http://www.gapinsaat.com/

---Lower Pressure Ammonia Synthesis

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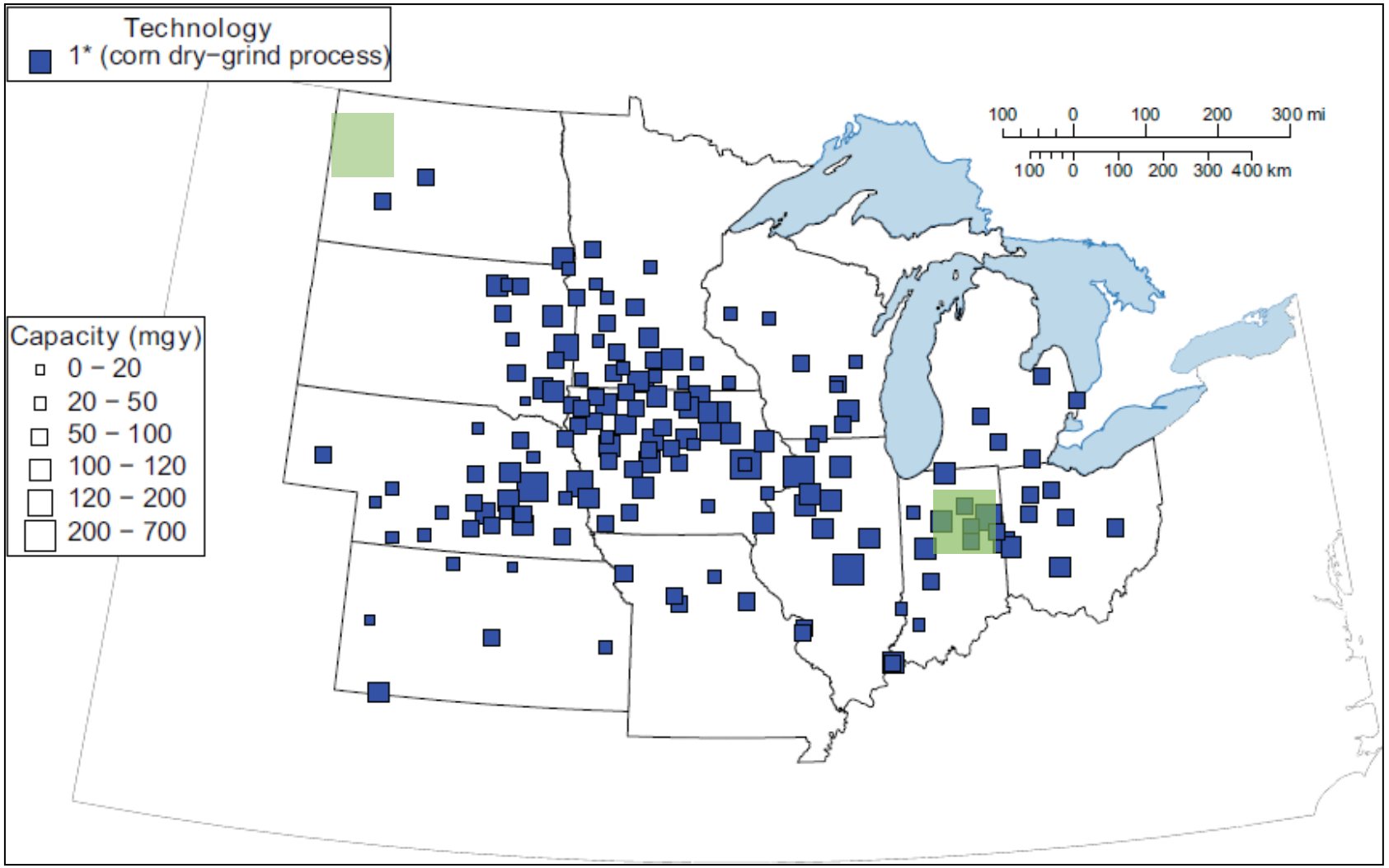
Driven to Discover

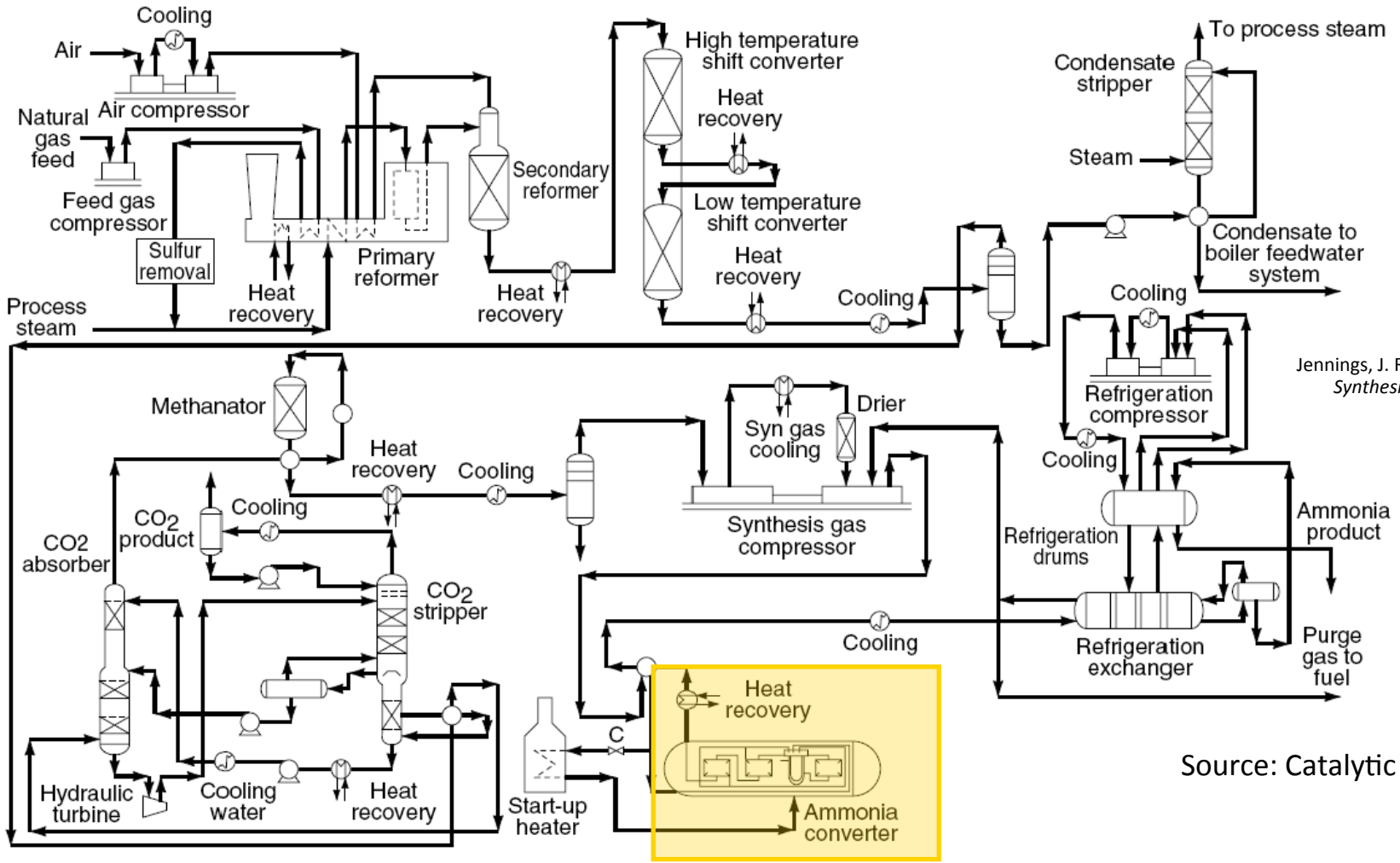
Ethanol [blue] vs Ammonia [green]

