Dynamic Modeling and Optimization of an Absorption Enhanced Ammonia Synthesis Process

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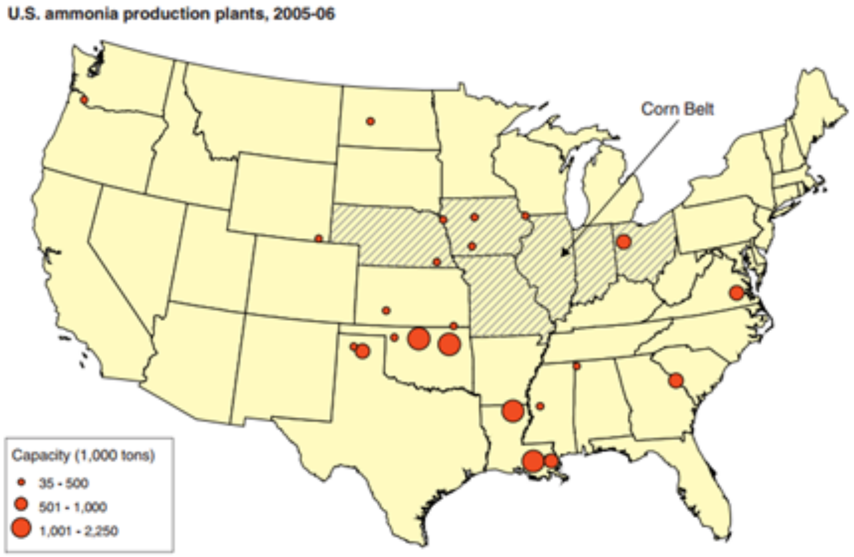
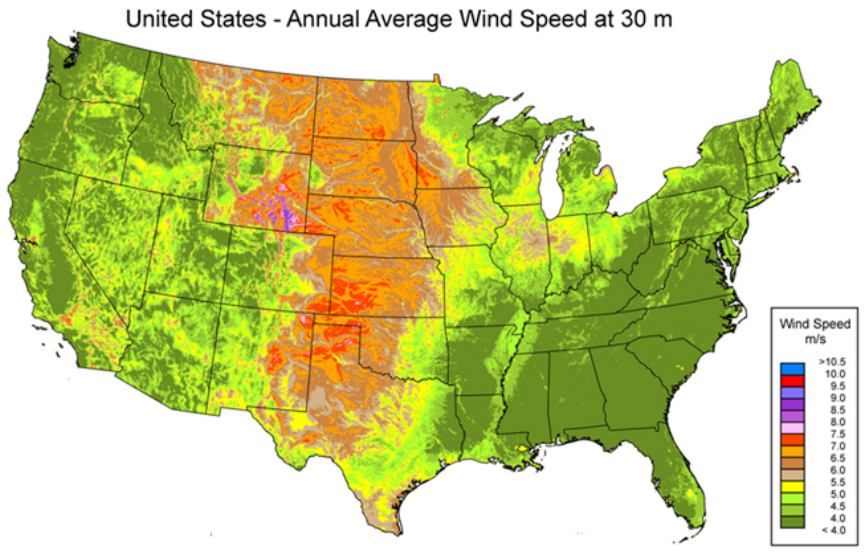
Motivation for Distributed Ammonia Production

- Energy intensive production: 2% of world's energy consumption[1]
- Long transportation distances: Gulf Coast to Midwest accounts for 20% of total cost[2]
- Alternative paradigm: Distributed ammonia production powered by electricity generated from renewables



Source: USDA, Economic Research Service



Source: NREL, GIS Division

[1] Worrell et al., *Energy Efficiency*, 2009, 2, 109-130.
[2] PotashCorp, *US Midwest Delivered Ammonia Cost*, 2014.

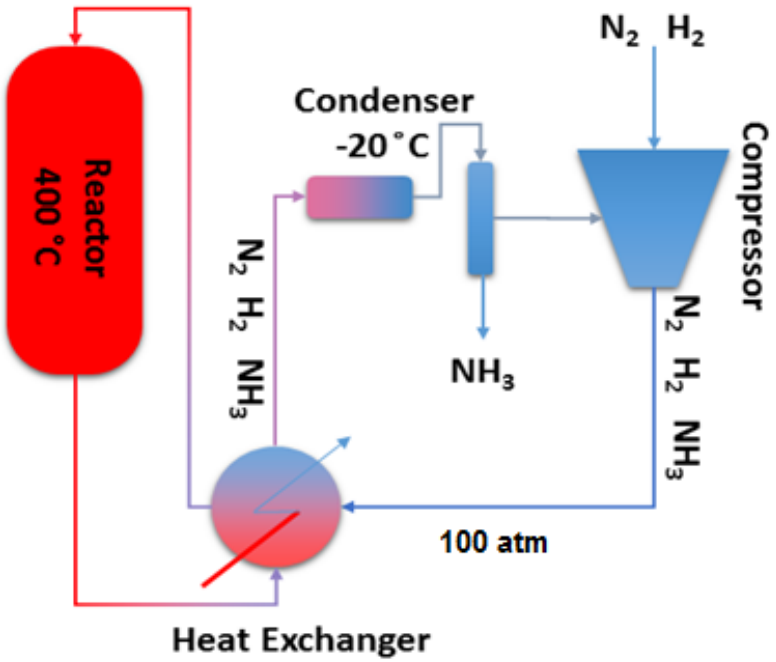
Small-Scale Haber Process

- Scaled down, wind-powered Haber process in Morris, MN
  - Hydrogen from electrolysis, nitrogen from PSA
  - Produces 65 kg/day[1]
  - Not economically competitive without incentives[2,3]

High capital cost and energy intensive

- Compression to high pressure
- Refrigeration for condensation
- Imperfect product separation[4]
  - More recycle, lowered reactor productivity

Haber Process



Source: M. Malmali

[1] Tiffany et al, *Econ. Eval. of Small Scale NH_3 Production*, 2015.
[2] Allman et al., *AIChE J.* 2017, 4390-4402.
[3] Allman and Daoutidis, *Chem. Eng. Res. Des.* 2017, accepted.
[4] Reese et. al, *Ind. Eng. Chem. Res.* 2016, 55, 3742-3750.

Absorption Enhanced Process

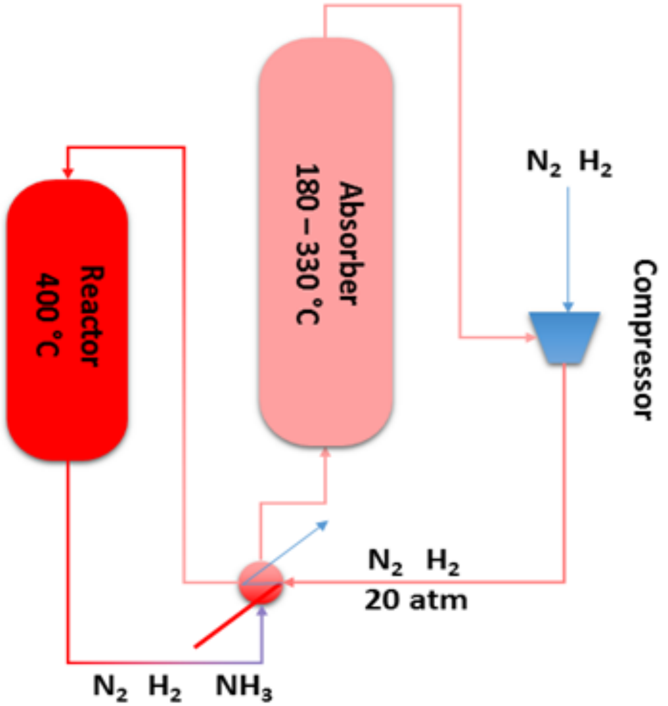
Proposed by Cussler, McCormick and colleagues:

- Ammonia separation by absorption into alkaline metal halide[1,2]

Key Advantages:

- Less compression (lower pressure)
- Higher separation temperature
  - Cooling water instead of refrigeration
- Near-complete separation
  - Less recycle, higher reaction rate

Absorbent Enhanced Process



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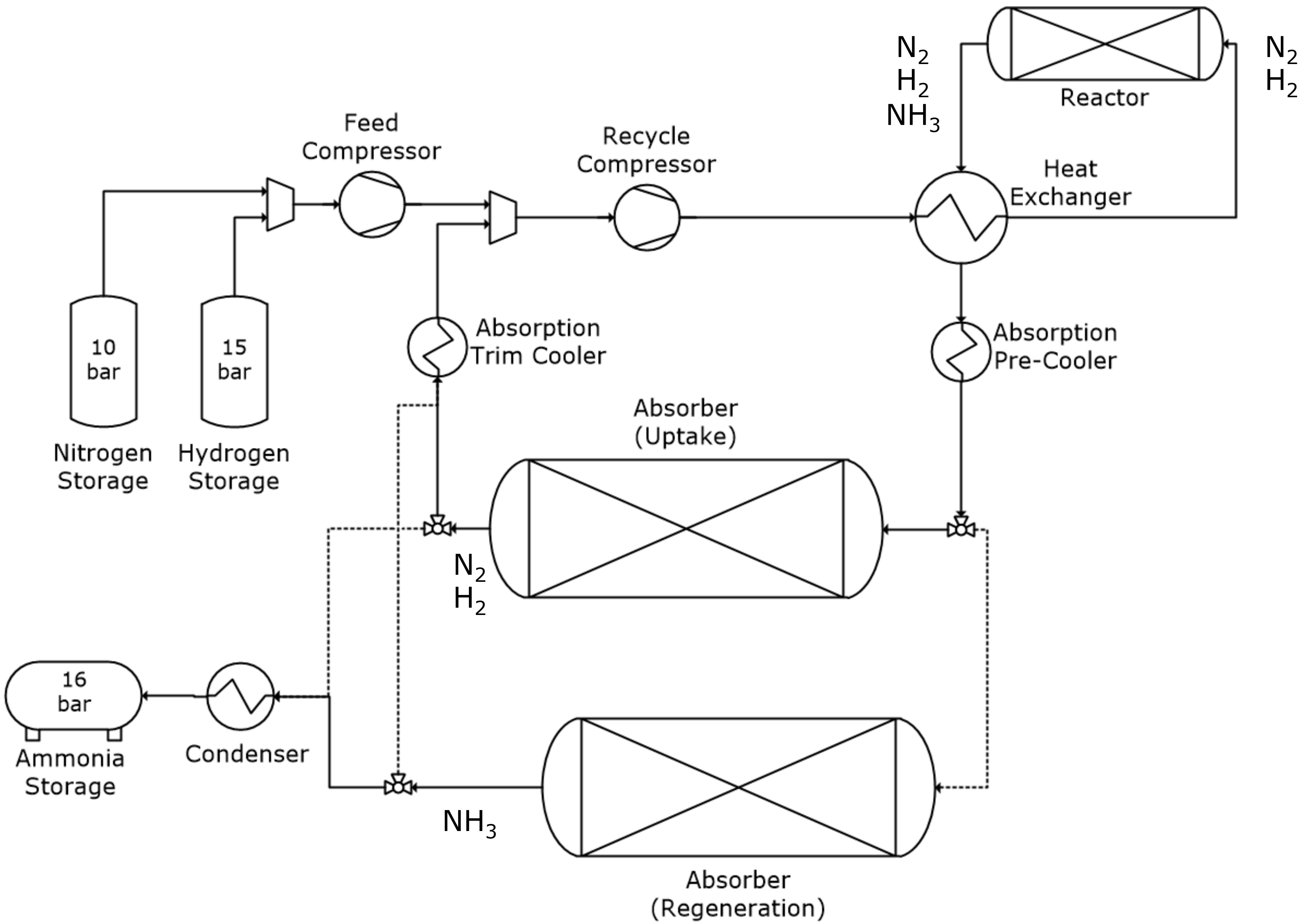
[1] Malmali et. al, *Ind. Eng. Chem. Res.* 2016, 55, 8922-8932.
[2] Himstead et. al, *AIChE J.* 2015, 61, 1364–1371.

Absorption Enhanced Process: Flowsheet



Absorption Enhanced Process: Experimental Work

- Experimental work performed by research groups under the direction of Cussler, McCormick

Areas of research:

- Bench-scale proof of concept[1,2]
- Selection, synthesis and testing of absorbents[1]
- Design of 1 kg/day prototype for installation in Morris

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This work: **Dynamic model of absorbent enhanced process from first principles**

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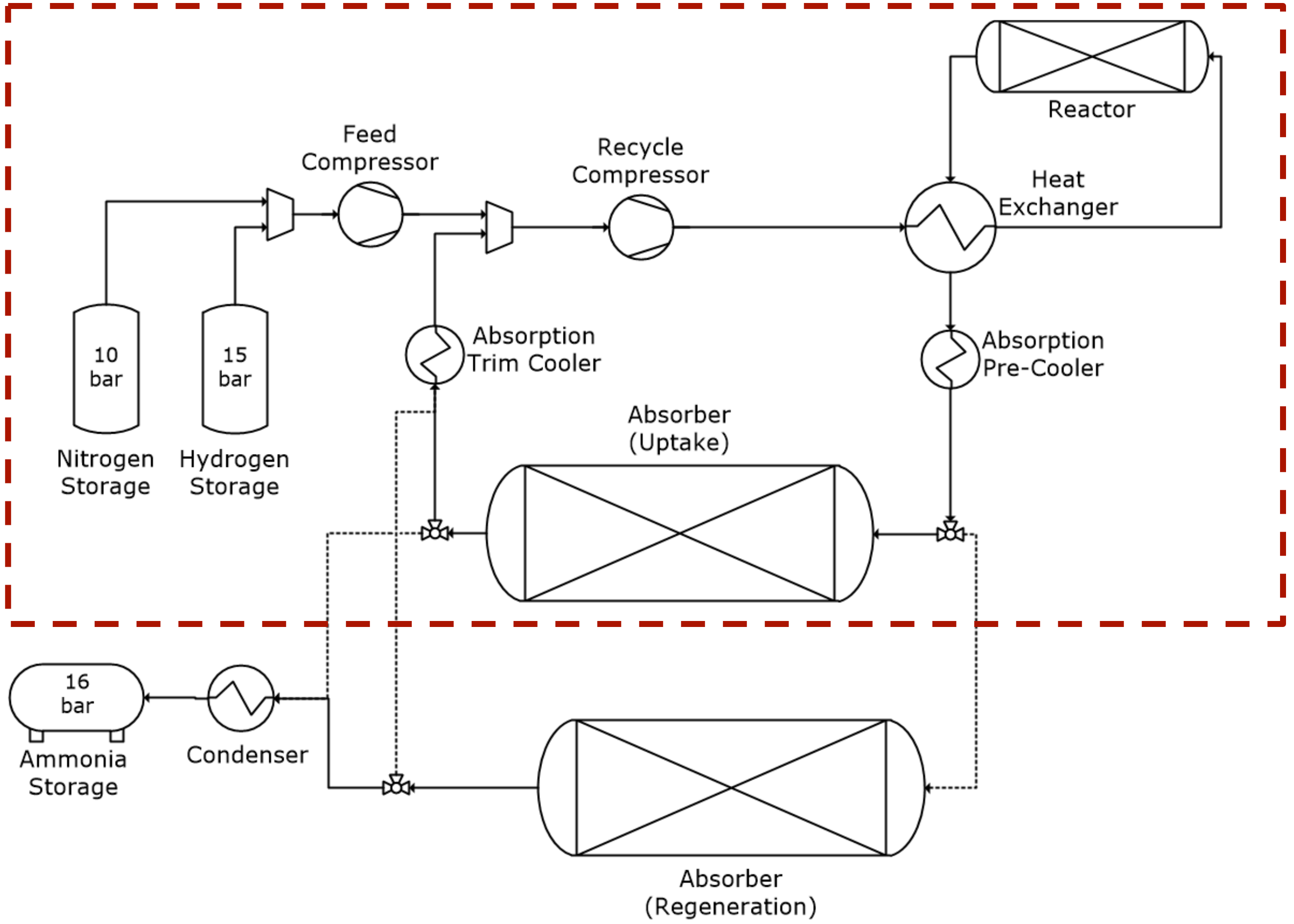
[2] Himstead et. al, *AIChE J.* 2015, 61, 1364–1371.

