NH$_3$ Fuel Conference 2015

Potential Strategies for Distributed Sustainable Ammonia Production

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University of Minnesota

Ed Cussler, Prodromos Daoutidis, Paul Dauenhauer, Lanny Schmidt, Roger Ruan, Doug Tiffany, Steve Kelley, Mike Reese

Potential Strategies for Distributed Sustainable Ammonia Production

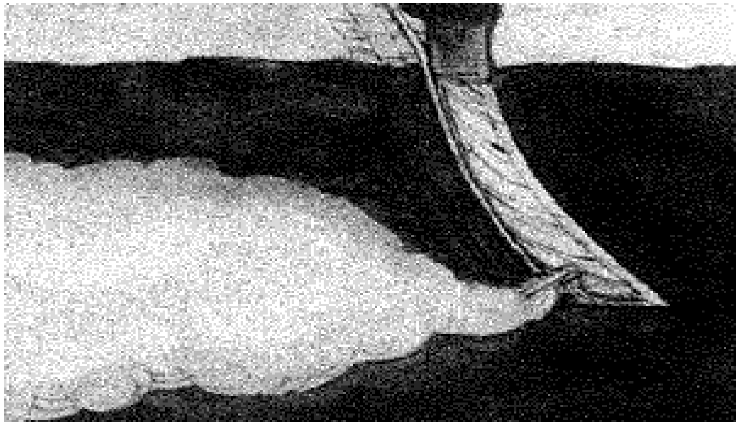
1. **Agriculture, wind power, and ammonia**
2. Zero emissions ammonia pilot plant
   - Reese & coworkers
3. Ammonia synthesis enhanced by absorption
   - Cussler, McCormick, & coworkers
4. Ammonia synthesis via non-thermal plasma - Ruan & coworkers
5. Modeling, economic, and public policy issues
   - Tiffany, Kelley, Daoutidis, & coworkers

Nitrogen Fertilizer in Corn Production

- 13 million metric tons annually, 80% goes to agriculture†
- Corn is most anhydrous ammonia intensive crop
- Dominant source of embedded energy in corn production
- Largest source of GHG emissions in corn production

†USDA (2011)

Source: www.countrysidefarmsimplements.com

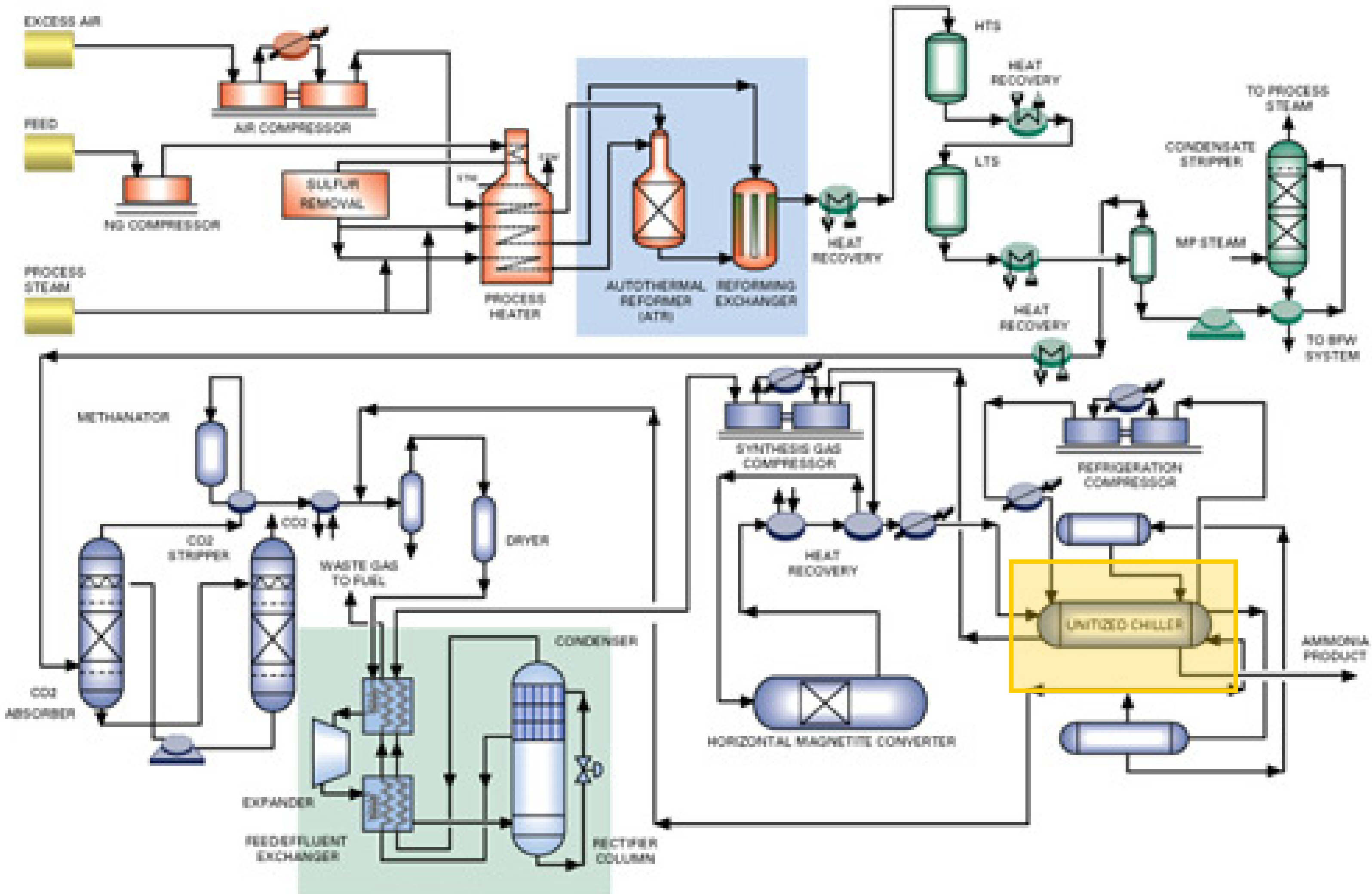


Source: U of M Extension, John M Shutske, "Using Anhydrous Ammonia Safely on the Farm.. FO-2326-C , April 2002

Ammonia Plants are very large…

IFC Ammonia & Urea plant in Wever, Iowa - 4 million tons/year capacity
Retrieved from http://www.2b1stconsulting.com/ Sep 2015

Example of Modern Large-Scale CH_4-Based Process

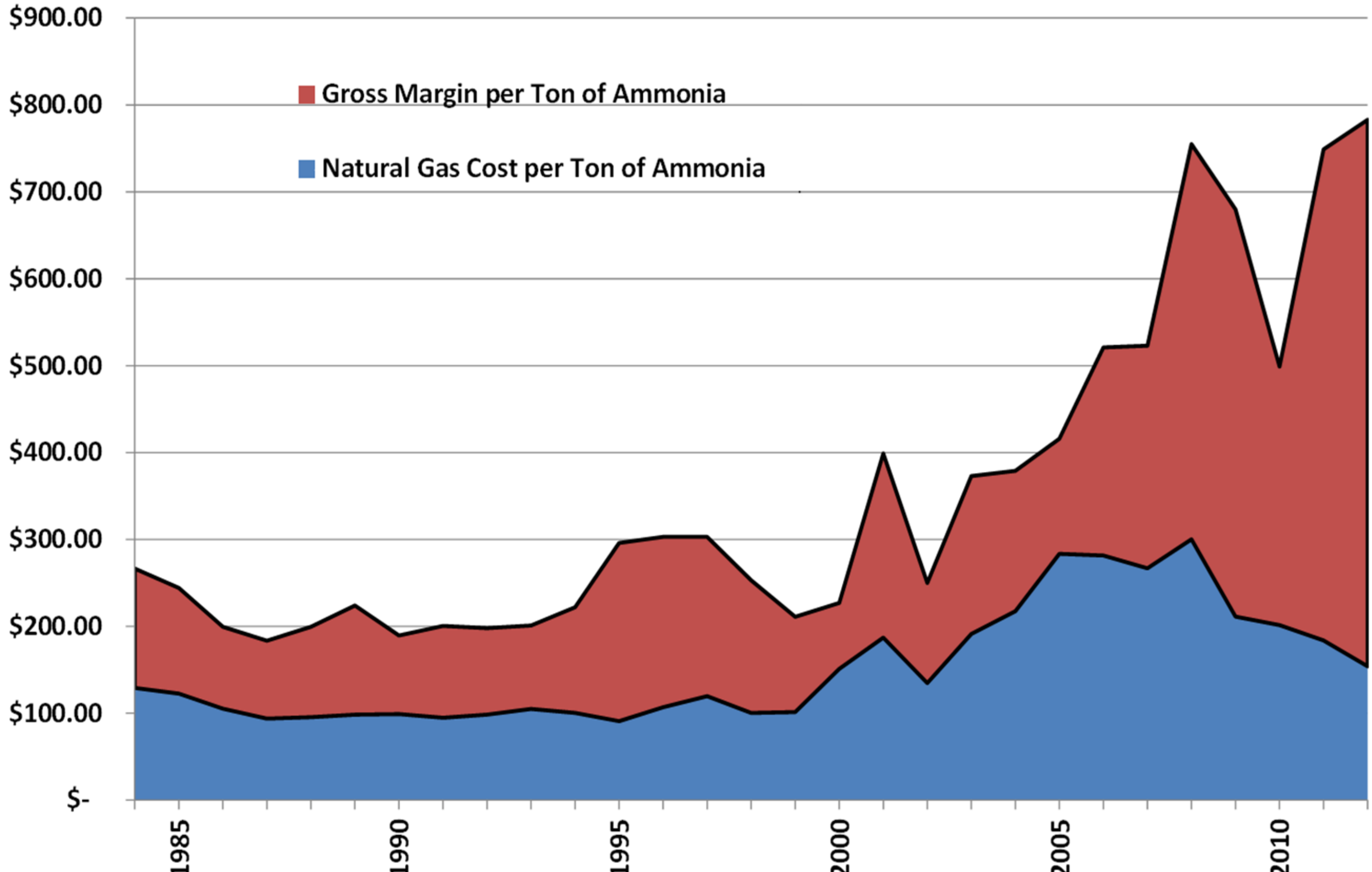


http://beta.kbr.com/Technologies/Process-Technologies/PURIFIERplus-Ammonia-Process/ Sept 2015

