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Technoeconomic Analysis of Chemical Looping Ammonia Synthesis Reactors to Enable Green Ammonia Production

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ABSTRACT

Chemical looping ammonia synthesis (CLAS) is a new ammonia synthesis method capable of efficiently synthesizing ammonia at atmospheric pressure. The low-pressure operation of CLAS systems could decrease the capital and operational costs of ammonia synthesis. Despite its early developmental stage, the use of standard process engineering equipment in CLAS makes it possible to reasonably assess its economic potential. In this study, we evaluated the technoeconomic potential of CLAS systems in comparison to a Haber-Bosch (HB) synthesis process in the context of green ammonia production. CLAS is more compatible with the separate nitrogen and hydrogen feedstocks used in green ammonia production, and cost savings from CLAS could improve the economic viability of green ammonia production. Ammonia synthesis loops were modeled in Aspen Plus and the levelized cost of ammonia (LCOA) of each system was calculated. Three CLAS systems; two high temperature and one low-temperature chemical loop, were compared to a conventional HB system of equivalent size. This study found that CLAS can reduce the synthesis cost by 90% and that the low temperature CLAS as more economically viable than the high temperature CLAS. The need for an external heater in the high temperature CLAS diminished any cost savings that would have been realized due to the low-pressure operation. This work highlights the potential of CLAS to reduce ammonia synthesis costs and emphasizes the need for further development of low-temperature CLAS systems.

Keywords: Aspen Plus, Food & Agricultural Processes, Modelling and Simulations, Technoeconomic Analysis, Process Design

INTRODUCTION

Ammonia is a vital chemical for our modern society. Most of the industrially produced ammonia is used as a fertilizer to feed the global population, and the remainder is used to manufacture pharmaceuticals, chemicals, or used as a refrigerant [1]. The high energy density of ammonia and hydrogen capacity per volume, makes ammonia an attractive solution as a carbon-free energy carrier [1]. Because of this, ammonia is expected to play a pivotal role in decarbonizing notoriously difficult to abate sectors like aviation, and maritime shipping [2-3]. However, ammonia production itself is a carbon-intensive and hard to abate sector. Global ammonia production emits 1.8% of annual CO_2 emissions while consuming 1% of the annual energy demand [1]. As global reliance on ammonia grows with the emergence of new applications, it is crucial to ensure that the rising demand for ammonia production does not lead to a corresponding increase in CO_2 emissions.

Industrial ammonia synthesis is performed by the Haber-Bosch (HB) process which combines nitrogen and hydrogen to synthesize ammonia via R1:

$$N_2 + 3H_2 \Leftrightarrow 2NH_3. \quad \text{(R1)}$$

Although the ammonia synthesis reaction doesn't directly emit carbon dioxide, it results in the emission of 2 tons of CO_2 for every ton of ammonia produced [1]. This significant carbon footprint stems largely from generating hydrogen via steam methane reforming and combusting natural gas to heat the process [1]. Consequently, adopting carbon-free sources for hydrogen and heating is essential to curtail CO_2 emissions associated with ammonia production.

Green ammonia production offers a low-carbon solution for ammonia synthesis. This approach typically involves generating hydrogen through water electrolysis and extracting nitrogen from air using an air separation unit (ASU). These gases are then reacted in a Haber Bosch (HB) reactor to produce ammonia, with the entire process powered by renewable energy, making it environmentally friendly [2]. While technically viable, green ammonia production is not yet economically feasible in most cases [1]. Current efforts to lower production costs have primarily focused on reducing electrolyzer costs, with less emphasis on cost savings within the ammonia synthesis loop. Additionally, the HB reactor's sensitivity to minor fluctuations poses a challenge in integrating with intermittent renewable energy sources, underscoring the need for a more robust synthesis loop [4].

