Process alternatives to stabilize small-scale ammonia production

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Abstract

Producing ammonia to offset the fluctuations in renewable energy is an energy storage approach with significant potential. Through the intermittent operation of a small-scale ammonia production process, ammonia can be produced, stored, and converted to electricity when additional power is required. The conventional ammonia synthesis reactor, however, is not designed for intermittent operation since minor changes in process conditions can cause catastrophic failures. In this study, we explored two reactor alternatives for stabilizing small-scale ammonia production. The first utilizes a Ru/C catalyst in a conventional reactor design to produce ammonia at a thermodynamically favorable temperature and the second utilizes a chemical looping reactor to decouple the ammonia synthesis reaction steps and eliminate reactor instabilities. Six disturbance tests were conducted in Aspen Dynamics to assess the stability of the process alternatives in comparison to a conventional small-scale Fe-based reactor. In response to disturbance testing, the Fe-based reactor exhibited runaway conditions, limit cycle behavior, and reaction extinction, whereas the two process alternatives remained stable throughout each disturbance test. The Ru/C-based reactor is a simple system, since it only requires the replacement of the catalyst in a conventional reactor. The chemical looping reactor requires additional equipment for separation and further reactor development. We demonstrate how engineering design considerations can aid in stabilizing small-scale ammonia production and enable carbon-free energy storage.

Keywords

Haber Bosch, Ammonia, Distributed Manufacturing, Chemical Looping, Ruthenium.

Small-scale ammonia production could play a pivotal role in establishing a grid powered entirely by renewable energy sources. Ammonia, unlike many other energy storage solutions, is a carbon-free energy carrier that can be produced on demand and stored for long periods of time without degradation. Thus, producing ammonia to offset fluctuations in intermittent renewable energy production is an energy storage approach that is gaining traction. In addition, the produced ammonia can be converted to hydrogen to support the growing hydrogen economy, or converted directly to electricity using established fuel cell technology. As a result, researchers are actively studying small-scale ammonia production systems as an energy storage solution of the future.

Proposals for small-scale ammonia production are conceptually straightforward. The excess energy from a renewable power project is used to generate hydrogen via electrolysis and nitrogen from pressure swing absorbers to feed a Haber-Bosch (HB) reactor producing ammonia (Reese et al., 2016). The HB process has been the dominant means of industrial ammonia production for the last 100 years, and is one of the most widely studied industrial processes. While considerable research efforts have been made to evaluate the economic feasibility (Lin et al., 2020), optimal geographical location (Palys and Daoutidis, 2020), and performance of these small-scale ammonia production proposals (Reese et al., 2016), little attention has been paid to the impact the temperamental HB process may have on these proposals.

The HB process produces ammonia from nitrogen and hydrogen over an Fe catalyst at 450 °C and 20.0 MPa via R1:

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 \cdot \tag{R1}$$

Ammonia is created during the process at a high temperature in order to carry out R1 at a kinetic rate that is economically viable. However, at high temperatures, the equilibrium of R1 narrowly favors the forward reaction. As a result, minor fluctuations in the process can disturb the equilibrium of R1 creating major fluctuations in reactor temperature, pressure, and flow rate (Morud and Skogestad, 1998). Consequently, HB reactors operate with a small margin of stability, which has been found to reduce with reactor size (Burrows and Bollas, 2022). Reactor disturbances are actively mitigated in large-scale HB reactors by using advanced controls (Araújo and Skogestad, 2008), which may be challenging to implement at a small-scale. It is, therefore, imperative that the HB reactor be stabilized through engineering design considerations wherever possible.

In this work, two potential solutions are explored to stabilize small-scale ammonia production. In the first solution ammonia synthesis at a lower temperature is explored as a

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more stable thermodynamic process. In the second solution a chemical looping ammonia synthesis (CLAS) reactor is explored to decouple R1, and avoid the instabilities associated with its equilibrium. To enable efficient ammonia synthesis at a lowered temperature, a Ru/C catalyst (Tripodi et al., 2021) is studied in a conventional HB reactor design. To decouple R1, a CaH_2/Ca_3N_2 chemical looping reactor system is studied (Burrows et al., 2021). The CaH_2/Ca_3N_2 chemical loop produces ammonia in a two-step process where CaH_2 is reacted with N_2 to produce Ca_3N_2 in R2 (Burrows et al., 2021):

