Comparative Technoeconomic Analysis of Absorbent-Enhanced and Traditional Ammonia Production

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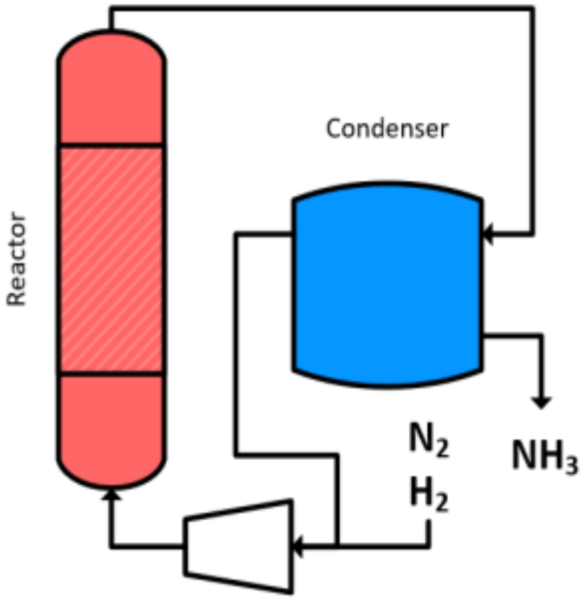
19 AIChE Annual Meeting, Orlando, FL

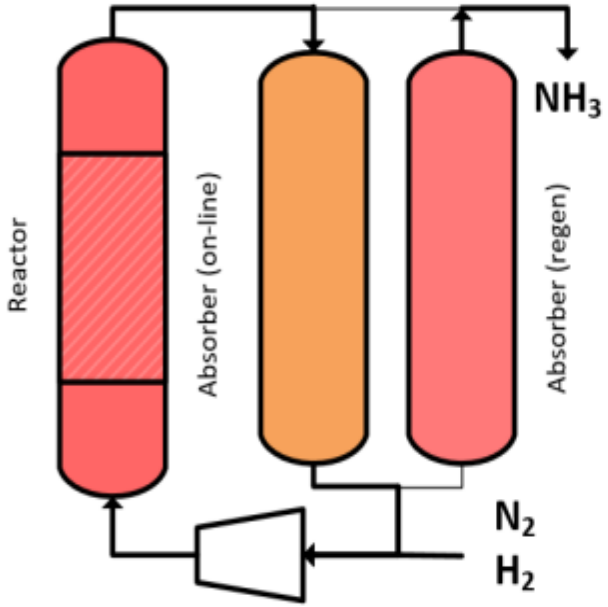
Absorbent-Enhanced Ammonia Production

- Alternative to traditional condenser-based process

Condenser-Based Process

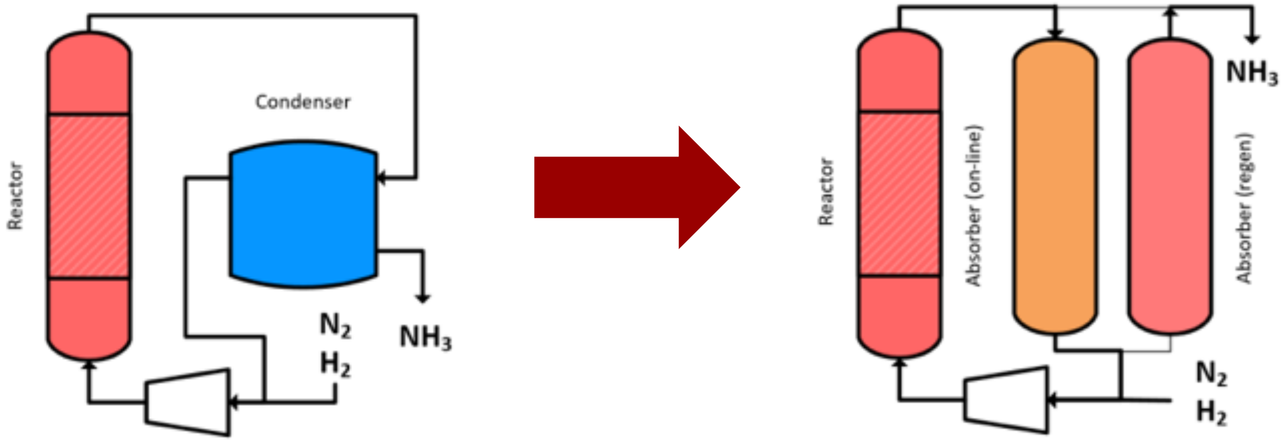


Absorbent-Enhanced Process



- Lower pressure
- Smaller temperature difference for separation
- More complete separation

Absorbent-Enhanced Ammonia Production



Condenser-Based Process

Absorbent-Enhanced Process

- Lower pressure
- Smaller temperature difference for separation
- More complete separation

Research at UMN:

- Absorbent and lab-scale performance experiments[1-3]
- Performance and energy consumption modeling[4,5]
- Optimal design for small-scale, wind-powered operation[6]

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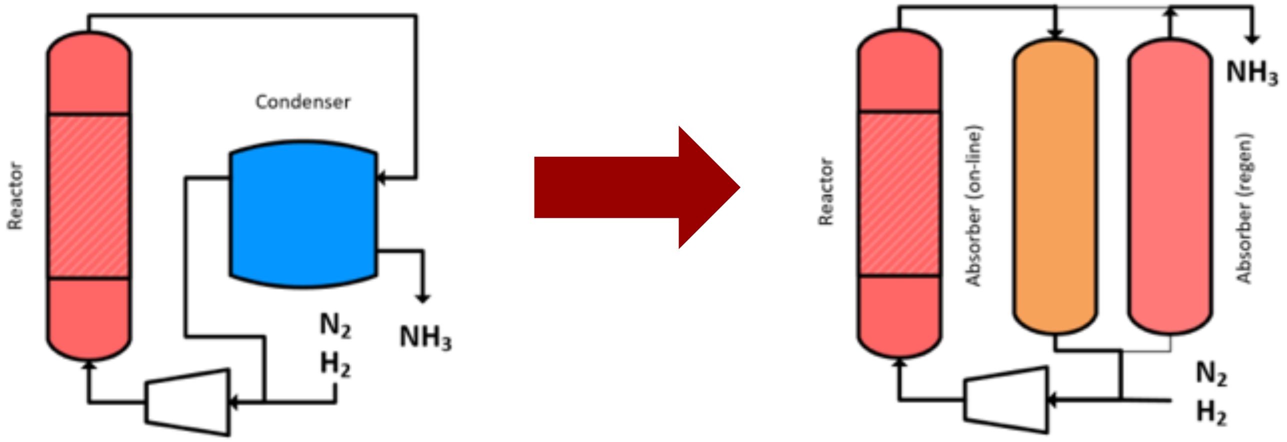
[1] Himstedt et al. (2015). *AIChE J.*, 61(4), 1364-1371.
[2] Malmali et al. (2016). *Ind. Eng. Chem. Res.*, 55(33), 8922-8932.
[3] Malmali et al. (2017). *ACS Sustainable Chem. Eng.*, 6(1), 827-834.
[4] Smith et al. (2019), *ACS Sustainable Chem. Eng.*, 7(4), 4019-4029.
[5] Palys et al. (2017). *AIChE Annual Meeting*
[6] Palys et al. (2018). *Processes*, 6(7), 91.

This Work: Comparative Technoeconomic Analysis

Condenser-Based Process → **Absorbent-Enhanced Process**



- Lower pressure
- Smaller temperature difference for separation
- More complete separation

- What is the *quantitative* benefit of these design changes?
- Feedstock and utility sources: Natural gas vs. renewable?
- Production scale?

Technoeconomic analysis of both processes

Comparative Technoeconomic Analysis Methodology

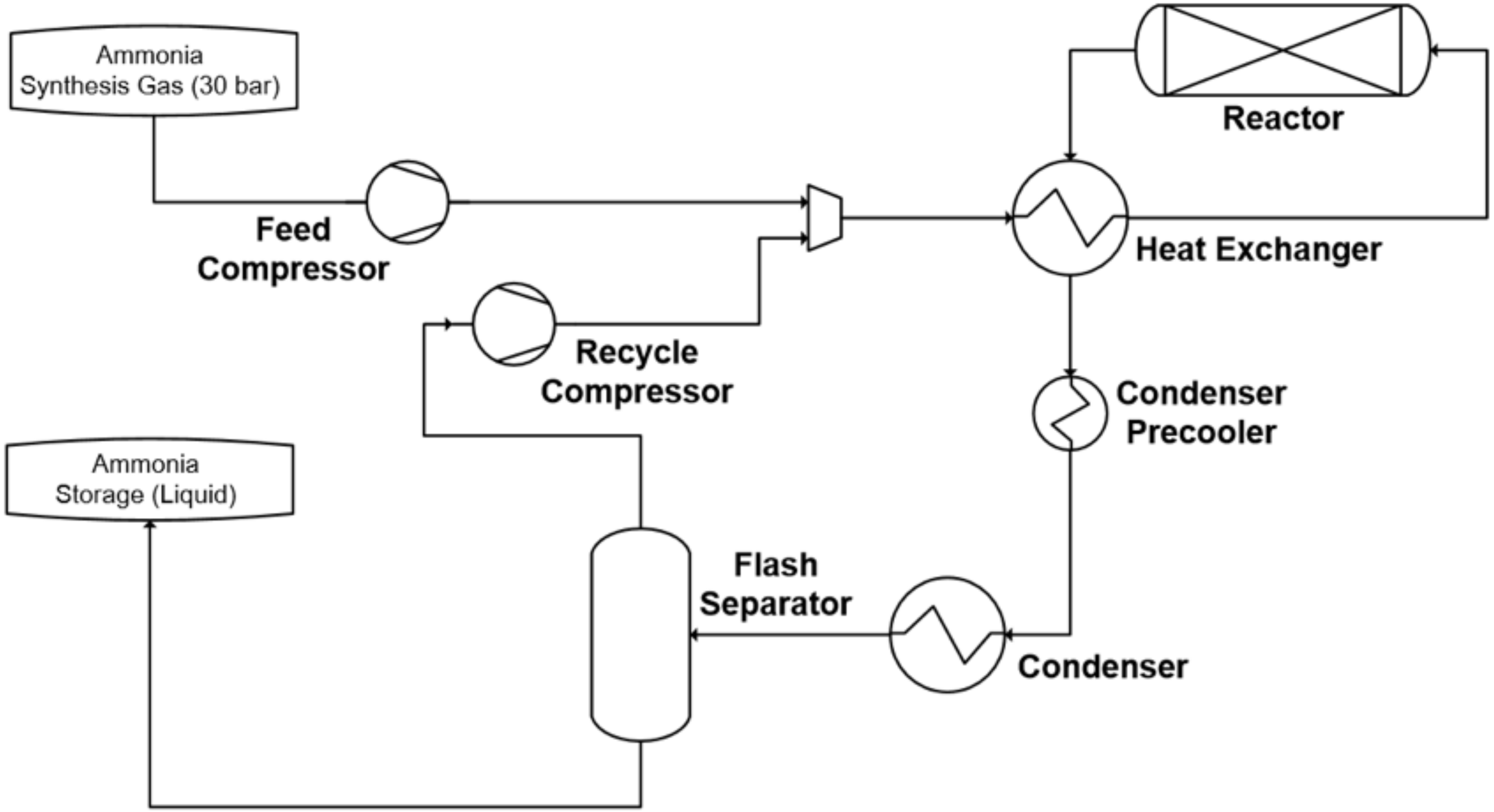
- Flowsheets modeled in gPROMS ProcessBuilder
  - Detailed modeling of ammonia production loops only
  - Ammonia synthesis gas available at 30 bar