Chemical Looping Ammonia Synthesis (CLAS) is a new ammonia synthesis method that enables efficient ammonia production at atmospheric pressure and mild temperatures (<300°C) [5]. CLAS synthesizes ammonia in two or more steps mediated by a carrier material, typically a metal catalyst. A generalized CLAS process is shown in R2-R3:

$$3M + N_2 \Leftrightarrow M_3N_2, \quad \text{(R2)}$$

$$M_3N_2 + 3H_2 \Leftrightarrow 3M + 2NH_3, \quad \text{(R3)}$$

where nitrogen is fixed to the metal catalyst in R2 and removed as ammonia in R3 using hydrogen. The primary benefit of CLAS is its ability to circumvent the equilibrium constraints of the traditional HB process (R1) [5]. This allows for ammonia production at reduced pressures and temperatures, which can significantly lower both capital and operational costs by enabling the use of more affordable compressors and reactors than those required for the HB process. Furthermore, CLAS is particularly well-suited for green ammonia production, which generates nitrogen and hydrogen in separate streams – a requirement for CLAS reactors. CLAS systems can vary in their number of steps, carrier materials, operating temperatures, and hydrogen sources making them difficult to assess [5]. Despite ongoing development of more CLAS systems, there's a gap in assessing their technoeconomic viability, especially as a direct replacement for the HB synthesis loop in green ammonia production proposals. Currently, CLAS has a low technology readiness level (TRL) of 3. However, its use of established technologies such as compressors, heaters, heat exchangers, and fixed bed reactors allows for a reasonably confident early-stage economic assessment. In this work we aim to assess the technoeconomic feasibility of CLAS reactors as a drop-in replacement for a HB synthesis loop in a green ammonia production system.

METHOD

In this study, HB and CLAS systems were simulated in Aspen Plus and their levelized cost of ammonia (LCOA) were compared. For the HB process, we simulated a state-of-the-art loop featuring a three-bed reactor. For the CLAS systems, we examined two high-temperature processes operating at 400°C using data from two preliminary catalysts (Catalyst A & B) studied in-house reported in [6], and a low-temperature process operating at 270°C utilizing Ni-BaH_2 [7]. Each synthesis loop was fed with 2,600 kmol/h of nitrogen and hydrogen in a ratio of 3:1 at a temperature of 80°C and a pressure of 5 atm to replicate the pressure from a PEM electrolyzer [1]. The capital cost of each equipment was calculated using published correlations [8]. The levelized cost of ammonia was calculated using a 20-year period and 5% discount rate. The effect of conversion and CLAS reactor configuration was studied in relation to LCOA. The details of this analysis are described in this section.

Chemical Looping Reactor Model

The chemical looping reactor models were simulated at cyclical steady state using adiabatic RSTOIC reactors with a fixed fractional conversion of N_2 [9]. In this context, cyclical steady state describes a condition in which the reactor performance is stabilized across multiple chemical looping cycles and reaches a steady state. In this work the single reactor model shown in Figure 1.a, and the three-reactor model shown in Figure 1.b were studied. In the single reactor model, the feed gas is heated to the set point temperature of the chemical loop before being reacted. Ammonia is separated from the reactor outlet using a separator, and the unreacted gases are recycled back to the reactor using a compressor. In the three-reactor setup three CLAS reactors are connected in series and the feed gas is preheated in a heat exchanger, before being sent to the heater that is set to the setpoint of the chemical looping reactor. Again, ammonia is separated from the reactor outlet, and unreacted N_2 and H_2 are recycled, forming the synthesis loop. Three CLAS configurations were examined, using preliminary production rates of 105 $\mu mol/g_{cat}{\cdot}h$ for Catalyst A, 2 $mmol/g_{cat}{\cdot}h$ for Catalyst B, and 28 $mmol/g_{cat}{\cdot}h$ for Ni-BaH_2 [7].

Haber-Bosch Reactor Model

The Haber-Bosch synthesis loop shown in Figure 1.c, was simulated as a three-bed reactor system with a preheater and quench splits [10]. The molar flow of the feed, shown in Figure 1.c, was split sending 23%, 13.9% and 12.7% to beds 1, 2, and 3, respectively and the balance sent to the preheater [10]. The catalyst beds were modeled as adiabatic plugged flow reactors with a catalyst void fraction of 0.33 and a density of 2200 kg/m^3. The iron-based catalyst kinetics are described by Eq. 1 [10]:

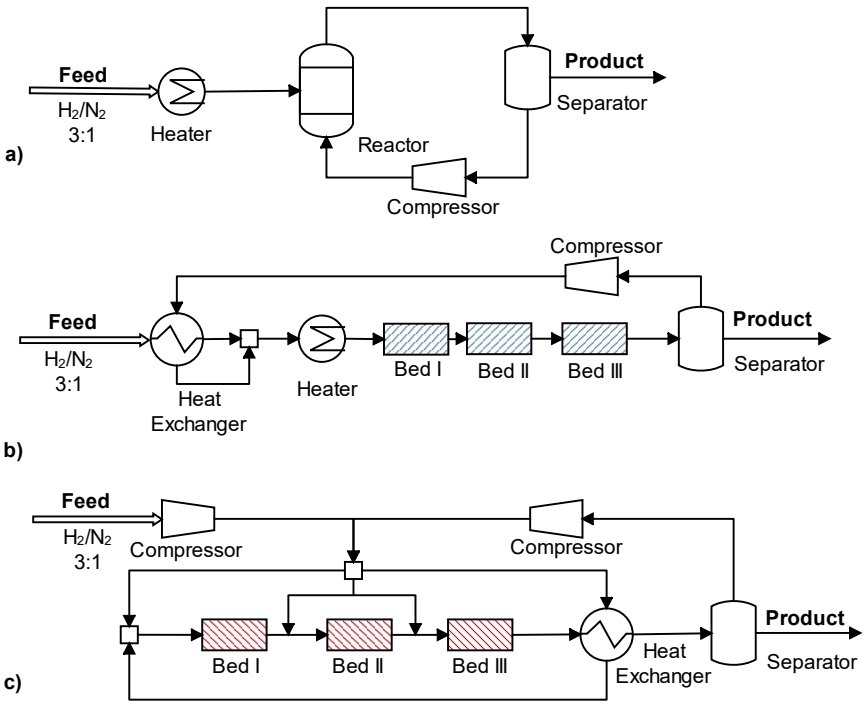

Figure 1: Diagrams of the ammonia synthesis loops modeled in this work where; a) is the single CLAS reactor model, b) is the three reactor CLAS model, and c) is the three bed Haber Bosch model.

$$r_{\mathrm{Fe}} = \frac{9.5}{\rho_{\mathrm{cat}}}\left(\frac{k_{\mathrm{Fe}} P_{\mathrm{N_2}} P_{\mathrm{H_2}}^{1.5}}{P_{\mathrm{NH_3}}} - \frac{k_{-\mathrm{Fe}} P_{\mathrm{NH_3}}}{P_{\mathrm{H_2}}^{1.5}}\right), \quad (1)$$

where ρ_{cat} is the catalyst bulk density, P_i is the partial pressure of component i in bar, and k_{Fe} and k_{-Fe} are the kinetic constants for the forward and reverse reactions of R1 respectively as:

$$k_{\mathrm{Fe}} = 1.79 \times 10^4 e^{\left(-\frac{87{,}090}{RT}\right)}, \quad (2)$$

$$k_{-\mathrm{Fe}} = 2.75 \times 10^{16} e^{\left(-\frac{198{,}464}{RT}\right)}, \quad (3)$$

where R is the universal gas constant, and T is the gas temperature in Kelvin.

Auxiliary Equipment

Auxiliary equipment was simulated to replicate realistic operation of each synthesis loop. A multistage compressor was used to elevate the pressure from 5 atm to 200 atm for the HB synthesis loop. The compressor includes an interstage cooler to reduce the outlet gases temperature to 250°C. The cooler was modeled as a heat exchanger with pumped cooling water as the working fluid. The pumps were modeled to increase the cooling water pressure by 1 atm with a 95% pump and driver efficiency. The cost of cooling water was not considered in this work. Compressors were simulated as isentropic using the ASME method with an efficiency of 95%. The compressors were powered by explosion proof drivers [8]. Heat exchangers were modeled with a 1 atm pressure drop across each side with a design specification to achieve a 50°C temperature change. The reported area of the heat exchangers was used to size the equipment. Heaters were modeled as electric heaters in Aspen Plus, and the duty of the heater was used to size the equipment. The separator used in each model assumed to be an absorbent based separator with a return stream of 250°C and a pressure drop of 1 atm [11]. The cost of separation was not included in the scope of this work.

Economic Calculations

The capital cost of each synthesis loop was calculated using Eq 4-6 :

$$C^{cap} = \sum_j^n C_j\,, \quad (4)$$

$$C_j = C_e \times AF \times P_e \times \frac{CEPCI}{1000}\,, \quad (5)$$

$$\log_{10} C_e = K_1 + K_2 \log_{10}(A) + K_3[\log_{10}(A)]^2, \quad (6)$$

where C^{cap} is the capital cost of the synthesis loop, C_j is the bare module cost of equipment j, n is the number of equipment in the synthesis loop, AF is the alloy factor used as 2.7 for stainless steel, P_e is the pressure adjustment factor for each equipment, and the chemical engineering plant cost index, $CEPCI$, was taken as 800 for 2023 [8,12]. C_e is the bare cost of the equipment defined by Eq. 6 where parameters $K1 - K3$ and A are described

in Table 1 for each equipment.