$$3\,CaH_2 + N_2 \rightleftharpoons Ca_3N_2 + 3\,H_2, \qquad \text{(R2)}$$

and Ca_3N_2 is reduced by H_2 to generate NH_3 in R3 (Burrows et al., 2021):

$$Ca_3N_2 + 6\,H_2 \rightleftharpoons 3\,CaH_2 + 2\,NH_3\,. \qquad \text{(R3)}$$

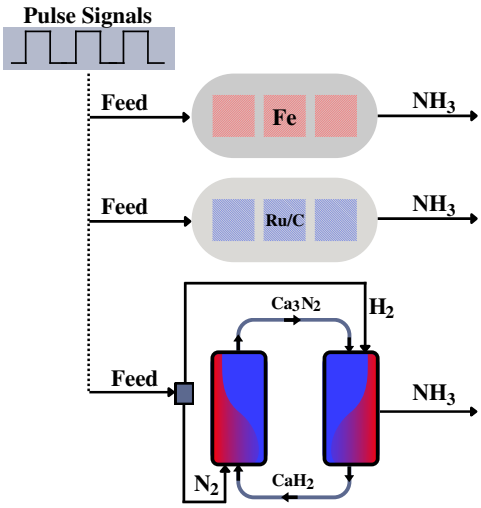

Figure 1: Schematic diagram of the disturbance tests performed on the Fe-based, Ru/C, and CaH_2/Ca_3N_2 chemical looping reactor model.

Figure 1 illustrates how reactor stability was assessed in this study. A conventional 3-bed ammonia synthesis reactor was used to model the Fe, and Ru/C reactor, and the chemical looping reactor was modeled with two reactors in a loop, as shown in Figure 1. Each reactor was subjected to pulse signals to simulate disturbances in reactor feed temperature, pressure, and flow rate. This paper presents and discusses the results of each of these disturbance test.

Methodology

In this work three ammonia synthesis reactors were modeled with a capacity of 150 tNH_3/day in Aspen Plus using the Redlich-Kwong-Soave equation of state. The steady state models were converted to flow-driven dynamic models and solved in Aspen Dynamics using the Gear integrator at a variable step size ranging from 0.001 h to 0.01 h. The reactors were subjected to disturbances in Aspen dynamics using a common feed in each case and their stability was measured. The reactor feed consisted of H_2 and N_2 in a ratio of 3:1 respectively, with an NH_3 composition of 4% at a temperature of 250 ^oC, and a pressure of 20 MPa (Morud and Skogestad, 1998). The details of each model and disturbance testing procedure are described in this section.

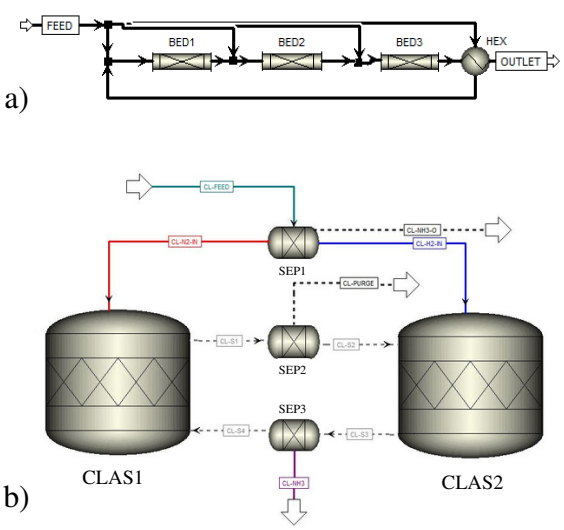

Figure 2: Aspen Plus model configuration for the : a) 3-bed ammonia synthesis reactor; and b) chemical looping ammonia synthesis reactor.

The Fe and Ru/C catalyst reactors were modeled using a conventional 3-bed plug flow reactor model (Morud and Skogestad, 1998) shown in Figure 2.a. The reactor beds were modeled with a diameter of 0.9 m, and lengths of 0.9585 m, 1.38 m, and 2.178 m, for beds 1, 2, and 3, respectively. The reactor beds operated adiabatically, and the pressure drop across each reactor bed was calculated using the Ergun equation in Aspen Plus. The molar flow of the feed, shown in Figure 2.a, was split sending 23%, 13.9% and 12.7% to beds 1, 2, and 3 respectively (Morud and Skogestad, 1998). The remainder of the feed was sent to the preheater, HEX shown in Figure 2.a, which was modeled as a heat exchanger with a constant heat exchange area of 25 m^2. The reactor beds were modeled with a void fraction of 0.33 and a catalyst density of 2200 kg/m^3 for Fe (Morud and Skogestad, 1998) and 590 kg/m^3 for the Ru/C catalyst (Tripodi et al., 2021).