- Natural gas and renewable feedstock/utility sources
  - Natural gas: Purchased synthesis gas, natural gas heating
  - Renewable: Electrolysis-derived hydrogen, electric utilities

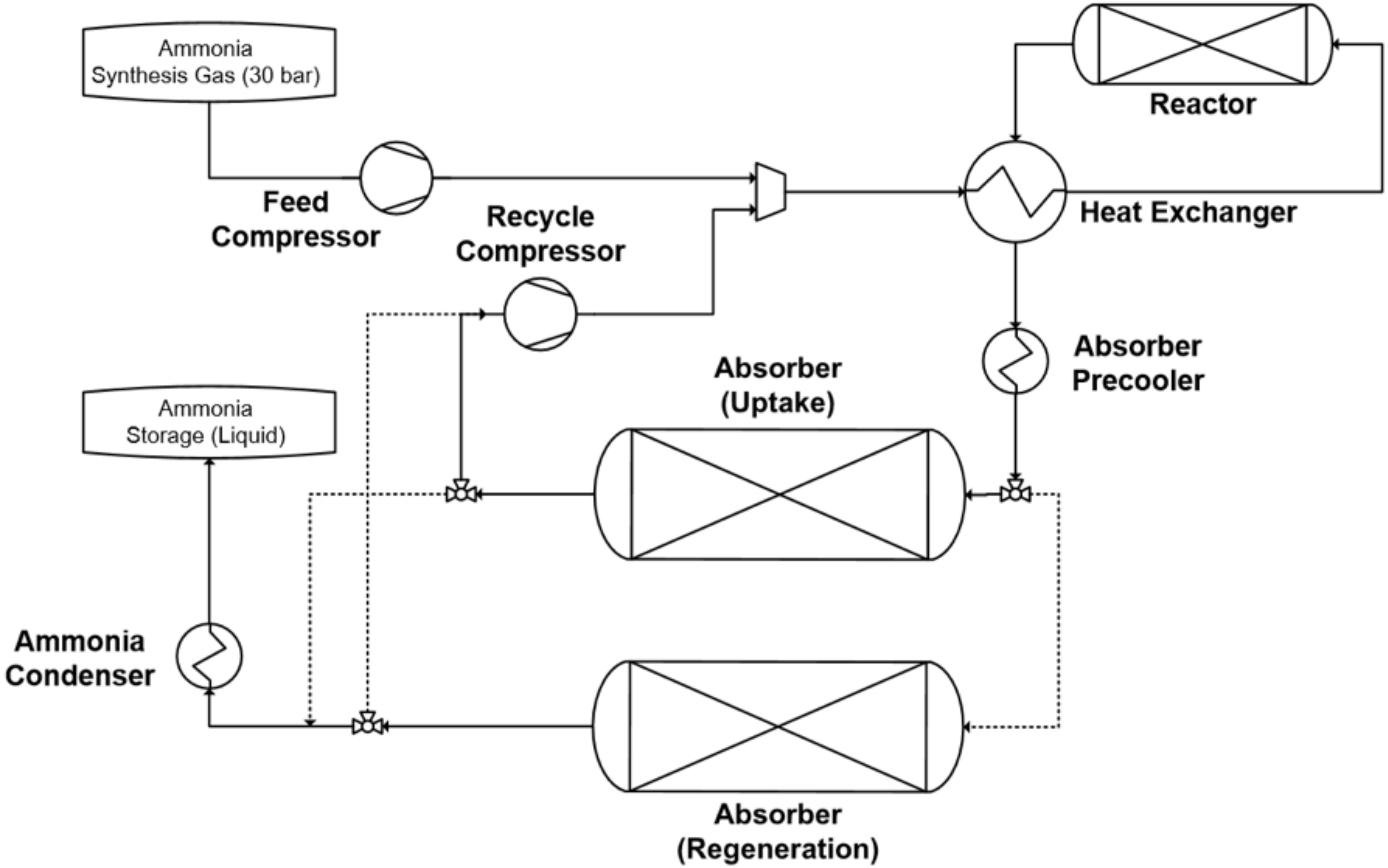
- Production scale range: 10,000 (distributed) to 1,500,000 ton/year (industrial)

- Optimal design of synthesis loops to minimize levelized cost

Condenser-Based Process Flowsheet



Absorbent-Enhanced Process Flowsheet



Unit Modeling

- Compressors, heat exchangers, flash separation standard models
  - Mass and energy balances
  - Thermodynamics and performance equations

- Ammonia synthesis reactor modeling:
  - Radial flow reactor
  - Adiabatic
  - Synthesis rate expression[1]: Non-infinite at zero ammonia partial pressures
  - Empirical catalyst effectiveness factor derived for low pressure[2]

[1] Sehested et al. (1999). *J. Cat.*, 188(1), 83-89.
[2] Dyson & Simon (1968). *Ind. Eng. Chem. Fundam.*, *7*(4), 605-610.

Absorption-Regeneration Modeling

- Multi-tubular fixed bed
- Isothermal operation: Cooling for absorption, heating for regeneration
- $MgCl_2$-Si absorbent capacity[1]: $0.1\ kg_{NH3}/kg_{abs}$

- Rates of absorption and regeneration[1]: $f\,(p_{NH_3} - p_{NH_3,eq})$
- Equilibrium pressure: Decreases with increasing temperature[2]
- Cycle time: 30 minutes
  - Regeneration
    - 5 minutes for heating/de-pressurization
    - 20 minutes for regeneration
    - 5 minutes for cooling/re-pressurization

[1] Smith et al. (2019), *ACS Sustainable Chem. Eng.*, 7(4), 4019-4029.
[2] Sørensen et al. (2008). *J. Am. Chem. Soc.*, 130(27), 8660-8668.

Key Economic Assumptions: Capital Costs

- Synthesis loop unit capital costs[1]

$$C_i = C_{i,ref}\left(\frac{S_i}{S_{i,ref}}\right)^{\beta_i} f(P_i)$$

- Electrolysis capital cost[2]: \$300/kW

- Outside battery limits (OSBL) costs[3]: 50% of inside battery limits (ISBL)
- Contingency costs[3]: 40% of ISBL+OSBL
- Maintenance costs[3]: 10% of ISBL/year

- Scaled project lifetime: 9.51 years (20 years at 10% discount rate)

[1] Woods (2007). *Rules of thumb in engineering practice*. Wiley.
[2] U.S. Dept. of Energy (2015). *Fuel cell technologies office multi-year research, development, and demonstration plan.*
[3] Towler and Sinnott (2017). *Chemical Engineering Design.* Elsevier.

Key Economic Assumptions: Operating Costs

- Electricity cost[1]: \$0.037/kWh

For natural gas feedstock and utilities

- Natural gas cost[2]: \$4.25/1000 cu. ft (2013-2018 average)
- Synthesis gas levelized cost[3]: \$1.55/kg (based on NG cost)

For renewable feedstock

- Electrolyzer energy use[1]: 44 kWh/kgH_2

[1] U.S. Dept. of Energy (2015). *Fuel cell technologies office multi-year research, development, and demonstration plan.*

[2] U.S. IEA (2019). *U.S. Natural Gas Industrial Price Data.*

[3] USDRIVE (2017). *Hydrogen Production Technical Team Roadmap.*

Levelized Cost Optimization

Objective: minimize Levelized Cost= $\frac{\text{Annualized Capital Cost+Operating Cost}}{\text{Production Scale}}$

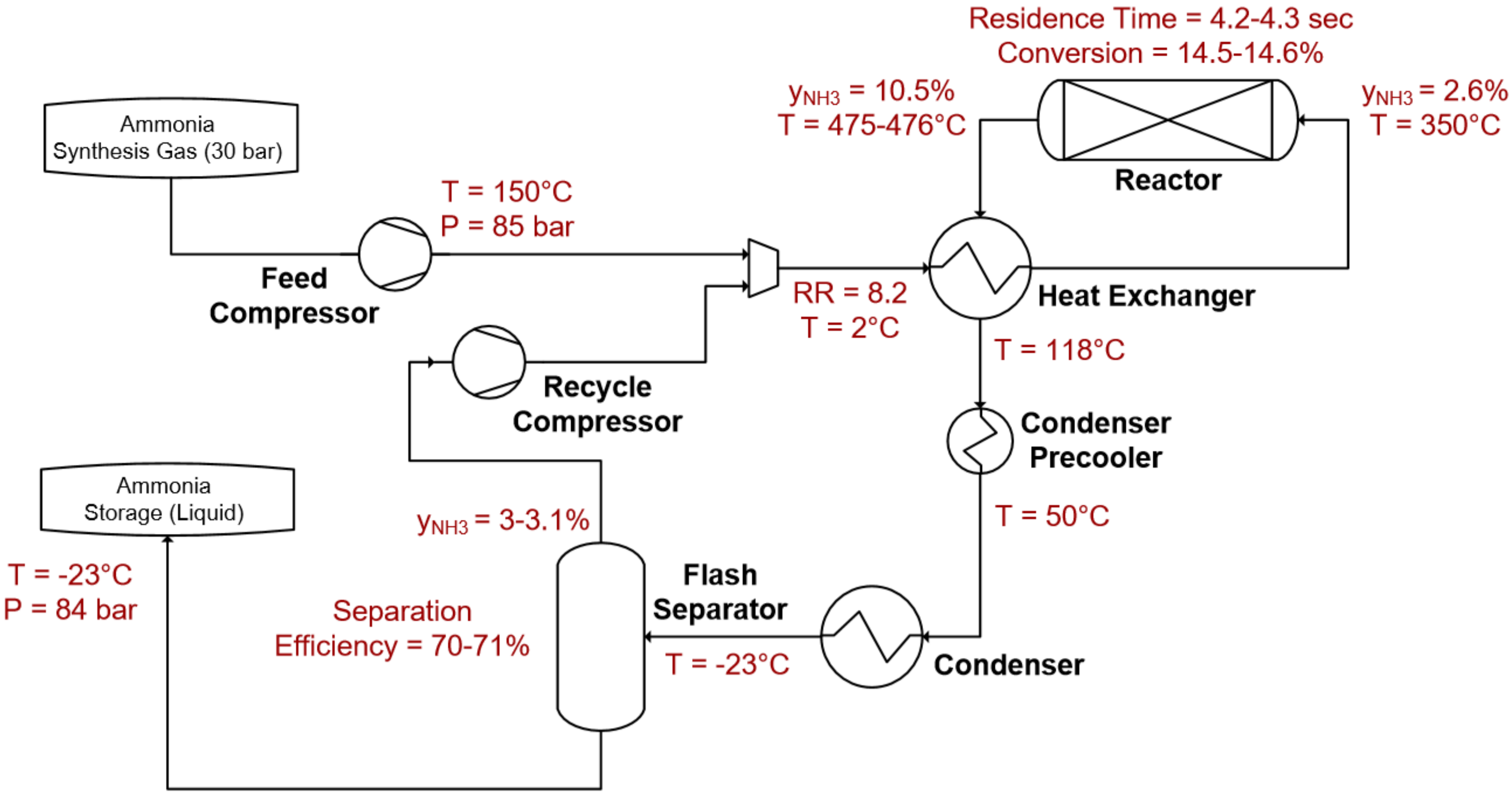
Decisions:

