

Video Article

Ammonia Synthesis at Low Pressure

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Abstract

Ammonia can be synthesized at low pressure by the use of an ammonia selective absorbent. The process can be driven with wind energy, available locally in areas requiring ammonia for synthetic fertilizer. Such wind energy is often called "stranded," because it is only available far from population centers where it can be directly used.

In the proposed low pressure process, nitrogen is made from air using pressure swing absorption, and hydrogen is produced by electrolysis of water. While these gases can react at approximately 400 °C in the presence of a promoted conventional catalyst, the conversion is often limited by the reverse reaction, which makes this reaction only feasible at high pressures. This limitation can be removed by absorption on an ammine-like calcium or magnesium chloride. Such alkaline metal halides can effectively remove ammonia, thus suppressing the equilibrium constraints of the reaction. In the proposed absorption-enhanced ammonia synthesis process, the rate of reaction may then be controlled not by the chemical kinetics nor the absorption rates, but by the rate of the recycle of unreacted gases. The results compare favorably with ammonia made from a conventional small scale Haber-Bosch process.

Video Link

The video component of this article can be found at <https://www.jove.com/video/55691/>

Introduction

Ammonia is a key industrial chemical. It is produced through the Haber-Bosch process, which is known as one of the most important innovations of the 20th century^{1,2}. Ammonia synthesis is carried out in the presence of a heterogeneous catalyst at elevated temperatures (> 375 °C) and pressures (>100 bar)³. Such high temperature and pressure requirements make ammonia synthesis very energy- and capital-intensive. Approximately, 150 million tons of ammonia are produced each year⁴, which accounts for 1-3% of the world's energy consumption, 5% of the natural gas consumption, and up to 3% of the climate-changing gas emissions^{5,6,7}.

Ammonia has two major potential uses. First, ammonia is a synthetic nitrogen fertilizer¹. Without this fertilizer, half of the current population would not have access to sufficient food. Second, ammonia can serve as an energy vector, either as a carbon-neutral liquid fuel or as an indirect hydrogen carrier^{8,9,10,11}. Typically, renewable resources (e.g. wind) are available in underpopulated rural areas, where it can be captured; this type of isolated wind and solar energy is called "stranded". In this scenario, the electrical and thermal energies from the renewable energy source are converted to energy-dense carbon-neutral liquid ammonia. The liquid ammonia produced can then be shipped to urban centers, where it can be directly used in ammonia-based fuel cells¹² and internal combustion engines¹³, or it can be decomposed into hydrogen and then be used in hydrogen fuel cells or hydrogen stations. As a result, we can move the wind of the U.S. prairies to the crowded urban areas of the U.S.

Mostly because of the fertilizer use, ammonia manufacture is a major industry. At room temperature, the ammonia synthesis reaction is exothermic and hence—at least, in principle—spontaneous¹⁴, however, achieving the reaction under ambient conditions is extremely difficult because of the strong nitrogen-nitrogen bond¹⁵. To overcome this, Fritz Haber famously used high temperatures to achieve fast kinetics, but these high temperatures meant that the reverse reaction inhibited the production. To reduce the inhibitions of this reverse reaction, Haber used high pressure to improve conversion. He carried out the large-scale reaction in a gun barrel, which still decorates the BASF plant in Ludwigshafen.

The necessity to use both high temperature and pressure when the reaction could potentially run under much more modest conditions has frustrated chemists for over a century². Even after the process was commercialized, Karl Bosch and a huge cohort at BASF churned through the entire periodic table looking for better catalysts. While Bosch had little success, the search still continues. Even last year, a new research program aimed at seeking a new catalyst was initiated^{16,17}. The detailed chemistry of ammonia synthesis is now well understood¹⁴, and if the search for the new catalyst is successful, it would certainly be worth the effort. However, in our view, the past failures reduce the chance of future success.

In the following text, small-scale ammonia synthesis process is described, and the motivation to investigate an alternative process is explained.

The Small-Scale Process:

Wind-Generated Ammonia

We are improving the Haber-Bosch process for synthesizing ammonia, seeking a much smaller, simpler process which can be operated locally but produces negligible amounts of carbon dioxide. The feasibility of local ammonia manufacture from wind has already been demonstrated in a pilot plant located in Morris, MN, and shown in **Figure 1**¹⁸. Morris sits on the Buffalo Ridge, a formation of sixty miles of rolling hills in the southwest corner of Minnesota. The ridge has unusually steady, strong wind, rolling across the prairie. As a result, it is a mecca for wind-generated electricity.

