#### **Supporting Information**

Performance of a Small-Scale Haber Process: A Techno-Economic Analysis Bosong Lin,<sup>†</sup> Theodore Wiesner,<sup>†</sup> Mahdi Malmali<sup>†\*</sup> † Department of Chemical Engineering, 807 Canton Ave, Texas Tech University, Lubbock, Texas 79409, United States \*Corresponding author email address: <u>mahdi.malmali@ttu.edu</u>; Tel.: (806) 834-8706; Fax: (806) 742-3552

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### Nomenclature

#### Abbreviations

CW	Cooling water
Q <sub>ch</sub>	Quench
RFG	Refrigerant
RXN-ABS	Reaction-absorption
RXN-CON	Reaction-condensation

## **Roman symbols**

$a_k$	Gas activity
$A_k$	Coefficient A of component k
b	Isotherm coefficient
$B_k$	Coefficient <i>B</i> of component <i>k</i>
C <sub>k</sub>	Molar concentration of species k in the bulk gas phase [mol/m <sup>3</sup> ]
$C_k$	Coefficient <i>C</i> of component <i>k</i>
$D_b$	Absorber diameter [m]
$D_{m,k}$	Molecular diffusion coefficient of component $k \text{ [m}^2/\text{s]}$
$D_{kn,k}$	Knudsen diffusion coefficient [m <sup>2</sup> /s]
$E_{z,k}$	Axial dispersion mass transfer coefficient of component $k \text{ [m}^2/\text{s]}$
F <sub>i</sub>	Inlet flow rate [kmol/h]
$J_{abs,K}$	Mass transfer rate due to absorption of component $k \text{ [mol/m}^3 \text{ s]}$
<i>k</i> <sub>2</sub>	Reverse reaction coefficient
$k_{f,k}$	Film resistance coefficient [m/s]
<i>K</i> <sub>3</sub>	Adsorption equilibrium constant
K <sub>a</sub>	Equilibrium constant
$K_{pk}$	Macro diffusion coefficient [m <sup>2</sup> /s]
L	Reactor bed length [m]
$M_k$	Molecular weight of component k [kg/mol]
$MTC_k$	LDF rate constant of component $k$ [1/s]
Р	Reaction pressure [bar]

$r_p$	Particle diameter [m]
r <sub>Pore</sub>	Pore radius [m]
R	Gas constant [J/K mol]
$R_{NH_3}$	Rate of $NH_3$ production [kmol/m <sup>3</sup> h]
Т	Reaction temperature [°C]
$v_g$	Gas velocity in axial direction [m/s]
$V_k$	Diffusion volume of component $k$
W <sub>k</sub>	Absorbent capacity of component k [mol/kg]
$w_k^*$	Equilibrium capacity of component $k \text{ [mol/kg]}$
W <sub>max</sub>	Maximum capacity [mol/kg]
$x_k$	Mole fraction of component $k$
X	Conversion
$y_{i,NH_3}$	Inlet mole fraction of $NH_3$
$y_{o,NH_3}$	Outlet mole fraction of $NH_3$
Ζ	Axial coordinate of the absorber column

## Greek symbols

$\varepsilon_i$	Interparticle voidage
$\varepsilon_p$	Intraparticle voidage
$\varepsilon_{abs}$	Total absorber column voidage
ξ	Extent of reaction
$\mu_g$	Gas dynamic viscosity [kg/m s]
$ au_p$	Tortuosity of the absorbent particle
τ	Tortuosity factor
$ ho_g$	Gas density [kg/m <sup>3</sup> ]
$ ho_s$	Absorbent density [kg/m <sup>3</sup> ]
$ ho_{abs}$	Absorber column density [kg/m <sup>3</sup> ]
$\psi$	Particle shape factor
Subscripts and	superscripts

abs A	Absorber column
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g	Gas
i	Interparticle
k	Component k
p	Particle
pore	Absorbent partible pore
max	Maximum

#### 1 Simulation

#### 1.1 Ammonia Synthesis Kinetics

To model the synthesis process, ammonia synthesis kinetics described by Nielsen et al. is adopted as shown in Table S1:<sup>1</sup>

Table	<i>S1</i> .	Ammonia	synthesis	kinetics	embedded	in the	reactor	of RXN	-CON	and RXN-A	ABS.
			-					./			

Description	Equation	No.	Reference
Rate of NH <sub>3</sub> production	$R_{NH_3} = \left[\frac{k_2\left(a_N K_a^2 - \frac{a_A^2}{a_H^3}\right)}{\left(1 + K_3 \frac{a_A}{a_H^\omega}\right)^{2\alpha}}\right] \frac{kgmole}{m^3 hr}$	(S1)	1
Equilibrium constant	$log_{10}K_a$ = -2.691122log_{10}(T) - 5.519265 × 10 <sup>-5</sup> T + 1.848863 × 10 <sup>-7</sup> T <sup>2</sup> + $\frac{2001.6}{T}$ + 2.6899	(S2)	2
Reaction rate constant	$k_2 = 3.945 \times 10^{10} \exp\left(-\frac{5622}{T}\right)$	(S3)	1
Adsorption equilibrium constant	$K_3 = 2.94 \times 10^{-4} \exp\left(\frac{12104}{T}\right)$	(S4)	1
Gas model	RKS-BM	(S5)	3
Gas activity	$a_{k}$ $= x_{k} P \exp\left[\frac{P}{RT}\left(B_{k} - \frac{A_{k}}{RT} - \frac{C_{k}}{T^{3}} + \left(A_{k}^{0.5} - \sum x_{k}A_{k}^{0.5}\right)^{2}\right)\right]$	(S6)	1

The values of  $A_k$ ,  $B_k$ , and  $C_k$  can be found in Table S2<sup>1</sup>. The reaction kinetics are implemented by a user Fortran subroutine.  $\omega = 1.523$  and  $\alpha = 0.654$  are used. Note that R = 0.0826 L·atm·K<sup>-1</sup>·mol<sup>-1</sup>, gas constant; *P*, the pressure in atm; *T*, the temperature in K.