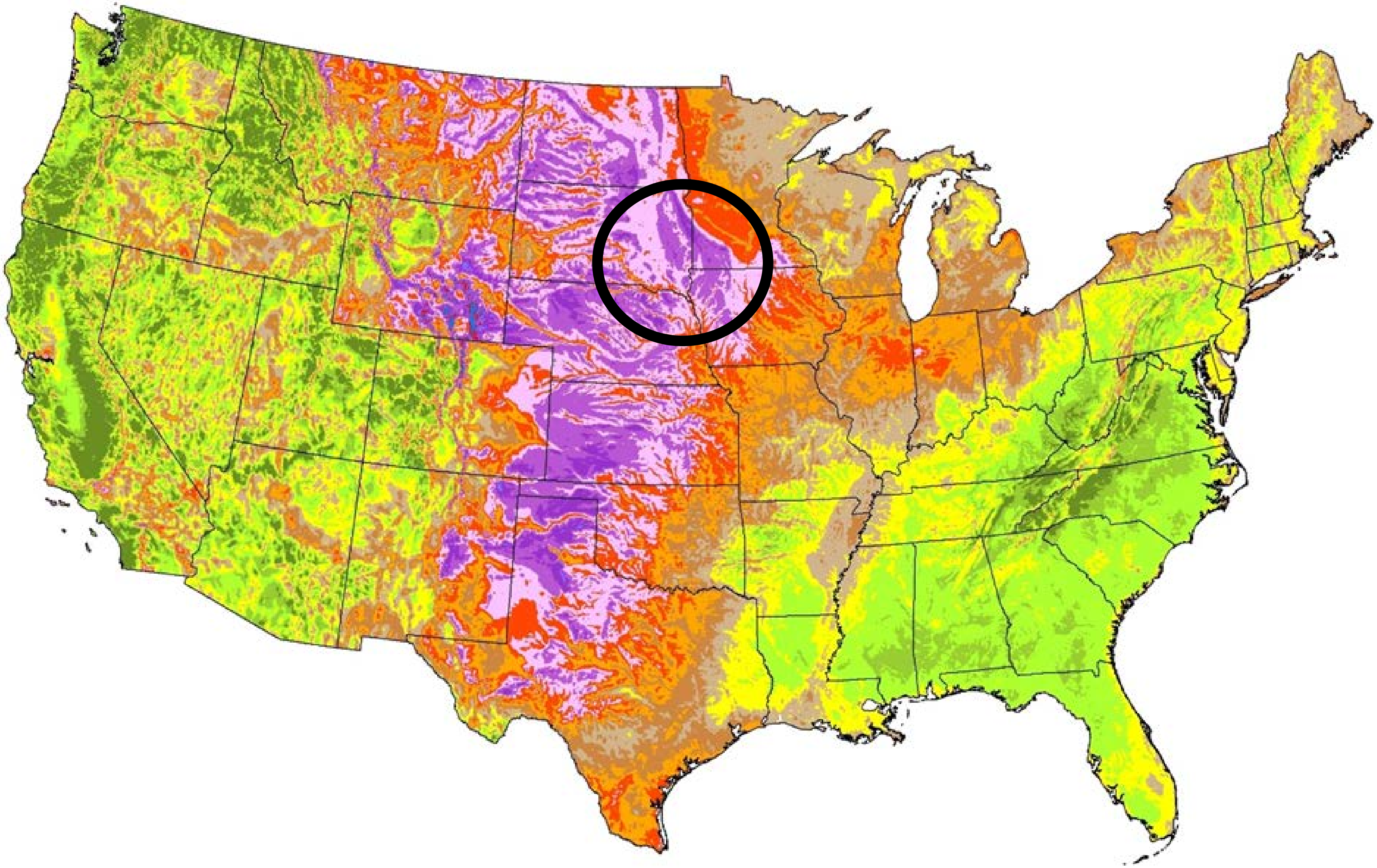
Cost of Natural Gas & Gross Margin in Sale Price of Anhydrous Ammonia

Derived by using Citygate natural gas prices and assuming 32.7 decatherms per ton of ammonia

Douglas G. Tiffany, University of Minnesota Extension

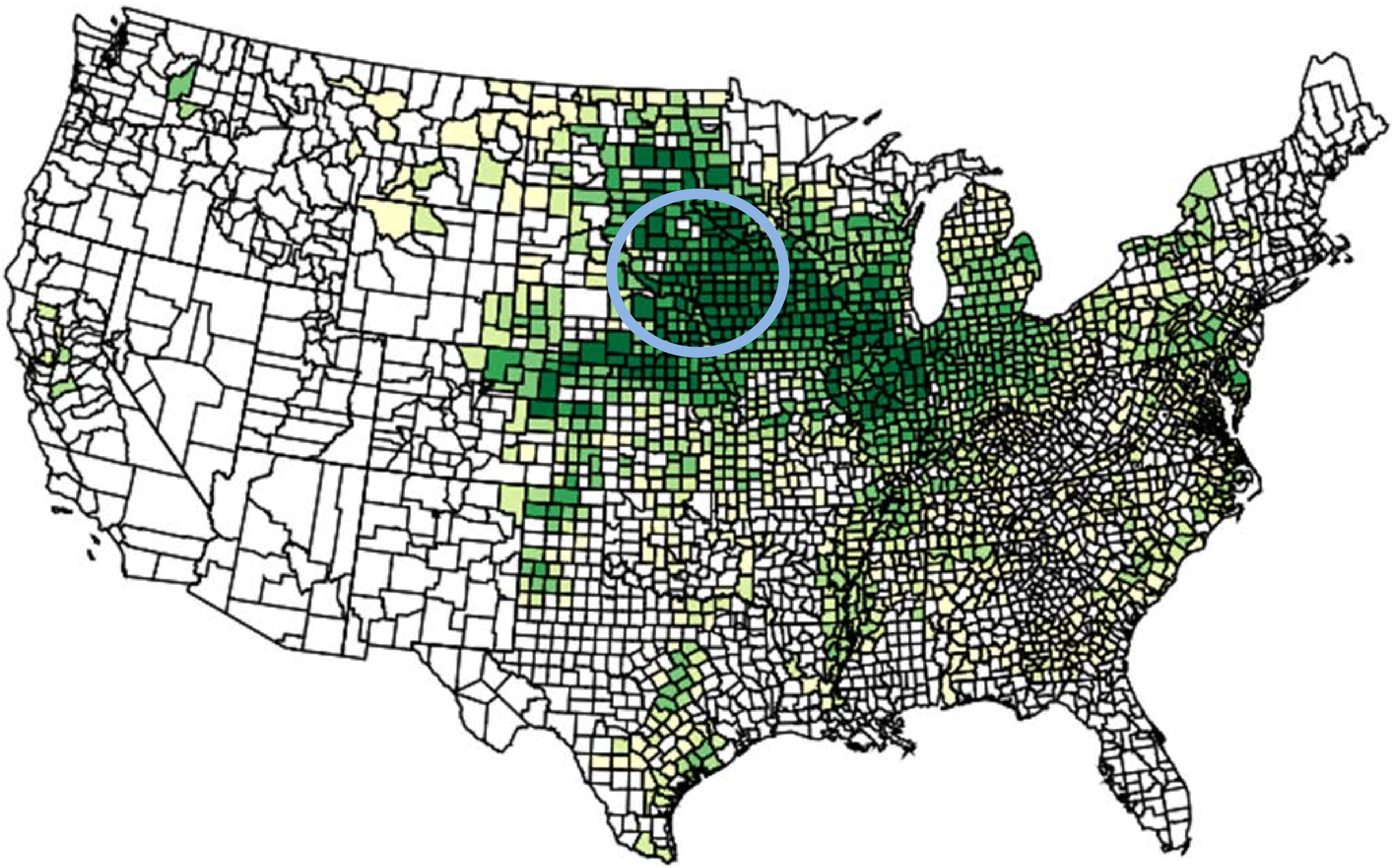


Stranded Wind Resources



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

Ammonia Demand



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

Sustainable NH_3: Oklahoma *vs* Minnesota

Costs	Oklahoma Production	Minnesota Production
Pipeline tariff - OK to MN	$40	0
Trucking—Mankato to Morris, MN	$22	0
Total Transportation Costs	$62 / ton NH_3	0

Pounds of CO_2 Produced		
Natural Gas in Production	3700	0
Electricity in Production	460	0
Pipeline Energy	50	0
Trucking	130	0
Total CO_2 Produced	4400 lbs CO_2 / ton NH_3	0

Source: Tiffany 2014 - MN Corn Research and Promotion Council Report

2. Zero-Emission Ammonia Pilot Plant

Mike Reese

Cory Marquart

Eric Buchanan

Joel Tallaksen

West Central Research & Outreach Center, Morris

University of Minnesota

Ammonia plant design and construction supported by:

College of Food, Agriculture, and Natural Resource Sciences, UMN

Institute for Renewable Energy and the Environment, UMN

State of Minnesota

Minnesota Corn Research and Promotion Council

Hydrogen facility: partial support from Environment and Natural Resources Trust Fund, State of Minnesota

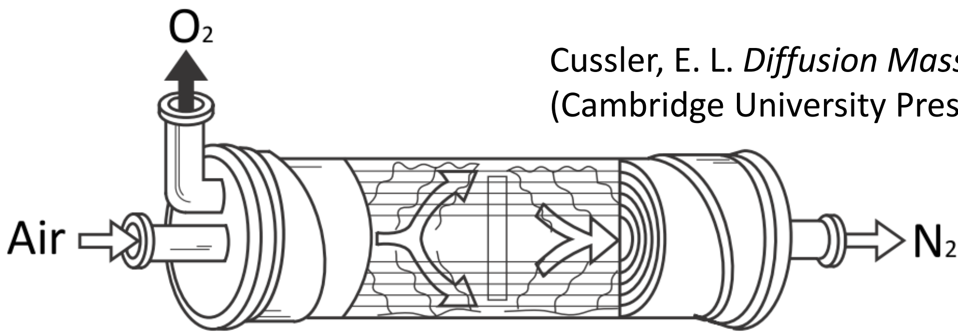
Photo Credit: http://wcroc.cfans.umn.edu/

Making Ammonia with Wind Energy:

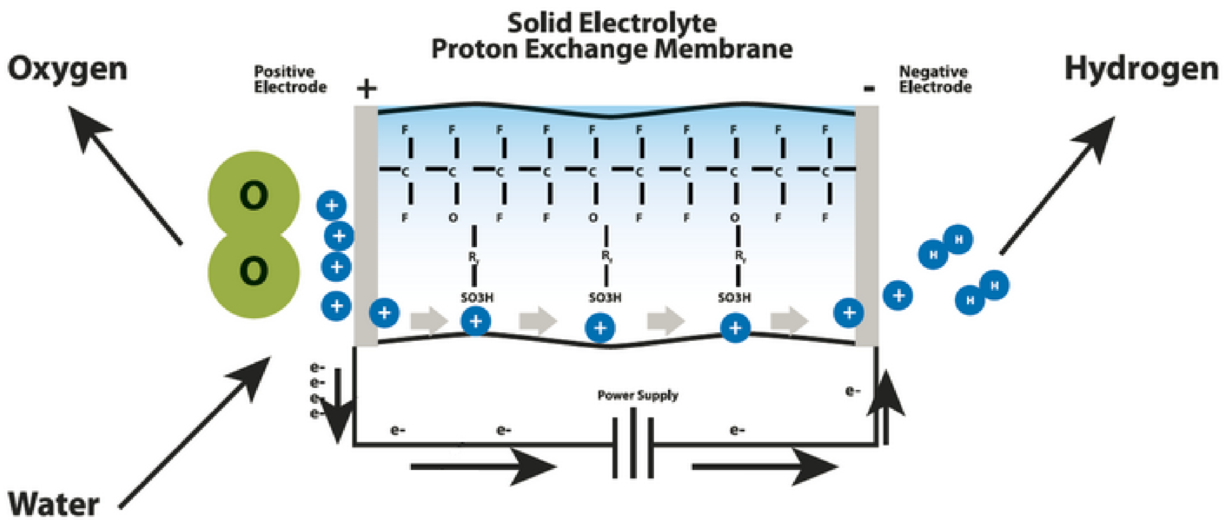
- Vestas turbine installed March 2005
- Produces 5.4 M kWh/yr
- Provides campus with over 50% of electricity needs
- NH_3 pilot plant construction 2012
- Pilot plant consumes 10% of turbine electricity production

Pilot plant: Sebesta Blomberg, Seppro, AGEC

N_2 from Air, H_2 from Water



Cussler, E. L. *Diffusion Mass Transfer in Fluid Systems*. (Cambridge University Press).