- Unit sizes
- Flowrates
- Temperatures
- Pressures

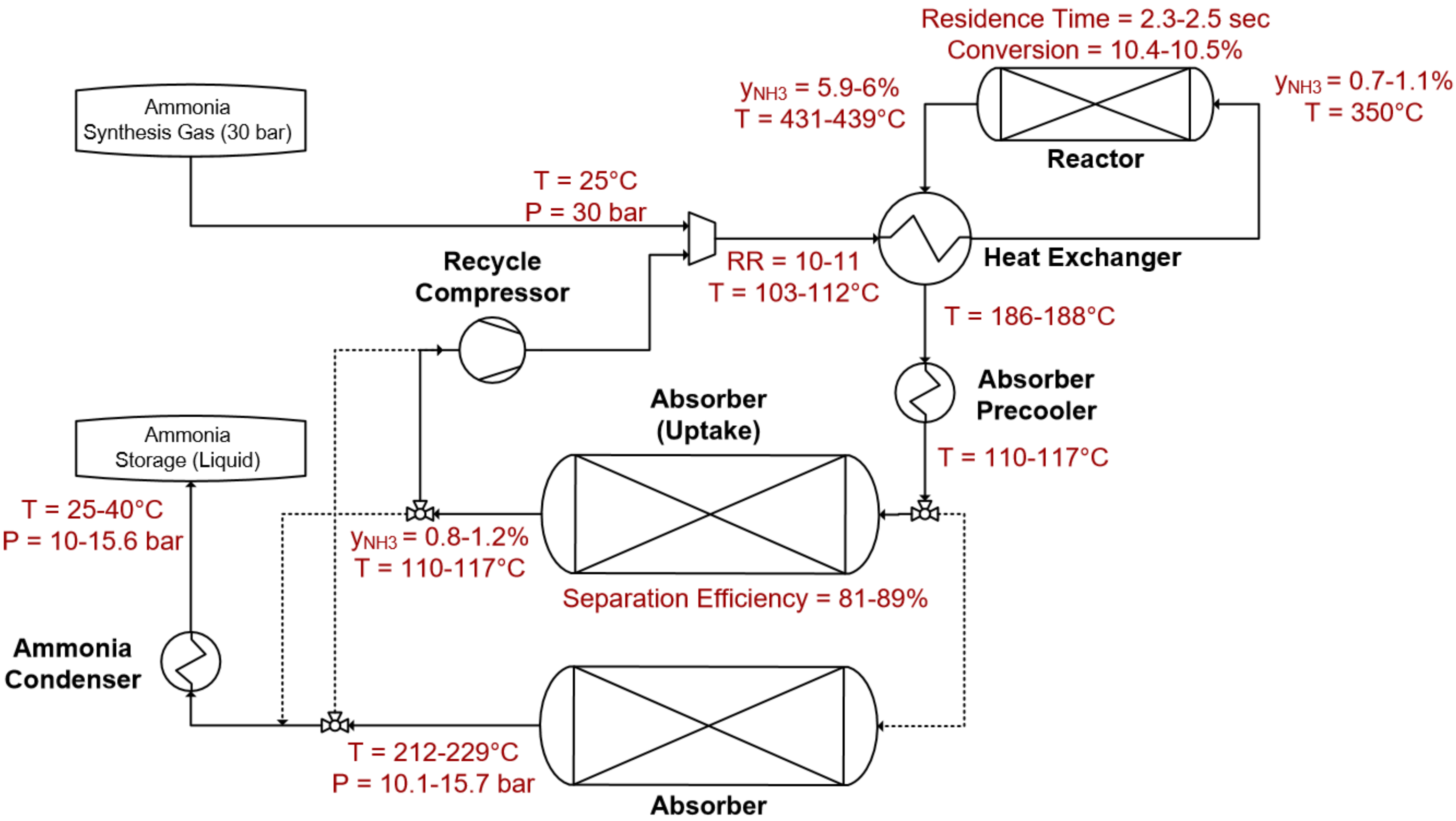
Constraints:

- Production requirement
- Liquefied ammonia product
- Decision bounds for safety, performance, model fidelity (i.e. kinetics)
- Process model