Table 1: Equipment capital cost parameters for Eq. 6 [8].

Unit	Basis (A)	K1	K2	K3
Heater	Duty (kW)	3.068	0.6597	0.0194
Heat Exchanger	Area (m^2)	2.7652	0.7282	0.0783
Compressor	Duty (kW)	2.2897	1.3604	-0.1027
Driver	Duty (kW)	2.4604	1.4191	-0.1798
Pump	Duty (kW)	3.3892	0.3161	0.1220

The reactor capital costs were calculated using Eq. 7:

$$C_{reactor}^{cap} = C_{fixed}^{cap} + f_P C_{ref}^{cap} \left(\frac{V}{20\ m^3}\right)^{0.52} + 15.50\, w_{cat}, \quad (7)$$

where w_{cat} is the catalyst weight in kg, V is the reactor volume in m^3, C_{ref}^{cap} is the reference reactor cost of \$268,000, C_{fixed}^{cap} is the fixed capital cost of the reactor at \$66,800, f_P is the pressure multiplier that accounts for the increase in vessel wall thickness at higher pressures, calculated as:

$$f_P = 0.125\left(\frac{P}{10}\right) + 0.875, \quad (8)$$

where P is in units of bar [11]. To calculate the volume of the RSTOIC reactors, we first established the required weight of the catalyst by dividing the ammonia production rate of each reactor by the catalyst production rate per gram of catalyst. Next, we determined the catalyst's volume using its density. Finally, we increased this volume by 25% to estimate the reactor volume. The HB catalyst cost was assumed to be \$15.5/kg [11] and the CLAS catalyst costs were calculated using the bare metal costs [13-15] plus an 80% markup.

The operating cost of each synthesis loop, C^{op}, was calculated using Eq. 5:

$$C^{op} = \sum_j^n C_j^{op}, \quad (9)$$

$$C_j^{op} = C_{j,duty} \times e_{cost} \times O_p, \quad (10)$$

where C_j^{op} is the operating cost of equipment j in the synthesis loop defined by Eq 10. $C_{j,duty}$ is the reported duty of equipment j, n is the number of equipment in the synthesis loop, e_{cost} is the cost of electricity assumed as 7 cents per kWh, and O_p is the operating period in hours. The levelized cost of ammonia was then calculated using Eq. 11 [16]:

$$\mathrm{LCOA} = \frac{\sum_{t=0}^{T} \frac{C_t^{cap} + C_t^{op}}{(1+r)^t}}{\sum_{t=0}^{T} \frac{m_{NH_3}}{(1+r)^t}}, \quad (11)$$

where T is the lifetime of the plant, t is the year, r is the discount rate, and m_{NH_3} is the annual ammonia production in tons. The LCOA was calculated for each synthesis loop using a 5% discount rate over the 20-year lifetime of the plant with an 90% uptime.

Parameter Analysis

Four studies were conducted to understand how different model parameters affect the levelized cost of ammonia in CLAS systems. The first study varied the reactor conversion rates between 1%, 5%, and 10%. The second study changed the number of reactors in a series, while varying the reactor conversion. The third study involved a sensitivity analysis on the three reactor Ni-BaH_2 CLAS system, where N_2 conversion, electricity cost, catalyst cost, and plant uptime were varied by ±20% individually to determine their impact on the LCOA. Lastly, in the fourth study, a six-reactor CLAS system was studied using the Ni-BaH_2 configuration with a conversion of 10% to determine the marginal cost of adding more reactors.