Ammonia [green] Isn't Sustainable and Dispersed



Source: https://www.ers.usda.gov/

A Simplified CH_4-Based Process



Jennings, J. R., *Catalytic Ammonia Synthesis*, Springer, 1991

Source: Catalytic Ammonia Synthesis

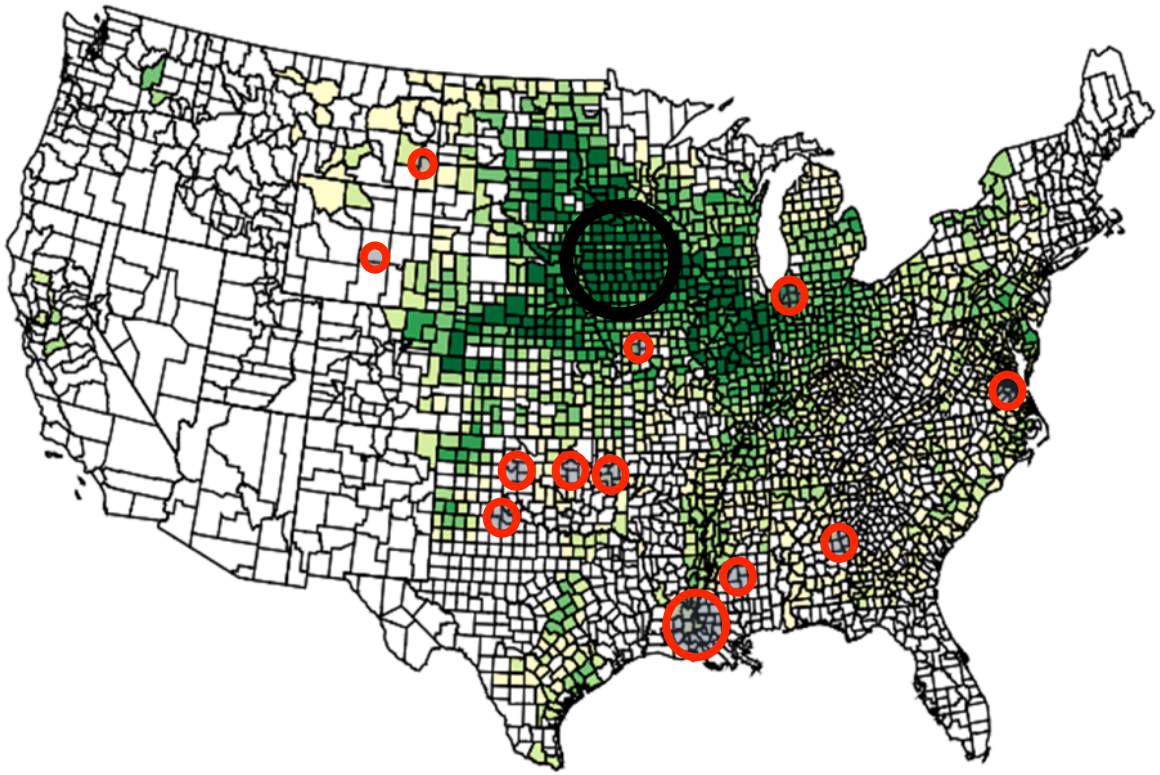
Requirements for Distributed Production:

1- Cheap Energy/Feed Resources

2- Simpler Process at Moderate Conditions

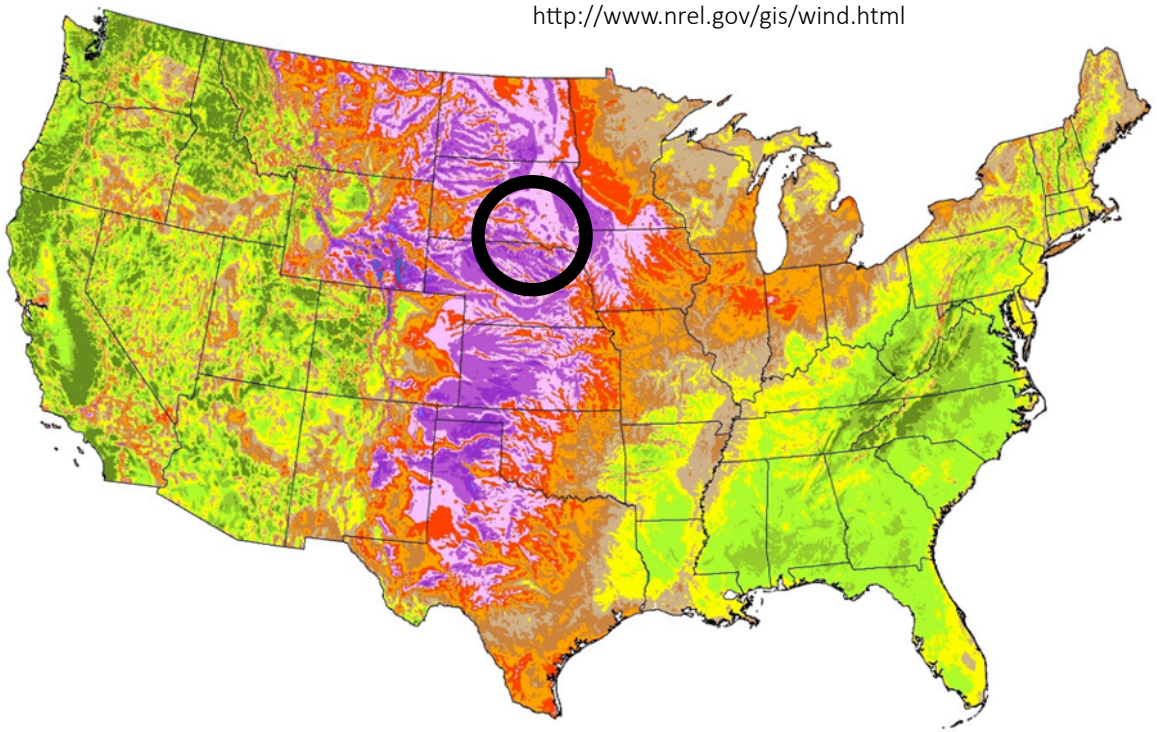
Wind Offers Sustainable Energy

Stranded Wind Resources Equals Ammonia Need

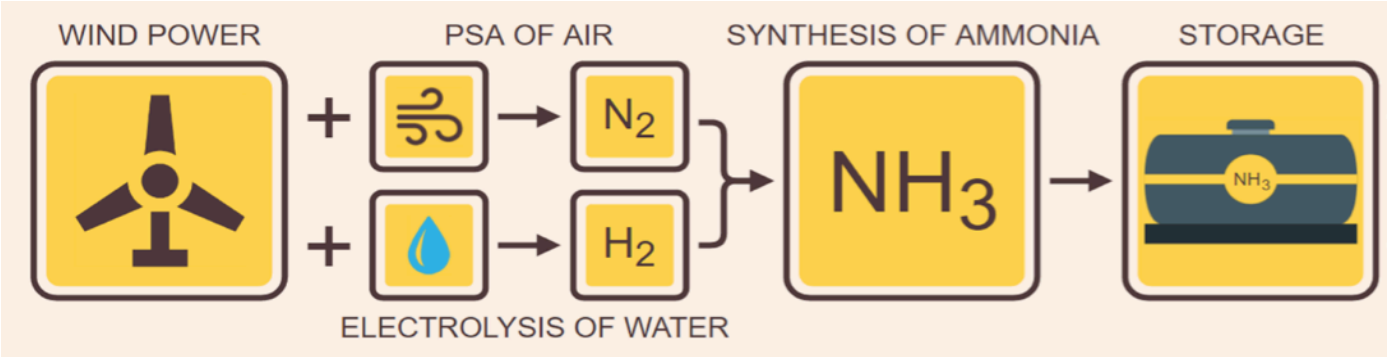


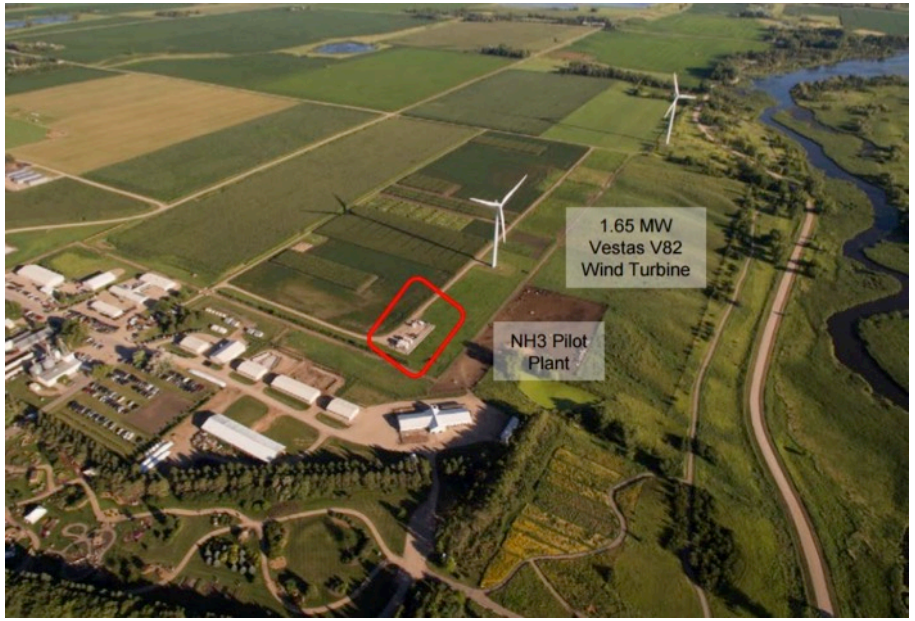
National Agricultural Statistics Service, United States Department of Agriculture. Planted Corn Acreage by County (2014). http://www.nass.usda.gov/Charts_and_Maps/Crops_County/#cr

National Renewable Energy Laboratory, United States Department of Energy. Wind Resource Map (2014). http://www.nrel.gov/gis/wind.html