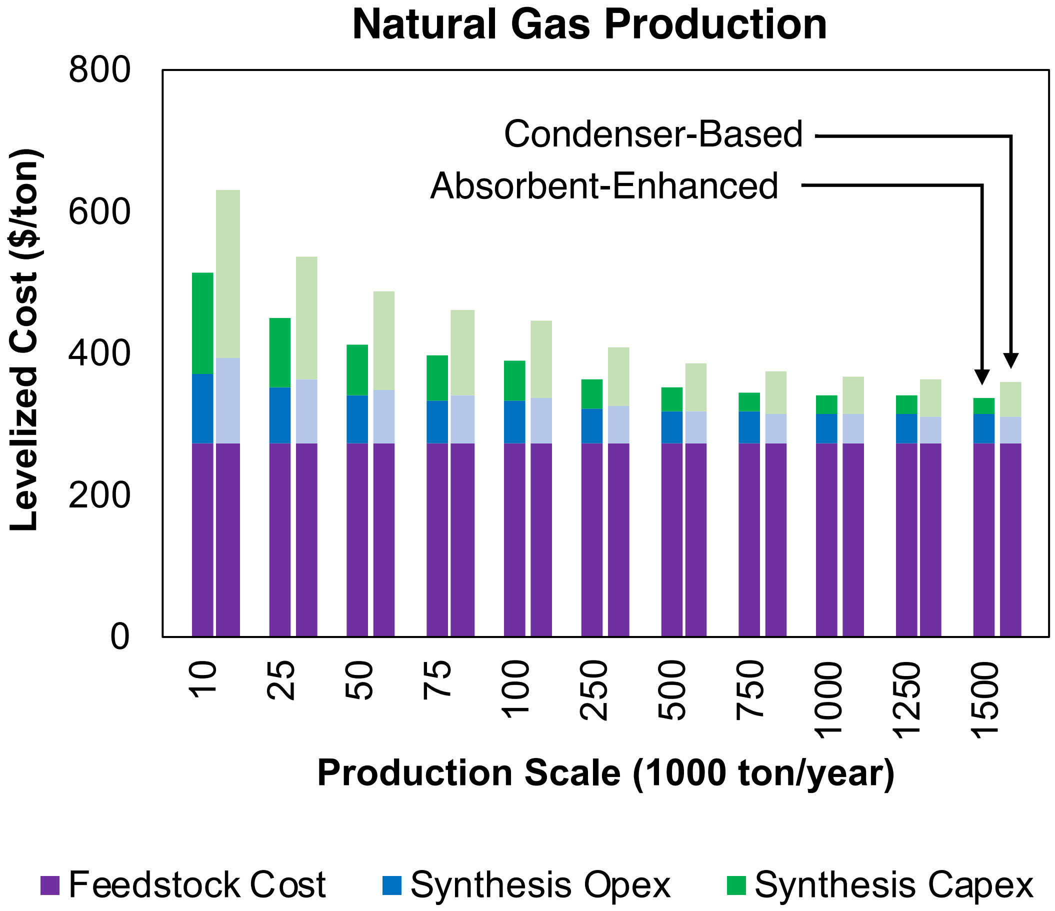
Condenser-Based Optimal Flowsheet

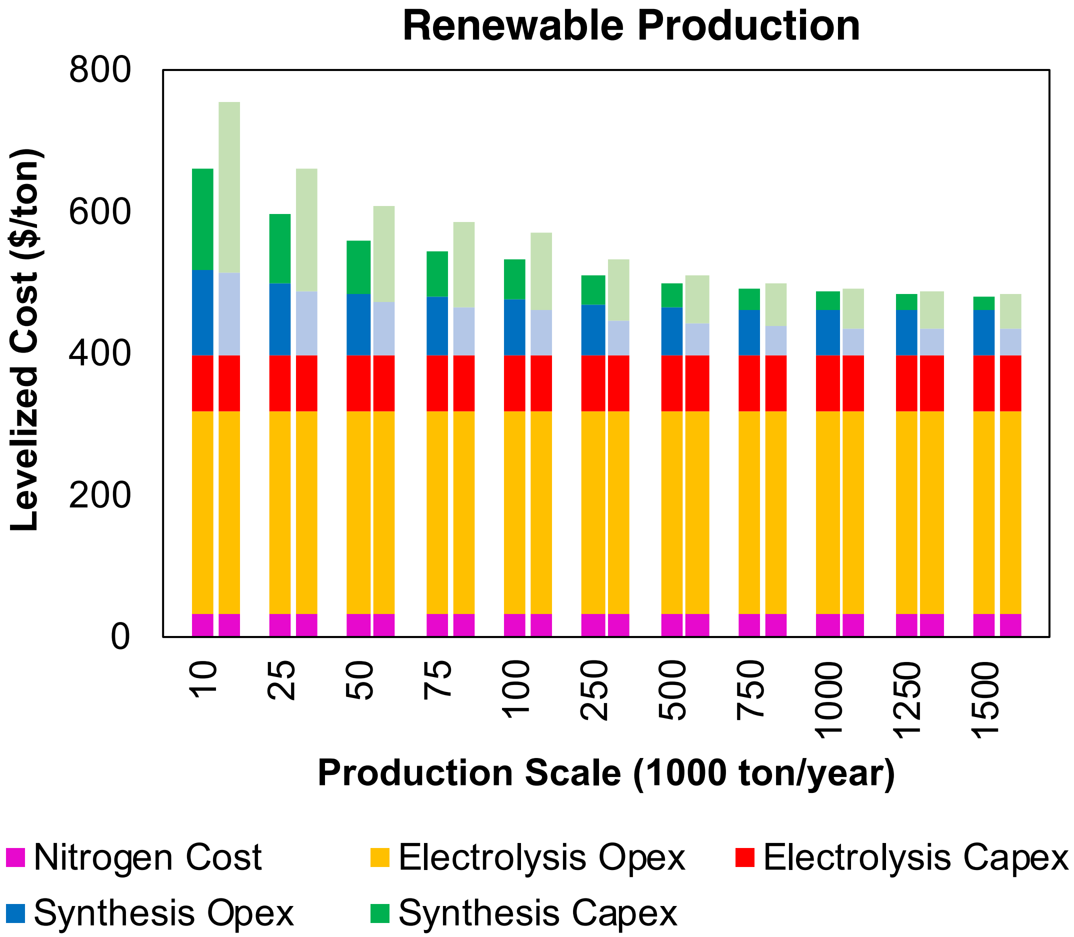


Absorbent-Enhanced Optimal Flowsheet



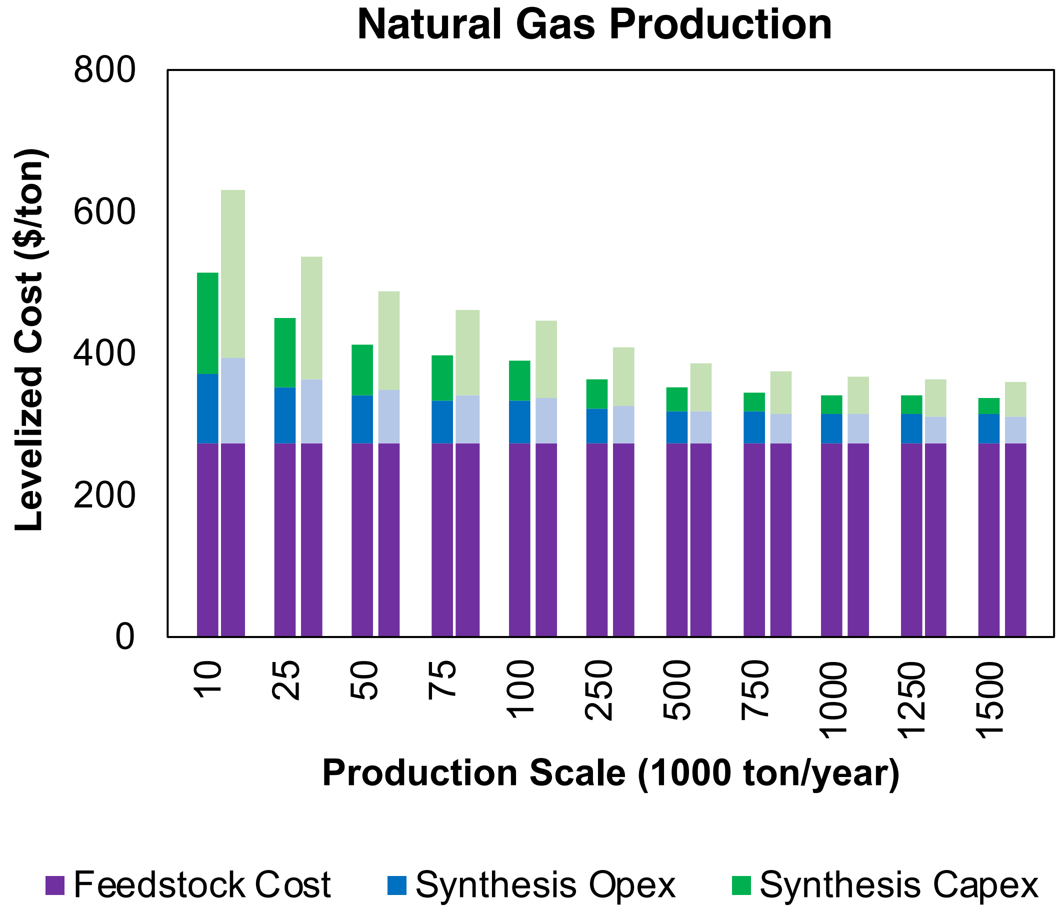
Levelized Cost of Ammonia Production

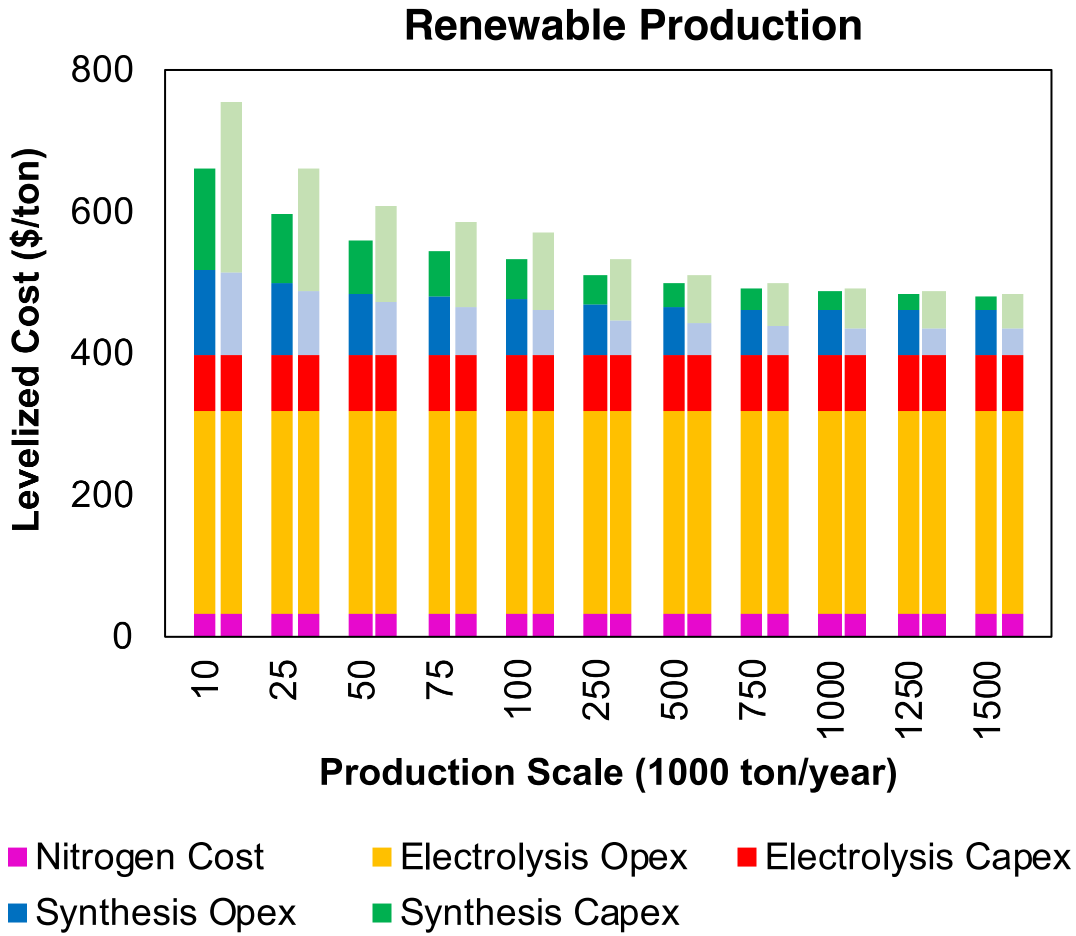




- Feedstock costs significant

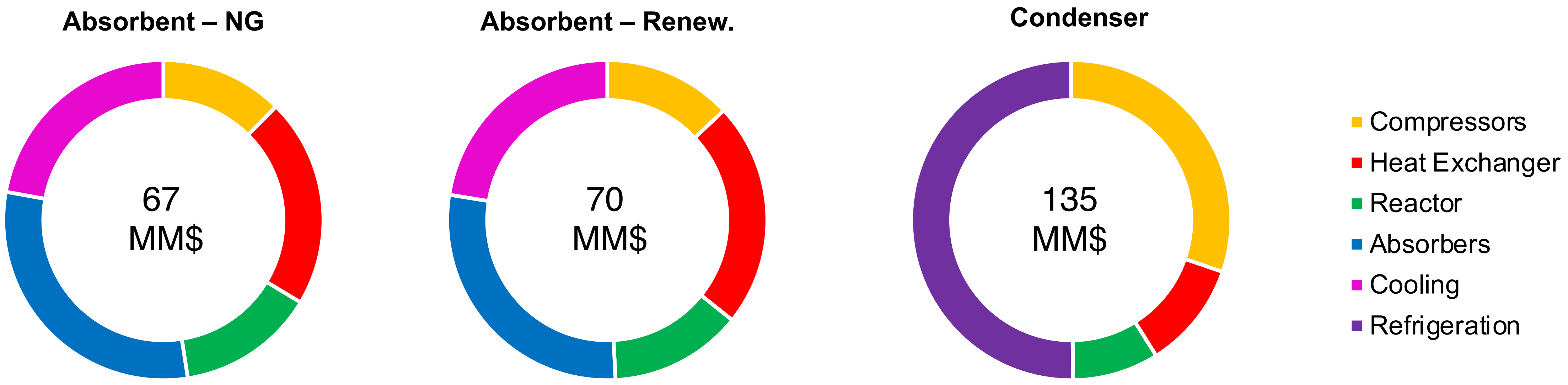
Levelized Cost of Ammonia Production


Natural Gas Production


Renewable Production

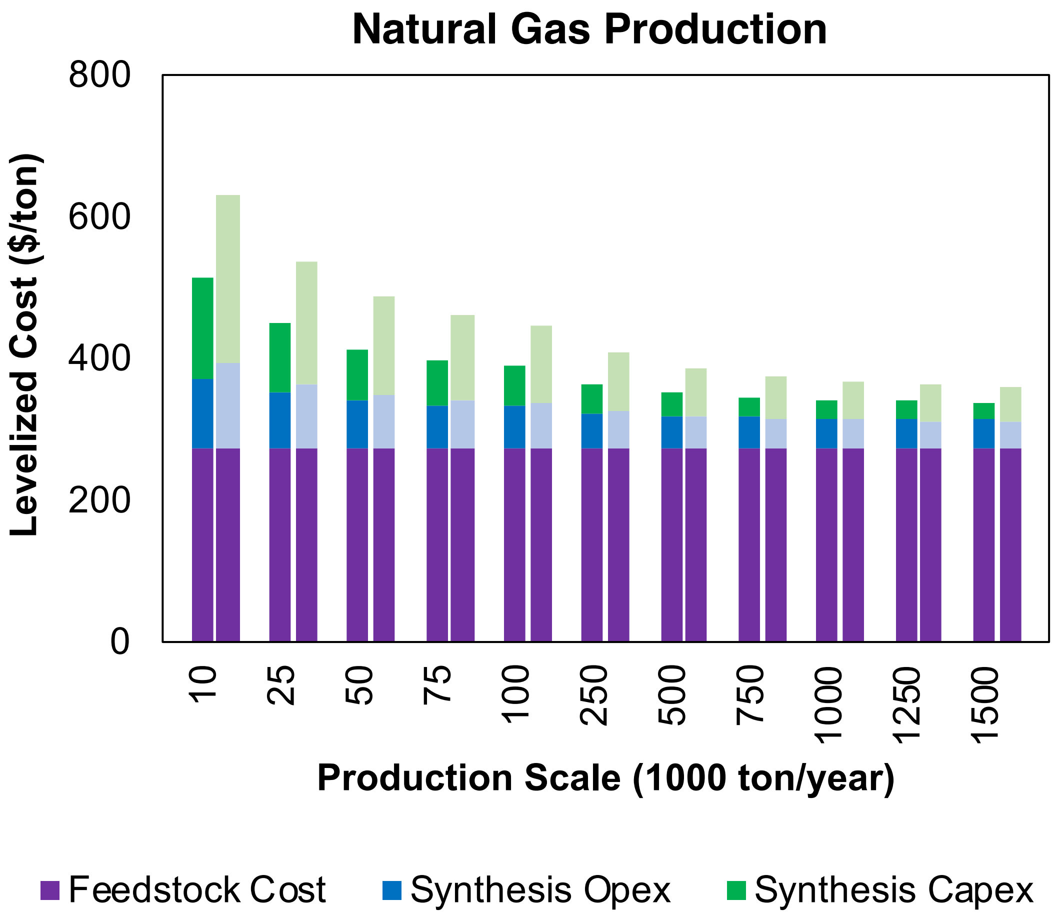
- Feedstock costs significant
- Absorbent-enhanced less expensive, especially scaled down: Synthesis capex

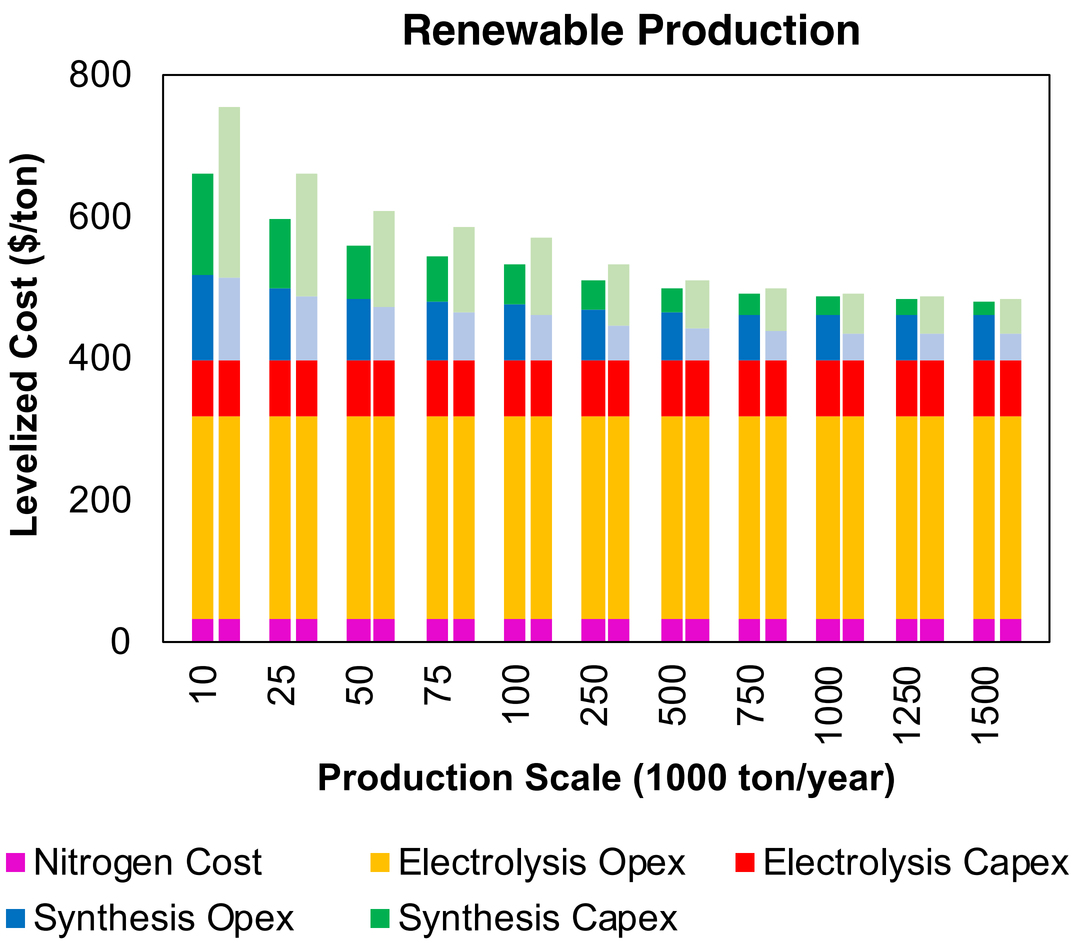
Capital Cost at 500,000 ton/year