Component, i	A <sub>k</sub>	B <sub>k</sub>	$C_k$
H <sub>2</sub>	1.975×10 <sup>-1</sup>	2.096×10 <sup>-2</sup>	$5.04 \times 10^{2}$
N <sub>2</sub>	1.3445	5.046×10 <sup>-2</sup>	$4.20 \times 10^{4}$
NH <sub>3</sub>	2.393	3.415×10 <sup>-2</sup>	$4.77 \times 10^{6}$

Table S2. Values for A, B, C for evaluating the activities for synthesis kinetics

As displayed in Figure S1, the equilibrium conversion was calculated based on Nielsen's kinetics above-mentioned, which is a function of temperature and pressure.



*Figure S1. Equilibrium conversion vs temperature. (RXN-CON at P=150 bar, RXN-ABS at 20 bar)* 

## **1.2** Process Design and Simulation

System/Component	Unit	<b>RXN-CON (110-150 bar)</b>	RXN-ABS (20-35 bar)			
Converter R-101						
Bed 1	m	0.5 (D), 0.5 (L)	0.5 (D), 1 (L)			
Bed 2	m	0.5 (D), 0.7 (L)	0.5 (D), 2 (L)			
Bed 3	m	0.5 (D), 1 (L)	0.5 (D), 3 (L)			
Total length	m	2.2	6			
Mainstream fraction	%	0.6	0.6			
Quench fraction	%	0.4	0.4			
Inlet temperature	°C	350	350			
Catalyst density	kg/m3	2200	2200			
Void fraction	%	05	0.5			
	Turbon	nachinery (C-101, C-102)				
Isentropic efficiencies	%	70	70			
Mechanical efficiencies	%	95	95			
		Cooling Water				
Inlet temperature	°C	20	20			
Outlet temperature	°C	35	35			
Pressure	bar	5	5			
Pump efficiency	%	85	85			
		Refrigerant				
Temperature	°C	-50	/			
	Absorbers					
Absorption	°C	/	150			
Desorption	°C	/	300			
No of absorber columns	/	/	3			

Table S3. Design specifications for RXN-CON and RXN-ABS processes

Results of ammonia mole fraction along the bed (see Figure S2) were obtained from simulation. In the RXN-CON process (Figure S2a), the gas mixture that enters the converter contains 1.5 mol% of ammonia because the phase-changing condensation is not capable of separating 100% of ammonia. On the other hand, the ammonia mole fraction in the gas mixture entering the converter in the RXN-ABS process (Figure S2b) is close to zero because the absorber column almost completely removes the ammonia from the recycle gas until it breaks through. As reactants enter the three-bed ammonia converter, ammonia mole fraction increases due to the formation of ammonia. At the end of the first and second beds, ammonia mole fraction decreases because the streams leaving the bed were diluted by the quench streams. The highest ammonia mole fraction in RXN-CON is about 2.5 times higher than that of RXN-ABS because of higher operating pressure in RXN-CON. Then these results as displayed in Figure S2 were converted into the conversion of nitrogen.



*Figure S2.* Ammonia mole fraction along the bed in RXN-CON (a) and RXN-ABS (b).

Table S4. Converting ammonia mole fraction to conversion based on simulation results

Description	Equation	No.
Outlet mole fraction of $NH_3$	$y_{o,NH_3} = \frac{F_i y_{i,NH_3} + 2\xi}{F_i - 2\xi}$	(S7)
Extent of reaction	$\xi = \frac{F_i(y_{o,NH_3} - y_{i,NH_3})}{2(1 + y_{o,NH_3})}$	(S8)
Conversion	$X = \frac{\xi}{F_i y_{i,N_2}} = \frac{2(y_{o,NH_3} - y_{i,NH_3})}{(1 + y_{o,NH_3})(1 - y_{o,NH_3})}$	(S9)

Stream	1	2	3	4	5	6	7
Temperature (°C)	25	25	24.7194	531.492	105.084	109.307	127.682
Pressure (bar)	10	10	9.5	150	146	150	149.5
Molar vapor fraction	1	1	1	1	1	1	1
Mole flows (kmol/h)	214.298	71.3942	285.693	285.693	1172.93	1172.93	1172.92
H <sub>2</sub> (kmol/h)	214.298	0	214.298	214.298	892.098	892.098	892.084
N <sub>2</sub> (kmol/h)	0	71.3942	71.3942	71.3942	267.606	267.606	267.617
NH <sub>3</sub> (kmol/h)	0	0	0	0	13.2228	13.2228	13.2225
Water (kmol/h)	0	0	0	0	0	0	0
Mole fractions							
$H_2$	1	0	0.750101	0.750101	0.760574	0.760574	0.760564
$N_2$	0	1	0.249899	0.249899	0.228152	0.228152	0.228163
NH <sub>3</sub>	0	0	0	0	0.0112734	0.0112734	0.0112731
Water	0	0	0	0	0	0	0
Mass flows (kg/h)	432	2000	2432	2432	9520.13	9520.13	9520.42
H <sub>2</sub> (kg/h)	432	0	432	432	1798.36	1798.36	1798.33
N <sub>2</sub> (kg/h)	0	2000	2000	2000	7496.58	7496.58	7496.9
NH <sub>3</sub> (kg/h)	0	0	0	0	225.192	225.192	225.187
Water (kg/h)	0	0	0	0	0	0	0
Mass fractions							
$H_2$	1	0	0.177632	0.177632	0.188901	0.188901	0.188892
$N_2$	0	1	0.822368	0.822368	0.787445	0.787445	0.787455
NH <sub>3</sub>	0	0	0	0	0.0236543	0.0236543	0.023653
Water	0	0	0	0	0	0	0