With this electricity, we already manufacture ammonia from wind, using this plant which is forty thousand times smaller than the existing commercial operations for fossil fuels. Some wind-generated electricity is used to make nitrogen from air by pressure swing adsorption, an established method for air separation used, for example, for patients with emphysema who need oxygen-enriched air. However, more of the electricity is used to make hydrogen by electrolysis of water. These gases are combined over a conventional catalyst in the process shown schematically in **Figure 2**. After the reaction, the gases are separated by chilling to condense the liquid ammonia. The unreacted gases, as well as the uncondensed ammonia, are recycled.

Details of the Pilot Plant

In our pilot plant, the University of Minnesota Renewable Hydrogen and Ammonia Pilot Plant, the electric power is provided from a co-located 1.65 MW wind turbine. The pilot plant uses approximately 10% of the power generated, with the remaining power used at the University of Minnesota, Morris campus.

The hydrogen production system uses an electrolyzer, a booster compressor, and a thermal chiller. This system produces 0.54 kg of hydrogen gas per hour, which is stored at 2,400 psi using 24 kWh of electricity. Water from an on-site well is purified using a reverse osmosis and deionization system. The water is then supplied to the electrolyzer at a rate of up to 15 L/h. Nitrogen is generated using a nitrogen generator, a pre-air compressor, an air dryer, and a booster compressor. The nitrogen gas is stored at 2,400 psi using approximately 6 kWh of electricity.

The synthesis of ammonia uses a custom skid. It includes a compressor, a reactor, a refrigeration cooling loop, and a 20 kW electric heater. The skid uses approximately 28 kWh of electricity to produce 2.7 kg of ammonia per hour which is then stored at 150 psi. The ammonia production process is controlled with integrated PLC and HMI systems. The produced hydrogen and nitrogen are stored on site in 18 nitrogen storage tanks and 54 hydrogen storage tanks. The ammonia is also stored onsite within a 3,100-gallon vessel.

Wind Generation is Expensive

The electricity for this process is made from wind, and so the fuel for making ammonia is free, without using any fossil fuel. However, the capital costs for this pilot plant are dominated by the investments for hydrogen production and for ammonia synthesis. The operations to date suggest that the cost of making small-scale ammonia are about twice that of conventional ammonia based on fossil fuels. While we continue to optimize our process, we believe that small-scale wind generated ammonia will not be competitive at the current natural gas prices. The capital costs per mass ammonia made could be reduced by a larger conventional process, or by an alternative process like that described next in this paper.

The Absorption Process:

Absorption Enhances Production

The catalyst used for ammonia synthesis has remained almost unchanged during the last century¹⁹. As a result, we have carried out a different approach in this research. We apply the current catalyst and operating temperature, but absorb ammonia at modest pressures as soon as it is formed. We recycle any unreacted hydrogen and nitrogen. The process is schematically like that in **Figure 3**, similar to the conventional process, but with a packed bed absorber replacing the condenser.

Initial Reaction Kinetics Do Not Change

Experiments with this system at low conversion show an initial reaction rate that is consistent with many of the earlier studies on this system^{3,14,15,20,21,22,23}, as shown in **Figure 4**. The left panel shows the initial rates, which vary strongly with temperature. While these rates also vary with pressure, the variations are smaller, as shown in the right panel. In our new process, we use the same catalyst and similar operating conditions, but seek ways to improve ammonia production by using absorption at a lower pressure. We thus hope to reduce the capital costs for ammonia synthesis.

Absorption Enhances Conversion

In our work, we replaced the condenser in the small process with a packed bed, which is a cylindrical vessel filled with small particles of the absorbent. We have emphasized absorbents made primarily of magnesium chloride and calcium chloride^{11,24}. Such ammine absorbents have two effects. First, they reduce the ammonia concentration present in the recycled gases to near zero. Second, they effectively reduce the time for separation to near zero. This strategy is productive^{25,26,27}. For example, in **Figure 5**, we show that the rate of making ammonia, which is proportional to the drop in the total pressure in the system, is much greater with absorption than without. In particular, the reaction at 90 bar, shown by the red circles, is less complete than the reaction with the absorbent, shown by the blue triangles²⁷. This is true even though the reaction without absorbent takes place at a pressure almost twice that of the reaction with absorption. In earlier experiments (not shown here), we also showed that the eventual conversion of the process is about 20% without absorbent but over 95% with absorbent.

The rate of reaction varies much less with temperature with absorption than without. This is shown in **Figure 6**, which again reports ammonia synthesis as total pressure *versus* time²⁷. Changing the reaction temperature by 60 °C has little effect on the reaction rate. This contrasts with the initial rates in **Figure 4**, which shows a change of reaction rate of almost an order of magnitude. The results in **Figure 4** and **Figure 6** are different because the effect of the reverse reaction has been reduced, so the chemical kinetics are no longer the only step responsible for the overall rate.