- Lower pressure for absorbent-enhanced: 30 bar vs. 85 bar
  - No feed compressor
  - Lower cost for same sized units
- Absorbent-enhanced avoids costly refrigeration

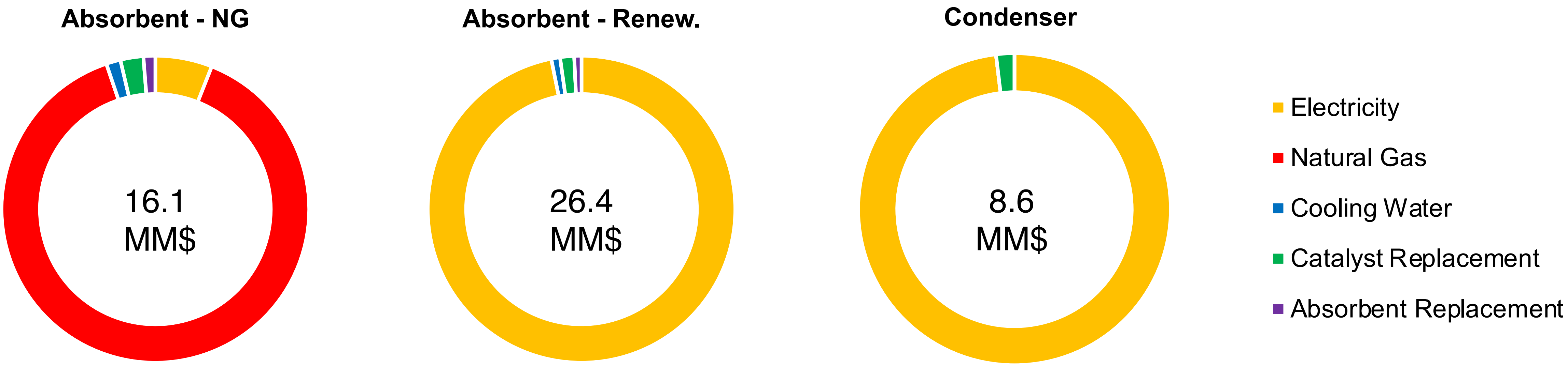
Levelized Cost of Ammonia Production





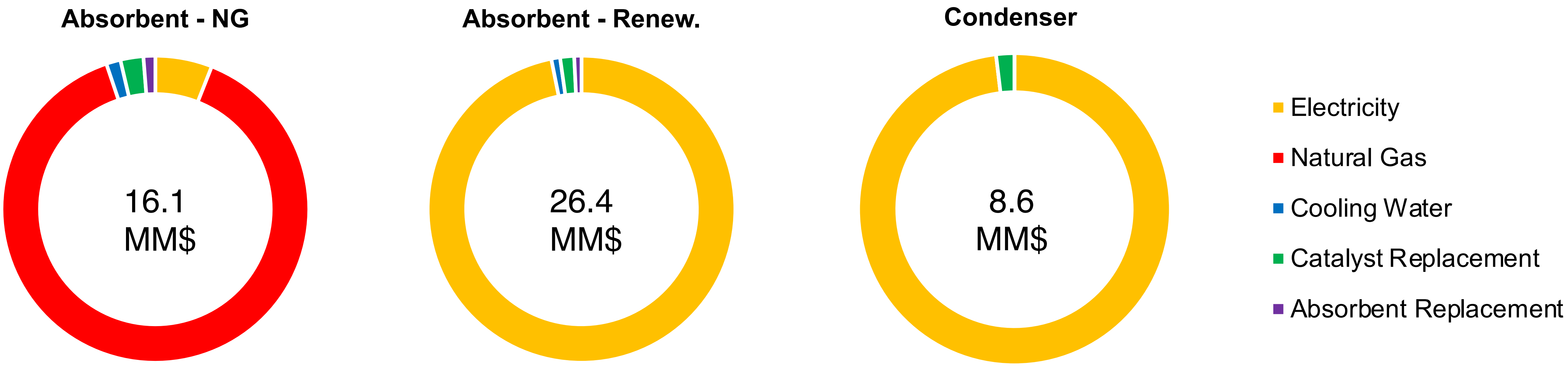
- Feedstock costs significant
- Absorbent-enhanced less expensive, especially scaled down
- Bigger cost difference for natural gas production: Synthesis opex

Variable Operating Cost at 500,000 ton/year



- Heating for regeneration drives absorbent-enhanced operating costs
  - Electrical heating is expensive
  - No absorption-regeneration heat integration