The chemical looping reactor was modeled in Aspen Plus using two RSTOIC reactor blocks shown in Figure 2.b. The first step of the chemical loop R2, was executed by the CLAS1 reactor shown in Figure 2.b, and the second step R3 was executed by CLAS2. The feed stream was separated using an ideal separator block, SEP1, to send N_2 to the CLAS1 reactor and H_2 to the CLAS2 reactor, shown in Figure 2.b. Ammonia in the feed stream was purged from the system also using SEP1. N_2 was reacted with CaH_2 in CLAS1 at a fixed N_2 conversion rate of 25% to generate Ca_3N_2 and H_2. The unreacted N_2 and the generated H_2 are separated from the chemical loop using an ideal separator block, SEP2, shown in Figure 2.b. The Ca_3N_2 generated in CLAS1 was reacted with H_2 from the feed in CLAS2 at a fixed H_2 con-

Table 1: Thermodynamic and kinetic inputs for the Ru/C Catalyst system (Tripodi et al., 2021)

Inputs to Aspen Plus LHHW kinetic formula Eq.4				
Kinetic constant	E_a (kcal mol^{-1})		k_0(kmol s^{-1}kg^{-1} $_{cat}$)	
	23.0		426.0	
Rate expression				
Exponents	N_2		H_2	NH_3
Forward term (v_r)	0.5		0.375	-0.25
Reverse term (v_p)	0		-1.125	0.75
Coefficients	A	B	C	D
Term 1 (K_{for})	-7.19	0	0	0
Term 2 (K_{rev})	-1.876	-4609	2.69	1.27×10^{-4}
Adsorption term				
Exponents	N_2		H_2	NH_3
Term 1 (v_i)	0		0	0
Term 2 (v_i)	0		0.3	0
Term 3 (v_i)	0		0	0.2
Coefficients	A	B	C	D
Term 1 (K_i)	0	0	0	0
Term 2 (K_i)	-10.3	4529	0	0
Term 3 (K_i)	-6.48	3523	0	0

version rate of 25% to generate ammonia. Lastly, ammonia and hydrogen from CLAS2 were separated from the chemical loop using SEP3 shown in Figure 2.b, and the solids, CaH_2 and Ca_3N_2, were recycled to CLAS1 to complete the chemical loop. CaH_2 and Ca_3N_2, were modeled in Aspen Plus as conventional solids, while the gasses, N_2, H_2, and NH_3, were modeled as conventional components. The reactors CLAS1 and CLAS2 were modeled as adiabatic reactors with a negligible pressure drop. Tear streams were used to solve the closed chemical loop in Aspen Plus, to produce 150 tNH_3/day from the feed stream.

The Fe-based catalyst kinetics are described by Eq. 1 (Morud and Skogestad, 1998):

$$r_{\mathrm{Fe}} = \frac{2f}{\rho_{\mathrm{cat}}}\left(k_{\mathrm{Fe}}\frac{P_{\mathrm{N_2}}P_{\mathrm{H_2}}^{1.5}}{P_{\mathrm{NH_3}}} - k_{\text{-Fe}}\frac{P_{\mathrm{NH_3}}}{P_{\mathrm{H_2}}^{1.5}}\right), \tag{1}$$

where f is the catalytic activity factor equal to 4.75 (Morud and Skogestad, 1998), ρ_{cat} is the catalyst bulk density equal to 2,200 kg/m^3, P_i is the partial pressure of component i in bar, and k_1 and k_{-1} are the kinetic constants for the forward and reverse paths of R1, respectively as:

$$k_{\mathrm{Fe}} = 1.79\times 10^4 e^{(-87{,}090/RT)}, \tag{2}$$

$$k_{\text{-Fe}} = 2.75\times 10^{16} e^{(-198{,}464/RT)}, \tag{3}$$

where R is the universal gas constant, and T is the gas temperature in K. The Ru/C catalyst rate equation was modeled using the built in LHHW formula in Aspen Plus described by Eq. 4:

$$r = \frac{\left(\mathrm{k_0}e^{-\frac{Ea}{RT}}\right)\left(\mathrm{K}_{for}\prod_r f_r^{v_r} - \mathrm{K}_{rev}\prod_p f_p^{v_p}\right)}{\left(\sum_i K_i\prod_i f_i^{v_i}\right)^e}. \tag{4}$$

Table 1 summarizes the inputs to Eq. 4 for the Ru/C catalyst.