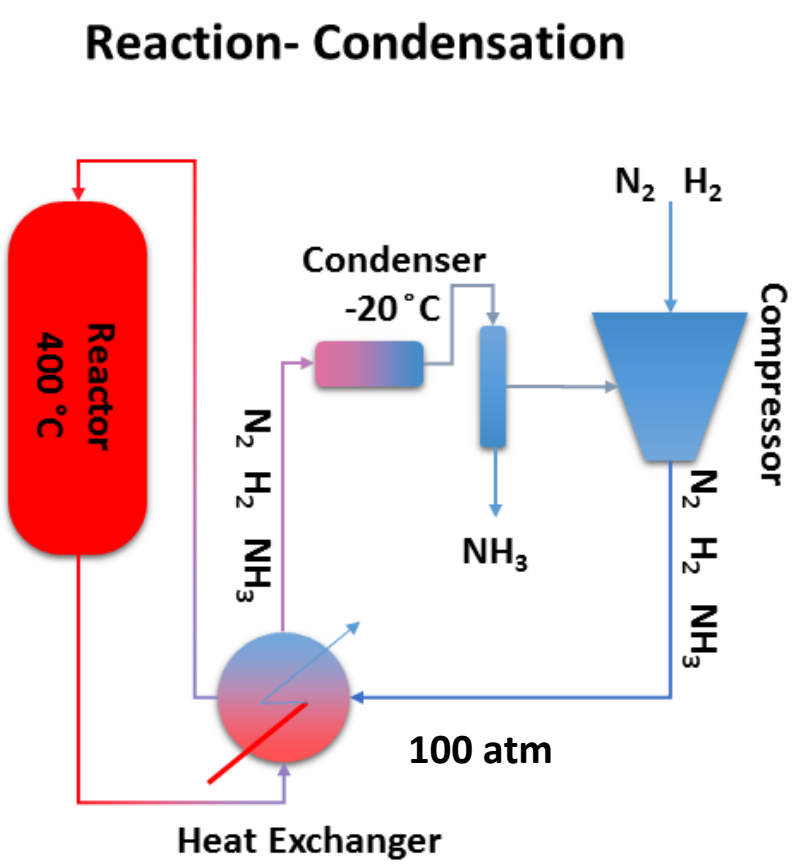


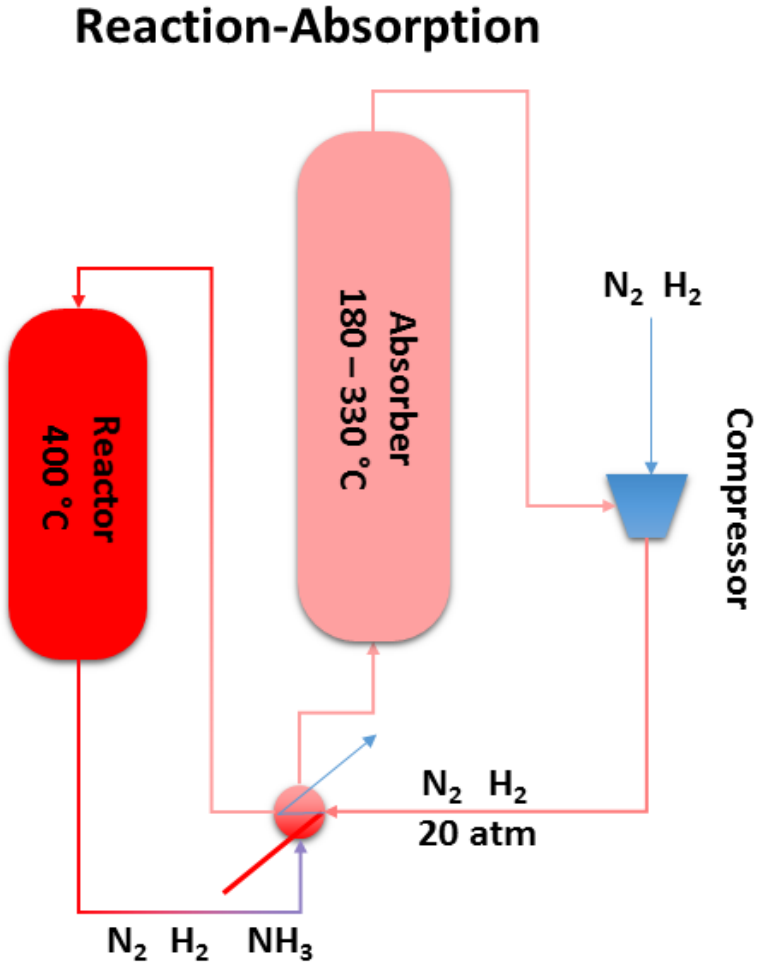
We are Making Renewable Ammonia Out of Thin Air





Absorption (staged) Replaces Condensation (mixed)

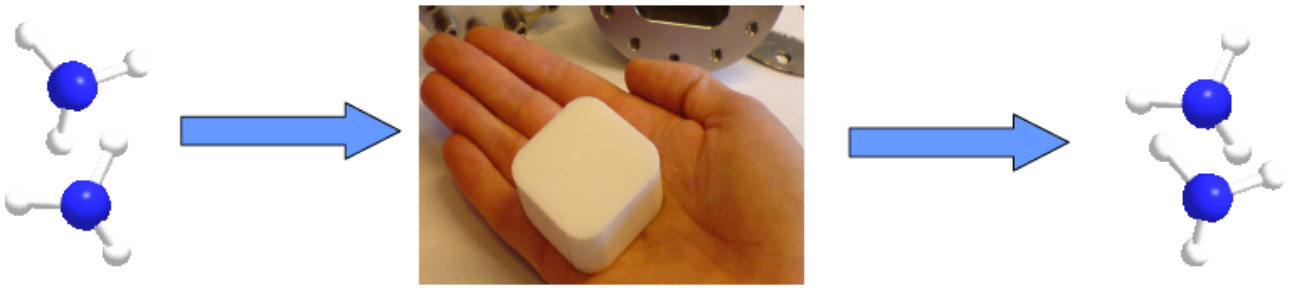


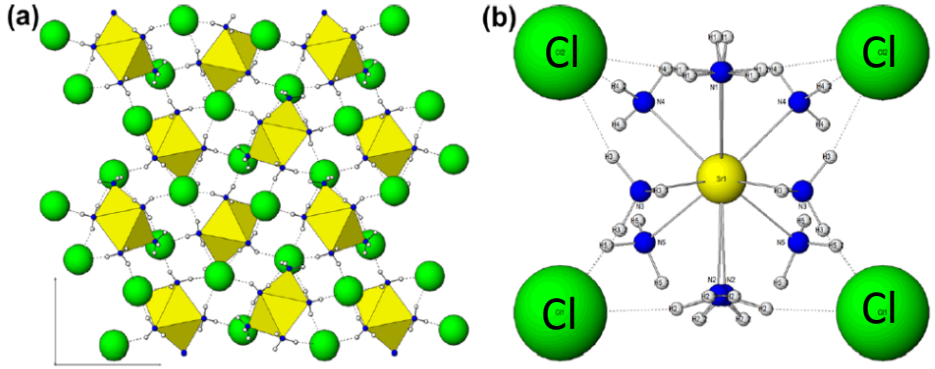


Malmali, M., Reese, M., McCormick, A., & Cussler, E. L. (2017) *ACS Sustainable Chemistry & Engineering*, Accepted.

Metal Halides with Remarkable Ammonia Uptake Capacity

100 *g* $MgCl_2$ block holds 135 L_{STP} NH_3





$Sr(NH_3)_8Cl_2$

$$MgCl_2 + NH_3 \rightleftharpoons Mg(NH_3)Cl_2$$
$$Mg(NH_3)Cl_2 + NH_3 \rightleftharpoons Mg(NH_3)_2Cl_2$$
$$Mg(NH_3)_2Cl_2 + 4NH_3 \rightleftharpoons Mg(NH_3)_6Cl_2$$

$$CaCl_2 + NH_3 \rightleftharpoons Ca(NH_3)Cl_2$$
$$Ca(NH_3)Cl_2 + NH_3 \rightleftharpoons Ca(NH_3)_2Cl_2$$
$$Ca(NH_3)_2Cl_2 + 2NH_3 \rightleftharpoons Ca(NH_3)_4Cl_2$$
$$Ca(NH_3)_4Cl_2 + 4NH_3 \rightleftharpoons Ca(NH_3)_8Cl_2$$

Johnsen, R. E., Jensen, P. B., Norby, P., & Vegge, T. (2014). *The Journal of Physical Chemistry C*, *118*(42), 24349-24356.

Strategies to Improve Haber-Bosch Process

1- Better Catalysis (Not Key Here)