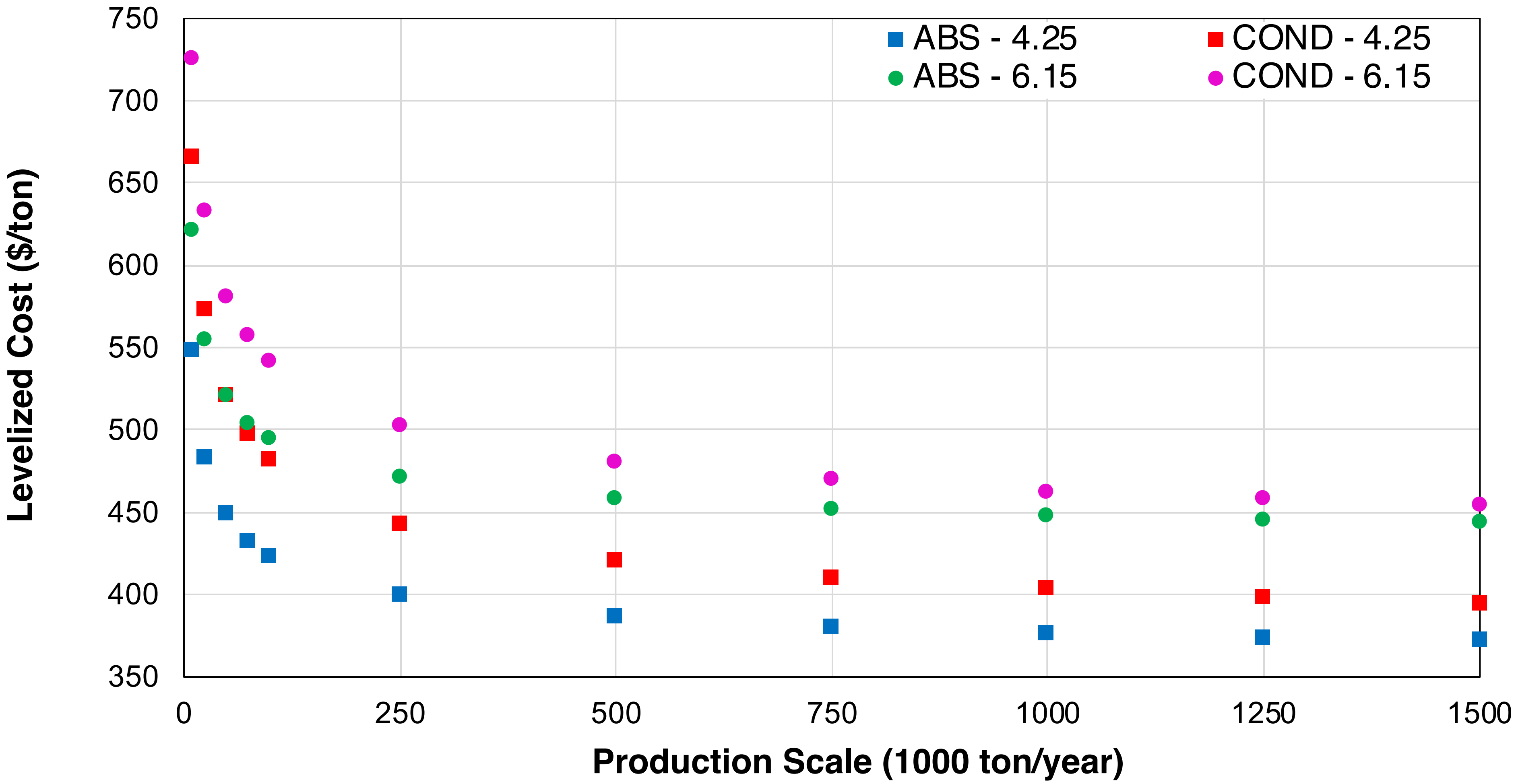
Variable Operating Cost at 500,000 ton/year



- Heating for regeneration drives absorbent-enhanced operating costs
  - Electrical heating is expensive
  - No absorption-regeneration heat integration

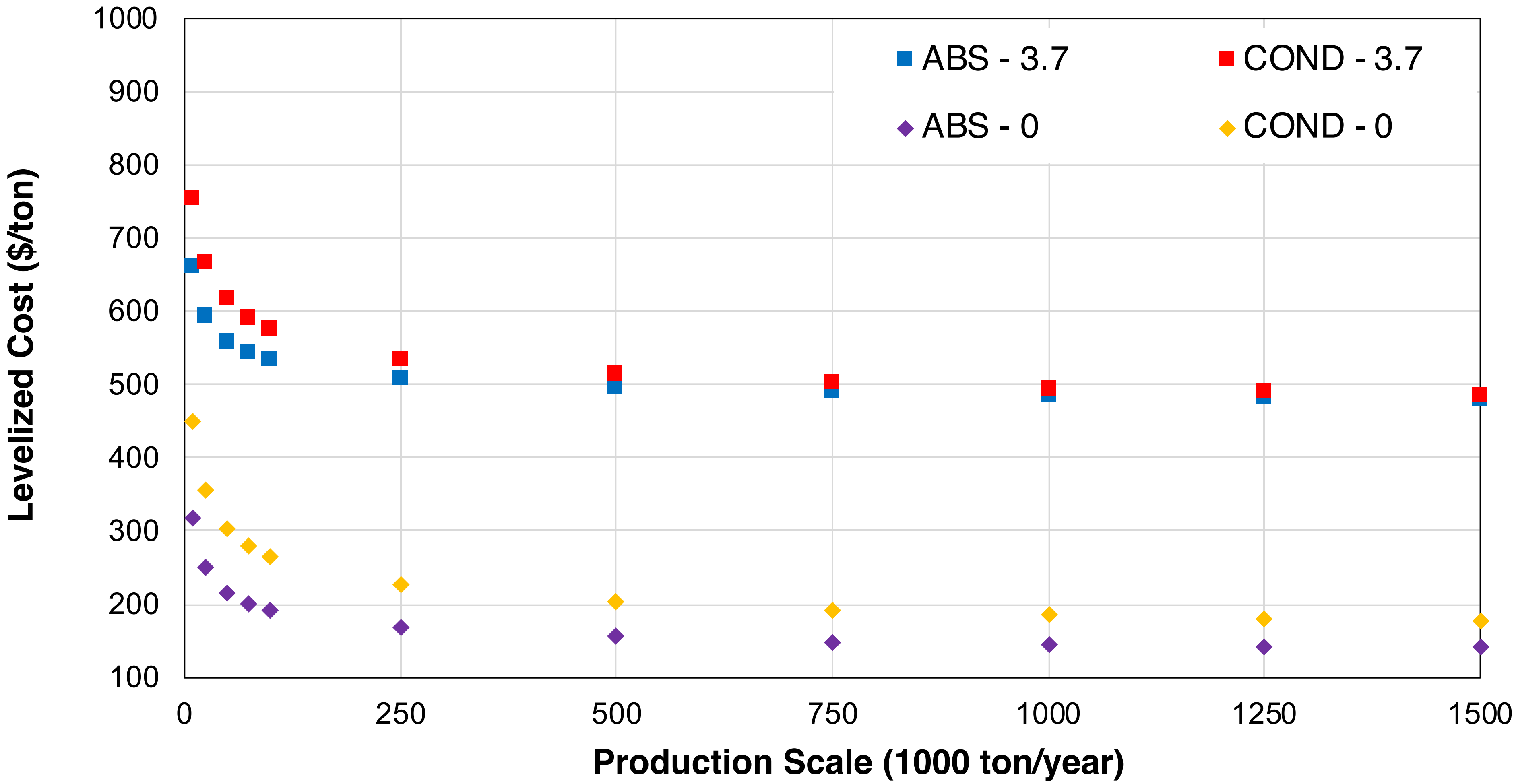
Utility costs more strongly affect feasibility of absorbent-enhanced process

Sensitivity to Natural Gas Price



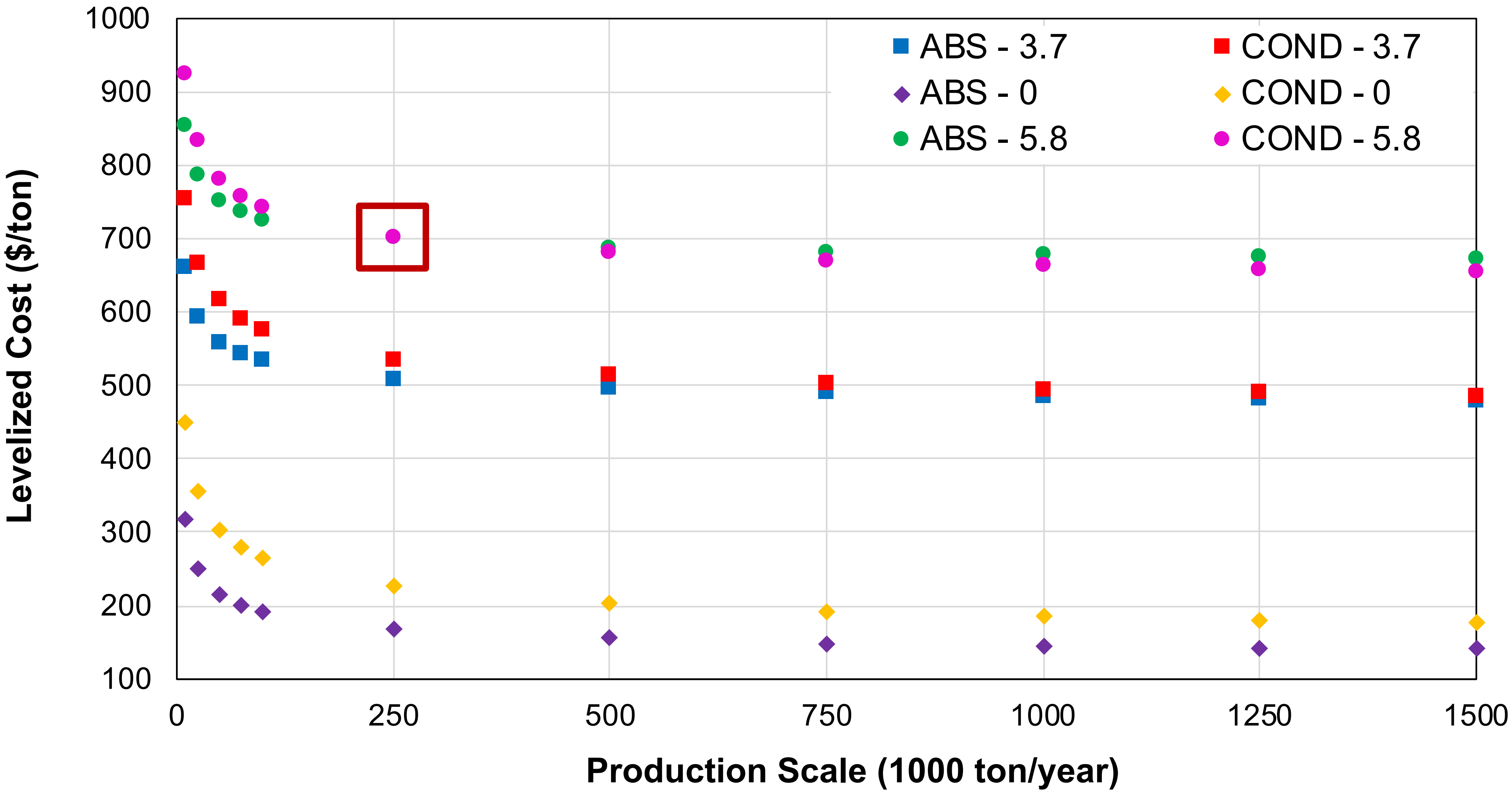
Still less expensive at $6.15/1000 cu. ft (2008-2013 avg.)

Sensitivity to Electricity Price in Renewable Production



Even more favorable with low-cost electricity: Stranded?