To validate the kinetic models, the transient performance of the Fe reactor and the steady state performance of the Ru/C reactor were compared to their respective references. The Fe-based reactor model studied in Morud and Skogestad (1998) was replicated in Aspen Plus and converted to a flow driven dynamic model in Aspen Dynamics. Thereafter, a disturbance was introduced to the reactor feed by simulating a drop in feed pressure from 20 MPa to 17 MPa for 0.3 h, then a subsequent pressure drop to 15 MPa for 1 h, before restoring the feed pressure to 20 MPa (Morud and Skogestad, 1998). For the Ru/C-based reactor, the reactor model in Yoshida et al. (2021) was replicated in Aspen Plus, and the outlet ammonia composition of each reactor bed was validated.

The disturbance tests were performed in Aspen Dynamics by subjecting each reactor model to a disturbance in feed temperature, pressure, and flow rate. Each process variable was subjected to a pulse test of $\pm$ 10% for one hour. The reactor response was measured at the outlet of the third reactor bed for the Fe and Ru/C reactor models, and at the outlet of the CLAS2 reactor for the chemical looping reactor model. To assess the overall stability of the reactor, non-stable reactor responses were categorized as faults and enumerated.

Table 2: Ru/C reactor validation of ammonia mole percentage at each catalyst bed outlet.

Catalyst Bed	I	II	III
Ru/C *(this work)*	9.87	14.7	18.0
Ru/C (Yoshida et al., 2021)	9.93	15.3	17.2

Results

Three small-scale ammonia synthesis reactors were modeled and subjected to the series of disturbance tests discussed earlier to assess their stability. The results of this work are presented in detail in this section.

The kinetic models were validated successfully and showed good agreement. The Ru/C kinetic model was validated against the reactor model in Yoshida et al. (2021) by comparing the ammonia mole fraction at the outlet of each reactor bed. The validation results are shown in Table 2, showing good agreement with the reference model (Yoshida et al., 2021). The minor difference in validation results can be attributed to the simplified LHHW kinetic formula used in this work, as opposed to the detailed FORTRAN subroutine used in Yoshida et al. (2021). The transient performance of the Fe-based reactor model was validated against its reference model in Morud and Skogestad (1998), shown in Figure 3. In response to the disturbance in feed pressure at time 0 h, the reactor outlet temperature oscillated $\pm$200 $^{\mathrm{o}}$C until the pressure was restored at time 2 h, shown in Figure 3.a. The Fe-based reactor model response had a similar behavior to its reference model shown in Figure 3.b., which oscillated $\pm$200 $^{\mathrm{o}}$C during the pressure disturbance.

Despite being fed with the same feed stream, the reactor models produced varying amounts of ammonia. The Fe-based reactor produced the most ammonia, 171 tNH_3/day at an outlet composition of 16.3 mol.% NH_3, operating through a temperature range of 361 - 520 $^{\mathrm{o}}$C. The Ru/C reactor model

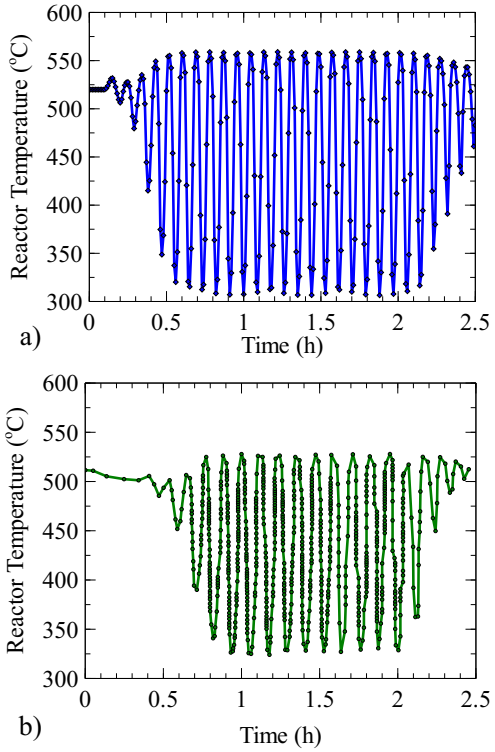

Figure 3: Fe-based reactor transient response validation for: a) this work and b) the reference model (Morud and Skogestad, 1998).

synthesized 161 tNH_3/day at an outlet composition of 15.2 mol.% NH_3 operating through a temperature range of 352 - 508 °C. On the other hand, the CLAS reactor model operated in a temperature range of 300 - 337 °C and produced 152 tNH_3/day at an outlet composition of 19 mol.% NH_3.