Absorption Enhanced Process: Dynamic Modeling

- Dynamic modeling required because absorption is transient
  - Absorption cycle modeled using gPROMS ModelBuilder
- Incorporates experimental data



Absorption Enhanced Process: Dynamic Modeling

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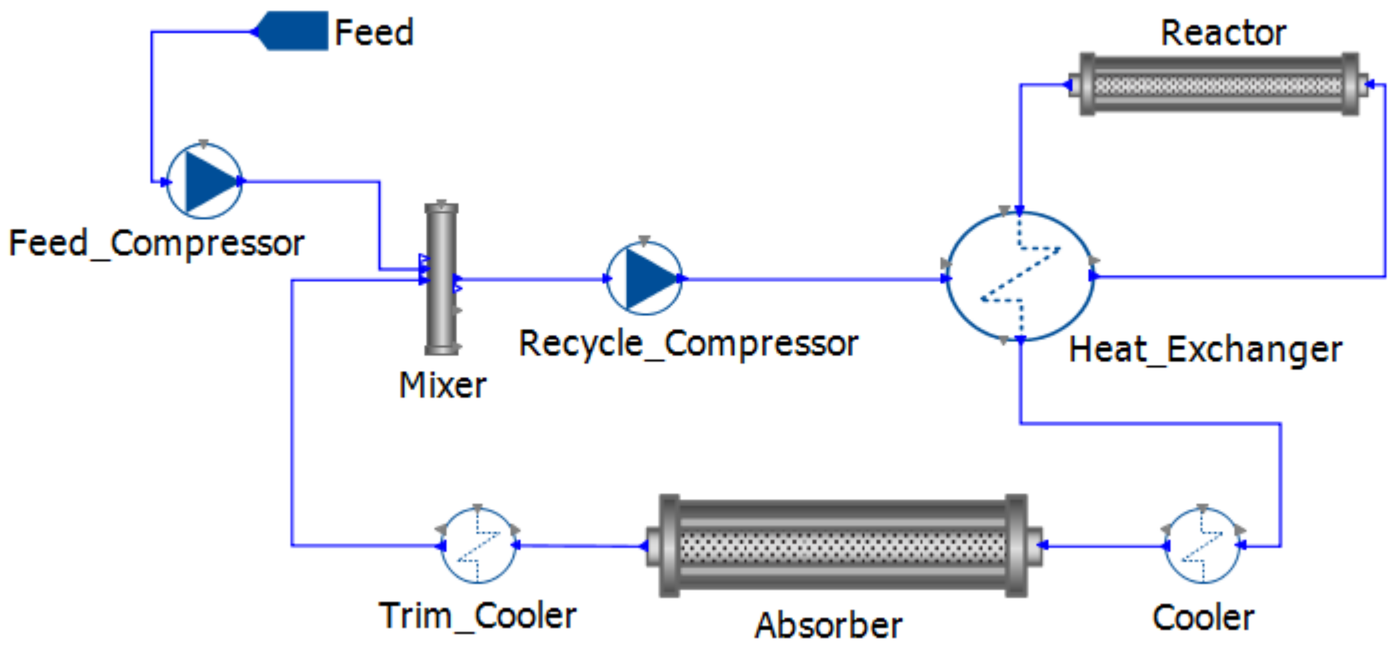
Absorbent Enhanced Process – gPROMS Flowsheet

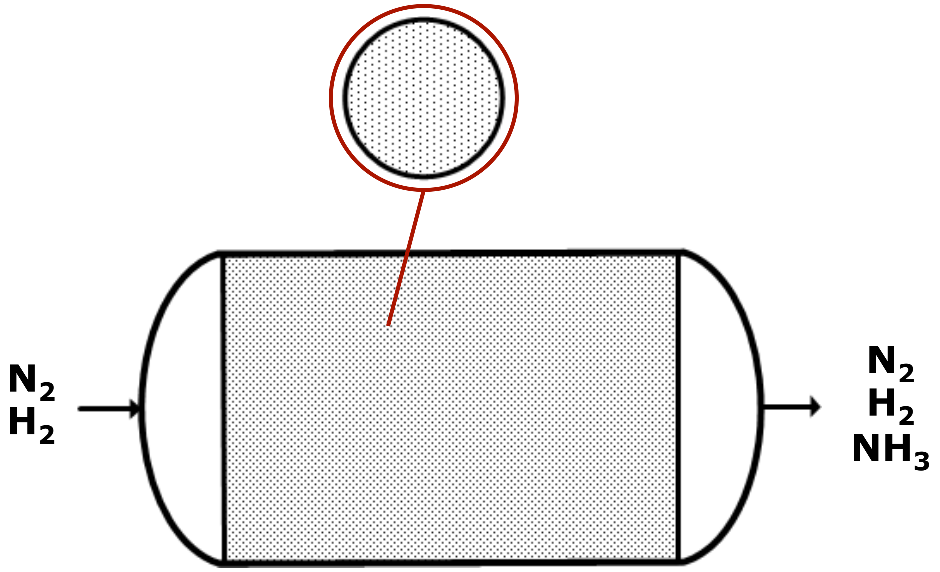


Reactor Modeling

- Adiabatic plug flow model
- Nielsen rate expression[1]

$$r_{NH_3} = k\left(p_{N_2}K_a^2 - \frac{p_{NH_3}^2}{p_{H_2}^3}\right)\left(1 + \frac{Kp_{NH_3}}{p_{H_2}^{\omega}}\right)^{-2\alpha}$$

$N_2 + 3H_2 \leftrightarrow 2NH_3$



- Minimal NH_3 at inlet
  - Internal diffusion limitation[2,3]
- Effectiveness factor from solution of particle mass balance[4]
  - Sampled over process conditions
- Generated empirical correlation

$$\eta = \frac{-\frac{3}{R_p} D_{NH_3,eff} \frac{P}{RT} \left.\frac{dy_{NH_3}}{dr}\right|_{r=R_p}}{2(1 + y_{NH_3}) \left.r_{NH_3}\right|_{r=R_p}}$$

$$\downarrow$$

$$\eta = \eta(y_{NH_3}, T, P)$$

[1] Nielsen, *Journal of Catalysis.* 1964, 3, 68-79.
[2] Liu, *Ammonia Synthesis Catalysts – Innovation and Practice*, 2010, 153-163.
[3] Appl, *Ammonia. Ullmann's Encyclopedia of Industrial Chemistry,* 2000, 24-26.
[4] Dyson and Symon*, Ind. Eng. Chem. Fundamen.* 1968, 7, 605–610.