Sensitivity to Electricity Price in Renewable Production

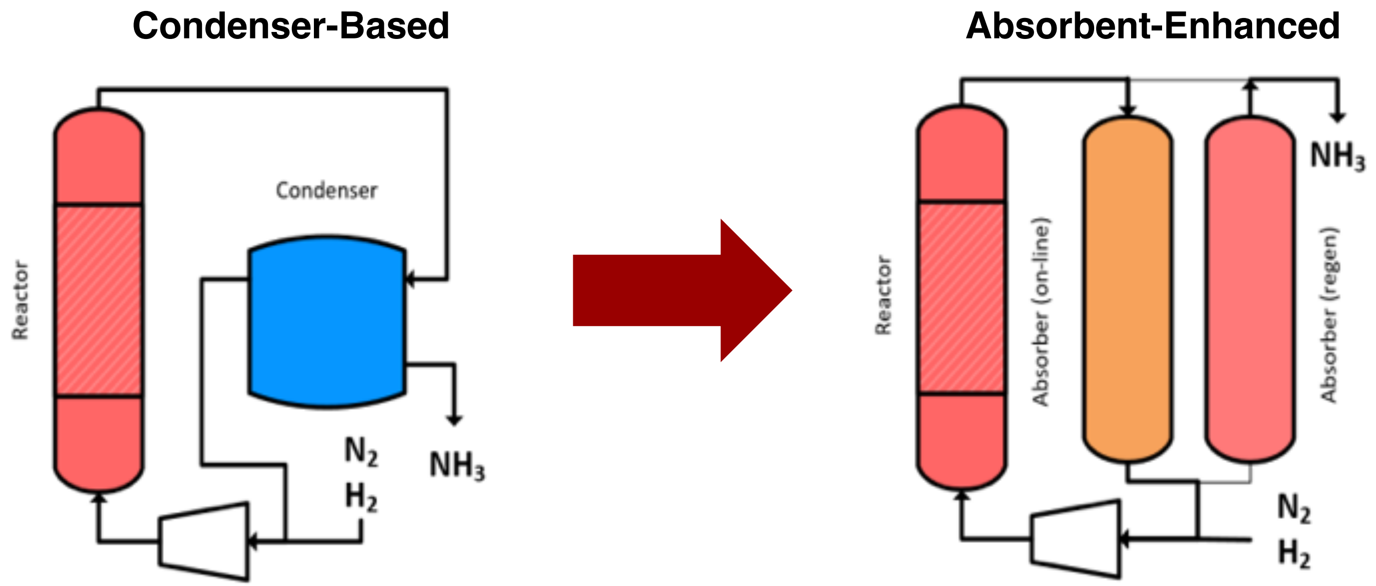


Not viable with standard electricity costs: Why renewable production?

Conclusions

- Absorption-enhanced process is viable alternative to condenser-based
  - Lower capital investment
  - Ideal for small-scale production with low-cost electricity: *Renewable*

- Next improvement: Reduce operating costs → Heat integration?



Acknowledgements

Daoutidis research group

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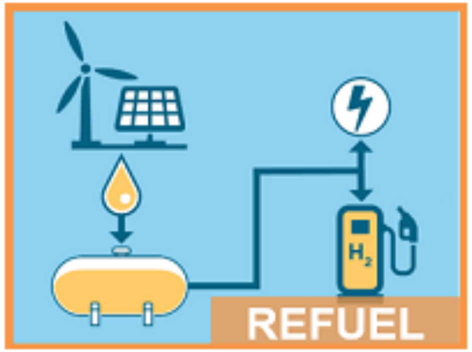

UMN Refuel Project Team

- NREL: Ling Tao, Michael Resch, Mary Biddy
- WCROC: Michael Reese, Cory Marquart

- Dr. Grigorii Solovichiek
- Dr. Madhav Acharya

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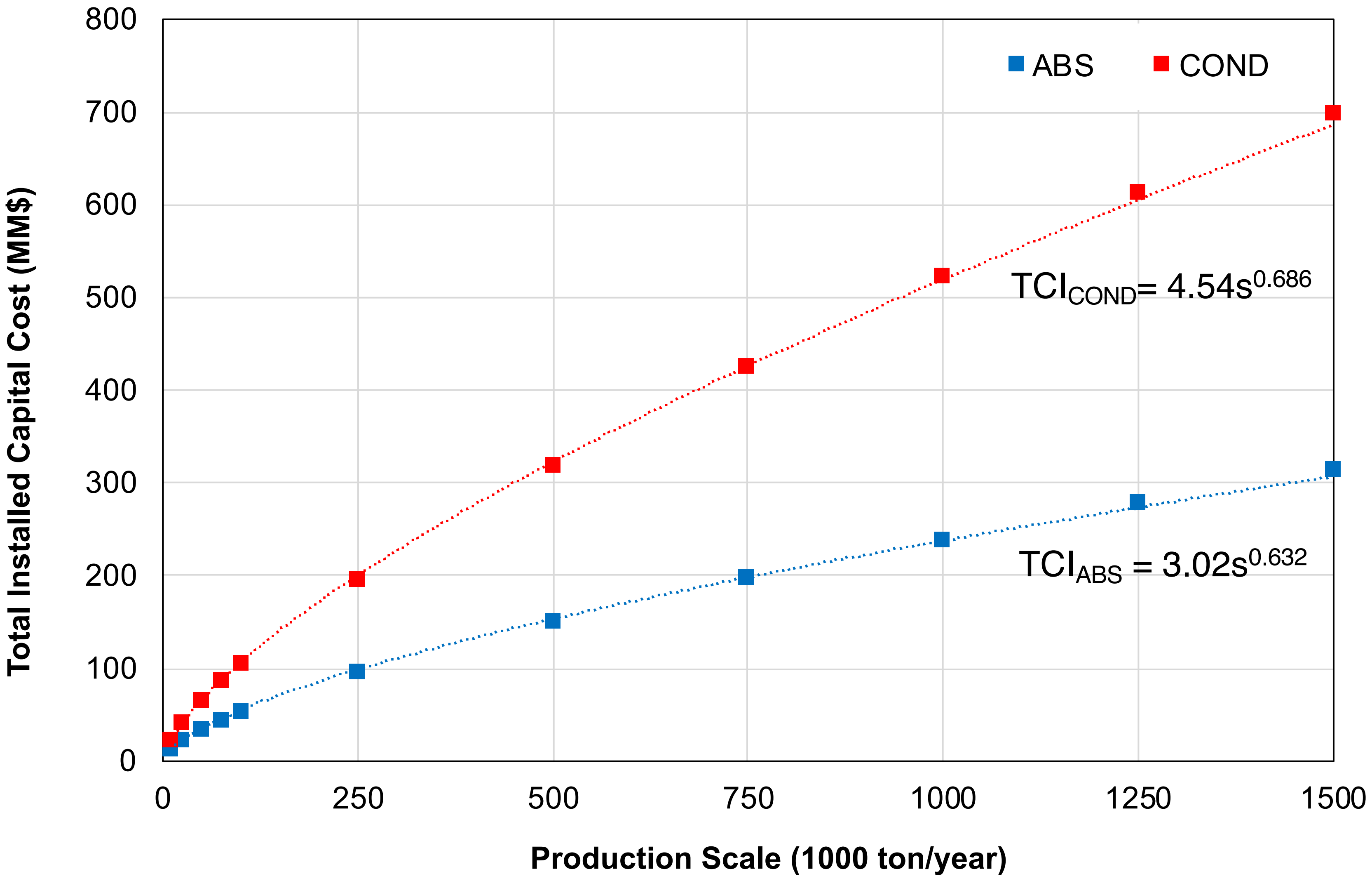
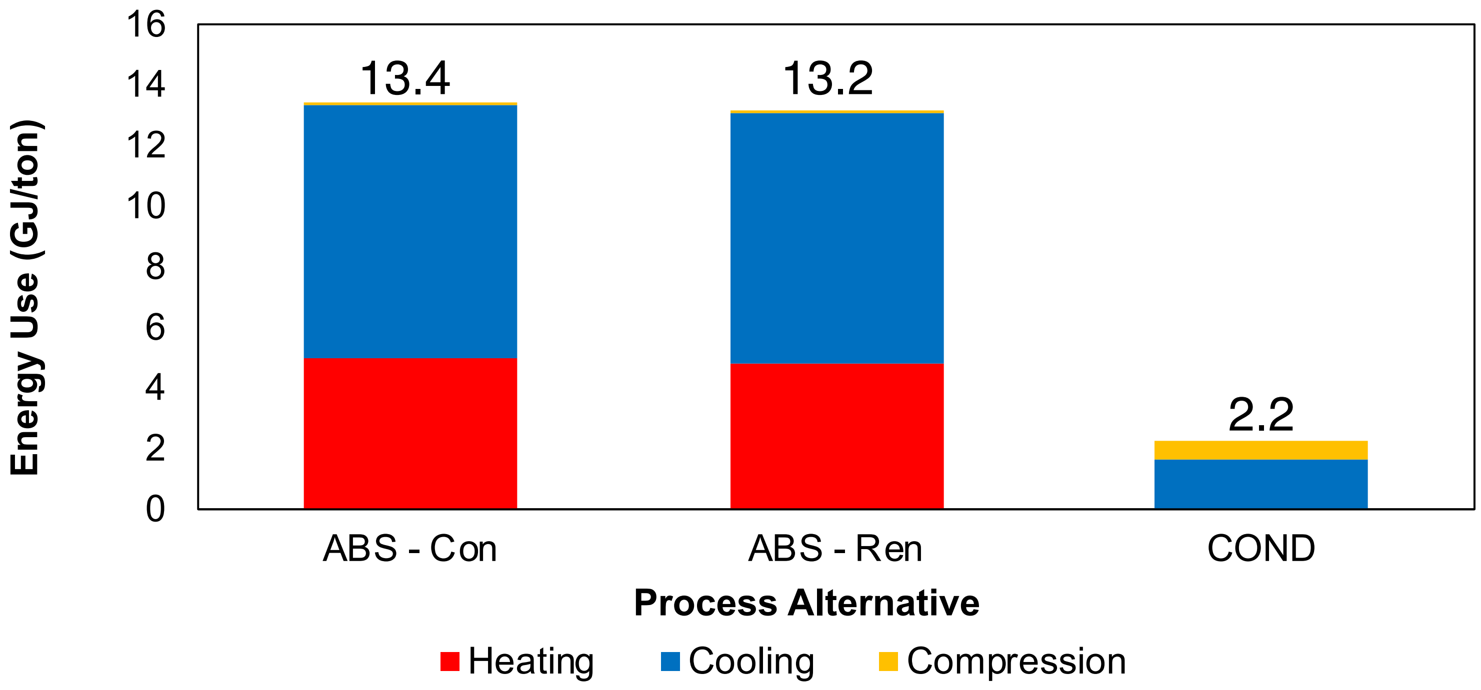
Capital Cost Scaling



Energy Use at 500,000 ton/year

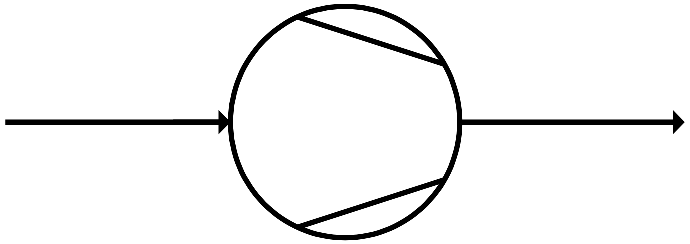


- Absorbent-enhanced requires more cooling, significant heating needed for ammonia recovery
- Not all forms of energy have same cost: Cooling water vs. refrigeration
- Reaction, absorption are exothermic, regeneration is endothermic: Better heat integration?