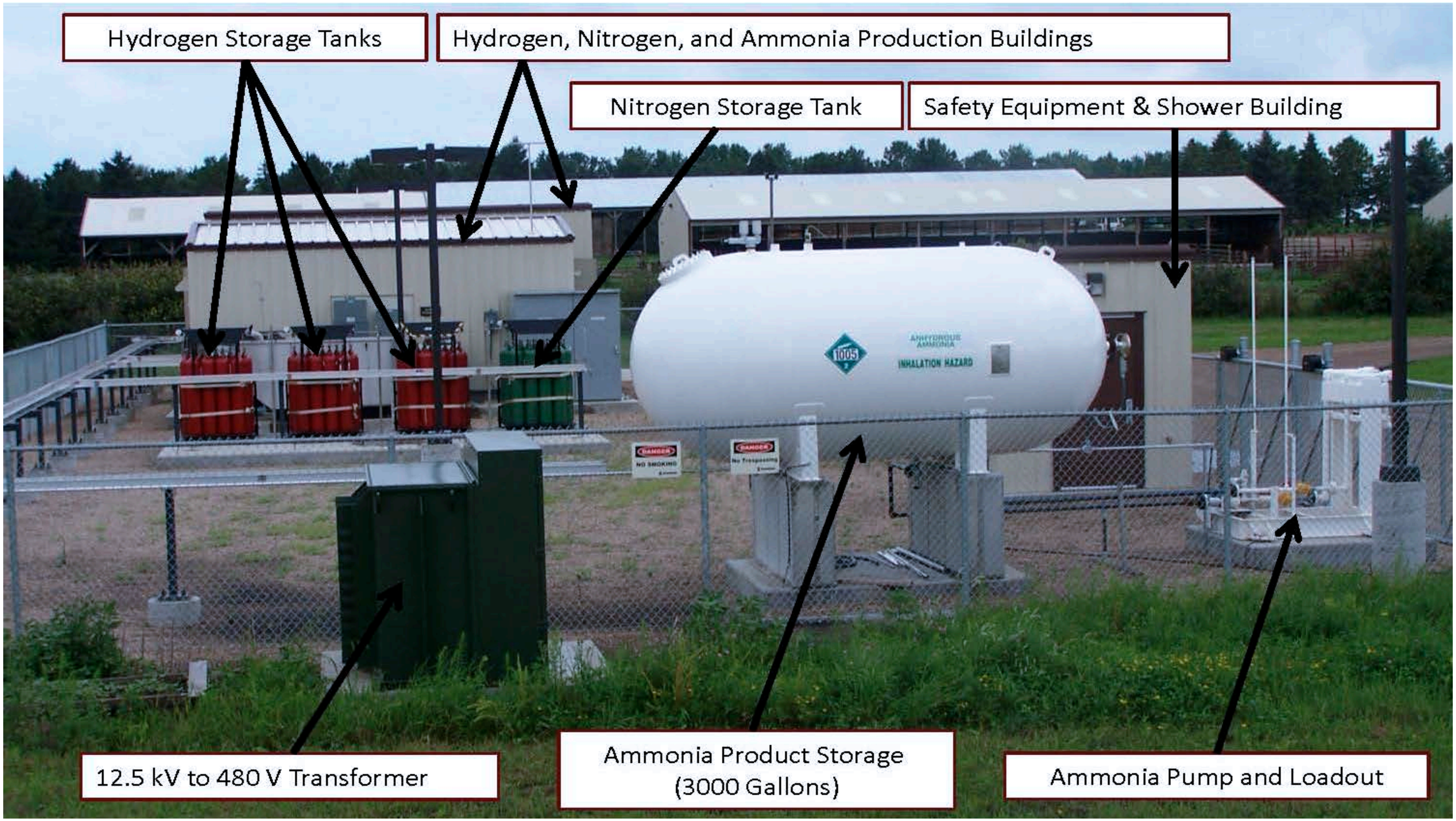


Source: http://protononsite.com/products/hydrogen-generator/

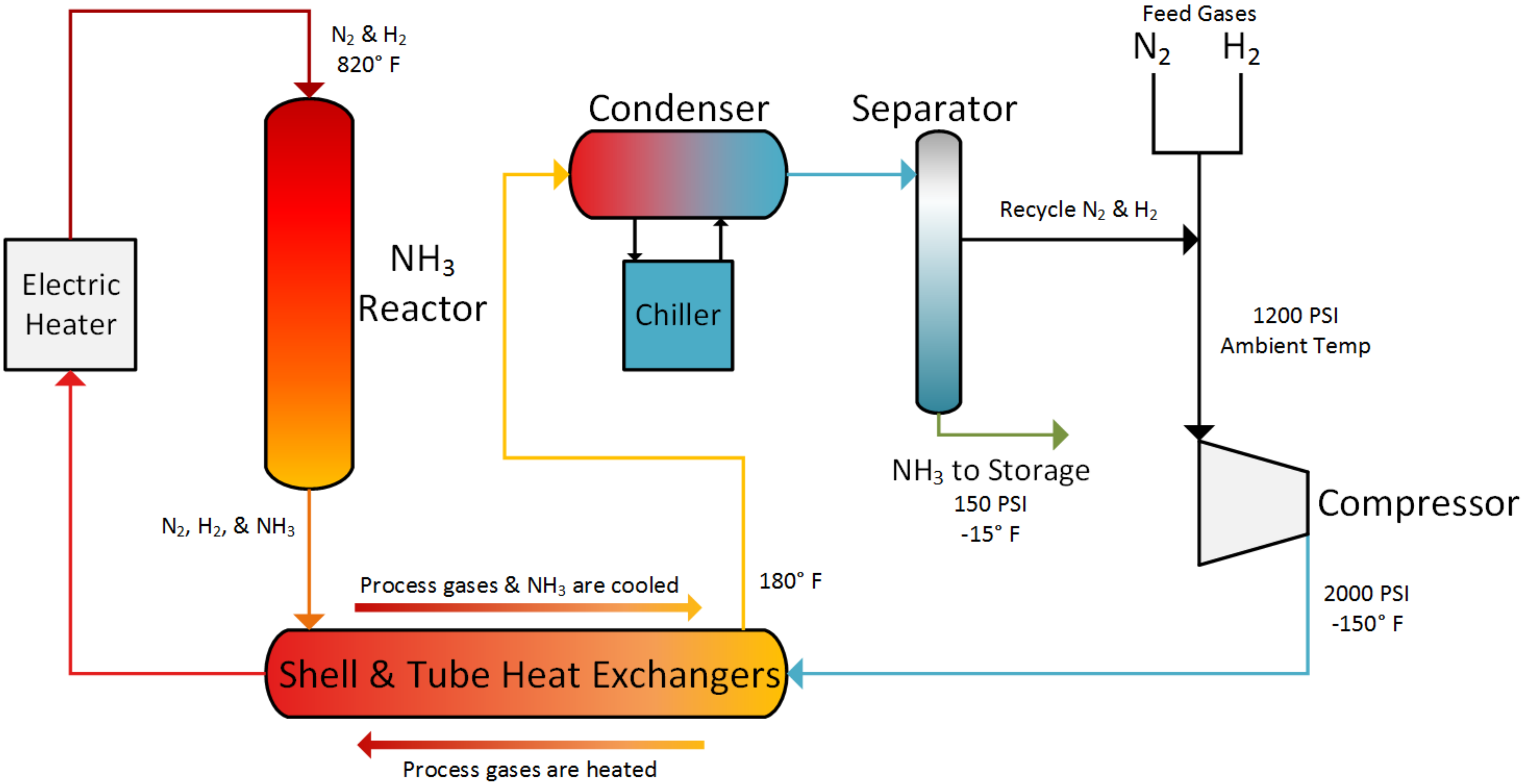
- Nitrogen via membrane or PSA separation
- Hydrogen via electrolysis of water

Morris, MN Ammonia Pilot Plant

Scaled down conventional Haber-Bosch process, 25 ton/yr capacity



Pilot Plant Process Flow



3. Absorbent Enhanced Ammonia Synthesis

Ed Cussler

Alon McCormick

Mahdi Malmali

Kevin Wagner

Lanny Schmidt, Paul Dauenhauer

Heath Himstedt

Mark Huberty

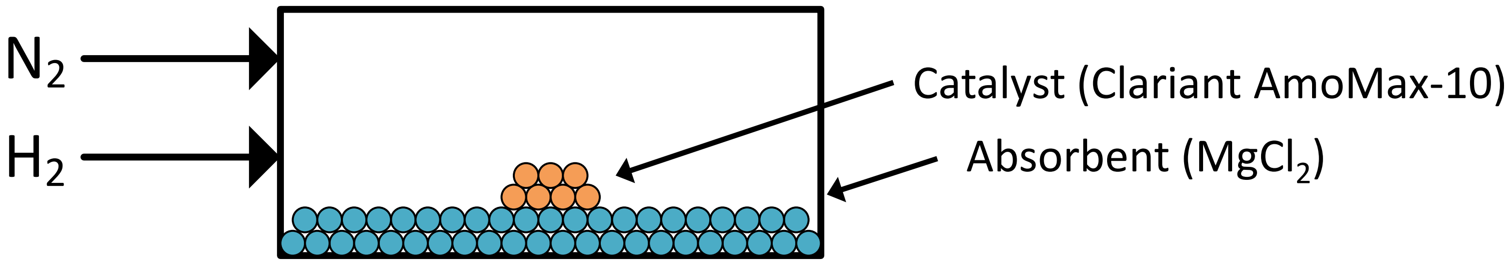
Chemical Engineering & Materials Science