Lower Pressure and Lower Temperature

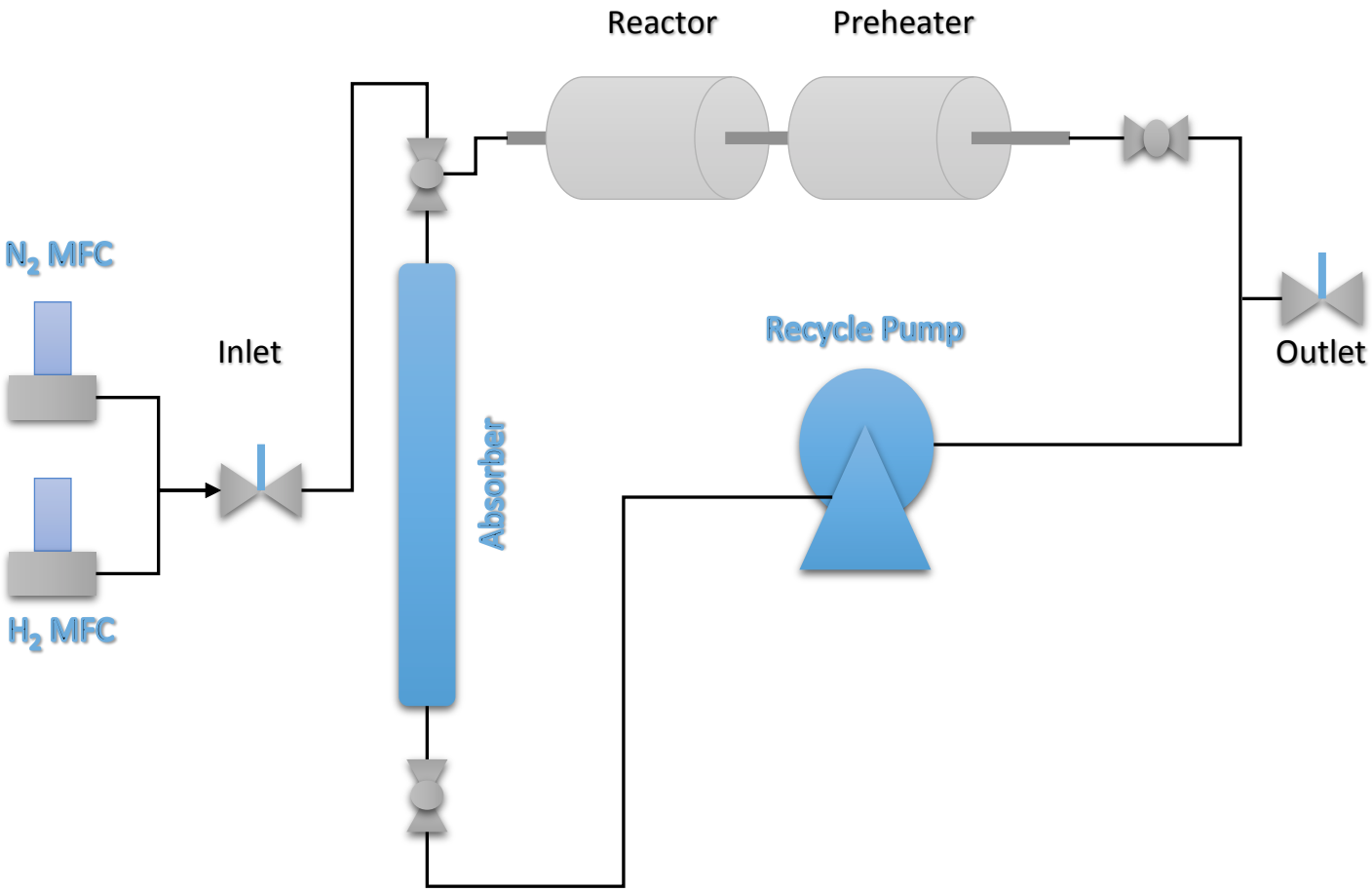
2- Lower Pressure

- Unraveling Mechanism of Reaction-Absorption Process

- Implication of a Lower Pressure Process

3- Better Separation/Better Sorbents

Reaction-Absorption Apparatus



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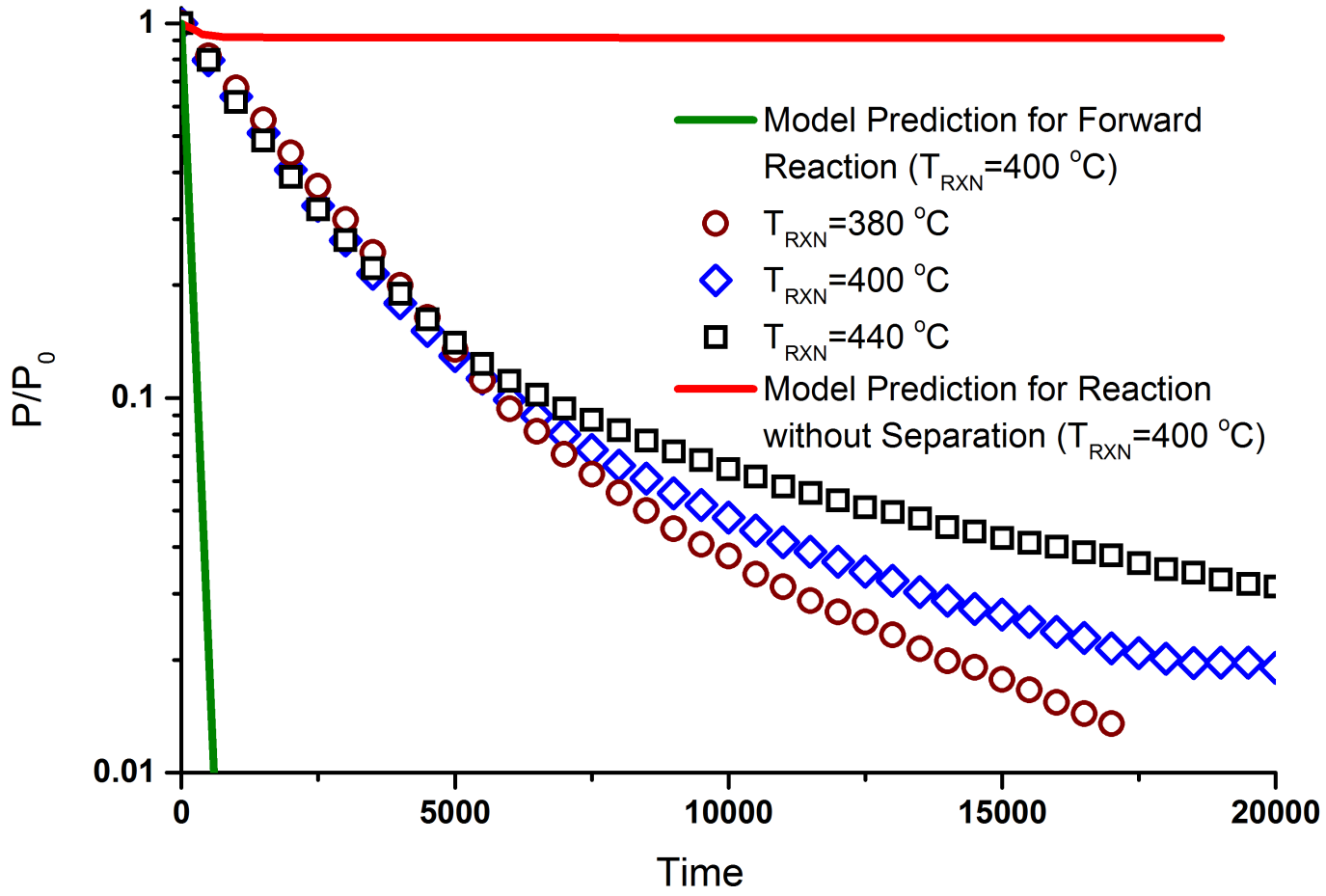
In Reaction-Absorption, Reaction Temperature has ~~Big~~ Little Effect on the Production Rate

$$\textbf{Production Rate} = C^{*} - C_{0} / 1/k_{R} M_{R} + 1/k_{abs} A_{abs} + 1 - C^{*} / C / m$$