The transient performance of the three reactor models was then compared through a series of disturbance tests summarized in Table 3. While the Ru/C and chemical looping reactor models remained stable throughout all disturbance tests, the Fe-based reactor model exhibited three faults. These faults of the Fe-based reactor model are highlighted in Figure 4, which shows the reactor models response to a 10% decrease in feed temperature and pressure, and a 10% increase in flow rate in Figure 4.a, b, and c, respectively. In response to the 10% decrease in feed temperature shown in Figure 4.a, the Ru/C and CLAS reactors remained stable, while the Fe-based reactor model exhibited a fault in operations. The decrease in temperature at time 0.5 h, caused the Fe-based reactor to cease ammonia production resulting in a rapid decrease in temperature. Then at time 1.5 h, the feed temperature was restored triggering an exponential increase in ammonia production and reactor temperature resulting in the runaway conditions shown in Figure 4.a. In response to the 10% decrease in pressure shown in Figure 4.b, the Ru/C and CLAS reactors remained stable, while the Fe-based reactor model exhibited another fault. The decrease in pressure at time 0.5 h, caused the Fe-based reactor to cease ammonia production resulting in a rapid decrease in temperature to the feed temperature of 250 °C. At the lowered pressure in the Fe-based reactor model, the forward reaction of R1 is no longer thermodynamically favored and the production of ammonia ceases. Lastly, in response to a 10% increase in flow rate at time 0.5 h, the Ru/C reactor model maintained stable operation during the disturbance and operated at a temperature 2% lower than the original temperature, shown in Figure 4.c. The chemical looping reactor model remained stable with no changes to its operating temperature shown in Figure 4.c. On the other hand, the Fe-based reactor model exhibited major oscillations in reactor temperature, with temperatures fluctuating ±200 °C.

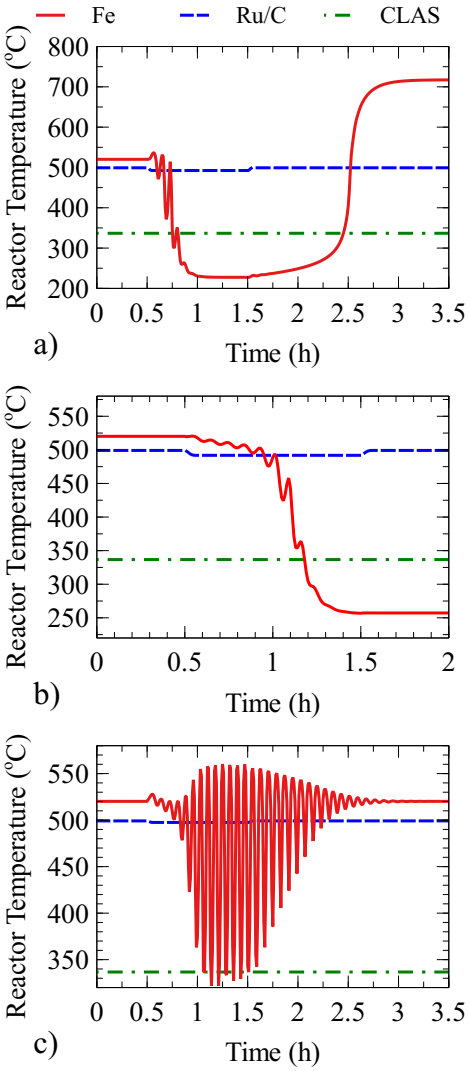

Figure 4: Ammonia reactor response to a: a) 10% decrease in feed temperature, b) 10% decrease in feed pressure, and c) 10% increase in feed flow rate.

Discussion

We presented two solutions to stabilize small-scale ammonia production through improved engineering design and intensification. Prior to this study the only solution to stabilizing ammonia production was through advanced control schemes. However, we showed that by operating at a lower tempera-

Table 3: Reactor response to each disturbance test where "-" denotes a stable response and "X" denotes a fault.

Test		Fe	Ru/C	CLAS
Temperature	+ 10 %	-	-	-
(^{o}C)	- 10 %	X	-	-
Pressure	+ 10 %	-	-	-
(MPa)	- 10%	X	-	-
Molar Flow Rate	+ 10 %	X	-	-
(kmol/h)	- 10%	-	-	-

ture, or by decoupling the HB reaction, ammonia production can be stabilized.