**Table S5.** Stream table for the operating condition for the RXN-CON process.

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Stream	8 (Qch-1)	9 (Qch-2)	9 (Qch-3)	10	11	12	13
Temperature (°C)	127.682	127.682	127.682	350	479.185	340.653	321.292
Pressure (bar)	149.5	149.5	149.5	149	147.5	147	146.5
Molar vapor fraction	1	1	1	1	1	1	1
Mole flows (kmol/h)	703.754	234.585	234.585	703.752	1030.32	1030.32	1030.32
H <sub>2</sub> (kmol/h)	535.25	178.417	178.417	535.248	678.175	678.175	678.175
N <sub>2</sub> (kmol/h)	160.57	53.5235	53.5235	160.57	196.315	196.315	196.315
NH <sub>3</sub> (kmol/h)	7.9335	2.6445	2.6445	7.93329	155.827	155.827	155.827
Water (kmol/h)	0	0	0	0	0	0	0
Mole fractions							
$H_2$	0.760564	0.760564	0.760564	0.760564	0.65822	0.65822	0.65822
$N_2$	0.228163	0.228163	0.228163	0.228163	0.190538	0.190538	0.190538
NH <sub>3</sub>	0.0112731	0.0112731	0.0112731	0.0112729	0.151242	0.151242	0.151242
Water	0	0	0	0	0	0	0
Mass flows (kg/h)	5712.25	1904.08	1904.08	5712.23	9520.4	9520.4	9520.4
$H_2 (kg/h)$	1079	359.667	359.667	1079	1367.12	1367.12	1367.12
N <sub>2</sub> (kg/h)	4498.14	1499.38	1499.38	4498.13	5499.46	5499.46	5499.46
NH <sub>3</sub> (kg/h)	135.112	45.0373	45.0373	135.108	2653.82	2653.82	2653.82
Water (kg/h)	0	0	0	0	0	0	0
Mass fractions							
$H_2$	0.188892	0.188892	0.188892	0.188892	0.143599	0.143599	0.143599
$N_2$	0.787455	0.787455	0.787455	0.787455	0.57765	0.57765	0.57765
NH <sub>3</sub>	0.023653	0.023653	0.023653	0.0236525	0.278751	0.278751	0.278751
Water	0	0	0	0	0	0	0

### Continued

Stream	14	15	16	17	CW-In	CW-Out	RFG-In	<b>RFG-Out</b>
Temperature (°C)	40	40	-29.121	-29.121	20	30.896	-50	-32.6067
Pressure (bar)	146	146	146	146	5	4.5	1.01325	1.01325
Molar vapor fraction	1	1	1	0	0	0	0	1
Mole flows (kmol/h)	1044.84	1030.32	887.24	143.076	9991.52	9991.52	206.392	206.392
H <sub>2</sub> (kmol/h)	669.734	678.175	677.814	0.361061	0	0	0	0
N <sub>2</sub> (kmol/h)	214.347	196.315	196.204	0.111256	0	0	0	0
NH <sub>3</sub> (kmol/h)	160.756	155.827	13.2228	142.604	0	0	206.392	206.392
Water (kmol/h)	0	0	0	0	9991.52	9991.52	0	0
Mole fractions								
$H_2$	0.640994	0.65822	0.763958	0.00252355	0	0	0	0
$N_2$	0.205149	0.190538	0.221139	0.000777601	0	0	0	0
NH <sub>3</sub>	0.153858	0.151242	0.0149032	0.996699	0	0	1	1
Water	0	0	0	0	1	1	0	0
Mass flows (kg/h)	10092.5	9520.4	7087.93	2432.47	180000	180000	3514.97	3514.97
$H_2$ (kg/h)	1350.1	1367.12	1366.39	0.727855	0	0	0	0
N <sub>2</sub> (kg/h)	6004.6	5499.46	5496.34	3.11668	0	0	0	0
NH <sub>3</sub> (kg/h)	2737.77	2653.82	225.191	2428.63	0	0	3514.97	3514.97
Water (kg/h)	0	0	0	0	180000	180000	0	0
Mass fractions								
$H_2$	0.133773	0.143599	0.192777	0.000299224	0	0	0	0
$N_2$	0.594958	0.57765	0.775452	0.00128128	0	0	0	0
NH <sub>3</sub>	0.271268	0.278751	0.0317711	0.998419	0	0	1	1
Water	0	0	0	0	1	1	0	0