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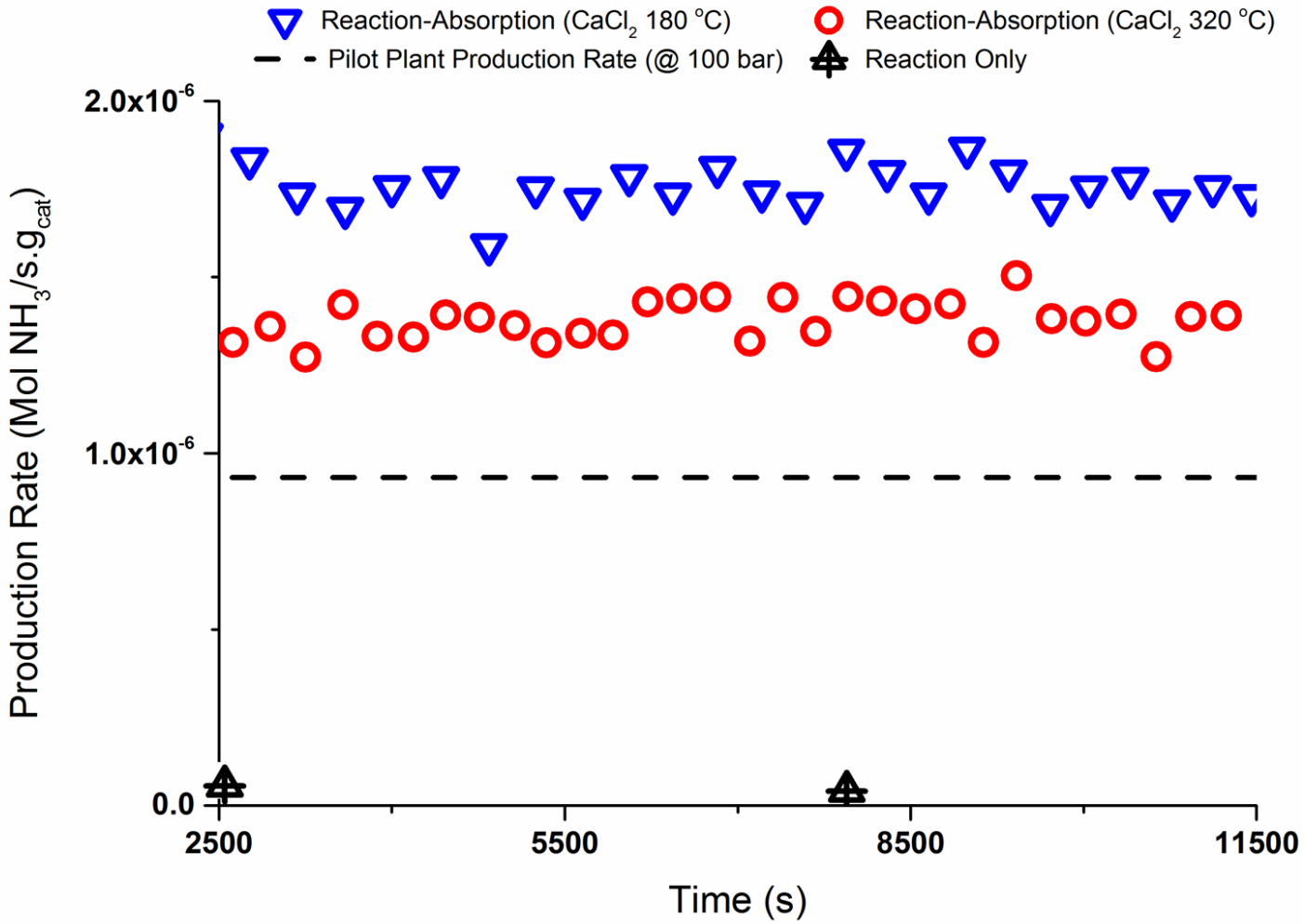
Malmali, M., Wei, Y., McCormick, A., & Cussler, E. L., Accepted.

Proof: Fedbatch at Constant Pressure



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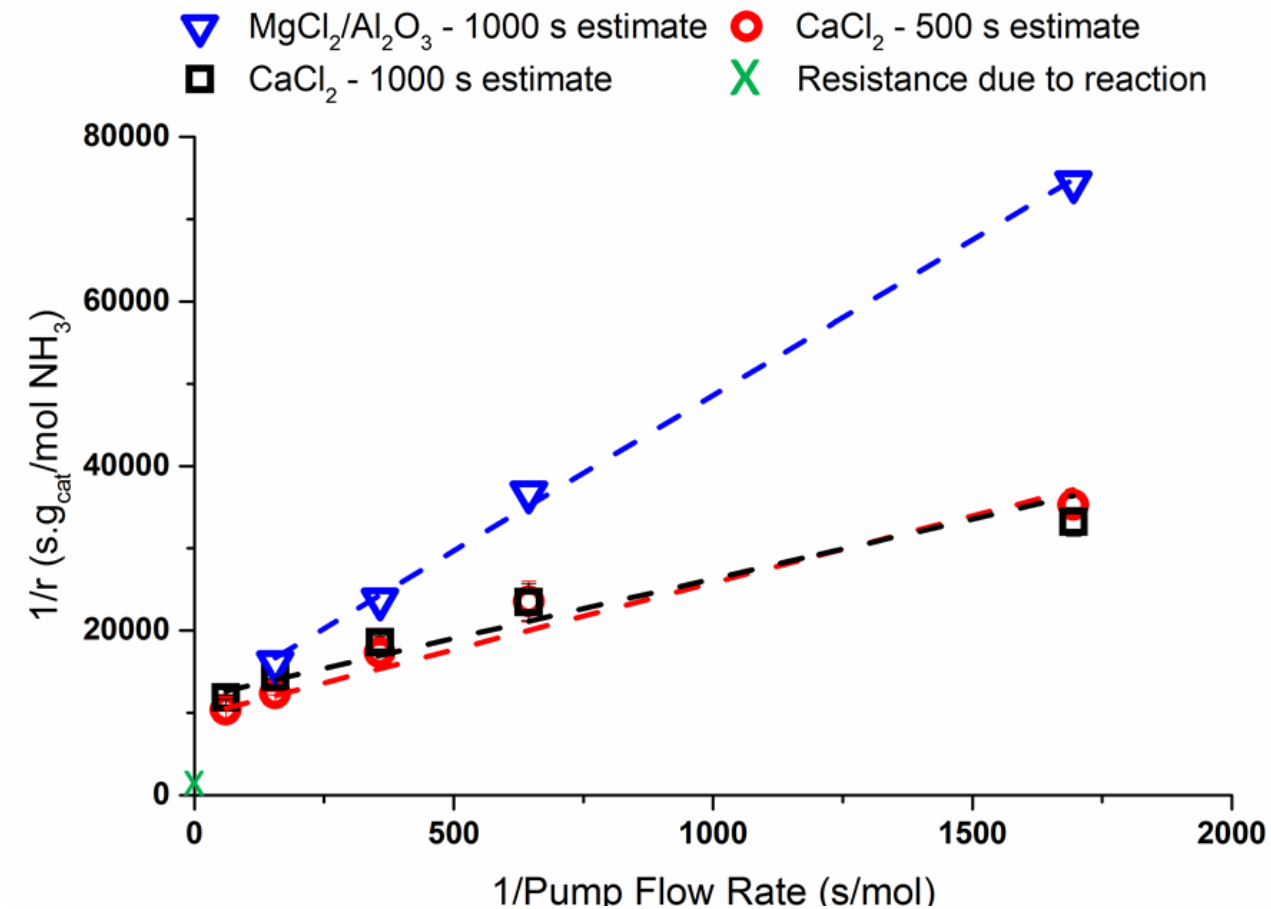
Synthesis More Affected by Recycle