RESULTS

Figure 2 shows the levelized cost of ammonia for the single and three-reactor CLAS systems using Catalyst A, B, and Ni-BaH_2. The figure identifies a "cost-effective" zone where CLAS systems are more economical than the HB synthesis loop, which costs \$63.9/ton. Catalyst A has the lowest production rate of the CLAS systems studied (105 μmol/g_{cat}·h), and due to this it is the least economical option. The low production rate requires more catalyst resulting in larger more expensive reactors and a higher LCOA. Increasing the number of reactors with Catalyst A did not make the system more economical than the HB process as shown in Figure 2. Catalyst B has a higher production rate (2 mmol/g_{cat}·h) than Catalyst A; however, it was only economically competitive in a three-reactor setup sized for a 10% conversion. In this case, the addition of more reactors reduced the LCOA of the configuration, to where it could be cost competitive with the HB process. The CLAS with Ni-BaH_2 is the only CLAS system that have economical configurations with the single reactor and the three-reactor setup. The Ni-BaH_2 configuration is less expensive overall due to its high production rate (28 mmol/g_{cat}·h) and low temperature operation. The high production rate reduces the amount of catalyst needed which in-turn reduces the reactor size and cost. Additionally, the low temperature operation eliminates

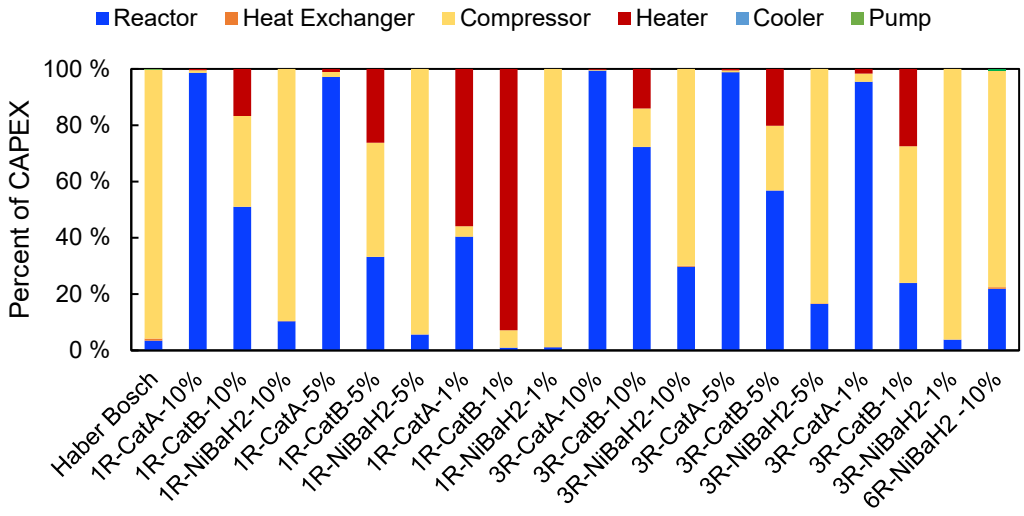

Figure 3: The capital contribution of each equipment in the synthesis loops studied where R represents the number of reactors and the percentage represents the N_2 conversion of the reactors.

the need for large external heaters. As a result, its single reactor configuration can achieve a LCOA lower than the HB process. A six-reactor configuration with Ni-BaH_2 was studied and shown to achieve a $9.73/ton LCOA, which represents an 84.8% reduction over the HB loop. The capital cost of the six-reactor synthesis loop is compared to the HB process in Table 2, showing an 82% reduction in capital costs. Table 2 shows that the compressor costs, inclusive of the driver costs, are the main differences between the two systems.

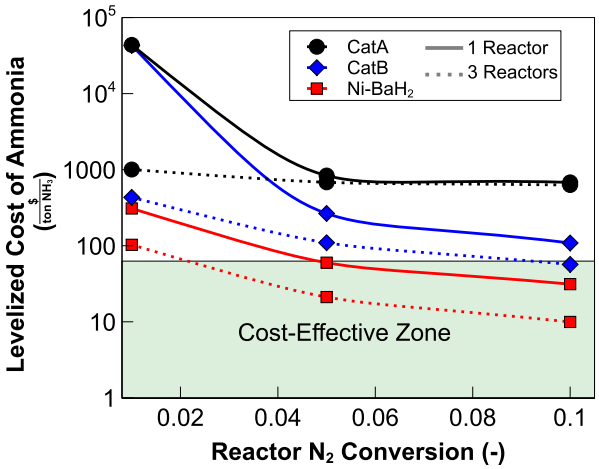

Figure 2: LCOA for each system, highlighting the "cost-effective zone" where systems outperform the HB loop.

The capital contribution of each equipment in the synthesis loop is shown in Figure 3. In the HB synthesis loop, over 95% of the capital expense is attributed to the compressor. In the CLAS systems, the major cost contributor varied significantly which each configuration. In the high temperature chemical loops, the need for an external heater drove up the capital cost making it a major cost contributor. In configurations with Catalyst A, the low production rate of the catalyst resulted in the reactor being the major cost driver in most configurations.