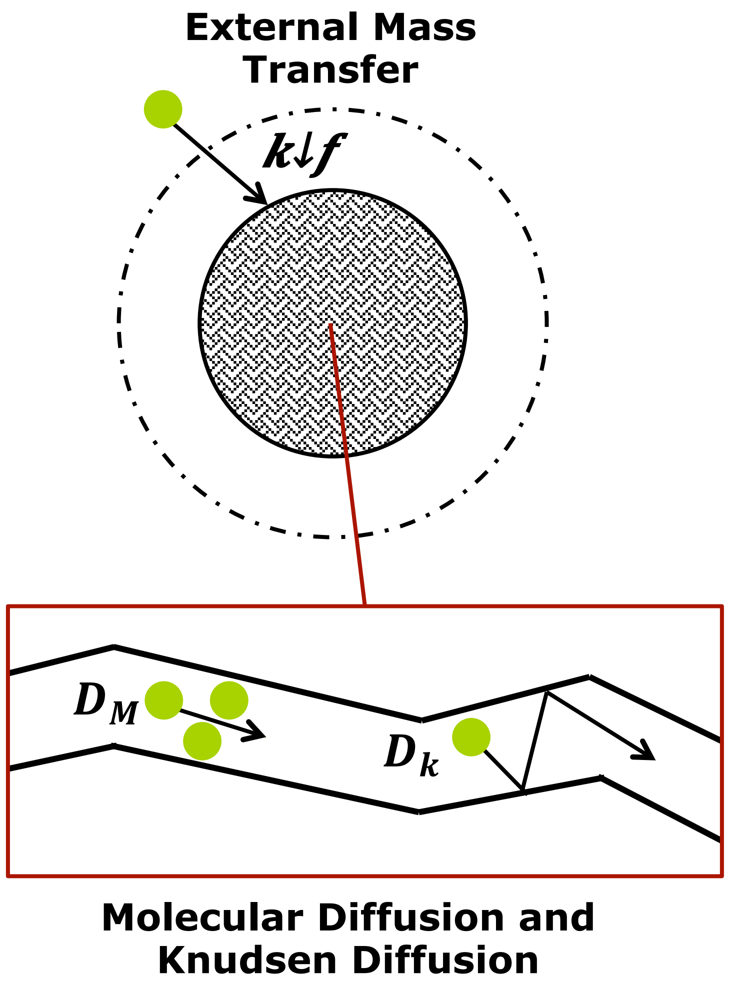
Absorber Modeling: Linear Driving Force

- Convection, axial dispersion in bulk fluid
- Volume averaged absorbent phase[1]
- Absorption rate: linear driving force (LDF)[2]

$$\frac{dq_{NH_3}}{dt} = K_{LDF}\frac{C_{NH_3}}{\rho_{ads}}\left(1 - \frac{q_{NH_3}}{q^*_{NH_3}}\right)$$

- LDF accounts for external mass transfer, molecular and Knudsen diffusion
- Generated empirical correlation for temperature and pressure dependence

$$K_{LDF} = \left(\frac{R_p}{3k_f} + \frac{R_p^2}{15\frac{\varepsilon_{ads}}{\tau_{ads}}(1/D_M + 1/D_k)^{-1}}\right)^{-1} \approx K_o\left(\frac{T}{T_o}\right)^{n_T}\left(\frac{P}{P_o}\right)^{n_P}$$

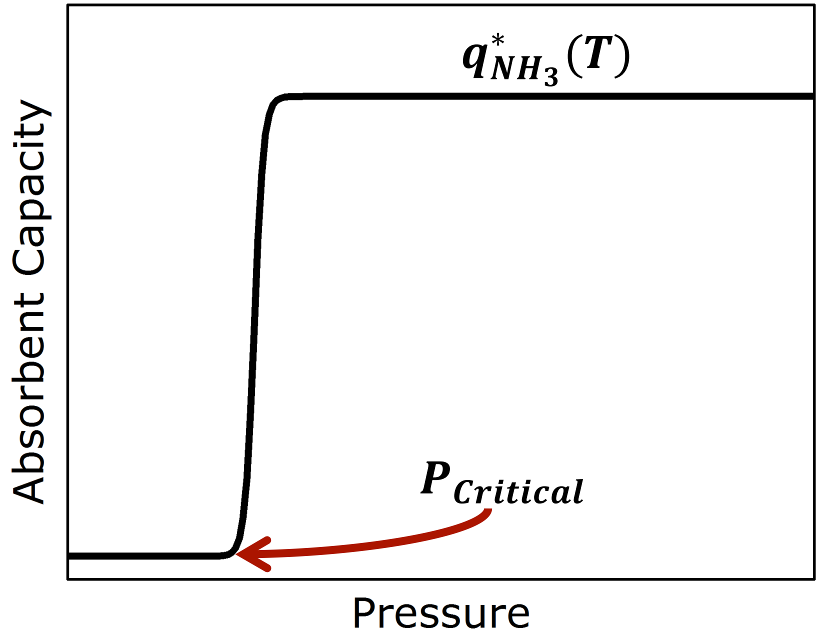


[1] Siahpoosh et al. *Iran. J. Chem. Chem. Eng.* 2009, 28, 25-44.
[2] Gorbach et al. *Adsorption.* 2004, 10, 29-46.

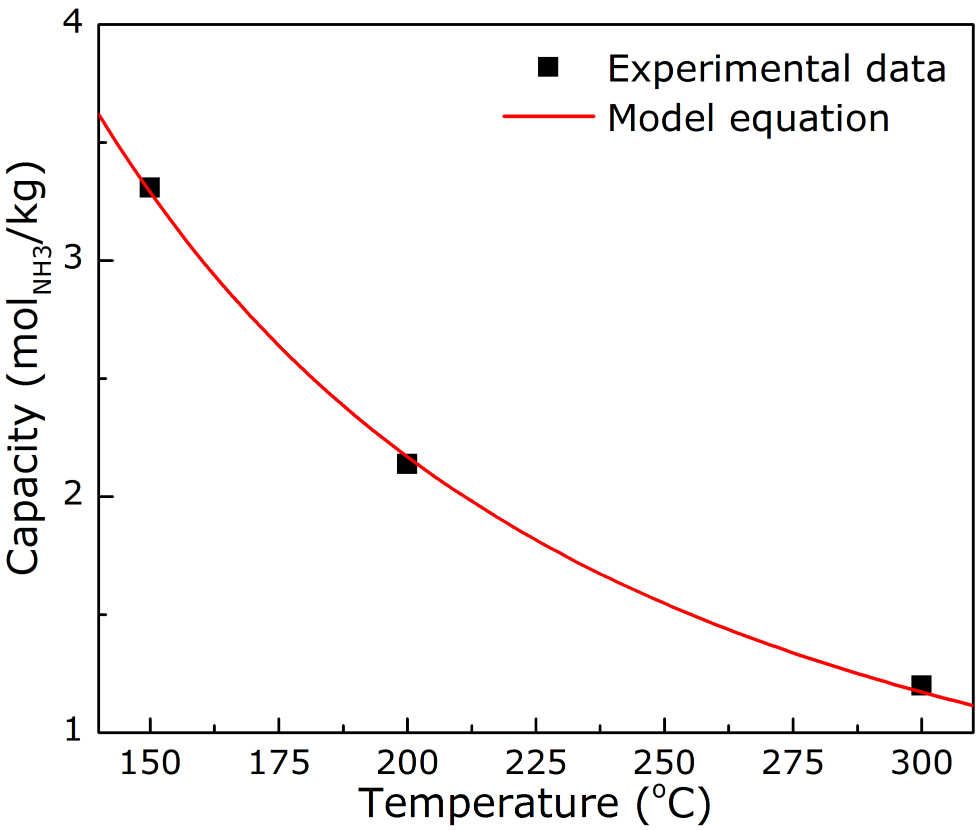
Absorber Modeling: Absorbent Capacity from Experiments

- Sharp absorption isotherm
- Step function at critical pressure

Sample Absorption Isotherm



Absorbent Capacity Temperature Dependence[1]