$$\textbf{Rate} = C\uparrow* - C\downarrow 0 \;/ 1/k\downarrow R\, M\downarrow R + 1/k\downarrow abs\, A\downarrow abs + 1 - C\uparrow* \;/ C \;/ m$$



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Strategies to Improve Haber-Bosch Process

1- Better Catalysis – Not Key Here

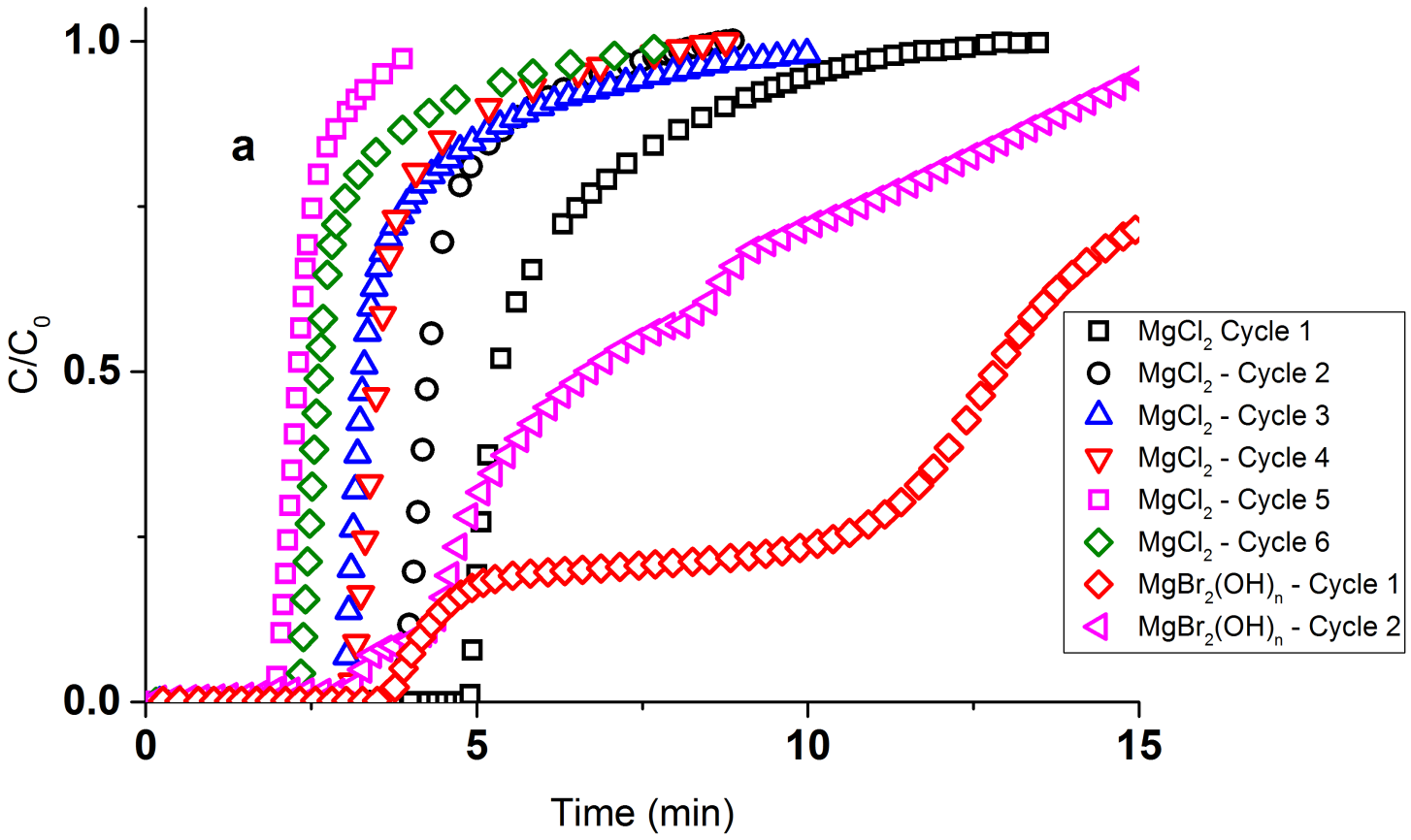
Lower Pressure and Lower Temperature

2- Lower Pressure

3- Better Separation/Better Conversion

Improving the RXN-ABS with Better Absorbents

Bulk Metal Halides Not Stable



Wagner, K., **Malmali, M.,** Smith, C., McCormick, A., Cussler, E. L., Zhu, M.Seaton, N. C. A. (2017) *AIChE J.*, *63* (7), 3058–3068.
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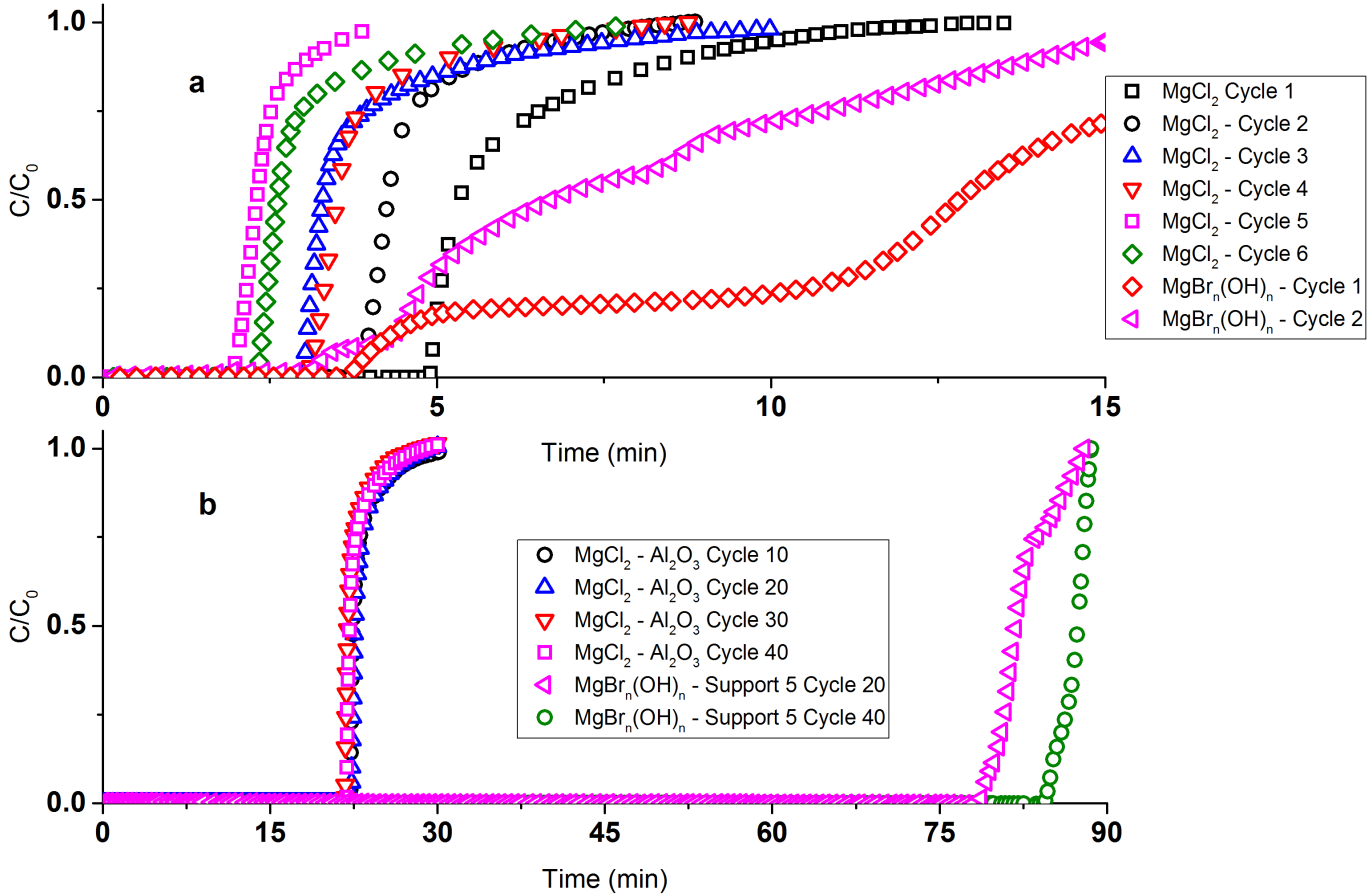