In this work, the conventional Fe-based reactor exhibited numerous faults that can have detrimental effects on plant economics, equipment longevity, and operator safety. The reactor exhibited runaway conditions, shown in Figure 3.a, when the disturbance momentarily interrupted the forward exothermic reaction of R1, causing a gradual decrease in reactor temperature followed by an exponential increase in reactor temperature as the reaction is triggered again. Then reactor extinction occurred when the disturbance completely stopped the forward reaction as shown in Figure 3.b, resulting in a gradual decrease of reactor temperature. In this case, the reduced pressure disturbed the equilibrium of R1 to no longer favor ammonia production. Then the reactor exhibited limit cycle behavior when the disturbance caused the equilibrium of R1 to be disturbed causing instabilities. Limit cycle behavior occurs when a disturbance perturbs the equilibrium of R1 to a point where the reactor cannot restore the equilibrium without large swings in reactor conditions as shown in Figure 3.c. This results in the reverse endothermic reaction competing with the forward exothermic reaction, oscillating reactor temperatures until the disturbance is removed or the equilibrium is restored.

The Ru/C reactor was proposed to enable efficient low-temperature ammonia production where ammonia synthesis is more favored thermodynamically. However, the reactor operated at relatively high temperatures for its application, about 12 ^{o}C lower than the Fe-based reactor on average, and remained stable. In practice, the Ru/C reactor should operate at temperatures below 500 ^{o}C to ensure the longevity of the catalyst and prevent methanation of its carbon-based support (Rossetti et al., 2005). The difference in reactor stability between the Ru/C and Fe-based reactor at comparable temperatures, may be explained by an investigation into their catalytic activity for ammonia decomposition at these temperatures and conditions. However, that investigation is outside the scope of this work. The Ru/C-based reactor provides a simple solution for stabilizing ammonia synthesis since it can be easily implemented into existing HB reactor configurations. Despite extensive research into Ru-based catalysts for low-temperature ammonia synthesis, the high cost of ruthenium makes them prohibitively expensive. However, a recent study showed that at small-scales, the Ru/C system becomes economically competitive with the Fe-based reactor systems (Yoshida et al., 2021). Therefore, Ru/C catalysts should be investigated further for use in small-scale ammonia production systems, since they may be more stable than the conventional Fe-based reactors.

Chemical looping ammonia synthesis is an emerging alternative ammonia synthesis route capable of decoupling the HB process and avoiding its associated instabilities. Instead of synthesizing ammonia in one step, where the forward and reverse reactions of R1 compete for dynamic equilibrium, chemical loops synthesize ammonia in two or more steps preventing this competition and instability. While this work shows how this can be achieved conceptually, further research and development is needed to create a complete solution for small-scale deployment. The chemical looping reactors were modeled as simplified stoichiometric reactors with a fixed fractional conversion. As a result, disturbances in the feed gas flow rate had no effect on the transient response of the reactor model. A comprehensive reactor model, yet to be published, is necessary to simulate the gas-solid interactions integral to the chemical looping reactor operation. Further, the chemical looping reactor requires separation equipment to direct gasses to specific reactors or purge streams. In this work, these separators were simulated with simplified models, however the optimal separation equipment for this task has yet to be studied.

Conclusion

The instabilities of a conventional Haber-Bosch reactor pose unique challenges for small-scale renewable energy storage applications. Stabilizing Haber-Bosch reactors generally involves advanced control schemes that can be difficult to implement at small scale where time scales are faster. In this work, a Ru/C-based reactor and a CaH_2/Ca_3N_2 chemical looping reactor were proposed to stabilize small-scale ammonia production through engineering design considerations. The stability of the proposed alternatives was compared to the stability of a conventional Fe-based Haber-Bosch reactor in Aspen Dynamics, subjected to disturbances in feed temperature, pressure, and flow rate. While the Fe-based reactor exhibited three unique faults in response to the six disturbance tests conducted, the process alternatives exhibited no faults. The Ru/C-based reactor provides a simple solution to stabilizing small-scale production because it only requires a change of catalyst in the conventional Haber-Bosch reactor configuration. On the other hand, the chemical looping reactor solution requires additional separation equipment and further reactor development. In this work we put forth two solutions to stabilize small-scale ammonia production to potentially enable robust intermittent operation for renewable energy storage projects.

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