University of Minnesota – Twin Cities

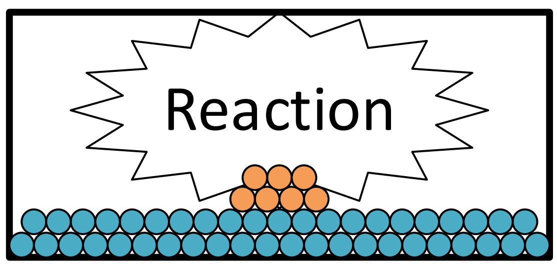
Photo Credit: http://twin-cities.umn.edu/

Batch Reaction with Absorbent

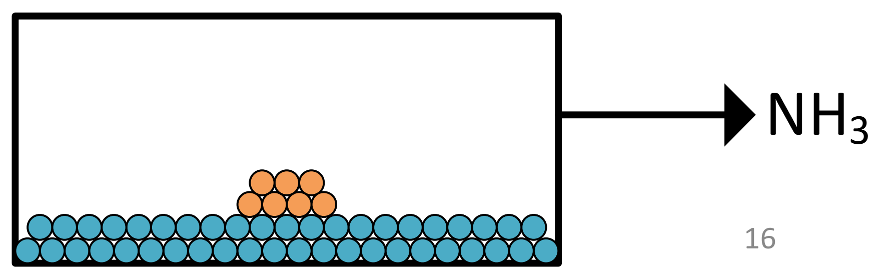
1. Feed the reactor



2. Reaction and Absorption

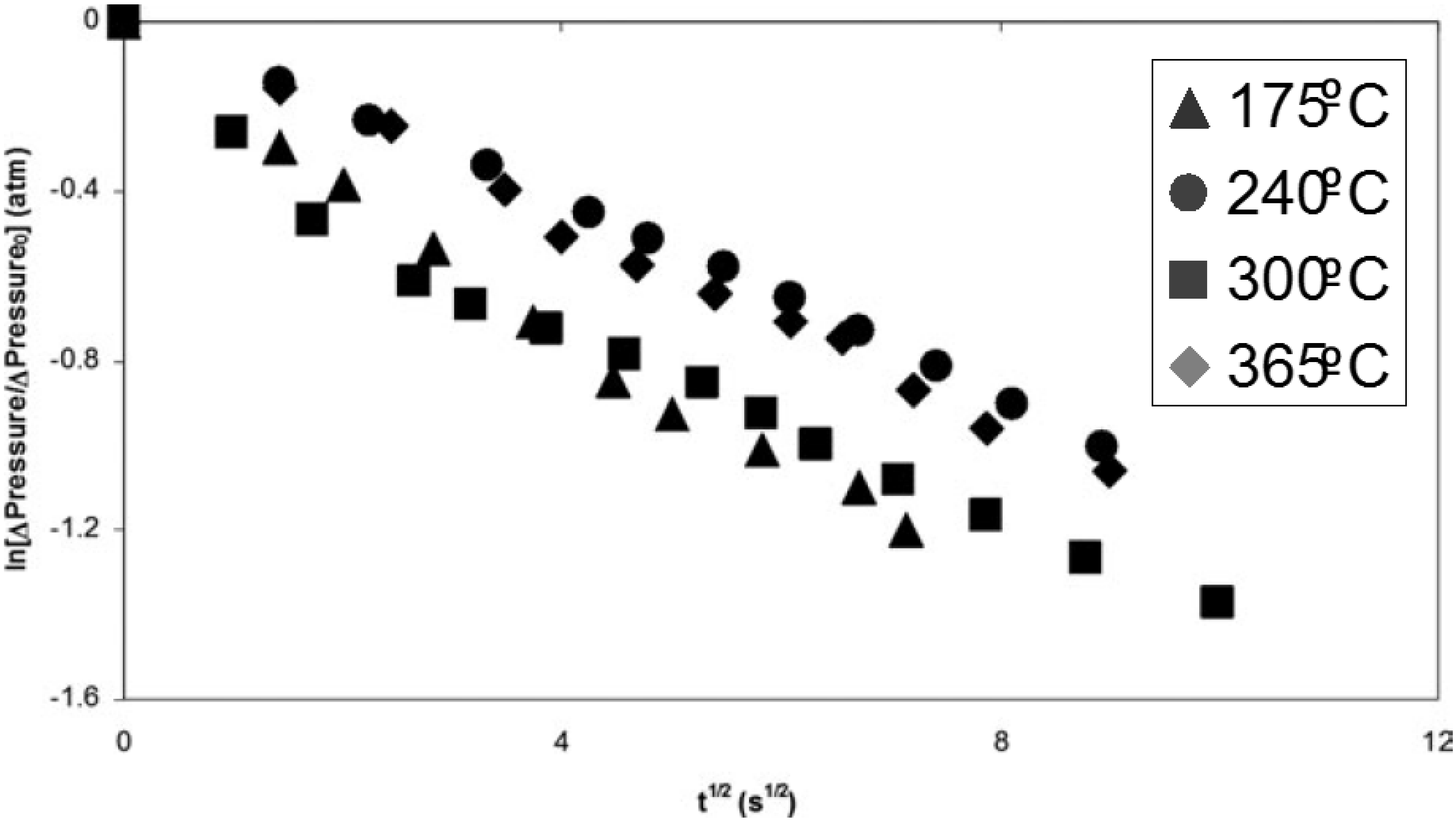


3. NH_3 Desorption



$MgCl_2$ Application	Researchers	Institute	Description	Year	Reference
Chemical Heat Pump	Saito et al.	University of Tokyo	Absorption of ammonia into alkaline earth metal halides	1994	Jpn. Kokai Tokkyo Koho JP 06136357
Low pressure ammonia synthesis & storage	Aika et al.	Tokyo Institute of Technology	Absorption isotherms of halide mixtures and phases	2002	Chem. Let. 31, 798-799
				2004	Procedure. Bull. Chem. Soc. Jpn. 77, 123-131.
				2004	Ind. Eng. Chem. Res. 43, 7484-7491
Ammonia Storage	Aristov et al.	Boreskov Institute of Catalysis	Alkaline earth metal confined in alumina	2005	React. Kinet. Catal. Lett. 1, 183-188
Hydrogen Storage as Ammonia	Christensen, Vegge, Norskov, Johannessen et al.	Technical University of Denmark	Opportunities for hydrogen storage	2005	J. Mater. Chem 15, 4106-4108
			Absorption/desorption difficulties	2006	J Am. Chem. Soc. 128, 16-17
			DFT studies for crystal structure	2010	Energy Environ. Sci. 3, 448-456
Desorption and characterization	Owen-Jones, Royce, David, et al	Oxford	Frontiers in characterization and understanding	2013-14	Chem Phys, 427, 38-43 2014 NH3FC
Distributed/facilitated Ammonia production	Cussler, McCormick et al.	University of Minnesota	Absorption of ammonia at Haber process conditions	2012	AIChEJ 58, 3526-3552
			Absorbent enhanced ammonia production	2015	AIChEJ 61, 1364-1371
Ammonia Storage Fuel Cell	Van Hassel et al.	United Technologies	Alkaline earth metal confined in activated carbon	2015	Sep. Purif. Technol. 142, 215-226

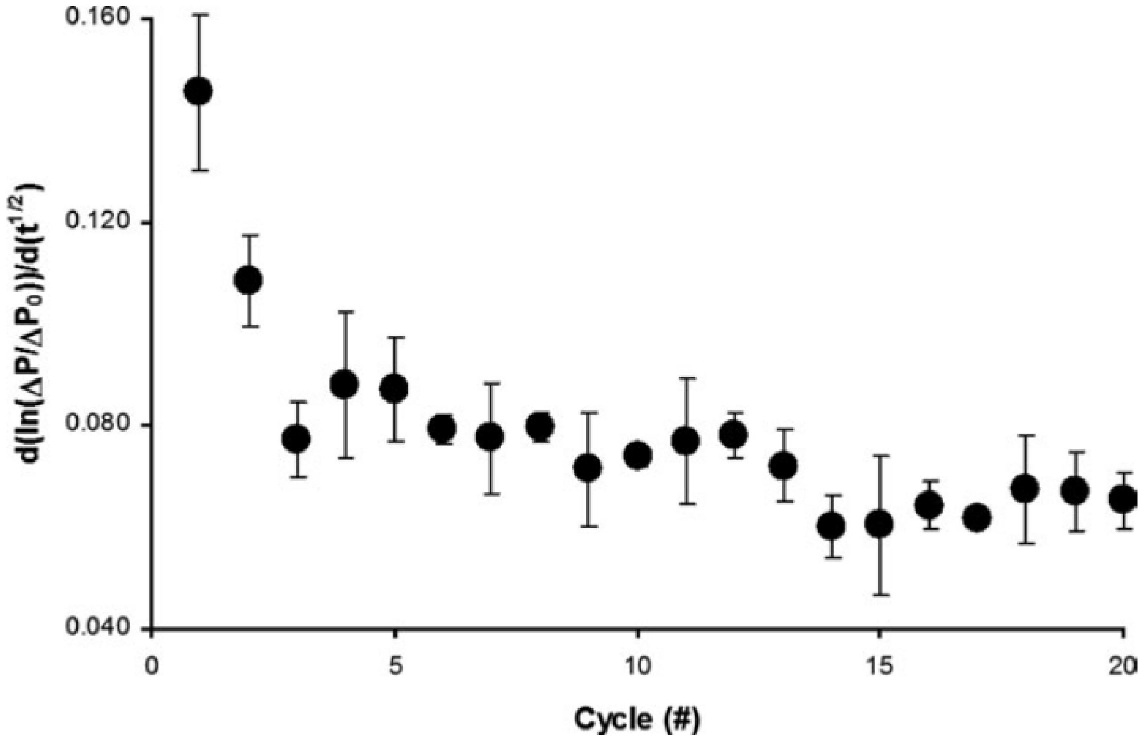
Ammonia Absorption in $MgCl_2$ can be Fast



Cussler et al. *AIChE J.* **58**, (2012) 3526–3532.