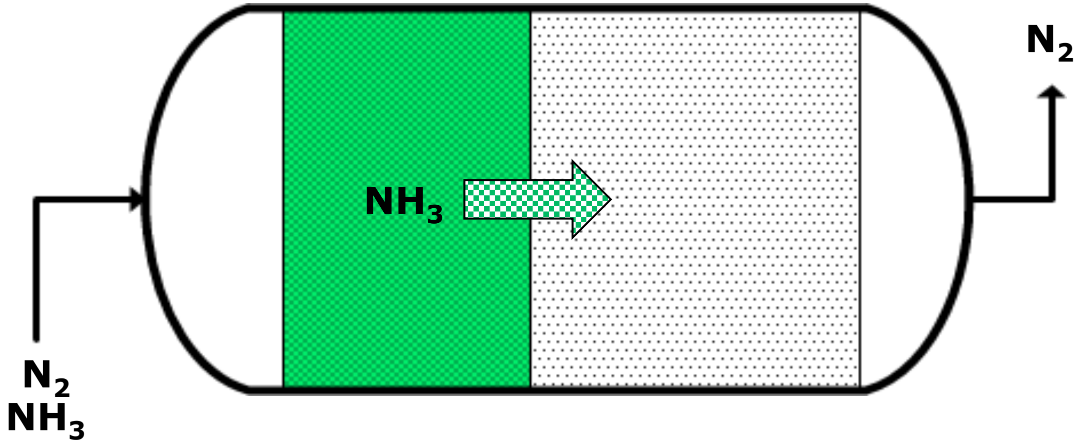
- Absorbent capacity temperature dependence from experimental data

$$q^*_{NH_3}(T) = 0.159 \exp\left(\frac{1669}{T}\right) \left[\frac{\text{mol NH}_3}{\text{kg}}\right]$$

[1] Experimental data from Cussler, Malami, Smith, McCormick

Absorber Modeling: Breakthrough Times

- Simulation of breakthrough experiments
  - Flow N2, NH3 until saturation
  - Isothermal

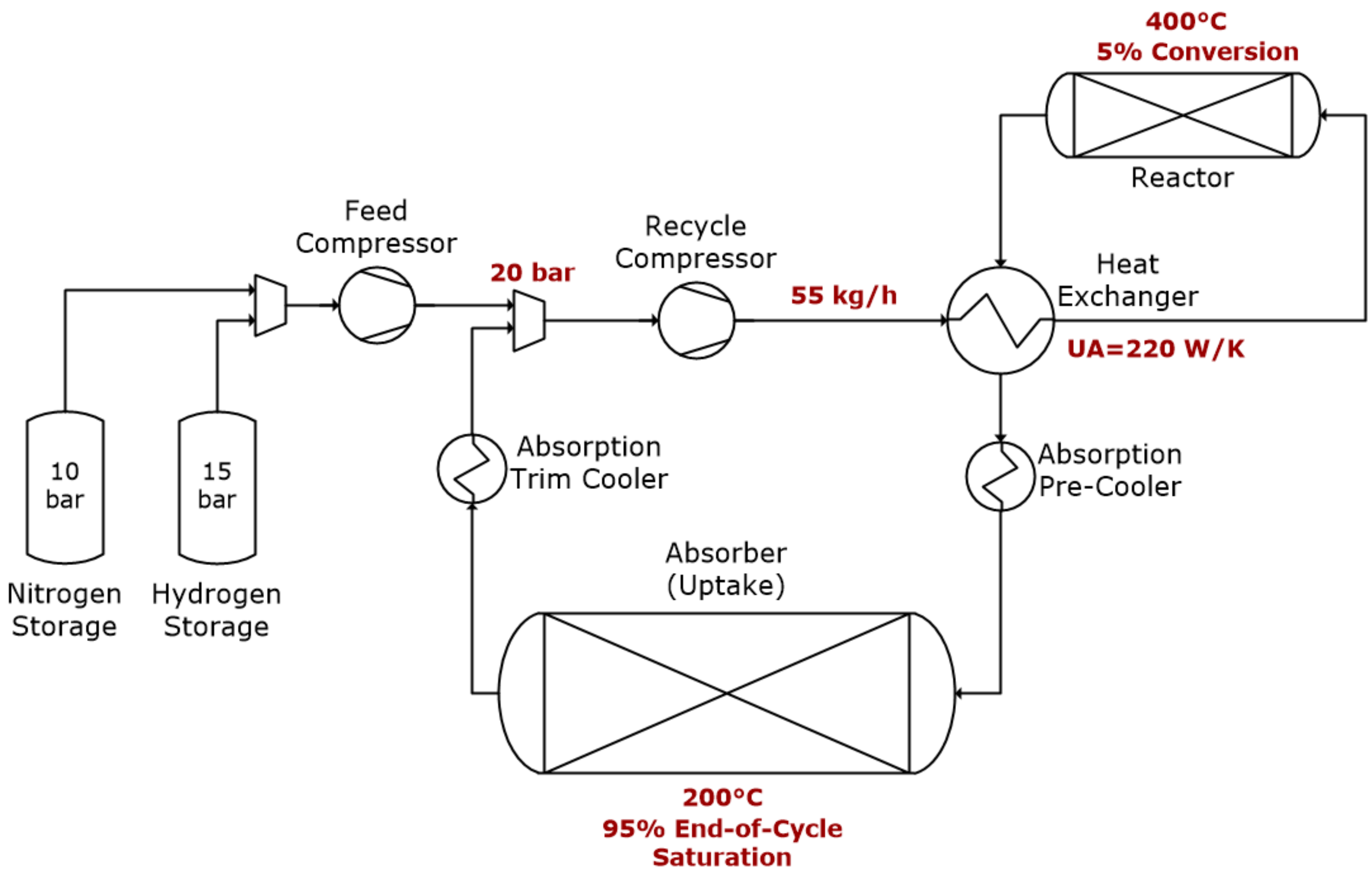


- Breakthrough times compare well for multiple absorbents at multiple temperatures

Temperature [°C]	Breakthrough Time [min]	
	Experiment[1]	*Simulation*
150	81	80.7
200	52	53.3
300	28	28.8

[1] Experimental data from Cussler, Malami, Smith, McCormick

Base Case Design of Absorbent Enhanced Process



Base Case Simulation Results

Electricity Consumption

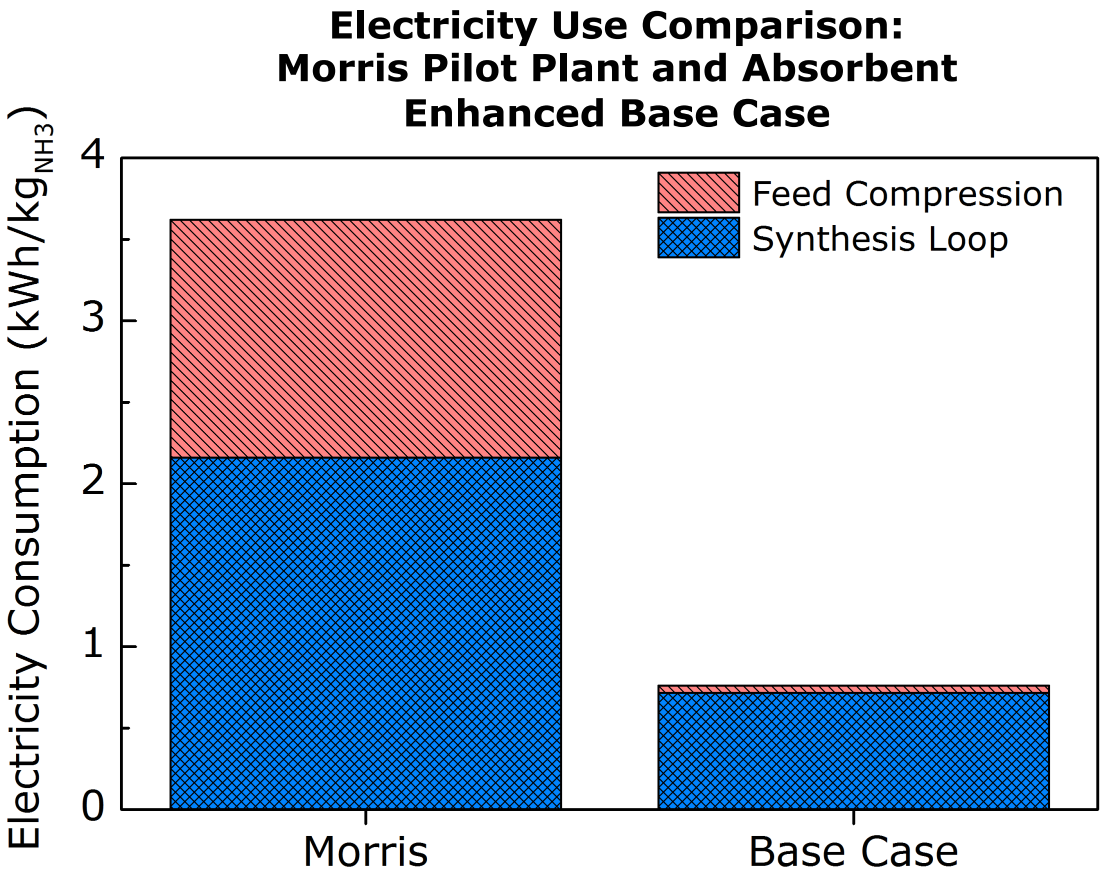
- Feed preparation not considered

Morris: 3.62 kWh/kgNH_3[1]

Base Case: 0.76 kWh/kgNH_3

- Compression
- Cooling
- Desorption
- Liquefaction

- Significant electricity savings:
  - Less compression
  - Cooling water instead of refrigeration



[1] Tiffany et al, *Econ. Eval. of Small Scale NH_3 Production*, 2015.