Stream	1	2	3	4	5	6	7	8 (Q <sub>ch</sub> -1)
Temperature (°C)	25	25	24.7194	125.914	148.317	166.638	290	290
Pressure (bar)	10	10	9.5	20	18	20	19.9	19.9
Molar vapor fraction	1	1	1	1	1	1	1	1
Mole flows (kmol/h)	214.298	71.3942	285.693	285.693	4076.29	4076.29	4076.29	2445.78
H <sub>2</sub> (kmol/h)	214.298	0	214.298	214.298	3057.25	3057.25	3057.25	1834.35
N <sub>2</sub> (kmol/h)	0	71.3942	71.3942	71.3942	1019.04	1019.04	1019.04	611.427
NH <sub>3</sub> (kmol/h)	0	0	0	0	0	0	0	0
Water (kmol/h)	0	0	0	0	0	0	0	0
Mole fractions								
$H_2$	1	0	0.750101	0.750101	0.750007	0.750007	0.750007	0.750007
$N_2$	0	1	0.249899	0.249899	0.249993	0.249993	0.249993	0.249993
NH <sub>3</sub>	0	0	0	0	0	0	0	0
Water	0	0	0	0	0	0	0	0
Mass flows (kg/h)	432	2000	2432	2432	34710	34710	34710	20826
H <sub>2</sub> (kg/h)	432	0	432	432	6163.05	6163.05	6163.05	3697.83
N <sub>2</sub> (kg/h)	0	2000	2000	2000	28547	28547	28547	17128.2
NH <sub>3</sub> (kg/h)	0	0	0	0	0	0	0	0
Water (kg/h)	0	0	0	0	0	0	0	0
Mass fractions								
$H_2$	1	0	0.177632	0.177632	0.177558	0.177558	0.177558	0.177558
$N_2$	0	1	0.822368	0.822368	0.822442	0.822442	0.822442	0.822442
NH <sub>3</sub>	0	0	0	0	0	0	0	0
Water	0	0	0	0	0	0	0	0

**Table S6.** Stream table for the operating condition for the RXN-ABS process.

### Continued

Stream	9 (Q <sub>ch</sub> -2)	9 (Q <sub>ch</sub> -3)	10	11	12	13	14	15
Temperature (°C)	290	290	350	387.847	351.419	343.459	218.108	150
Pressure (bar)	19.9	19.9	19.8	18.3	18.2	18.1	18	18
Molar vapor fraction	1	1	1	1	1	1	1	1
Mole flows (kmol/h)	815.259	815.259	2445.78	3933.68	3933.68	3933.68	3933.33	3933.33
H <sub>2</sub> (kmol/h)	611.45	611.45	1834.35	2843.33	2843.33	2843.33	2843.07	2843.07
N <sub>2</sub> (kmol/h)	203.809	203.809	611.427	947.737	947.737	947.737	947.652	947.652
NH <sub>3</sub> (kmol/h)	0	0	0	142.614	142.614	142.614	142.605	142.605
Water (kmol/h)	0	0	0	0	0	0	0	0
Mole fractions								
$H_2$	0.750007	0.750007	0.750007	0.722816	0.722816	0.722816	0.722816	0.722816
$N_2$	0.249993	0.249993	0.249993	0.240929	0.240929	0.240929	0.240929	0.240929
NH <sub>3</sub>	0	0	0	0.036255	0.036255	0.036255	0.036256	0.036256
Water	0	0	0	0	0	0	0	0
Mass flows (kg/h)	6942	6942	20826	34710	34710	34710	34707	34707
$H_2 (kg/h)$	1232.61	1232.61	3697.83	5731.81	5731.81	5731.81	5731.29	5731.29
N <sub>2</sub> (kg/h)	5709.39	5709.39	17128.2	26549.4	26549.4	26549.4	26547	26547
NH <sub>3</sub> (kg/h)	0	0	0	2428.79	2428.79	2428.79	2428.64	2428.64
Water (kg/h)	0	0	0	0	0	0	0	0
Mass fractions								
$H_2$	0.177558	0.177558	0.177558	0.165134	0.165134	0.165134	0.165134	0.165134
$N_2$	0.822442	0.822442	0.822442	0.764892	0.764892	0.764892	0.764891	0.764891
NH <sub>3</sub>	0	0	0	0.069974	0.069974	0.069974	0.069976	0.069976
Water	0	0	0	0	0	0	0	0

### Continued

Stream	16	Product	CW2-In	CW2-Out	CW1-In	CW1-Out
Temperature (°C)	150	36	20	35.0005	20	35
Pressure (bar)	18	15.4	1.01325	1.01325	1.01325	0.91325
Molar vapor fraction	1	0.029844	0	0	0	0
Mole flows (kmol/h)	3790.6	142.979	3346.86	3346.86	6142.62	6142.62
H <sub>2</sub> (kmol/h)	2842.95	0.280076	0	0	0	0
N <sub>2</sub> (kmol/h)	947.65	0.094073	0	0	0	0
NH <sub>3</sub> (kmol/h)	0	142.605	0	0	0	0
Water (kmol/h)	0	0	3346.86	3346.86	6142.62	6142.62
Mole fractions						
$H_2$	0.75	0.001959	0	0	0	0
$N_2$	0.25	0.000658	0	0	0	0
NH <sub>3</sub>	0	0.997383	0	0	0	0
Water	0	0	1	1	1	1
Mass flows (kg/h)	32278	2431.84	60294.6	60294.6	110661	110661
H <sub>2</sub> (kg/h)	5731.05	0.5646	0	0	0	0
N <sub>2</sub> (kg/h)	26547	2.6353	0	0	0	0
NH <sub>3</sub> (kg/h)	0	2428.64	0	0	0	0
Water (kg/h)	0	0	60294.6	60294.6	110661	110661
Mass fractions						
$H_2$	0.177553	0.000232	0	0	0	0
$N_2$	0.822447	0.001084	0	0	0	0
NH <sub>3</sub>	0	0.998684	0	0	0	0
Water	0	0	1	1	1	1

Note: the stream table was generated from the steady state model, with the absorber column desorbing at 300 C. The integration between the absorber and reactor is not considered in the calculation of the temperature for S12 and S13.