Absorption only, no catalyst

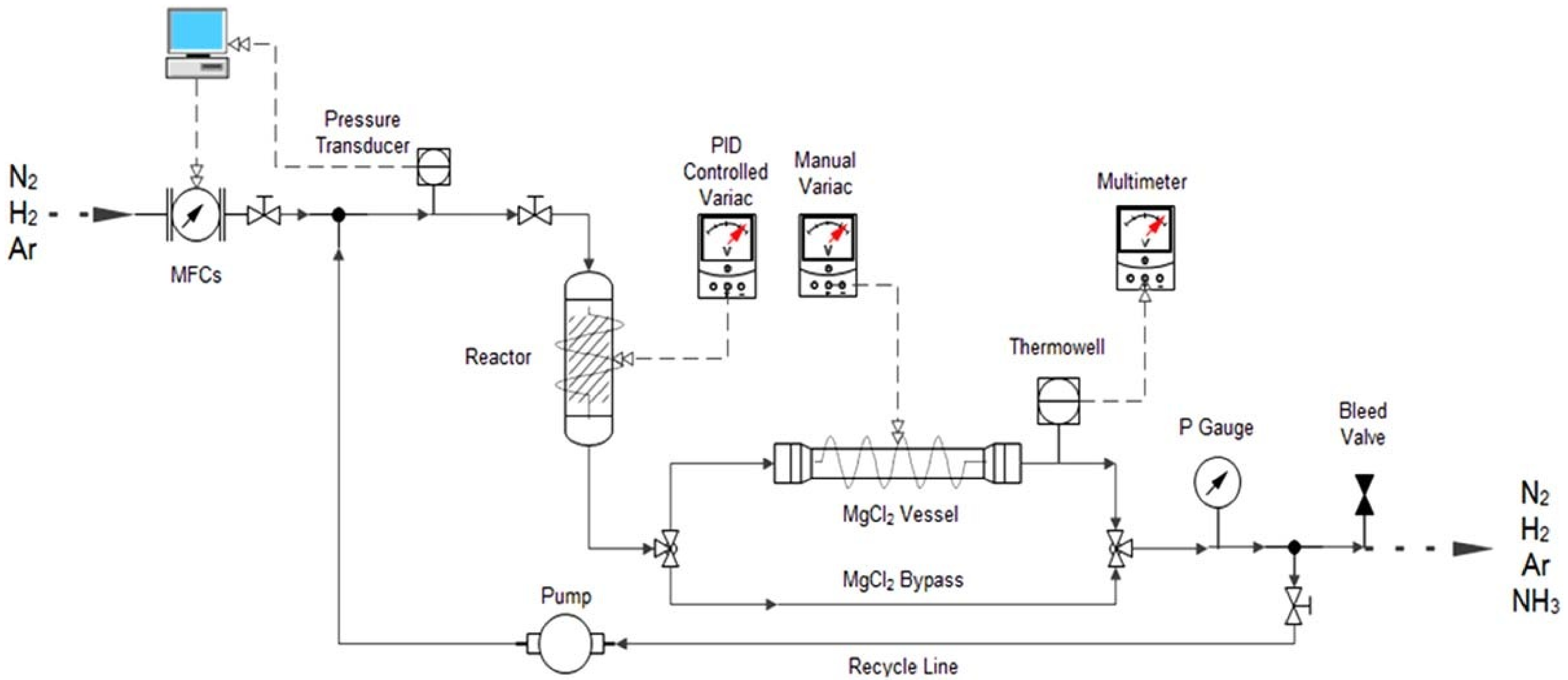
$MgCl_2$ can be loaded with NH_3 over many cycles



Cussler et al. *AIChE J.* **58**, (2012) 3526–3532.

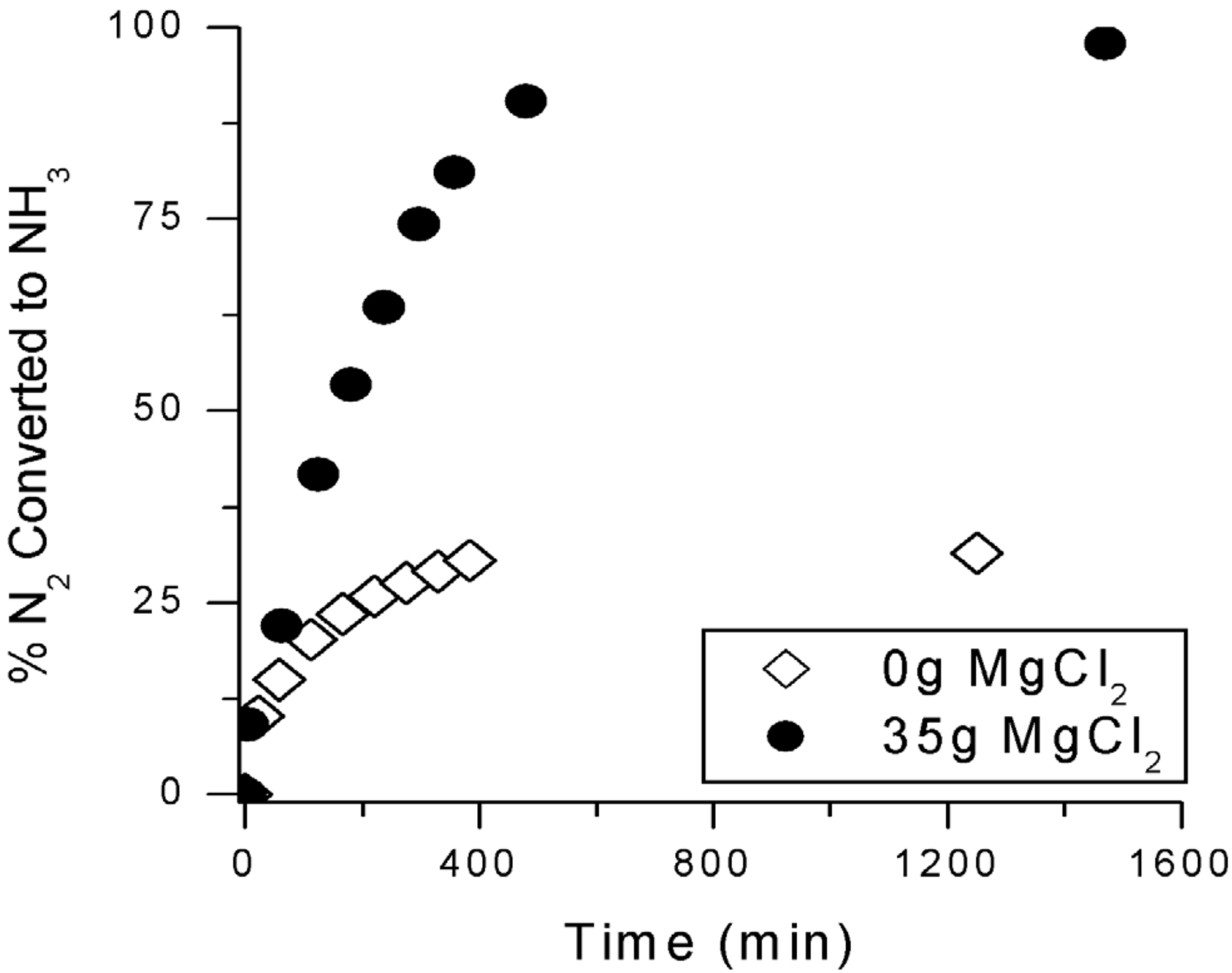
Absorption only, no catalyst

Combined Catalysis and Absorption



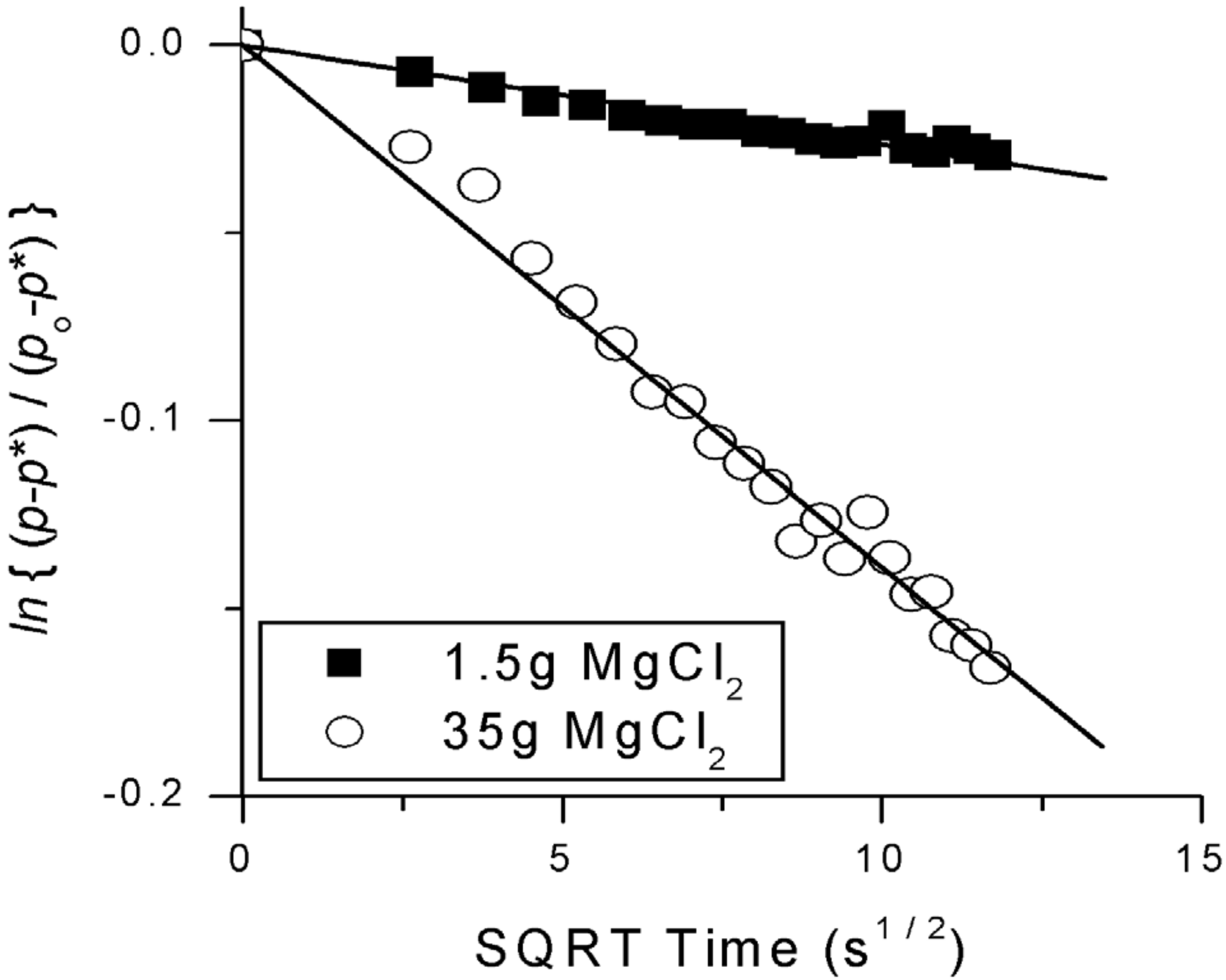
Cussler, et al. *AIChE J.* **61,** (2015) 1364-1371.