Table 2: Synthesis loop capital cost ($Millions USD), comparing the six-reactor Ni-BaH_2 system to the HB.

Stream	Haber-Bosch	Chemical Loop
Compressor	29.1	4.2
Reactor + Catalyst	0.98	1.10
Heat Exchanger	0.21	0.06
Pump	0.04	0.04
Total	30.33	5.4

A sensitivity analysis was performed on the three-reactor Ni-BaH_2 CLAS system at 5% conversion. The reactor conversion, electricity cost, catalyst cost, and plant uptime were varied ± 20% and the effects on the LCOA were recorded. Figure 4 presents the change in LCOA as a result of the sensitivity analysis showing that the LCOA is most sensitive to changes in the reactor conversion. A 20% decrease in conversion increased the LCOA by 47%, while a 20% increase in conversion decreased LCOA by 25.5%. A ±20% change in electricity costs resulted in a proportional ±11% change in LCOA. Finally, a ± 20% change in catalyst cost and uptime had little effect on the LCOA.

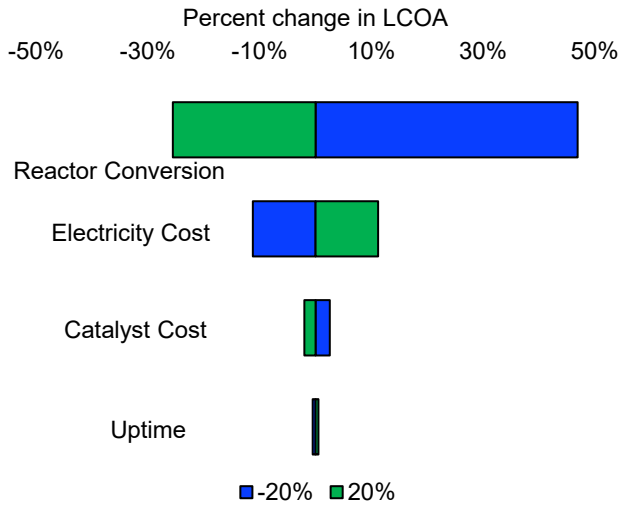

Figure 4: Percent change in Levelized Cost of Ammonia (LCOA) in response to a ± 20% change in various model parameters: Tornado Diagram Analysis.

Figure 5 shows the energy demand of the Ni-BaH_2 CLAS configurations compared to the HB system. Figure 5 shows that the CLAS systems can reduce energy demand by 86% compared to the HB process, when a six-reactor configuration is used. However, CLAS systems with low conversion (< 1%) can consume more energy than the HB process. Low conversion systems have a higher recycling rate which requires more energy to operate their compressors. On the other hand, CLAS systems with higher conversion have reduced recycling needs and consequently lower energy demands. Nevertheless, CLAS is a more energy-efficient method for ammonia synthesis as the majority of configurations studied are more energy efficient than the HB system.

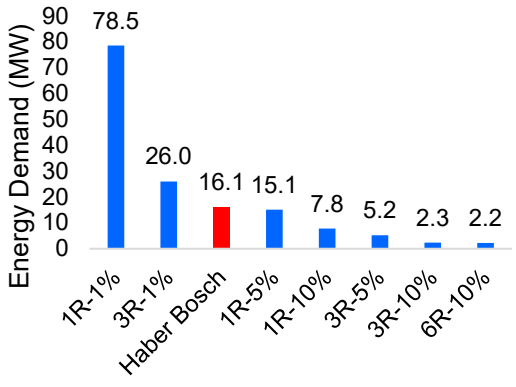

Figure 5. Energy required to produce 585 tons NH_3 per day from the Ni-BaH_2 CLAS systems compared to the HB system.