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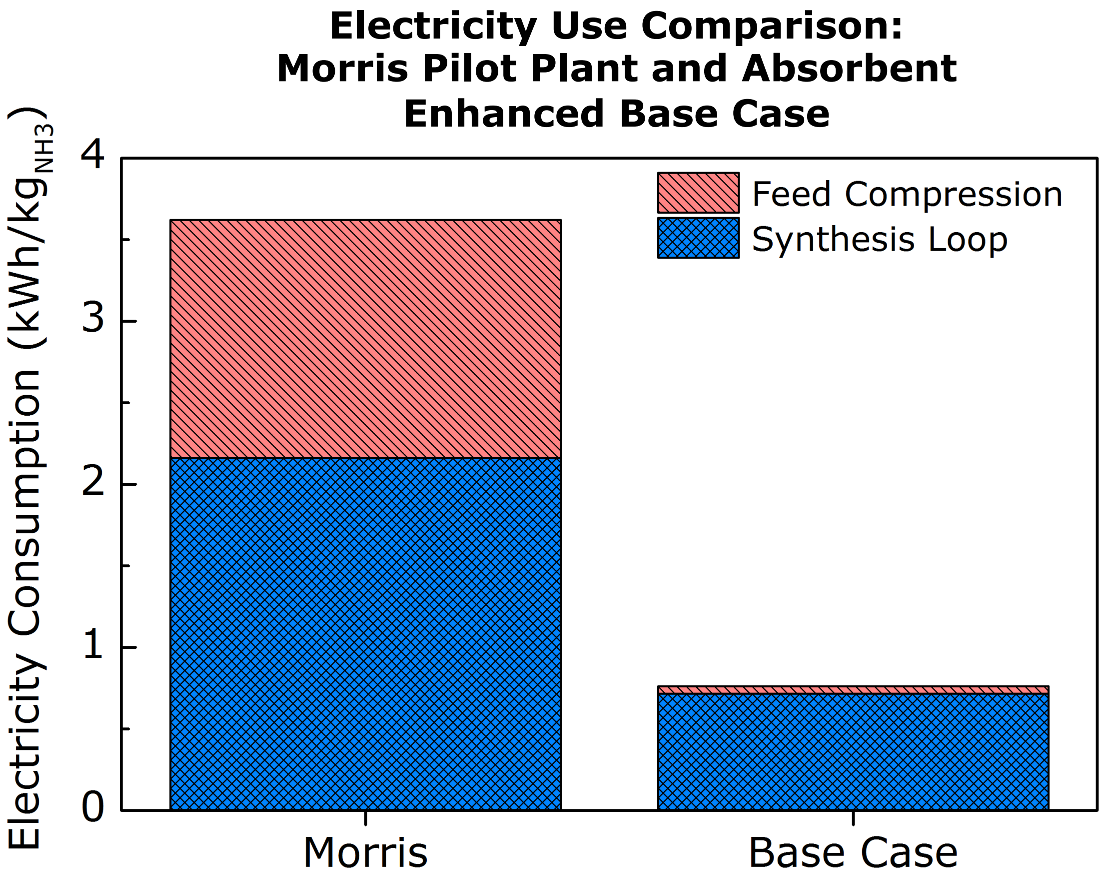


How much further can electricity consumption be reduced?

[1] Tiffany et al, *Econ. Eval. of Small Scale NH_3 Production*, 2015.

Absorbent Enhanced Process Optimization: Formulation

- Objective: Minimize total electricity consumption
  - Process powered by renewable-generated electricity

$$
\begin{aligned}
E_{total} = {} & y_{N_2}^{o}\left[\int_0^{3600} \dot{m}_{add}(t)dt + m_{initial}\right]\widehat{W}_C^{N_2} && \text{Nitrogen Feed Compression} \\
& + y_{H_2}^{o}\left[\int_0^{3600} \dot{m}_{add}(t)dt + m_{initial}\right]\widehat{W}_C^{H_2} && \text{Hydrogen Feed Compression} \\
& + \int_0^{3600}\left[P_{RC}(t) + \frac{\widehat{P}_{cw}\, Q_{Cool}(t)}{c_p^{cw}\left(T_{out}^{cw} - T_{in}^{cw}\right)}\right]dt && \text{Recycle Compression and Cooling Water Recirculation}
\end{aligned}
$$

  - Electricity for desorption and liquefaction still considered but constant

Absorbent Enhanced Process Optimization: Formulation

- Objective: Minimize total electricity consumption
- Decisions Variables: $\dot{m}_{RC}$ P T_{R_o} T_{A_o} L_R D_R L_A D_A UA
  - Recycle flowrate
  - Pressure
  - Reaction and absorption temperatures
  - Unit sizes

Absorbent Enhanced Process Optimization: Formulation

- Objective: Minimize total electricity consumption
- Decisions Variables: $\dot{m}_{RC}$ P T_{R_o} T_{A_o} L_R D_R L_A D_A UA
- Constraints:
  - Decision variable bounds: physical reasoning, design practicality
  - Minimum ammonia production rate – same as Morris pilot plant