Conversion Increases with $MgCl_2$



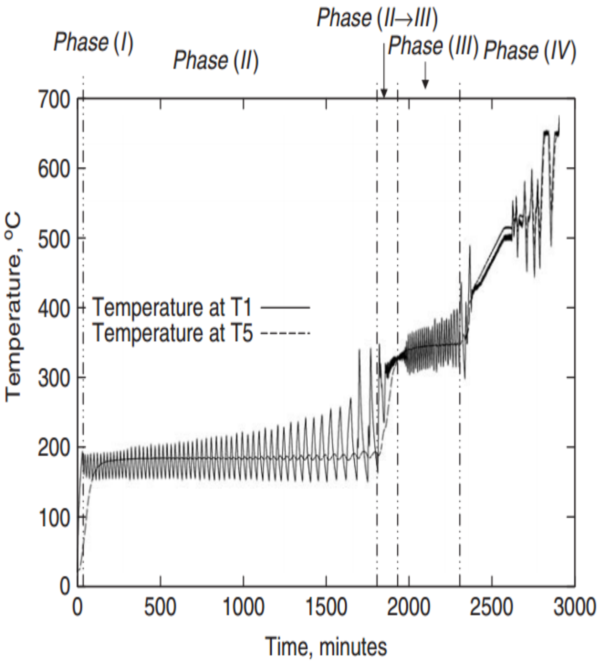
Cussler, et al. *AIChE J.* **61,** (2015) 1364-1371.

Conversion Increases with $MgCl_2$

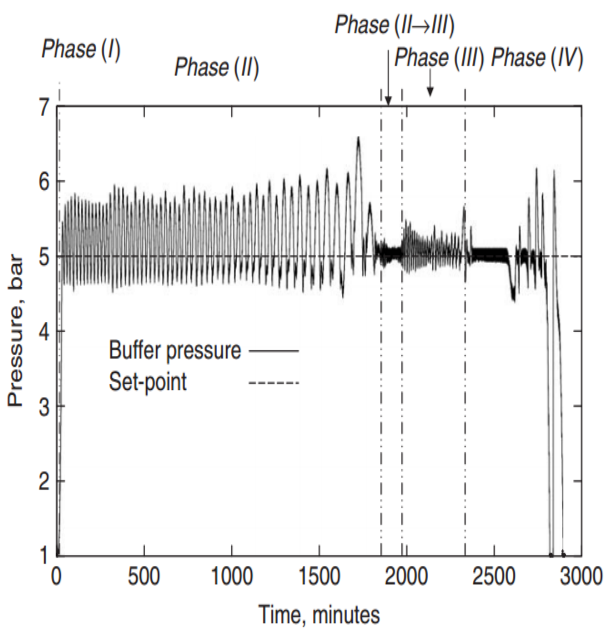


Cussler et al. *AIChE J.* **61,** (2015) 1364-1371.

Complex Ab/De-sorption



T_1: absorbent bed wall temperature
T_5: absorbent bed center temperature



Johannessen et al., *Chem. Eng. Sci.* **61** (2006) 2618-2625

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

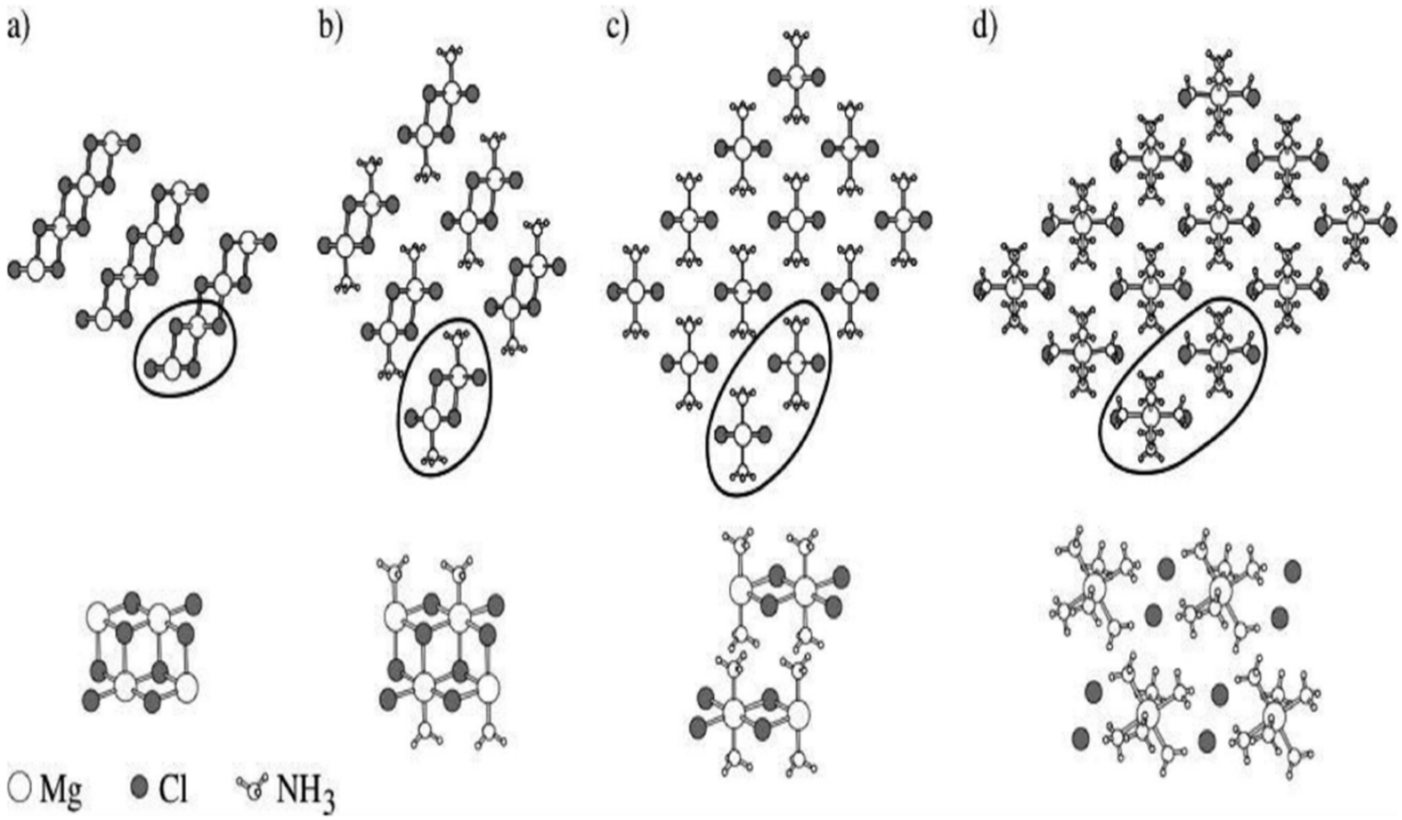
$$Mg(NH_3)_2Cl_2 \rightleftharpoons Mg(NH_3)Cl_2 + NH_3$$

$$Mg(NH_3)Cl_2 \rightleftharpoons MgCl_2 + NH_3$$

Revealing desorption demonstration
Phase I: warm up
Phase (II): first four moles are desorbed
Phase (II to III): transition phase
Phase (III): fifth mole of ammonia desorbs
Phase (IV): sixth mole of ammonia desorbs

Absorbent Structure Changes as Ammonia is Absorbed

Christensen et al. *J. Am. Chem. Soc.*, 2008, **130**, 8660.



Calculated structures found by Danish group for $MgCl_2(NH_3)_x$.