Cost Correlations: Compressor

Assumptions:

- Polytropic efficiency: 80%
- Electrical efficiency: 75%



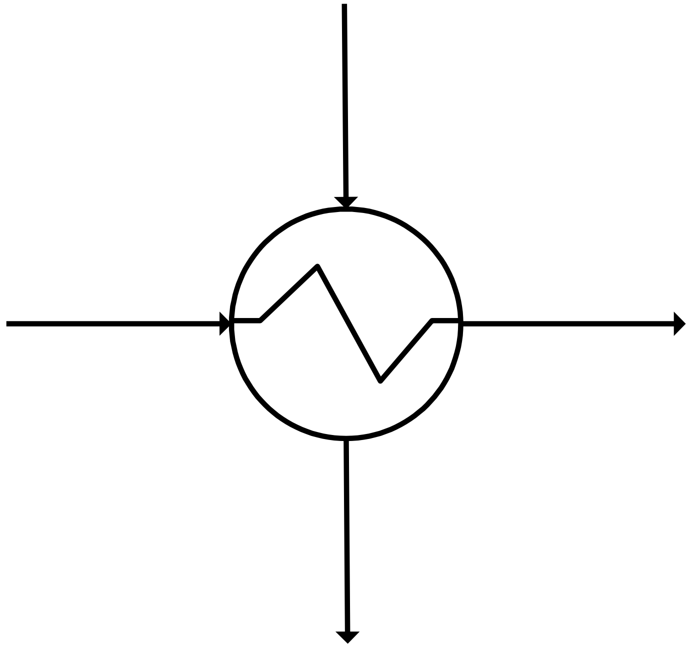
$$\dot{W}_{elec} = \dot{W}_{comp}/0.75$$

$$C_{comp} = 7.1\left(\frac{\dot{W}_{elec}}{1{,}000\ kW}\right)^{0.65}$$

Cost Correlations: Process Stream Heat Exchanger

Assumptions:

- Shell and tube heat exchanger
- Overall heat transfer coefficient: $\mathrm{U} = 0.15 \frac{kW}{m^2\ K}$



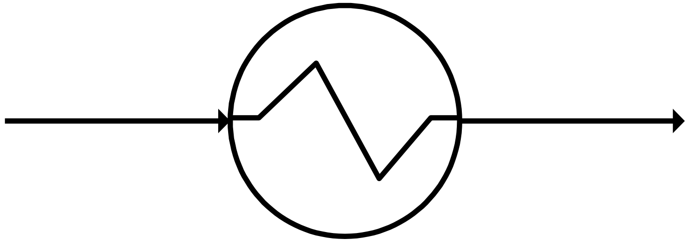
$$A_{HEX} = \frac{\dot{Q}_{HEX}}{\Delta T_{\ell m} U}$$

$$C_{HEX} = 0.44 \left(\frac{A_{HEX}}{100\ m^2}\right)^{0.71} (0.98 + 0.0026P + 3.5\times 10^{-5} P^2)$$

Cost Correlations: Cooler with Water

Assumptions:

- Shell and tube heat exchanger
- Cooling water as heat transfer fluid
- C.W. inlet temperature: 20°C
- C.W. outlet temperature: 40°C
- Overall heat transfer coefficient: $\mathrm{U} = 0.3\,\frac{kW}{m^2\ K}$
- C.W. pumping requirement: 1.9 kJ/kg



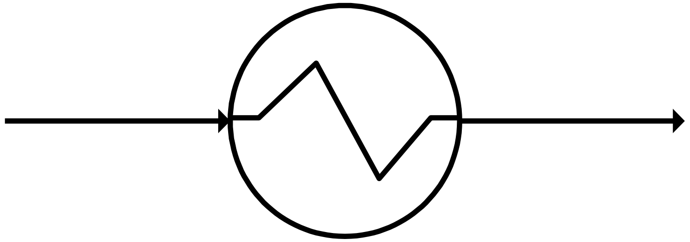
$$A_{COOL} = \frac{\left|\dot{Q}_{COOL}\right|}{\Delta T_{\ell m} U} \qquad \dot{m}_{H_2O,COOL} = \frac{\left|\dot{Q}_{COOL}\right|}{20\mathrm{°C} \times C_{p,H_2O}} \qquad \dot{W}_{H_2O,COOL} = 1.9{\times}\dot{m}_{H_2O,COOL}$$

$$C_{COOL} = 0.44\left(\frac{A_{COOL}}{100\ m^2}\right)^{0.71}(0.98 + 0.0026P + 3.5{\times}10^{-5}P^2)\ + 0.265\left(\frac{\dot{W}_{H_2O,COOL}}{23\ kW}\right)^{0.79}$$

Cost Correlations: Cooler with Refrigeration

Assumptions:

- Shell and tube heat exchanger
- Cooling water as heat transfer fluid
- Refrigerant temperature: -30°C
- Overall heat transfer coefficient: $\mathrm{U} = 0.3\,\frac{kW}{m^2\ K}$
- Refrigeration COP: 3.5



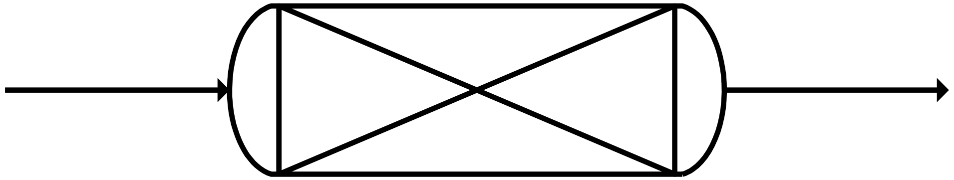
$$A_{COOL} = \frac{\left|\dot{Q}_{COOL}\right|}{\Delta T_{\ell m} U}$$

$$C_{COOL} = 0.44\left(\frac{A_{COOL}}{100\ m^2}\right)^{0.71}\left(0.98 + 0.0026P + 3.5{\times}10^{-5}P^2\right) + 2.77\left(\frac{\dot{Q}_{COOL}}{1000\ kW}\right)^{0.77}$$

Cost Correlations: Ammonia Synthesis Reactor

Assumptions:

- Catalyst density: 3000 kg/m^3
- Bed void fraction: 40%
- Catalyst lifetime: 5 years
- Catalyst cost: $15.50/kg



$$C_{RCTR} = 7.72\left(\frac{V_{RCTR}}{100\ m^3}\right)^{0.4}(0.72 + 0.018P)$$

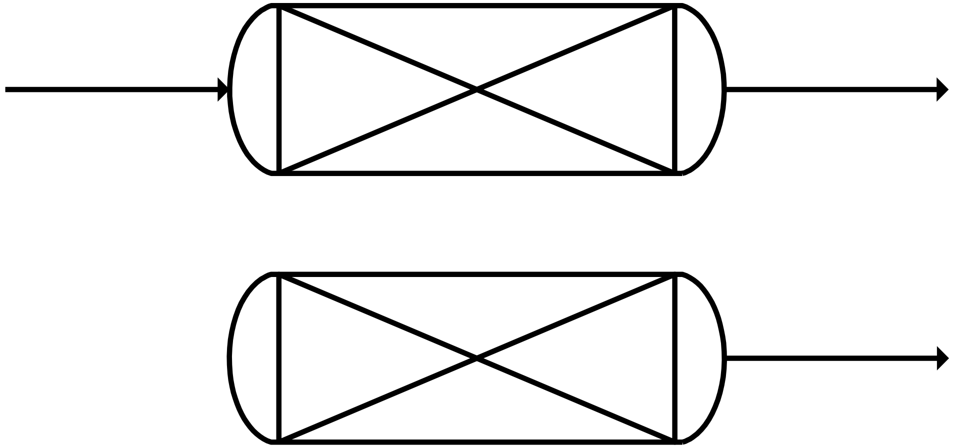
$$W_{CAT} = \rho_{CAT}(1 - \varepsilon_{CAT})V_{RCTR}$$

Cost Correlations: Ammonia Absorbers

Assumptions:

- Heat of absorption: -55.7 kJ/mol
- Absorbent density: 1700 kg/m^3
- Total void fraction: 70%

- C.W. inlet temperature: 20°C
- C.W. outlet temperature: 40°C
- Overall heat transfer coefficient: $\mathrm{U} = 0.3\,\frac{kW}{m^2\ K}$
- C.W. pumping requirement: 1.9 kJ/kg



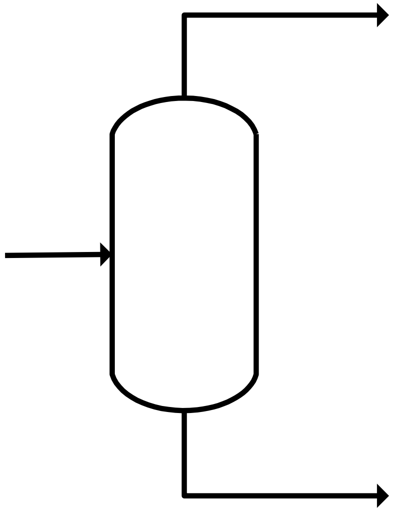
$$A_{UP} = \frac{|\dot{Q}_{UP}|}{\Delta T_{\ell m} U} \qquad \dot{m}_{H_2O,UP} = \frac{|\dot{Q}_{UP}|}{20°\mathrm{C} \times C_{p,H_2O}} \qquad \dot{W}_{H_2O,UP} = 1.9 \times \dot{m}_{H_2O,UP}$$

$$C_{ABS} = 2\left[0.24\left(\frac{V_{ABS}}{20\ m^3}\right)^{0.52} (0.72 + 0.018P)\ +\ 0.21\left(\frac{A_{ABS}}{100\ m^2}\right)^{0.71} (0.98 + 0.0026P + 3.5\times10^{-5}P^2) + 0.265\left(\frac{\dot{W}_{H_2O,COOL}}{23\ kW}\right)^{0.79}\right]$$

Cost Correlations: Flash Separation

Assumptions:

- Length-to-Diameter Ratio = 3



$$u_v = 0.107\sqrt{\frac{\rho_\ell - \rho_v}{\rho_v}} \qquad D = \sqrt{\frac{4\dot{m}_v}{\pi\rho_v u_v}} \qquad V_{FS} = \frac{3\pi D^3}{4}$$

$$C_{FS} = 0.474\left(\frac{V_{FS}}{20\ m^3}\right)^{0.52}(0.72 + 0.018P)$$