DISCUSSION

This study demonstrates the significant potential of chemical looping ammonia synthesis reactors in reducing ammonia production costs. By operating at a lower pressure (5 atm) compared to the Haber Bosch (HB) reactor (200 atm), CLAS can decrease the synthesis loop cost from $63.9/ton to $9.95/ton at a scale of 585 tNH3/day. This study shows that the cost reduction in CLAS systems is largely due to lower compressor costs, a major cost factor in the HB synthesis loop. However, these savings are not just due to reduced pressure but also because CLAS operates at lower temperatures, eliminating the need for costly external heating. In contrast to the adiabatic HB reactor, CLAS requires active temperature control. Therefore, focusing on mild temperature (T < 300°C), low-pressure CLAS systems could significantly lower ammonia production costs compared to the HB process. This reduction in synthesis cost is achievable today using a Ni-BaH_2 CLAS with reported production values. Among the studied systems, the Ni-BaH_2 CLAS had the lowest LCOA due to its high production rate (28 mmol/g_{cat}·h) and low temperature and pressure operation. A three-reactor system using Ni-BaH_2 had a LCOA of $9.95/ton while the six-reactor system had a LCOA of $9.73/ton. The additional reactors did not significantly improve the LCOA beyond the three-reactor system.

Despite its low TRL, the equipment similarities between CLAS and HB systems enable early economic evaluations of CLAS. This research highlights contrasting cost dynamics between the equipment in a HB system and a CLAS system. While the HB system has low catalyst costs and high reactor vessel costs, the CLAS system have low reactor vessel costs and high catalyst costs. These cost differences effectively balance each other out when the total reactor costs are considered. In the HB system, the compressor costs are high because of the elevated pressure, whereas the compressor costs in the CLAS system is driven by the high recycle rate. Notably, if reactor conversion in CLAS is too low (≤1%), its compressor costs can surpass those of the HB system. CLAS need an external heater, which is an important consideration to factor into future CLAS developments. In this work external heat was provided by an electrically driven heater, alternative renewable heating sources could be studied to reduce the heating costs.

This early economic evaluation sheds light on the economic potential of CLAS systems in development. However, there are three limitations in this work. Firstly, the catalyst production rate at 1 atm is assumed to be the same at 5 atm. CLAS production rates have not been extensively studied at elevated pressures therefore the reported production rate at 1 atm is used. Presumably, elevated pressures would increase the production rate of the CLAS improving the performance of the CLAS studied

and reducing their LCOA. Secondly, the analysis assumes the catalyst can last for the lifetime of the plant. There's a lack of long-term data on catalyst longevity and methods for their regeneration in CLAS systems. Shorter regeneration cycles and rising catalyst costs could significantly impact the levelized cost of ammonia by necessitating frequent expensive catalyst replacement. Lastly, the equipment sizing assumes that nitrogen and hydrogen are present in each equipment simultaneously. This is not accurate because CLAS alternate gas flows, which results in the CLAS equipment being oversized. While this is not optimal, it does provide a margin of contingency in relation to the CLAS cost estimates.

Future research into CLAS should focus on two key areas: the development of low-temperature CLAS systems and the exploration of strategies to maintain catalyst activity. The emphasis on low-temperature CLAS is crucial due to the economic challenges posed by high-temperature systems, which require substantial external heating. On the other hand, given the significant impact of catalyst costs on CLAS economics, finding ways to prolong catalyst life is essential. This involves conducting long-term tests to establish replacement timelines and understand degradation processes. Additionally, it is important to develop environmentally friendly methods for catalyst regeneration.

CONCLUSION

This study evaluated the technoeconomic potential of chemical looping ammonia synthesis (CLAS) reactors compared to a state-of-the-art Haber Bosch loop using Aspen Plus simulations. Three CLAS configurations were studied, two high temperature CLAS using preliminary catalyst performance data and one low-temperature CLAS using Ni-BaH_2 as a catalyst. Studies were performed focusing on the number of reactors in series, their conversion, and a sensitivity analysis on operating variables. The chemical loop with the lowest LCOA was the low temperature Ni-BaH_2 chemical loop, due to its efficient operation at low temperature and pressure. The Ni-BaH_2 chemical loop could reduce the LCOA by 90% when compared to the HB process, when 6 reactors were simulated in series. The study emphasizes the significance of operating CLAS at moderate temperatures to maximize cost savings because the need for an external heater can diminish the cost benefits of low-pressure operation, as was seen in the high temperature chemical loops. Despite CLAS's low TRL, its integration of existing technologies like compressors, heat exchangers, heaters, and fixed bed reactors make it possible to evaluate their economic viability even at this early stage. Future research should focus on the long-term catalyst degradation and regeneration, and performance at varied pressures to optimize CLAS further. This study underscores the need for ongoing research to make ammonia synthesis more cost-effective and sustainable.

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