Protocol

1. Pilot Plant Start-up

1. Nitrogen production system

1. Turn on the air dryer, the air compressor, and the nitrogen generator. Verify that there is at least 800 kPa of air in the air compressor tank. This keeps sending nitrogen to the buffer tank until there is no more than 0.004% (40 ppm) oxygen in the nitrogen.
2. Turn on the nitrogen gas booster. The gas booster starts to fill the nitrogen supply tanks, at pressures as high as 17 MPa.

2. Hydrogen production system

1. Turn on the chiller, the water deionization unit, and the electrolyzer. The electrolyzer will not operate without a venting system, because there is a flow sensor that measures the negative pressure venting in order to let the electrolyzer start. The hydrogen is produced with a rate of 0.54 kg/h, and the discharge pressure will be about 1.5 MPa.
2. Turn on the hydrogen gas booster. Verify that the chiller is operational and the cooling liquid is flowing through. The hydrogen supply tanks will be filled up to 17 MPa.

3. Ammonia skid start-up

1. Use the computer in the control room to do the following:
 1. Verify the emergency exits for the building.
 2. Make sure that the oxygen, hydrogen, and ammonia concentrations in the building are less than 20%, 19 ppm, and 35 ppm, respectively.
 3. Verify that the hydrogen and nitrogen supply tanks are charged to 17 MPa.
 4. Make sure that the ammonia sampler and the weight tank valves are bypassed.
 5. Pressurize the skid with nitrogen by setting the skid's nitrogen inlet regulator to 2.5 MPa. Set the nitrogen pressure regulator to 300 psi and then open the nitrogen bypass valve to fill the skid with nitrogen to 300 psi. Then close the nitrogen valve when that pressure is reached. Set the hydrogen regular to 1,200 psi and open the hydrogen valve to allow the skid to fill to 1,200 psi. Then close the hydrogen bypass valve.
 6. Open the hydrogen inlet valve and set the skid's hydrogen inlet regulator to 10 MPa.
 7. Set the NH_3 pressure regulator to 1 MPa.
 8. Use the GUI controlling software to close/open multiple bypass valves on the skid, the compressor, and the air valves.
 9. Use the GUI controlling software to turn a couple of the PID controllers to ensure that the skid is fed with a 1:3 ratio of $\text{N}_2:\text{H}_2$.
 10. From the control room, and using the master GUI controlling software, start the skid. The compressor starts to recirculate the gas in the skid, and inject the fresh feed.
 11. In the GUI controlling software, set the reaction and condensation temperature. The reactor and condenser temperatures are set at 440 °C and -25 °C, respectively.
- NOTE: It takes up to 4 days for the reactor to get to the set point temperature and achieve a steady state condition.

2. Experimental Apparatus Start-up

1. Reactor preparation and reduction

1. Weigh 3 g of the pre-reduced catalyst. Reduce the particle size of the catalyst particles to less than 1 mm using a mortar and pestle.
2. Load the catalyst into 0.25 in tubing, and place quartz wool on both sides.
3. Use a PID controller, and increase the reactor temperature to the reaction temperature (400 °C) with appropriate ramps, while flowing hydrogen through the reactor with a flow rate of 500 standard cubic centimeters per minute (SCCM). Use the ramps (summarized in Table 1).

NOTE: The temperature increase should be very smooth in order to obtain the proper catalyst activity.

4. Continue the reduction process for 24 h. Ensure that no air or impurity comes into contact with the catalyst. Always keep the reactor under a nitrogen blanket.

2. Absorber preparation

1. Load 80 g of the CaCl_2 absorbent into the absorber column (ID: 2.3 cm, Length: 30 cm). According to different absorbent sizes, different absorber packing supports will be used on both sides of the absorber, in order to immobilize the packed bed.
2. To remove any humidity, increase the absorber temperature to 350 °C while flowing nitrogen with the flow rate of 200 SCCM for 24 h.

3. Starting reaction separation tests

1. Increase the reactor and absorber temperature to 400 °C and 180 °C, respectively.
NOTE: Use proper temperature ramps to increase the reactor temperature. Use transformers to make the temperature control smoother. Keep the system in idle mode under the nitrogen blanket. Before starting any test, charge the system with nitrogen to 5 MPa a few times, and then release the pressure.
2. Use the GUI to control the hydrogen and nitrogen mass flow controllers.
3. Charge the apparatus to the target pressures with nitrogen and hydrogen, with the ratio of 1:3.
4. Once the target pressure is achieved, close the inlet valves, open the reactor outlet valve, and turn on the recirculating pump. Due to the exothermic reaction and absorption, the reactor and absorber temperatures might require more careful control at the beginning of the process.
5. Continue the test for 5 h, until the point when the absorber starts to breakthrough.

4. Desorption of ammonia

1. Open the inlet and outlet valves.
2. Reduce the system's pressure to atmospheric pressure and increase the temperature of the absorber while flowing nitrogen with a flow rate of 100 SCCM for 5 h to desorb ammonia from the absorbent material.