$$m_{NH_3}^{ads}(t = 3600) \geq 2.7 \text{ kg}$$

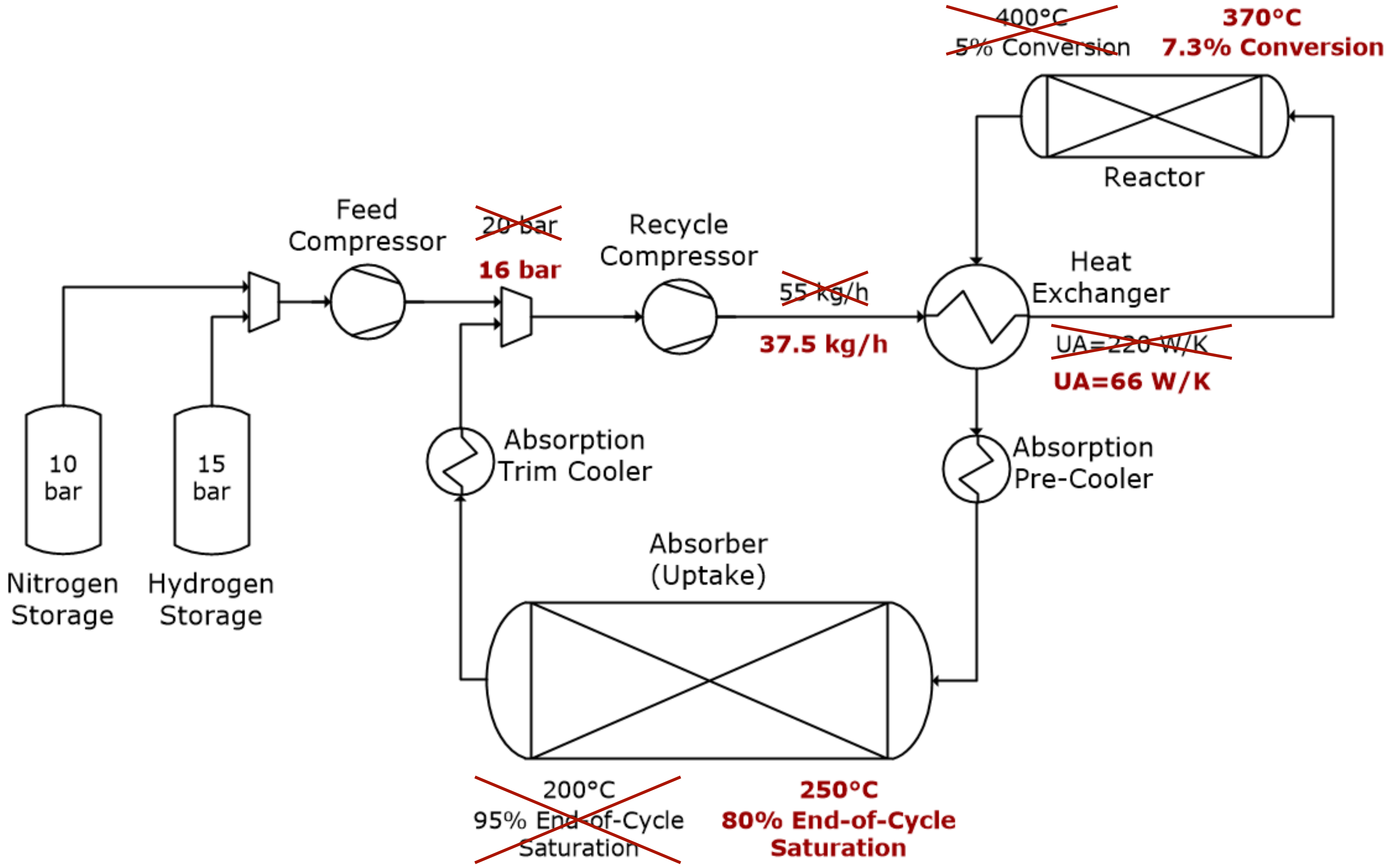
  - Minimum absorber saturation of 80%

$$\frac{1}{L_A}\int_0^{L_A} \frac{q_{NH_3}(z)}{q_{NH_3}^*(z)} dz \geq 0.8$$

  - Minimum reactor and absorber L/D ratios of 2

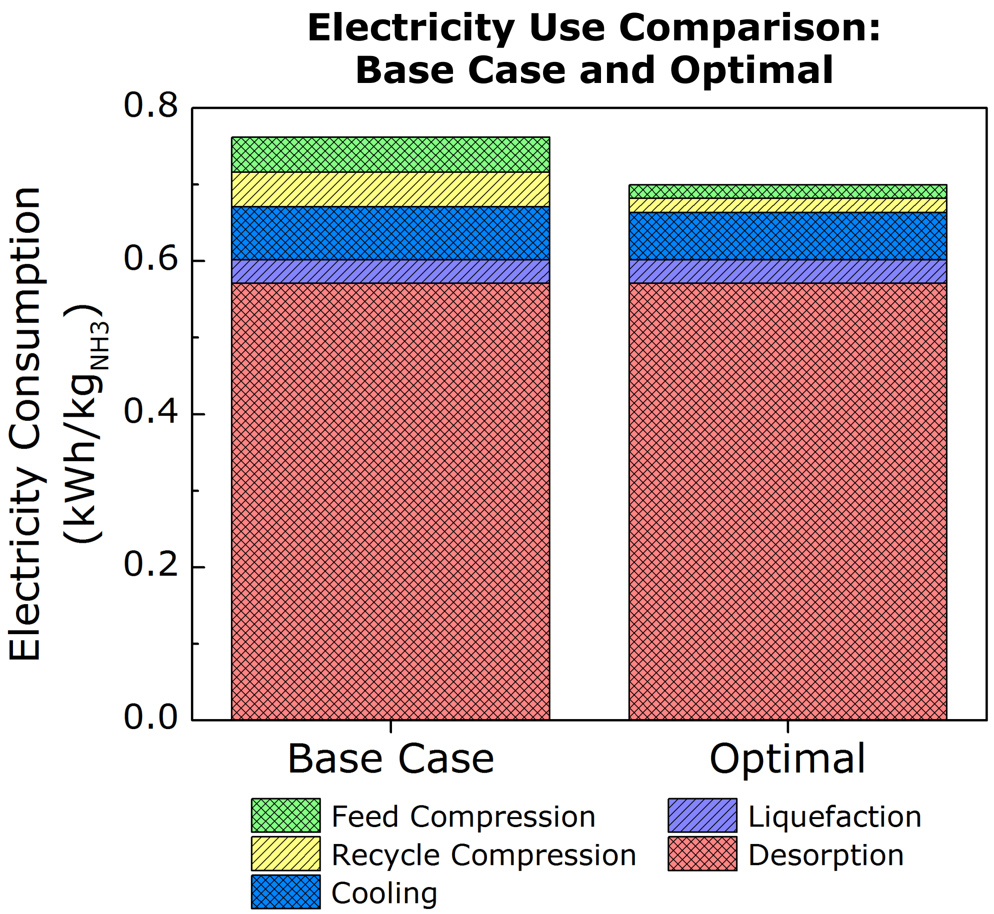
$$\frac{L_R}{D_R} \geq 2 \qquad \frac{L_A}{D_A} \geq 2$$