4. Non-Thermal Plasma Catalytic NH_3 Production

Roger Ruan

Yun Li

Paul Chen

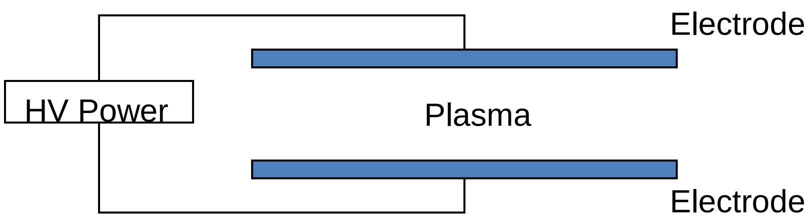
Bioproducts & Biosystems Engineering

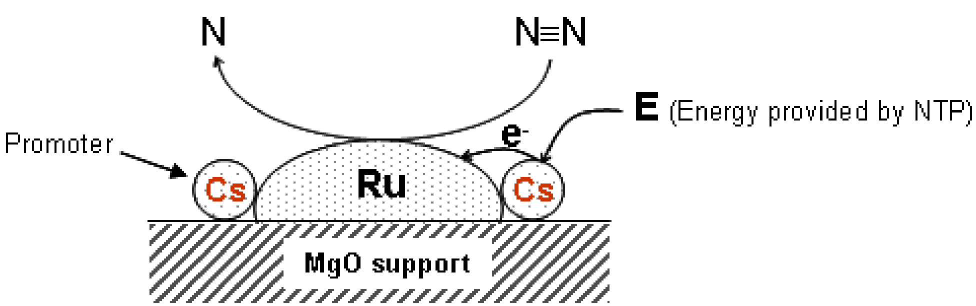
University of Minnesota – Twin Cities

Photo Credit: http://twin-cities.umn.edu/

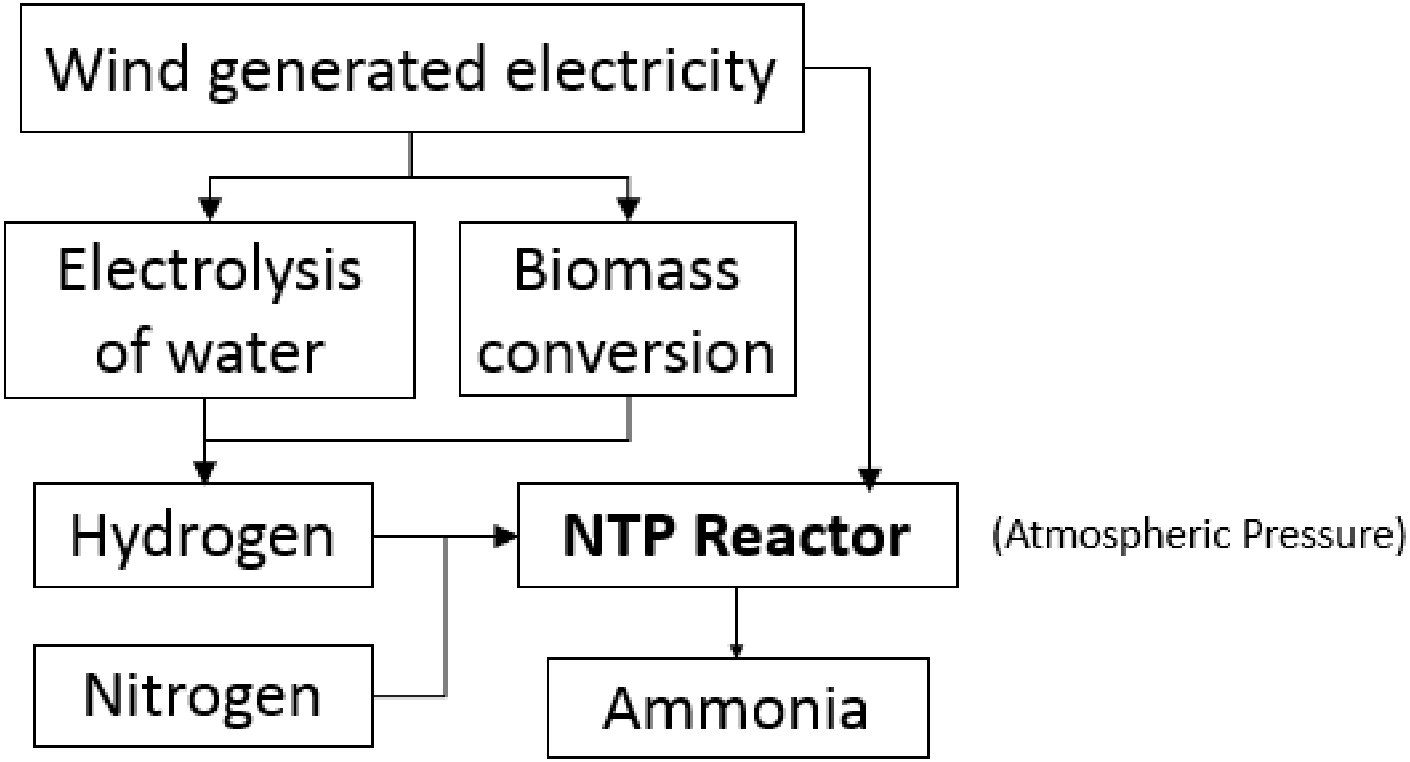
Non-Thermal Plasma (NTP) Assisted Catalysis

- NTP - energized ions and highly reactive radicals made in *non pressurized* gas with electrical discharge
- Catalyst with Promoter: triple bond of dinitrogen weakened by passing electron into the anti-bonding orbital of N_2 through the d-orbital of Ruthenium

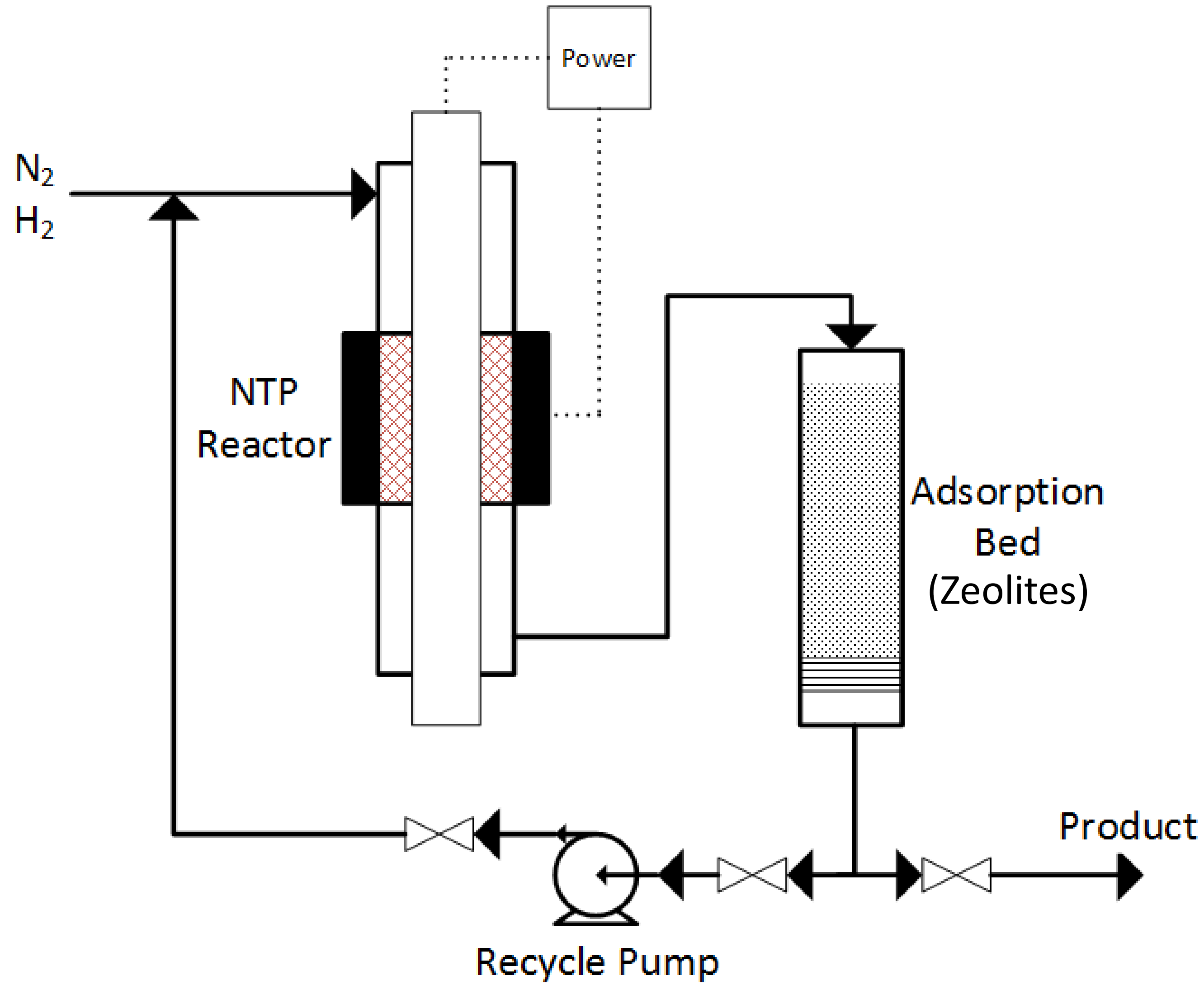




Potential Advantages of NTP



Plasma Assisted Catalysis



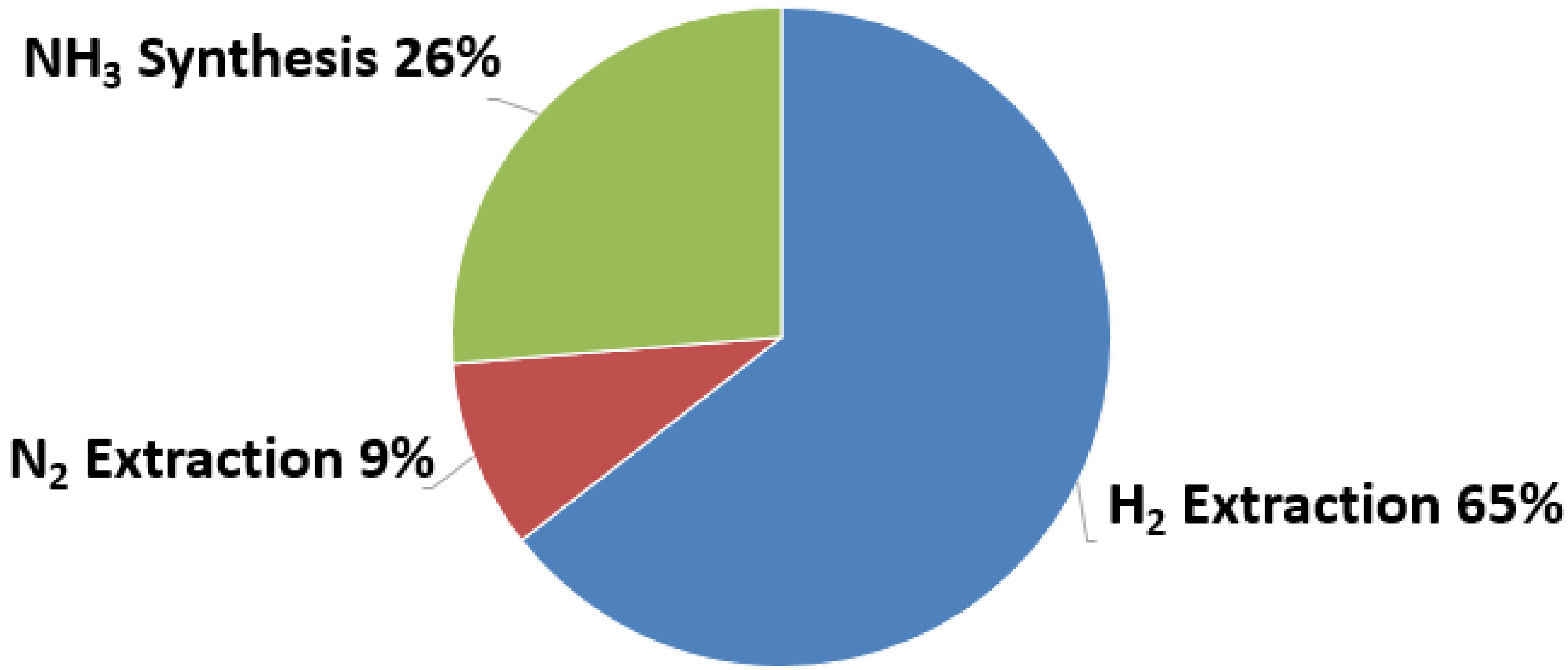
5. Modeling, Economic, & Policy Analysis

Doug Tiffany*
Steve Kelley†
Prodromos Daoutidis‡

*Applied Economics
†Humphrey Institute Public Affairs
‡Chemical Engineering & Materials Science
University of Minnesota – Twin Cities