Representative Results

A pilot plant in Morris, MN has demonstrated the feasibility of using wind for local ammonia manufacture¹⁸, as shown in **Figure 1**. The wind generates electricity, which is used to make nitrogen and hydrogen through the pressure swing absorption of air and through the electrolysis of water, respectively. A reactor uses a conventional catalyst to combine the nitrogen and hydrogen gases, making ammonia. The ammonia is then separated using a condenser.

The method described here includes a process to recycle any unreacted hydrogen and nitrogen. The overall procedure is similar to that demonstrated in **Figure 3**, the conventional process, except the condenser is replaced with a packed bed absorber. The absorbents are primarily made with magnesium chloride and calcium chloride. The initial reaction rates demonstrated by this system at low conversion are consistent with many earlier studies, as demonstrated in **Figure 4**. The total pressure drop in the system is proportional to the ammonia production rate. This rate is much greater with absorption than without, as illustrated in **Figure 5**. Also, with absorption, the rate of reaction varies much less with temperature (**Figure 6**). With absorption, a temperature change of 60 °C has little effect on the reaction rate, while the initial reaction rates (**Figure 4**) demonstrate almost an order of magnitude change.

At the temperatures and pressures used here, pure amines are not stable. At a given flow, the amount of ammonia absorbed by the bed is reduced after its repeated use (**Figure 7**). Stabilizing the absorbent can improve its capacity. As demonstrated in **Figure 8**, this stability over many cycles can be achieved by trapping small magnesium chloride crystals in fissures of the alumina. Additional improvements to the absorbent are currently being investigated.

With absorption, chemical and absorption kinetics are less able to limit ammonia production, as illustrated in **Figure 9**. The intercept at infinite pump flow includes the resistances of reaction and absorption. When this reciprocal is small, the chemical reaction values are large. Higher pump flows correspond to rate increases; at infinite pump flow, the rate can be extrapolated to a finite limit.



Figure 1. The Small-scale Plant. [Please click here to view a larger version of this figure.](#)

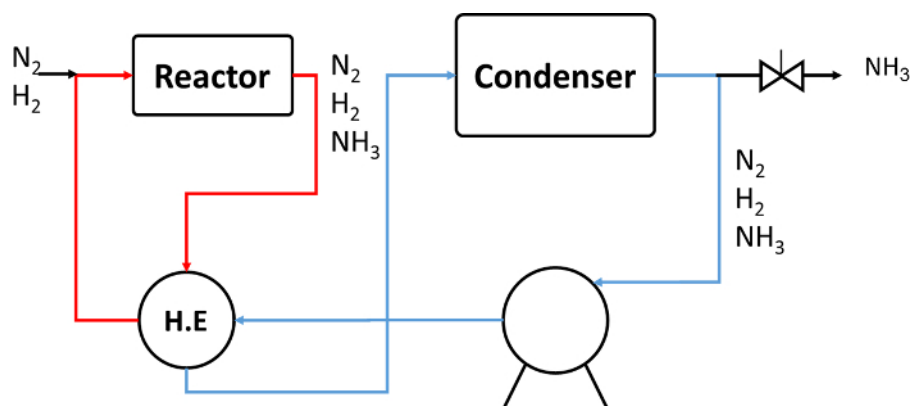


Figure 2. A Schematic Drawing of the Small-scale Plant. [Please click here to view a larger version of this figure.](#)

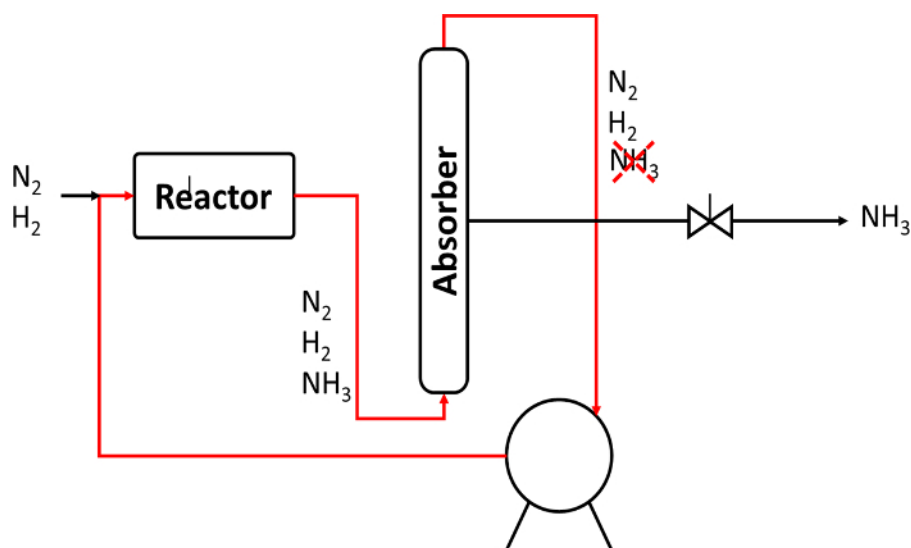


Figure 3. The Absorbent Process. [Please click here to view a larger version of this figure.](#)