Optimal Design of Absorbent Enhanced Process



Absorbent Enhanced Process Optimization: Results

- Base Case: 0.76 kWh/kgNH_3
- Optimal: 0.7 kWh/kgNH_3



Absorbent Enhanced Process Optimization: Results

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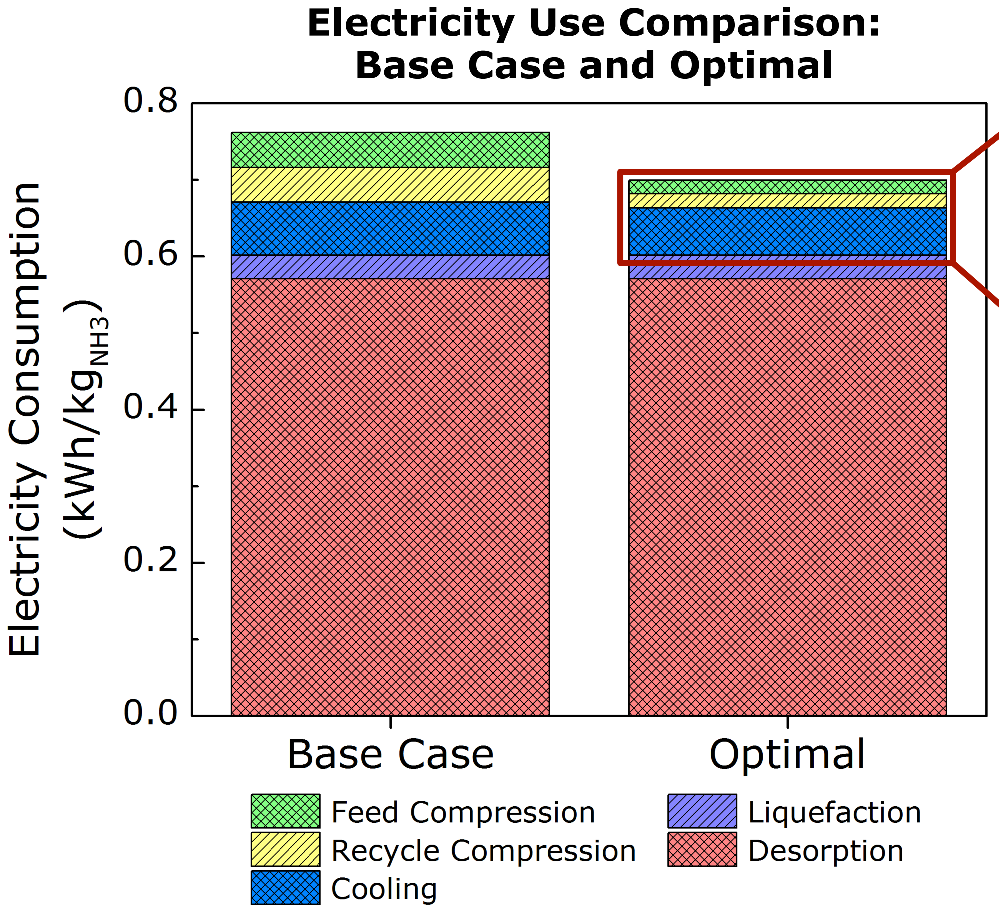
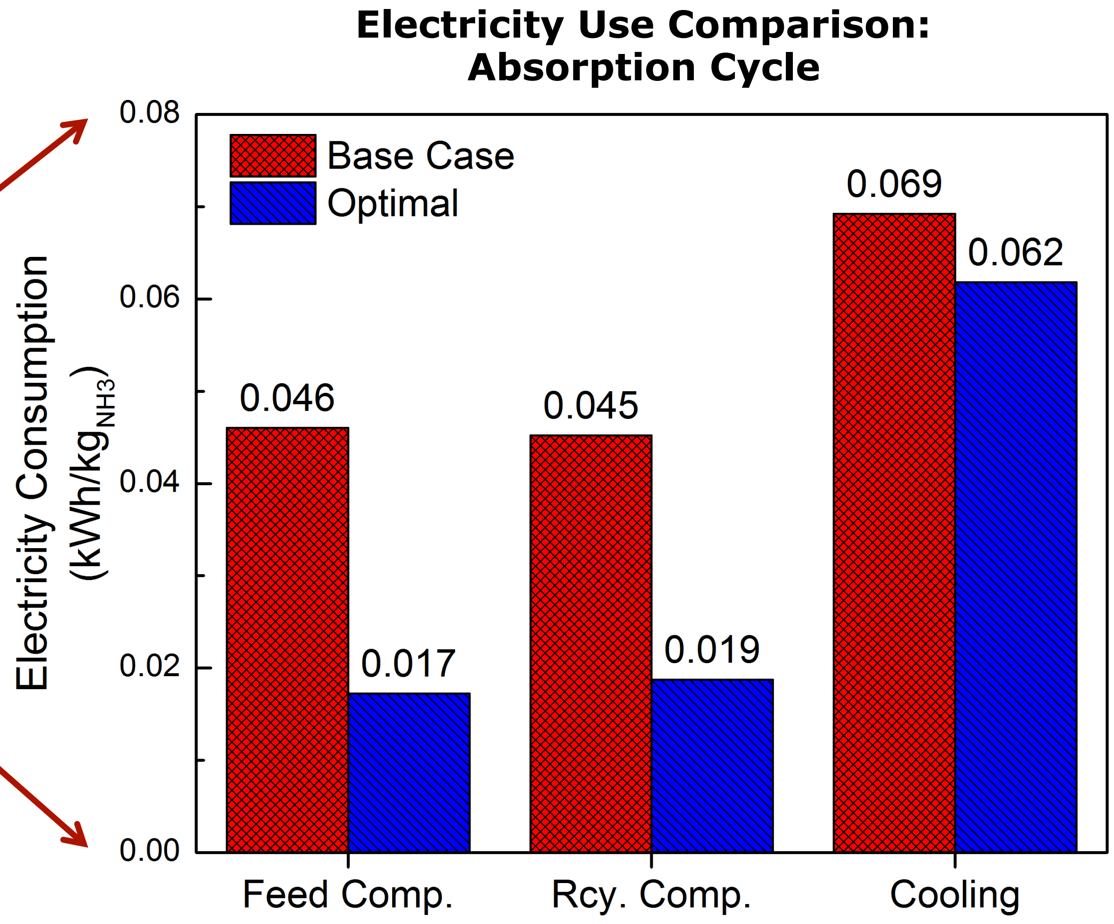
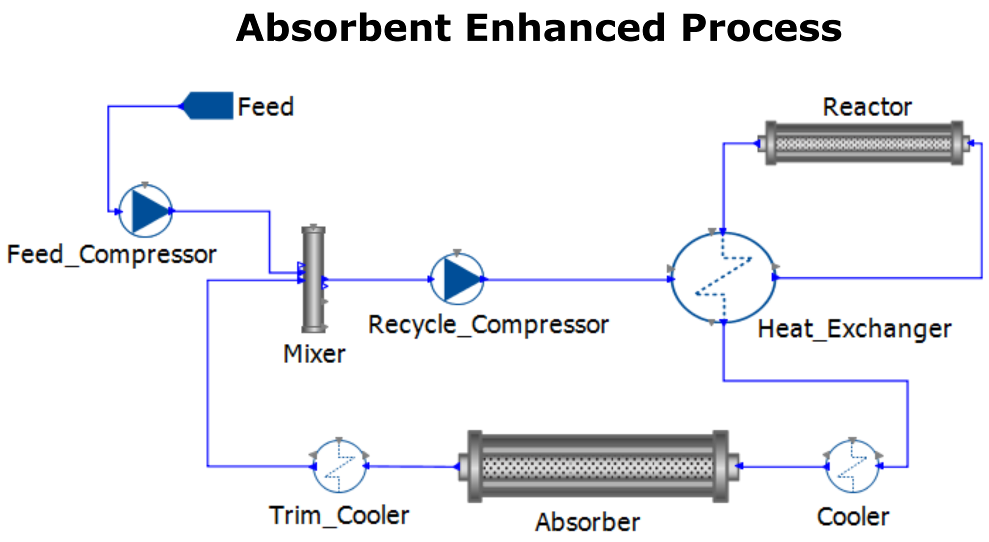


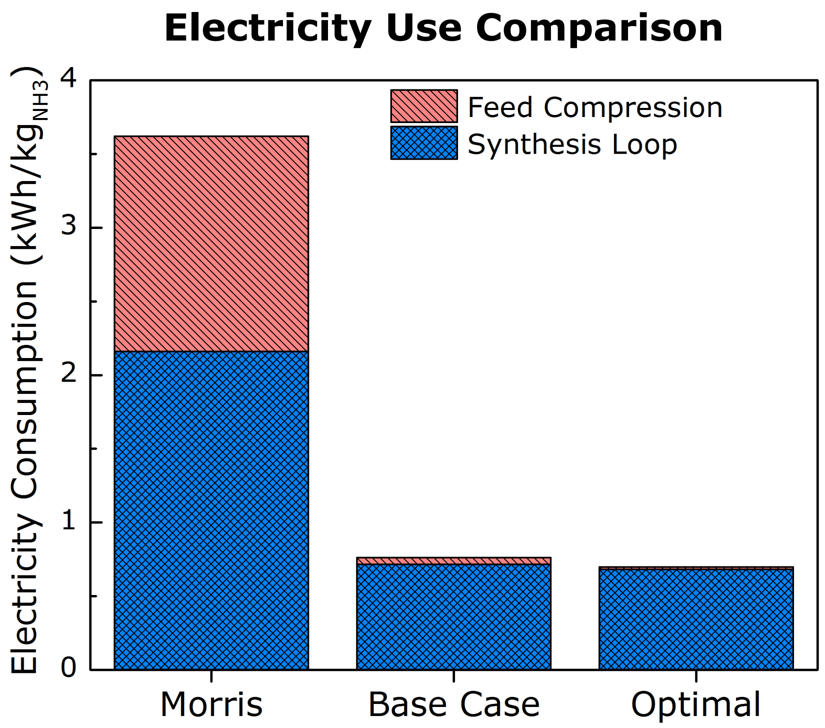


Lower pressure
Less recycle

Conclusions

- Dynamic model of absorbent enhanced ammonia synthesis process
  - Incorporates experimental data
  - Quantitatively demonstrates significant reduction in electricity use
  - Can be used for optimization
    - Minimized electricity consumption in this work





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CHANGING WHAT'S POSSIBLE

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