## 1.3 Dynamic Modeling of an Absorption Column

Table S7. Summary of the equations of the dynamic absorption Column model.<sup>4</sup>

Description	Equation	No.
Mass balance for the	$-\varepsilon_i E_{zk} \frac{\partial^2 c_k}{\partial z^2} + \frac{\partial (v_g c_k)}{\partial z} + \varepsilon_B \frac{\partial c_k}{\partial t} + (1 - \varepsilon_i) J_{abs} = 0$	(S10)
gas phase		
Mass transfer due to	$J_{abs} = \rho_s \frac{\partial W_k}{\partial t}$	(S11)
absorption		
Kinetic model	$\frac{\partial w_k}{\partial t} = MTC_k(w_k^* - w_k)$	(S12)
Linear driving force	dt kan k	
Equilibrium capacity	$w_k^* = w_{max} \frac{bp_k}{1 + bp_k}$	(S13)
Gas model	RKS-BM	(S14)
Momentum balance:	$\frac{dp}{dp}$	(S15)
Ergun equation	dz	
	$=\frac{1.5\times10^{-3}(1-\varepsilon_{i})^{2}\mu v_{g}}{(2r_{p}\psi)^{2}\varepsilon_{i}^{3}}+\frac{1.75\times10^{-5}M\rho_{g}(1-\varepsilon_{i})}{2r_{p}\psi\varepsilon_{i}^{3}}v_{g}^{2}$	
Dispersion	$E_{gk} = 0.73D_{mk} + \frac{v_g r_p}{1}$	(S16)
coefficient	$\varepsilon_i \left( 1 + 9.49 \frac{\varepsilon_i D_{mk}}{2 v_g r_p} \right)$	
Effective molecular	$10^{-3}T^{1.73}\left(\frac{1}{1}+\frac{1}{1}\right)^{1/2}$	(S17)
diffusion coefficient	$D_{mk} = \frac{10^{-1} (M_k + M_m)}{P[(\Sigma V_k)^{1/3} + (\Sigma V_m)^{1/3}]^2}$	
Effective mass	$1 - r_p - r_p^2$	(S18)
transfer coefficient	$\overline{MTC_k} = \frac{1}{2k_{fk}} + \frac{1}{15\varepsilon_p K_{pk}}$	
Film resistance	$k_{cl} = Sh_l \frac{D_{mk}}{dl}$	(S19)
coefficient	$r_{fk} = 5r_k 2r_p$	
Macro diffusion	1 (1 + 1)	(S20)
coefficient	$\overline{K_{pk}} = l \left( \frac{1}{D_{kn,k}} + \frac{1}{D_{mk}} \right)$	
Knudsen diffusion	$D = 0.7\pi \left(\frac{T}{T}\right)^{0.5}$	(S21)
coefficient	$D_{kn,k} = 9/r_{Pore} \left( \frac{M_k}{M_k} \right)$	
Total column	$\varepsilon_B = \varepsilon_i + (1 - \varepsilon_i)\varepsilon_p$	(S22)
voidage		

Reynolds number	$Re = \frac{v_g d_p \rho_g}{\mu_g}$	(\$23)
Schmidt number	$Sc_k = \frac{\mu_g D_m}{\rho_g}$	(824)
Sherwood number	$Sh_k = 2 + 1.1Sc^{1/3}Re^{0.6}$	(S25)
Tortuosity factor	$\tau = \tau_p + 1.5(1 - \varepsilon_p)$	(S26)
Initial conditions	$c_{k,i} = 0; w_{k,i} = 0; i = 0, 1, 2, \cdots$	(S27)
Boundary conditions	$c_{k,0} = c_{k,feed}; v_g = v_{g,feed}; P = P_{feed}$	(S28)

The mathematical model is solved by the finite difference method with initial conditions and boundary conditions. The model is then validated by experimental data of breakthrough time for the selected absorbent.

### **1.4** Absorber Specifications



*Figure S3.* Breakthrough time of ammonia absorption with MgBr2-Si at 100 °C, 200 °C, and 300 °C. Conditions used in simulation are consistent with those in experiments<sup>5</sup>. The breakthrough time threshold is 5% of the feed concentration.

*Table S8. Experimental results vs simulation results (Breakthrough time of ammonia absorption with MgBr2-Si at 100 °C, 200 °C, and 300 °C)* 

Temperature	Breakthrough Time [min]						
[ °C]	Experimental Results	Simulation Results	Error [%]				
150	81	82.1	1.4				
200	52	52.4	0.8				
300	28	27.0	3.6				

The ammonia capacity of the selected absorbent, MgBr<sub>2</sub>-Si, at different temperatures (423 K, 473 K, and 573 K):<sup>5</sup>



*Figure S4.* Ammonia capacity of MgBr<sub>2</sub>-Si at 100 °C, 200 °C, and 300 °C (experiments retrieved from<sup>5</sup>)

The expression for the fitted curve:

$$W_{max} = 0.05411 \exp\left(\frac{1780}{T(^{\circ}C) + 273.15}\right)$$
(S29)

Lab-scale result can provide us an initial guessing of the absorber size, specifically, the size can be simply calculated based on the hourly ammonia production and the coordination number of the ammine complex of MgBr<sub>2</sub>-NH<sub>3</sub>. Given that 2428.8 kg/hr. of ammonia is synthesized in the proposed ammonia plant, the amount of ammonia absorbed by MgBr<sub>2</sub> for 30 minutes in an absorber column during a PSA/TSA cycle can be obtained as follows:

$$2,428.8\frac{kg}{hr} \cdot 1000 \cdot \frac{kmol}{17.031kg} \cdot \frac{1}{2} = 71,436.32 \ mol$$

Given that the complex  $Mg(NH_3)_{1.5}Br_2$  is formed during absorption, the amount of  $MgBr_2$  in one absorber bed is

71436.32 
$$\frac{mol}{1.5} \cdot \frac{kmol}{1000 \ mol} \cdot \frac{184 \ kg}{kmol} = 8768 \ kg$$