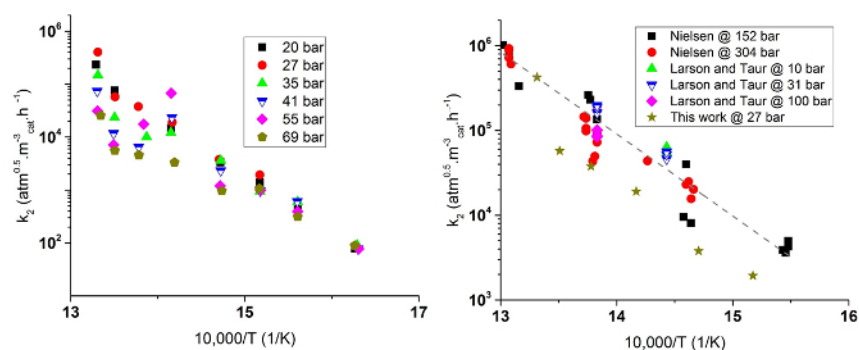


Figure 4. Initial Reaction Rates. [Please click here to view a larger version of this figure.](#)

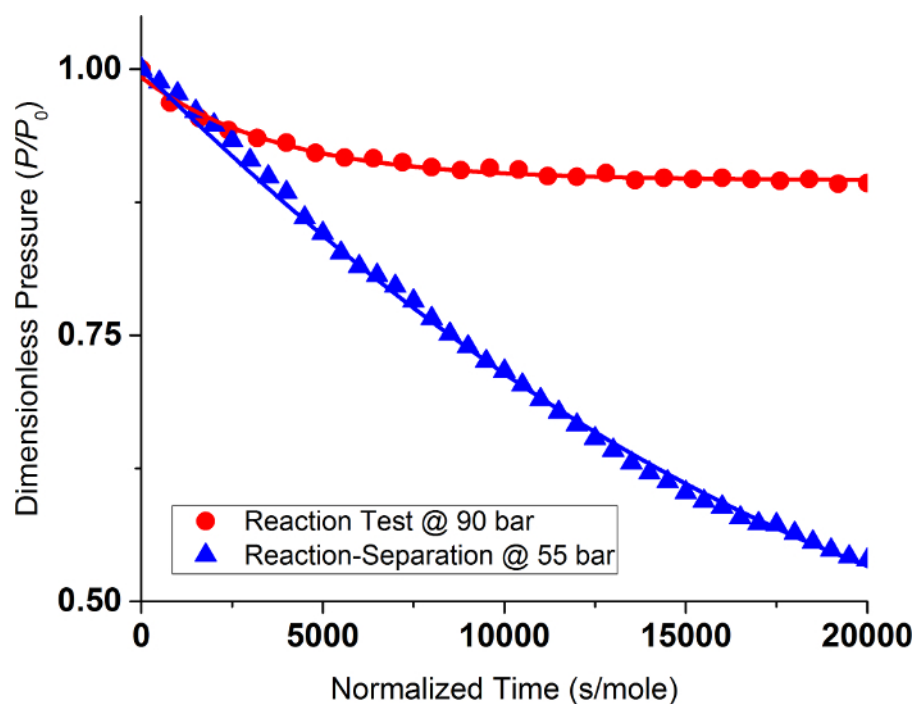


Figure 5. Conversion Without and With Separation by Absorption. [Please click here to view a larger version of this figure.](#)