Better Absorbent: Improved by 10X

10 g Salt Packed in Column
BET: less than 1 m^2/g

10 g Sorbent (5% and 40% loading) Packed in Column
BET: less than 400 m^2/g



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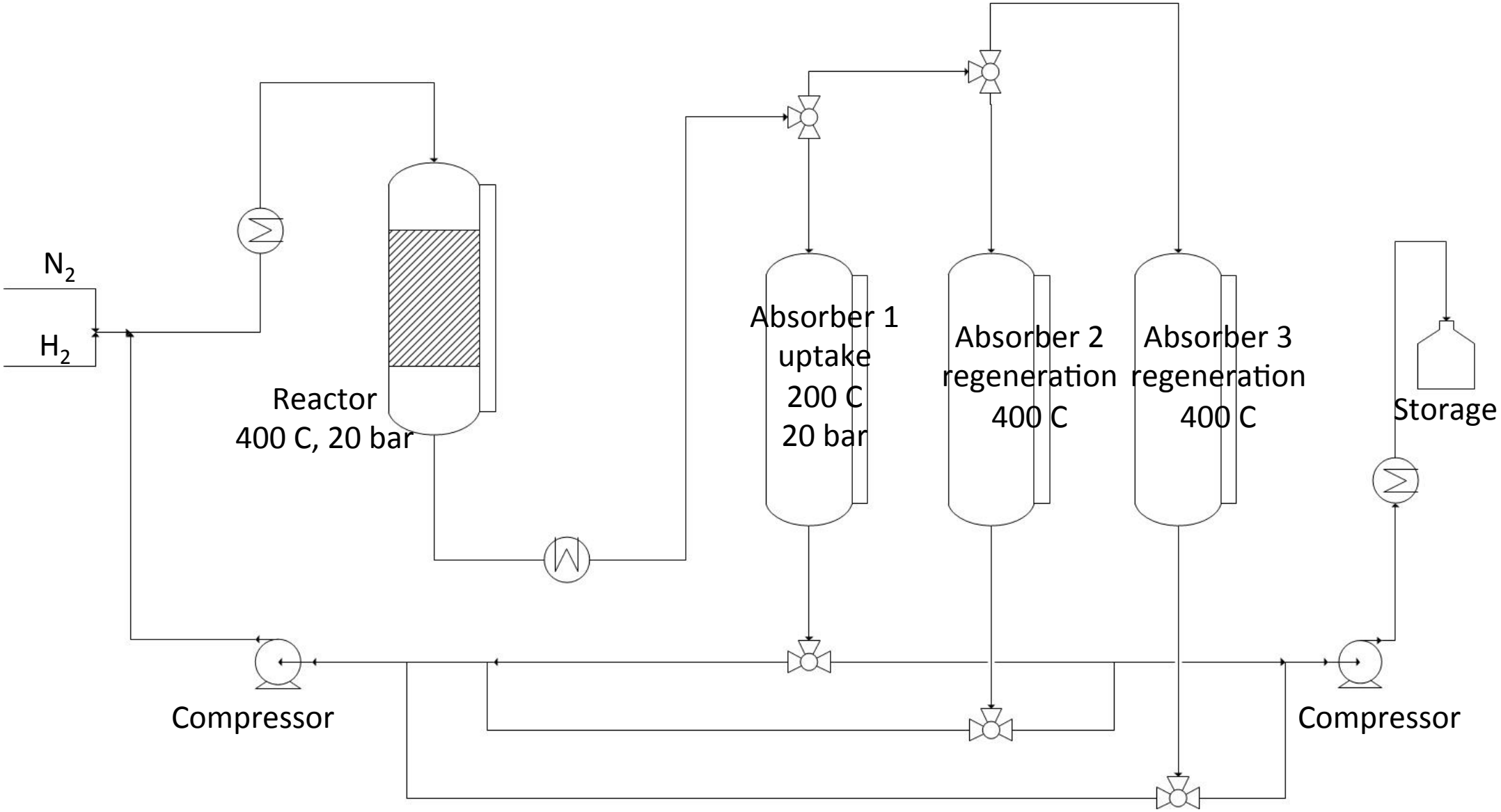
Proposed Process Flow Diagram (PFD)



Conclusions: Distributed Sustainable Ammonia

1. Reactive-Separation Promises Faster Rates
2. Absorption is Promising, we improved absorbents by 10X
3. Distributed Renewable Ammonia Possible with Lower CapEx
4. We want to Test the Reaction-Absorption Benchmark

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- Joshua Prince (UROP)
- Collin Smith
- Michael Ho (UROP)

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