With the density of  $3720 \text{ kg/m}^3$  of MgBr<sub>2</sub>, bed voidage of 0.32, and particle voidage of 0.4, the volume of the absorber can be calculated as

$$V = 8768 \ kg/3720 \frac{kg}{m^3} / \frac{1}{(1 - 0.32)(1 - 0.4)} = 5.74 \ m^3$$

If the length-to-diameter ratio is 2.5, back-calculate the length and diameter with the formula below, thus, D = 1.43 m and L = 3.58 m.

$$V = \frac{LD^2\pi}{4} = \frac{2.5D^3\pi}{4}$$

When the initial size was used in our dynamic modeling of an absorber column, it shows that breakthrough happens at 11 mins, shown as a black line in Figure S5, which indicates the discrepancy between the lab scale and the proposed scale. The space velocity from the simulation is also not close to that of the lab scale. The volumetric flow of the stream entering the absorber was 11301 m<sup>3</sup>/h while the flow rate in the las scale was 0.005578 m<sup>3</sup>/h with the bed size of  $1.92 \times 10^{-5}$  m<sup>3</sup>. The resulted space velocity of the proposed design and the lab scale was 1968/h and 289/h, respectively. Therefore, it is important to note that the coordination number of the complex ammine obtained in the lab scale could not be achieved in the proposed design.

The final size of the absorber column was tuned to achieve the absorption time of 30 mins. A red line in Figure S5 denotes the outlet composition of the absorber in the final design (4.70 m length, 1.88 m diameter, with volume of 13.87 m<sup>3</sup>), indicating that breakthrough will happen at 30 mins. Thus, this size was used in the design.



**Figure S5**. Breakthrough time for initial and final design of the absorber size. NH<sub>3</sub> mole fraction was normalized by the initial composition of NH<sub>3</sub> before entering the absorber. Breakthrough takes places as  $C/C_o$  reaches 0.05. The black line represents the initial size (5.74 m<sup>3</sup>) inspired from the lab-scale result, showing that breakthrough happens at 11 mins. The red line denotes the outlet composition of the absorber in the final design (13.87 m<sup>3</sup>), indicating that breakthrough will happen at 30 mins.

#### 1.5 RXN-ABS Heat Integration Strategy

To summarize, in the reaction-absorption process (RXN-ABS), the reactor effluent stream will be directed to the absorber that in the desorption mode and at preheating stage (Step 2). Specifically, the absorber is chosen to be a shell-and-tube column, therefore heat of reaction can be recovered as the reactor effluent flows via the shell side of the regenerating column. This stream will be further cooled with cooling water and then directed to the absorber column in the process line (Step 1) for the separation of ammonia. In addition to the sensible heat needed for raising the temperature of absorber column and absorbent, the heat of desorption of ammonia should be also provided. The specific heat capacity of stainless-steel absorber column and absorbent particles is about  $0.50 \text{ J/(g} \cdot \text{C})^6$  and  $0.32 \text{ J/(g} \cdot \text{C})^7$ . Integrating heat from reaction for the regenerating column was carried out via ASPEN Plus, from which we obtain information on the streams in a steady state.

In general, the whole process is exothermic. We assume that reactor and absorber column can be tightly heat integrated, while the heat of reaction released from the ammonia synthesis can be directed to cancel the heat requirements beyond the pinch point (minimum temperature approach of  $10^{\circ}$ C). For this design, we simply used the water cooling for reducing the temperature of the reactor effluent before the separation and refrigeration and to keep the temperature of the absorber constant during the absorption stage (Step 1). We found that these costs are insignificant and had less than 1% effect on the final LCOA. See the calculation of absorber cooling costs during Step 1 in Section 1.9).

# 1.6 Capital Costs of RXN-CON and RXN-ABS

	Capital Investment [\$ millions]							
Subsystem	RXN-CON	%	RXN-ABS	%				
Hydrogen production	21.04	62	21.04	67				
Nitrogen production	0.68	2	0.68	2				
Synthesis loop	12.43	36	10.29	31				
Total	34.26	100	32.11	100				

Table S9. Total Capital Costs for RXN-CON at 150 bar and RXN-ABS at 20 bar.

Equipment	<i>K</i> <sub>1</sub>	<i>K</i> <sub>2</sub>	<i>K</i> <sub>3</sub>	Capacity, Units	Min Size	Max Size
Centrifugal	2.2897	1.3604	-0.1027	Fluid Power,	450	3000
Compressors				kW		
Rotary	5.0355	-1.8002	0.8253	Fluid Power,	18	950
Compressors				kW		
Electric Drives	1.956	1.7142	-0.2282	Shaft Power,	75	2600
				kW		
Floating Head	4.8306	-0.8509	0.3187	Area, m <sup>2</sup>	10	1000
Heat Exchangers						
Reciprocating	3.8696	0.3161	0.1220	Shaft Power,	0.1	200
Pump				kW		
Packed Tower	3.4974	0.4485	0.1074	Volume, m <sup>3</sup>	0.3	520
(Reactor/Absorber)						

*Table S10.* K values for estimation of equipment cost used with Eq. (2).<sup>8</sup>

Equipment	Equipment	F <sub>BM</sub>	$C_{P}^{0}$ (\$)	<i>C<sub>BM</sub></i> (\$)
No.	Туре		(2001)	(2019)
E-101	Heat Exchanger	7.48	3,730	44,550
E-102	Heat Exchanger	7.43	2,210	26,221
E-103	Heat Exchanger	8.04	18,640	239,284
R-101	Reactor	76.98	2,310	284,020
C-101	Compressor	5.80	321,547	2,978,808
C-102	Compressor	5.80	15,822	146,571
V-101	Vessel	66.51	1,726	183,331
D-101	Drive	1.50	119,790	287,000
D-102	Drive	1.50	23,330	55,895
P-101	Pump	1.85	6,560	19,384
E-104	Heat Exchanger	8.04	19,994	256,669
Refrigeration				
E-201	Heat Exchanger	8.04	21,649	277,922
C-201	Compressor	5.80	163,813	1,517,562
D-201	Drive	1.50	124,216	297,605
P-201	Pump	1.85	3,950	11,672
Total				6,626,494
CEPCI	634 (Oct 2019)	397 (Sep	o 2001)	