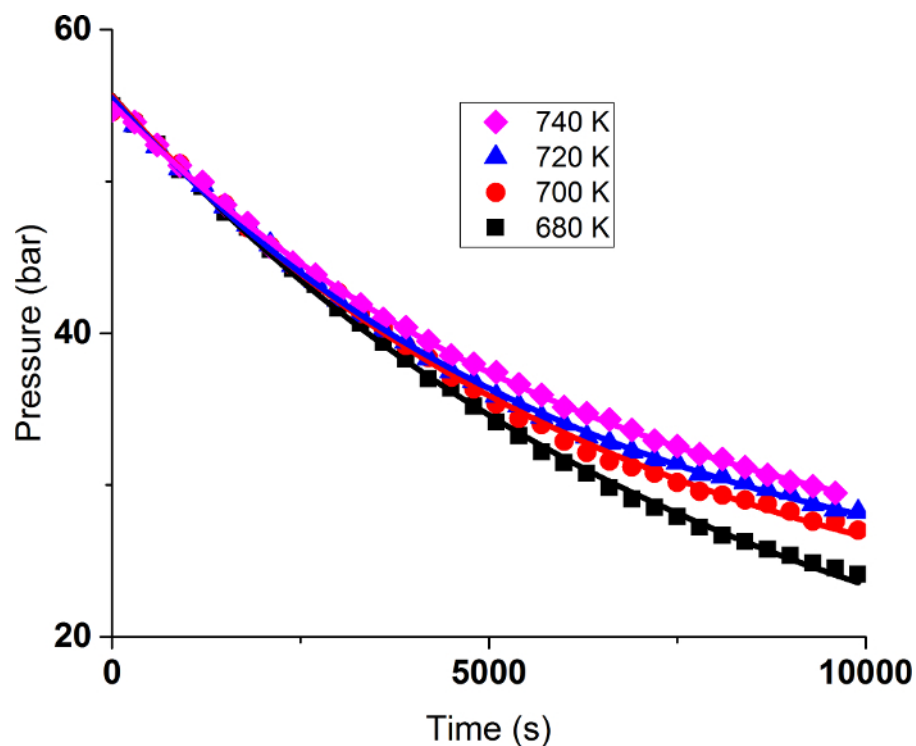


Figure 6. Reaction with Absorption. [Please click here to view a larger version of this figure.](#)

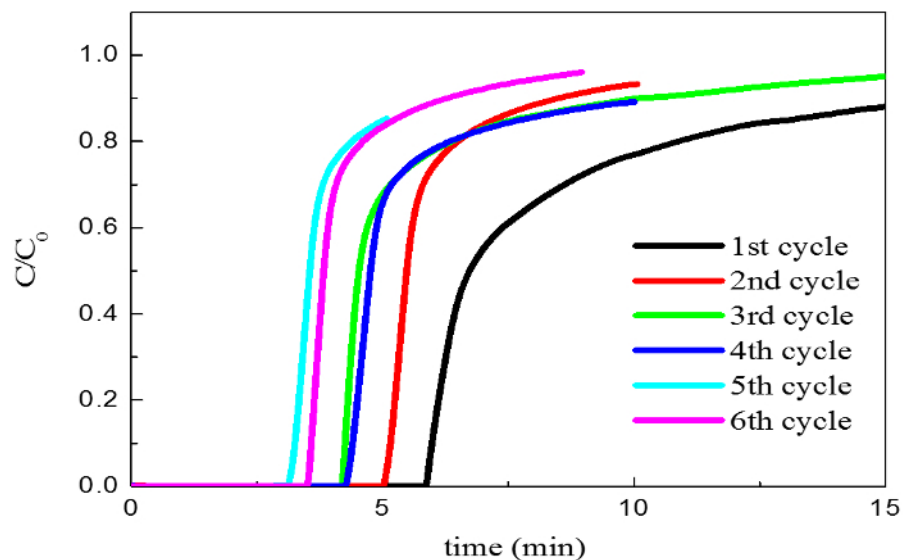


Figure 7. Current Absorbents are Limited. [Please click here to view a larger version of this figure.](#)

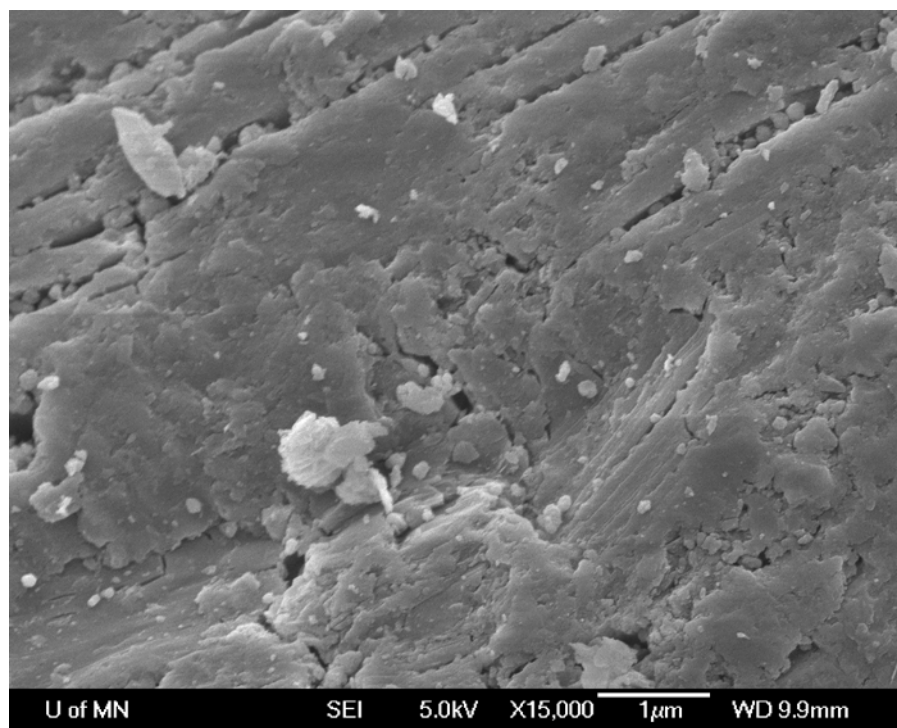


Figure 8. Micrographs of Absorbents. [Please click here to view a larger version of this figure.](#)

