy by integrating the entire Haber Bosch process with solar power. Analyzing these case studies at different current densities and time intervals gave insights on the effects of solar radiation and battery capacity on the ammonia production rate.

The battery system employed is large but not beyond currently used industrially sized systems. The key conclusion explained from the analysis shows that, the scale of the ammonia plant is necessary for the renewable energy to be economical. Several small-scale renewable plant is more cost effective than one large renewable plant. The results also show that case study 2 is more economical for the ammonia plant because it is much closer to the equator, therefore more energy can be harvested and stored in the battery for night-time. Lastly, the results also show a promising future holds for a renewable ammonia plant although this focuses on a smaller production scale. Future studies will perform MINLP optimization to minimize battery requirements and thus improve overall sustainability.

References

Akinlabi, Charles O., Dimitrios I. Gerogiorgis, Michael C. Georgiadis, and Efstratios N. Pistikopoulos. 2007. 'Modelling, design and optimisation of a hybrid PSA-membrane gas separation process.' in Valentin Pleşu and Paul Şerban Agachi (eds.), *Computer Aided Chemical Engineering* (Elsevier, Amsterdam).

Argyle, Morris D., and Calvin H. Bartholomew. 2015. 'Heterogeneous Catalyst Deactivation and Regeneration: A Review', *Catalysts*, 5: 145-269.

Bard, Allen J, and Larry R Faulkner. 2002. 'Electrochemical Methods: Fundamentals and Applications'.

Ciobanu, Madalina, Jeremy P. Wilburn, Morgan L. Krim, and David E. Cliffel. 2007. '1 - Fundamentals.' in Cynthia G. Zoski (ed.), *Handbook of Electrochemistry* (Elsevier: Amsterdam).

Hao, Pingjiao, J. G. Wijmans, Jay Kniep, and Richard W. Baker. 2014. 'Gas/gas membrane contactors – An emerging membrane unit operation', *Journal of Membrane Science*, 462: 131-38.

Himma, Nurul F., Anita K. Wardani, Nicholaus Prasetya, Putu T.P. Aryanti, and I Gede Wenten. 2019. 'Recent progress and challenges in membrane-based O2/N2 separation', *Reviews in Chemical Engineering*, 35: 591-625.

Martín, Mariano Martín. 2016. '*Industrial chemical process analysis and design*' Elsevier, Amsterdam.

Murali, R. Surya, T. Sankarshana, and S. Sridhar. 2013. 'Air Separation by Polymer-based Membrane Technology', *Separation & Purification Reviews*, 42: 130-86.

M. Guezgouz, J. Jurasz, B. Bekkouche, T. Ma, M.S. Javed, A. Kies Optimal hybrid pumped hydro-battery storage scheme for off-grid renewable energy systems112046 *Energy Conservation Management, 199* (2019)

Palys, Matthew J., Alon McCormick, E. L. Cussler, and Prodromos Daoutidis. 2018. 'Modeling and Optimal Design of Absorbent Enhanced Ammonia Synthesis', *Processes*, 6: 91.

Wu, Yiqian, Yanlei Xiang, Lei Cai, Haitian Liu, and Ying Liang. 2020. 'Optimization of a novel cryogenic air separation process based on cold energy recovery of LNG with exergoeconomic analysis', *Journal of Cleaner Production*, 275: 123027.