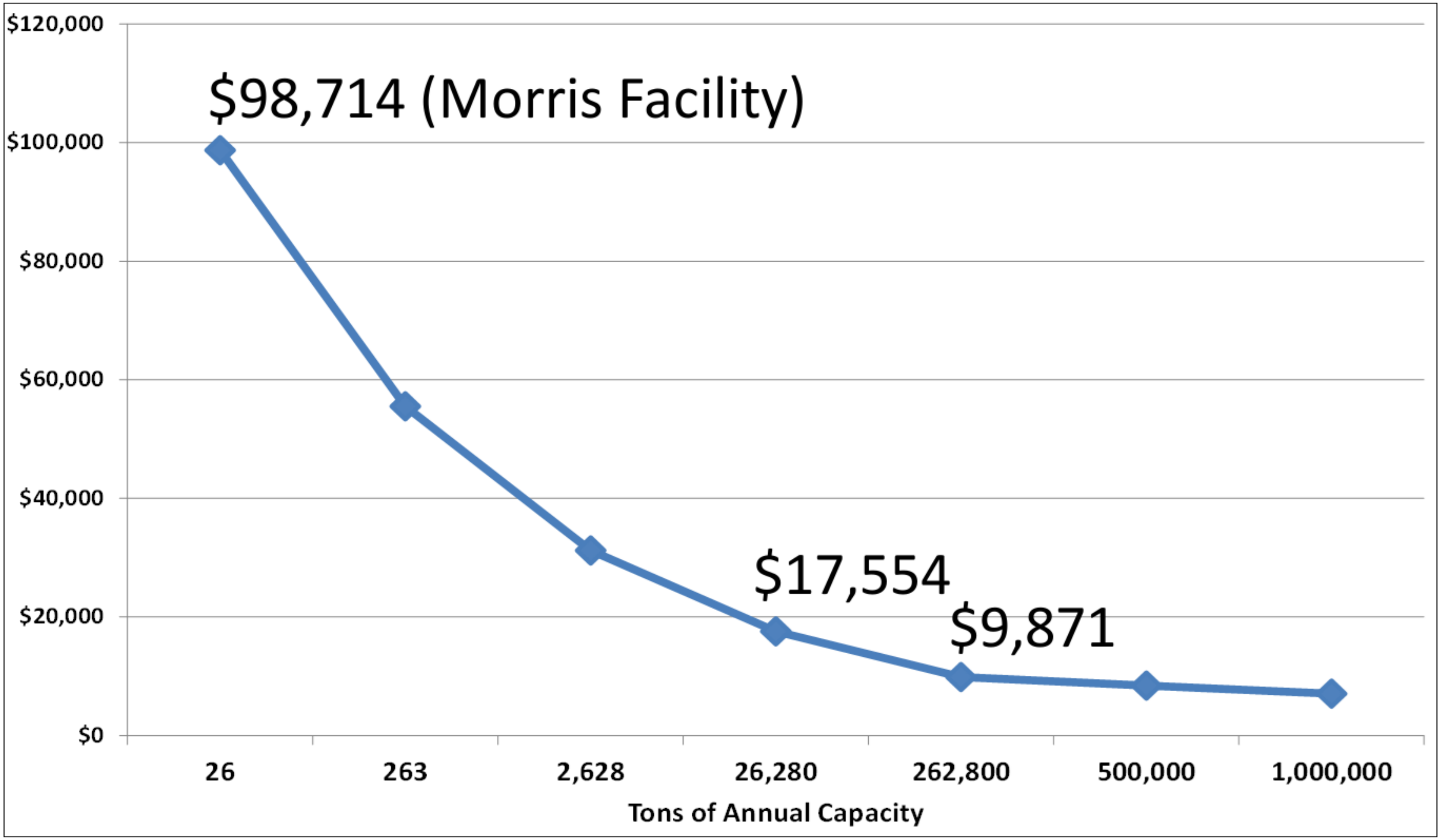
Photo Credit: http://twin-cities.umn.edu/

Tiffany – Current Pilot Plant Energy Consumption



Tiffany – Effect of Scale

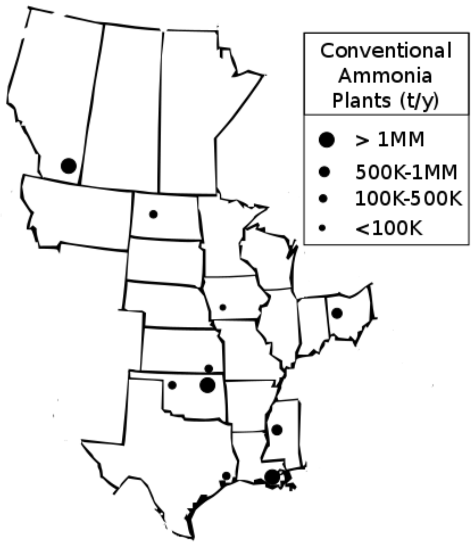
Estimated plant capital cost per ton of capacity of ammonia – including electrolysis, excluding wind turbine



Tiffany & Kelley – Effect of Policy?

Daoutidis - Supply Chain Formulation

Purchase from conventional plants



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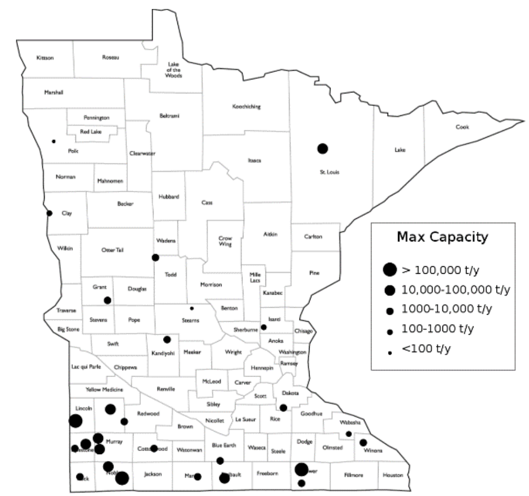
Candidate renewable sites



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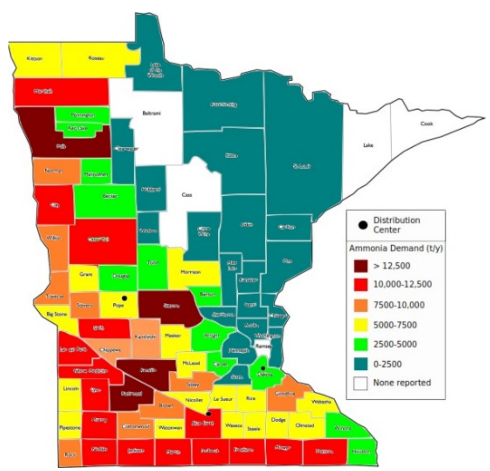
Distribution and demand



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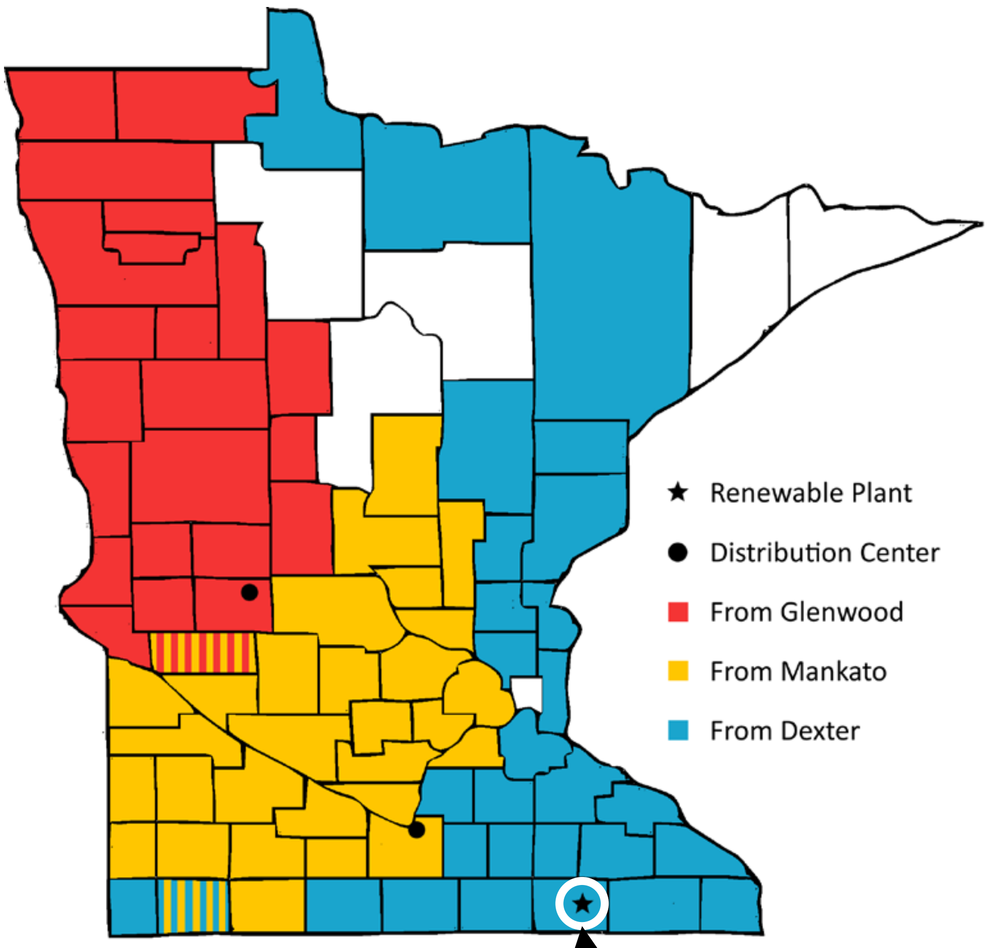
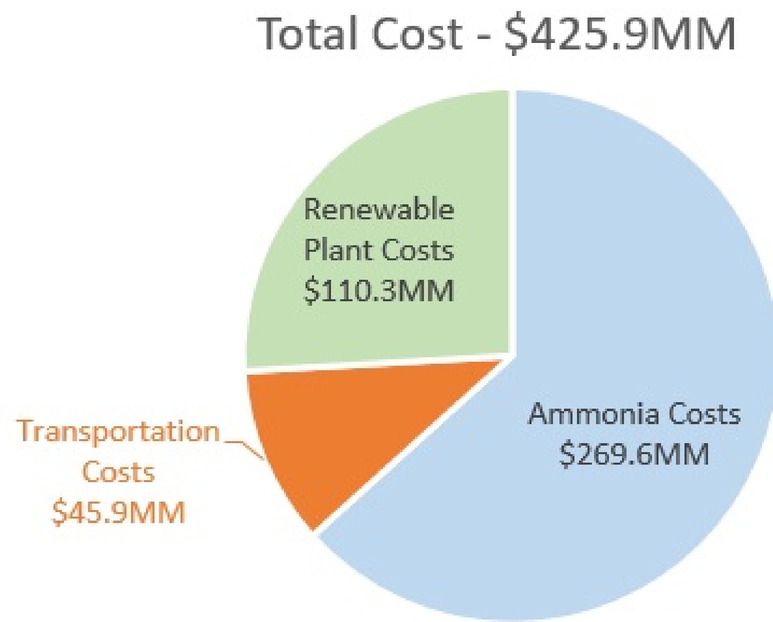
Nonlinear program formulation for optimal supply chain

Daoutidis - Renewable Plant Favorable in Base Case





140K t/y capacity built in Dexter, MN

Conclusions: Distributed Sustainable Ammonia

1. Cuts CO_2 emissions
   - Pilot plant offers benchmark study
2. New technologies can promise lower capital
   - But must be robust and efficient
3. Distributed renewable ammonia possible
   - new technology
   - scale, economic scenario
   - location and policy

Acknowledgment for support of research results shown in this presentation:

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- *MNDrive program, University of Minnesota VP for Research*
- *Minnesota Corn Growers Association*