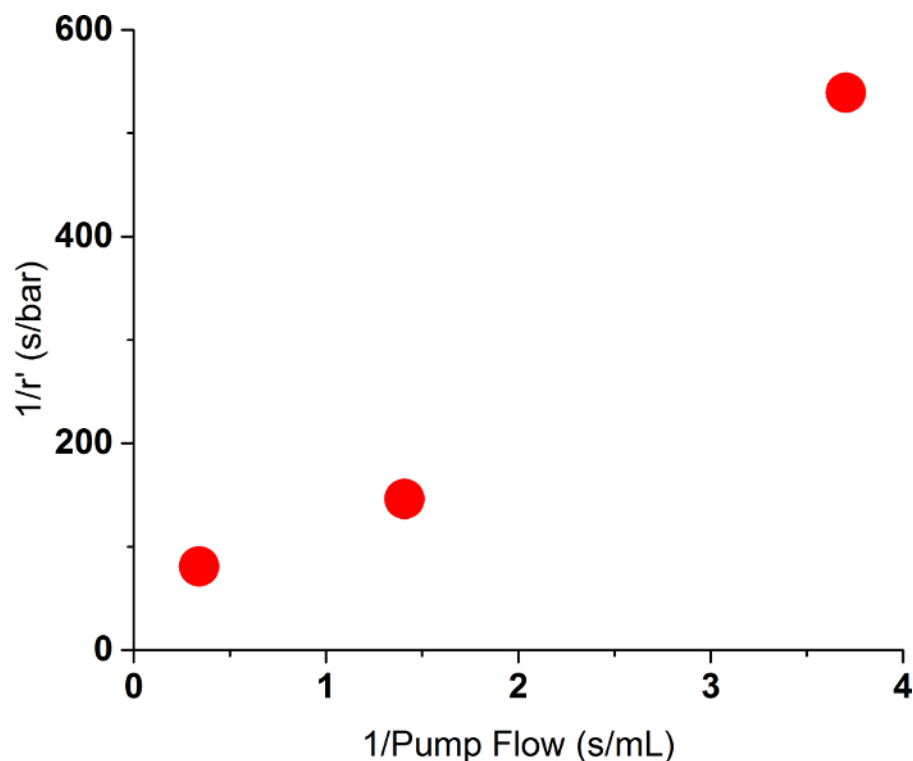


Figure 9. Reaction versus Recycle Flow. [Please click here to view a larger version of this figure.](#)

Peak Temperature Range (°C)	Max. Rate of Temperature Increase (°C/h)	Time in Heating Steps (h)	Time (h)
Ambient-340	40	8	8
340-370	15-20	2	10
370-400	10-May	5	15
400-430	0-5	28	43
430-470	5	8	51
	Hold Inlet Temperature at 450 (°C) for 4 h		

Table 1. Temperature Ramps Used to Activate the Catalyst.

	7/14/2014	9/2/2014	9/17/2014	10/29/2014	1/9/2015
Reactor T	569	575	563	565	557
Pressure p	112	72	124	117	128
Condenser T	404	365	425	413	420
Reaction	9	3	17	14	30
Condensation	0.019	0.012	0.021	0.02	0.022
Recycle	0.004	0.005	0.004	0.003	0.003

Table 2. Typical Rate Data from Pilot Plant Operation.

The times for reaction, condensation, and recycle show that the chemical kinetics has the largest time, and hence the slowest rate. Units: T (°C), p (bar)

Discussion

Critical Steps of the Reaction-absorption Experimental Apparatus:

Make sure that there is no impurity in the nitrogen and hydrogen system. The absorbent materials will change after each cycle. In most cases, at high temperature and in the presence of ammonia, the absorbent materials fuse and form a large solid concrete. According to the thermodynamic properties of each metal halide and ammine complex, the appropriate temperatures for absorption and desorption should be

employed. Before each test, the pressure drop across the system (absorber, reactor, tubing, valves, fittings, etc.) should be checked, to make sure that the recirculation loop, absorber, or reactor are not imposing large pressure drops across the system.