**Table S11.** Bare module cost factors for the equipment purchased in ammonia synthesis loop inRXN-CON (150 bar)

Equipment	Equipment	F <sub>BM</sub>	$C_{P}^{0}$ (\$)	С <sub>ВМ</sub> (\$)
No.	Туре		(2001)	(2019)
E-101	Heat Exchanger	1.74	18,528	51,492
E-102	Heat Exchanger	1.74	24,365	67,716
E-103	Heat Exchanger	1.74	18,540	51,525
R-101	Reactor	36.89	7,045	415,076
C-101	Compressor	5.80	86,619	802,438
C-102	Compressor	5.80	183,990	1,704,488
D-101	Drive	1.50	56,282	134,843
D-102	Drive	1.50	91,283	218,701
P-101	Pump	1.85	2,760	8,156
P-102	Pump	1.85	2,493	7,365
V-101	Absorber	36.61	22,692	2,492,109
	Columns			
Total				5,953,909
CEPCI	634 (Oct 2019)	397 (Sep	2001)	

**Table S12.** Bare module cost for the equipment purchased in ammonia synthesis loop RXN-CON(150 bar) and RXN-ABS (20 bar).

## 1.7 Operating Costs of RXN-CON and RXN-ABS

*Table S13. Raw Materials, Utilities, Waste Treatment, and Operating Labor for RXN-CON (150 bar).* 

	Current Price, Amount Purchased, Annual Cost,			
KAN-CON (150 bar)	\$/kg	kg/yr.	\$/yr.	
Raw Materials				
Feed Water, kg	0.005	31,764,246	143,383	
Iron Catalyst, kg	2.700	6,476	17,486	
Total Raw Material Costs, C <sub>RM</sub>			160,869	
Utilities				
Cooling Water, kg	2.58×10 <sup>-5</sup>	10,790,114,112	278,321	
Refrigerants, GJ	14.3	103,753	1,487,824	
Electric Power, kWh	0.04	193,951,966	7,952,031	
Total Annual Utility Cost, $C_{UT}$			9,718,176	
Waste Treatment, C <sub>WT</sub>	_	-	-	
	Total Number	Operator Base	Cost of	
	of Operators	Wages +Benefits,	Operating	
		\$/yr.	Labor, \$/yr.	
Operating Labor, C <sub>0L</sub>	28	54,080	1,514,240	

DVN ADS (20 hor)	Current Price,	Amount	Annual Cost,
KAN-ADS (20 Dar)	\$/kg	Purchased, kg/yr.	\$/yr.
Raw Materials			
Feed Water, kg	0.005	31,764,246	143,383
Iron Catalyst, kg	2.700	17,663	47,689
Absorbent, kg	1	174,248	174,248
Total Raw Material Costs, C <sub>RM</sub>			365,320
Utilities			
Cooling Water, kg	2.58×10 <sup>-5</sup>	14,700,096,000	379,176
Electric Power, kWh	0.04	187,221,604	7,676,086
Total Annual Utility Cost, $C_{UT}$			8,055,261
Waste Treatment, $C_{WT}$	-	_	_
	Total Number	Operator Base	Cost of Operating
	of Operators	Wages +Benefits,	Labor, \$/yr.
		\$/yr.	
Operating Labor, C <sub>0L</sub>	28	54,080	1,514,240

*Table S14. Raw Materials, Utilities, Waste Treatment, and Operating Labor for RXN-ABS (20 bar).* 

#### 1.8 Wind Generation Capacity



*Figure S6.* Wind generation in TTU's GLEAMM microgrid facility, located at Lubbock, TX operating at a stream factor of 0.94 (total working hours of 8760 hours).

#### **1.9** Power Requirement for Cooling in Absorption Step

We evaluated the possible heat released during ammonia uptake. Malmali et al.<sup>5</sup> reported that the coordination number of MgBr<sub>2</sub>-NH<sub>3</sub> is 1.5 mol<sub>NH3</sub>/mol<sub>salt</sub> at 150 °C. If the complex  $Mg(NH_3)_{1.5}Br_2$  is formed during absorption, the amount of heat released due to absorption can be obtained by multiplying the ammonia produced by the heat of absorption as follows:

$$Q = \Delta H_{abs} \cdot P_{NH_3} \cdot MW_{NH_3}$$

$$= (90.80 + 84.10 * 0.5) \frac{kJ}{mol} \cdot 2428 \frac{kg}{hr} \cdot 17.031 \frac{kg}{kmol} = 5,493,516 \frac{kJ}{hr}$$

We assumed that the generated heat can be removed by cooling water, without design a heat integration with other processes. The amount of cooling water can be calculated by

$$M_{water} = \frac{Q}{C_p \cdot \Delta T}$$

which results in  $M_{water} = 65,680 \frac{kg}{hr}$  ( $C_p = 4182 \frac{J}{kg^{\circ}C}, \Delta T_{difference} = 20$ ).

The pumping power is then obtained by heuristics as follows:

$$P_{pump} = \frac{1.67 \cdot M_{water} \left(\frac{m^3}{\min}\right) \cdot \Delta P}{\eta_{pump}}$$

If the reciprocating pump is assumed to have a pressure drop of 2 bar with a pump efficiency of 85%, then the total pumping power is 4.30 kW, approximately 0.017 kWh/kg  $NH_3$ , which is about 0.18% of total energy consumption. Therefore, it is reasonable to assume that the power requirement for cooling can be negligible.

The utility cost resulted from this amount of cooling water can be calculated by multiplying the amount of cooling water during by its costs – with an annual stream factor of 0.94,

$$C_{ut,water} = M_{water} \cdot 2.58 \times 10^{-5} \frac{\$}{kg} \cdot 365 \ days \cdot 24 \ hr \cdot 0.94 = \$14,000/year$$

The additional utility cost for cooling,  $C_{ut,water}$  results in increasing the operating cost by \$17,220/year using Eq. 6 in the manuscript, which results in an increase on LCOA by \$1.41 MT

of NH<sub>3</sub>. Therefore, it is reasonable to assume that cost of cooling water for the absorption step has negligible impact on the result.

Overall, heat management of such process is a multi-objective optimization problem and needs its own dedicated study, which is beyond the scope of this work.

#### **1.10** Improving Economics by Selling Oxygen

Oxygen is produced during nitrogen production via PSA and hydrogen production via electrolysis of water. Also, we assume that PSA can produce high-purity oxygen with additional facilities. PSA produces 607.6 kg/hr.  $O_2$ , given that nitrogen mass flow is 2000 kg/hr., the weight ratio of 1:3.29, while electrolysis of water produces 3428.8 kg/hr.  $O_2$ , given that hydrogen mass flow is 428.6 kg/hr. and the weight ratio of 1:8. Therefore the total amount of oxygen generated is 4036.4 kg/hr.  $O_2$  will be stored in medical E oxygen tanks which have service pressure of 2,015 psi with a volume of 682 L. The cost of an empty medical tank is \$64.60/cylinder.<sup>9</sup> After packaging the oxygen in the cylinder,  $O_2$  can be sold for \$125/tank.<sup>10</sup>

The volume of the amount of oxygen produced can be calculated using the ideal gas law:

$$V = \frac{\dot{m}RT}{MP} = \frac{4036.4 \cdot 1000 \frac{g}{hr} \cdot 0.0821 \frac{L \cdot atm}{mol \cdot K} \cdot 298.15 K}{32 \frac{g}{mol} \cdot 137.11 atm} = 22.520 \frac{L}{hr}$$

The number of tanks needed per hour can be calculated by

$$N_{\underline{tanks}} = \frac{V}{Volume/tank} = \frac{22,520 \frac{L}{hr}}{682 \frac{L}{tank}} = 33 \frac{tanks}{hr}$$

Cost of tanks per year can then be found by:

$$Cost_{tank} = 33 \frac{tanks}{hr} \cdot 64.60 \frac{USD}{tank} \cdot 24 \frac{hr}{day} \cdot 365 \frac{days}{year} \cdot 0.94 = 17,619,410 \frac{USD}{year}$$

The resulting income from selling the oxygen can be estimated by:

$$Cost_{O2} = 33 \frac{tanks}{hr} \cdot 125 \frac{USD}{tank} \cdot 24 \frac{hr}{day} \cdot 365 \frac{days}{year} \cdot 0.94 = 33,988,061 \frac{USD}{year}$$

Then the net profit from selling the oxygen is

$$Cost_{02} - Cost_{tank} = 33,988,061 \frac{USD}{year} - 17,619,410 \frac{USD}{year} = 16,368,650 \frac{USD}{year}$$

#### 1.11 Cash Flow (RXN-ABS) – Selling Oxygen

This 20,000 MT/year ammonia plant can be profitable if selling oxygen produced from PSA and electrolysis of water. As in Table S15, a cash flow table was constructed assuming a 20-year project life span with an additional 2 years added before the project begins for investment and plant construction. Total capital investment, annual revenue (from selling oxygen and ammonia), annual operating cost, after-tax Rate of return, cost of capital, and NPV at cost of capital are summarized. In Figure S7, non-discounted cash flow diagram show that the plant can profit after 5 years.

Executive Summary		
Total Capital Investment, TCI	\$31.61 million	
Selling Price of Ammonia	\$598/MT of ammonia <sup>11</sup>	
Annual Revenue: Ammonia	\$11.96 million	
Annual Revenue: Oxygen	\$16.37 million	
Annual Revenue, R	\$28.33 million	
Annual Operating Cost, <i>COM<sub>d</sub></i>	\$15.59 million	
After-Tax Rate of Return, DCFROR	27.50%	
Cost of Capital, <i>i</i> <sub>coc</sub>	7.0%	
NPV at Cost of Capital, CDCF	\$58.47 million	

Table S15. Executive Summary (RXN-ABS, 20 bar)





RXN-ABS: Non-Discounted Cumulative Cash Flow

## 1.12 Cash Flow (RXN-CON) – Selling Oxygen

In Figure S8, non-discounted and discounted cash flow diagram show that the plant can profit after 6 years.

Table S16. E	Executive	Summary	(RXN-CON,	150 bar	)
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Executive Summary		
Total Capital Investment, TCI	\$34.26 million	
Selling Price of Ammonia	\$598/MT of ammonia <sup>11</sup>	
Annual Revenue: Ammonia	\$11.96 million	
Annual Revenue: Oxygen	\$16.37 million	
Total Annual Revenue	\$28.33 million	
Annual Operating Cost, COM <sub>d</sub>	\$17.26 million	
After-Tax Rate of Return, DCFROR	21.83%	
Cost of Capital, <i>i<sub>coc</sub></i>	7.0%	
NPV at Cost of Capital, CDCF	\$46.06 million	





RXN-CON: Non-Discounted Cumulative Cash Flow

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