Limitations: The Best Absorbents Known Now Are Unstable:

The ammine absorbents used to separate ammonia have a large potential capacity, as much as six moles of ammonia per mole of calcium. This absorption is controlled by the diffusion in the solid, and hence is much slower than diffusion in the surrounding gases. Absorption at the high temperatures and pressures like those in the synthesis reactor has a smaller capacity, but is still usually more than the amount collected by surface adsorption.

However, the absorbents themselves, especially magnesium chloride, are not stable²⁸. As a result, breakthrough curves in packed bed experiments are not reproducible, as shown in **Figure 7**. This figure reports the breakthrough curves of ammonia-nitrogen mixtures flowing through a packed bed of particles of magnesium chloride. As expected, the bed does absorb the ammonia, but the amount absorbed at a given flow drops as the bed is repeatedly used. At the same time, the solids in the bed change from a free-flowing powder to a single concrete mass. This fusion makes the kinetics of absorption much slower. To overcome this, we made a packed bed of alumina supporting the small crystals of magnesium chloride. Such a bed does show stable breakthrough curves, apparently stabilized by the small chloride crystals trapped within fissures of the alumina and shown in **Figure 8**²⁸. Further improvement in the absorbent remains an active research focus.

Significance of the Method: Recycle of Unreacted Gas Now Controls:

The controlling step is now, largely, the rate of recycle of the unreacted gases, as shown in **Figure 9**. This figure plots the reciprocal of the pressure change versus the reciprocal of the pump flow. The pressure change is, of course, the same measure of reaction that we used in **Figure 5** and **Figure 6**: the small values of this reciprocal correspond to the large values of the chemical reaction. The reciprocal of the pump flow, shown on the x-axis, is simply a convenient way to investigate what happens as the pump flows approach infinity. As can be seen, the rate increases at higher pump flows, and extrapolates to a finite limit at infinite pump flow. This limit is close to the fastest reaction rate possible, that is, the forward reaction rate without the constraints of either the reverse reaction or separation. The slope on this line measures the effect of recycling the unreacted gases.

The results shown above confirm the viability of the reaction absorption process for the enhanced production of ammonia at significantly lower pressures. For example, in one set of measurements, we obtained more than 80% conversion with relative fast ammonia synthesis rates. This suggests that high production rates at pressures as low as 25 bar are viable when ammonia is removed from the system efficiently. The absorption separates the synthesized ammonia from the reaction environment and induces the reverse reaction.

The data for the current pilot plant and for our absorption studies show that the reaction rate for moles ammonia synthesized per time equals the ammonia concentration in the system at equilibrium minus the true ammonia concentration, divided by three characteristic times. The first of these times is the time of reaction, the second is the time of separation, and the third is the time for recycle. Examples of these times are shown in **Table 1**, where the absorption step is by partial ammonia concentration. At present, the time of reaction is the largest, so that the existing pilot plant's productivity is controlled by the chemical reaction rate. We can increase the reaction rate by increasing the temperature. We are doing this, and the plant is running well.

Future Applications and Directions:

The data for both the pilot process and the absorption process can also be analyzed in terms of a concentration difference divided by three characteristic times. More specifically,

$$\frac{\text{Production Rate}}{\text{Volume}} = \frac{C - C^*}{\tau_{rxn} + \tau_{sep} + \tau_{recycle}}$$

where C and C^* are the nitrogen concentrations actually present and present at equilibrium, respectively, and τ_{rxn} , τ_{sep} , and $\tau_{recycle}$ are times of reaction, separation, and recycle, respectively. In the small plant and in our initial rate measurements, the time of reaction is the largest, that is, the slowest. It controls the overall rate. Therefore, we are trying to run the pilot plant at higher temperatures.

However, in our absorption process, the concentration at equilibrium C^* is near zero because of absorption. Also, the times of reaction and absorption in an unsaturated bed are somewhat smaller than the time of recycle. Thus, the plot of inverse reaction rate versus the reciprocal of recycle flow should give a straight line roughly like that in **Figure 9**. The slope on this line should correspond to the recycle flow, and the intercept will represent any contributions of the chemical rates and absorption rates. Our preliminary data support this prediction, and suggest ways in which our synthesis can be further improved.

While these results are preliminary, they still permit speculation about the design of a small, efficient process that manufactures ammonia at reduced pressure. This obviously depends on an efficient absorbent. In the experiments to date, we have not focused on the rate of uptake of the absorbent and hence on its physical geometry. We have found this geometry is not always stable under reactor conditions, and hence represents a major area for continued development. We also have not worried about the amount of absorbent required: to get more absorption, we simply have used more absorbent. In addition, we have not worried about the absorbent lifetime; we have noted absorbent properties frequently deteriorate with use, both by forming fines and by apparently showing reduced surface area. All of these issues, dealing both with the absorbent and with the absorber design, must be resolved to further clarify the potential of this process. At the moment, however, the prognosis is good.

Disclosures

The authors have nothing to disclose.

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