Optimizing the Conditions for Ammonia Production using Absorption

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Abstract

Ammonia is made from hydrogen and nitrogen over a catalyst operating at high temperature and pressure. More ammonia can be produced by changing how the ammonia synthesized is separated, i.e. by replacing the current condensation of ammonia with absorption in salts like magnesium chloride. This paper uses the concept of resistances in series in conjunction with experiments of absorption and a well-established theory of reaction to identify conditions where the rate of ammonia synthesis can be increased. For example, in one case, if a condenser in a conventional process is simply replaced with an absorber, the increase in production rate per mass of catalyst is capped at 10%. However, if the recycle rate is simultaneously increased, the increase in production rate per gram of catalyst can exceed 1000%.

Keywords: Ammonia, absorption, condensation, optimization, production rate

Introduction

This work is concerned with the synthesis of ammonia, made by reacting nitrogen and hydrogen via the Haber–Bosch process.[1] The conventional feedstock for this synthesis uses fossil fuels.[2] In one common case, methane is partially burned in air and steam to produce a mixture of nitrogen, hydrogen, and carbon dioxide. After the carbon dioxide is carefully removed, the nitrogen and hydrogen are combined at high pressure and temperature over a catalyst to produce a mixture of ammonia and unreacted nitrogen and hydrogen. The ammonia is removed by condensation; the unreacted gases are recycled and supplemented with more hydrogen and nitrogen to make more ammonia.

The Haber-Bosch process is remarkably effective, responsible for feeding about a third of the world's population and for supplying up to 80% of the nitrogen atoms in our bodies.[3] However, because the process uses fossil fuels to make hydrogen and to generate the high temperature and high pressure required, it is responsible for around two percent of global carbon dioxide emissions, and hence is a major contributor to global warming.[4] Hence, efforts to improve the process continue at a large scale.

Much of the research on a substitute to the Haber-Bosch process tries to find a new, more effective catalyst.[5] This work is spurred by the fact that the process is based on a reaction with a negative Gibbs free energy, and hence can potentially run under more modest conditions. This research has been incompletely successful, at least in terms of finding a more active, stable, inexpensive catalyst. This incomplete success is probably because of the high strength of the nitrogen-nitrogen bond. As a result, many have looked for electrochemical syntheses,[6] either by looking at catalysts making hydrogen more efficiently, by depending on a proton selective membrane, or by using non-thermal plasma.[7] None of these efforts have results which allow abandoning the existing process, at least for now.

The sustainable process being developed in our laboratories accepts the existing wustite based doubly promoted iron catalyst but changes the separation of the ammonia produced. It replaces fossil fuels used now with air, water, and wind-generated electricity.[8] Using the electricity, nitrogen is made from air using pressure swing adsorption; and hydrogen is made from water by electrolysis. The nitrogen and hydrogen are combined over the conventional catalyst to make ammonia, which is separated not by condensation, but by absorption.[9, 10] The result aims at faster sustainable ammonia production at lower pressure, lower energy usage, and near zero carbon dioxide emissions.

In this paper, we shift our attention from the general absorbent based low-pressure process to the specific implementation of an absorbent either in a conventional commodity process or newer, more sustainable synthesis. In the following, we discuss two cases of the absorption-based process. The first, which runs at constant pressure, is close to the existing ammonia synthesis, but replaces the condenser with an absorber. The second combines the reactor and the absorber in one unit operation, which sacrifices optimization of each operation to obtain more process integration. From earlier experiments, we know that each of these two cases can work; here, we are trying to estimate the conditions for better operation.

Theory

Unsteady State Processes at Constant Pressure

We begin with the case of constant pressure ammonia synthesis, where ammonia absorption replaces ammonia condensation. This change is shown schematically in Figure 1. The left of the figure illustrates the key parts of the conventional process. A stoichiometric mixture of hydrogen and nitrogen at high pressure and temperature is fed to a catalytic reactor, operating at about 400 °C, where the gases are partially converted to ammonia. These gases are chilled to about -20 °C to condense liquid ammonia, which is removed until the pressure of ammonia is approximately 1.9 bar. The remaining nitrogen, hydrogen, and ammonia vapor are heated back to the reactor temperature and supplemented with more nitrogen and hydrogen to replace that converted. The process runs close to steady state. While there are many important details, like the removal of any argon produced when the nitrogen is made from combustion of natural gas in air, these need not concern us here.

The alternative process, shown on the right of Figure 1, replaces the ammonia condenser with an ammonia absorber. Such an absorber captures the ammonia inside of a solid salt, like $MgCl_2$.[11, 12] Such an absorption can occur at considerably higher temperatures than most adsorptions. Absorption in salts can also be much more selective than adsorption on, for example, activated carbon; and absorption in salts can have a greater high temperature capacity than adsorption in zeolites or MOFs. The absorption-based process can remove the ammonia more completely than condensation does; and because the process can produce ammonia at a similar rate but at lower pressure, it requires a smaller compressor and less energy for operation. However, the absorber will not remove the ammonia completely under all process conditions, a point sometimes glossed over in earlier work.

An absorbent bed implicitly operates in unsteady state, so an absorbent-based process must contain at least two beds. At any given time, one bed will be absorbing ammonia, and the other bed will be regenerated, releasing it. As a result, the kinetics of absorption and desorption will be central to the entire process.[13]

Desorption Kinetics at Constant Pressure We first review the kinetics of desorption of a loaded absorption bed, a key step in ammonia synthesis using conventional catalysts but a separation based on absorption, not condensation. Desorption typically takes place at a temperature around 350 °C, but it could be higher or lower depending on the metal halide salt. In most of the ammonia absorbents studied to date, the ammonia does not follow the normal form of Henry's law, where the concentration in the solid varies roughly linearly with the ammonia pressure, that is, the concentration of the ammonia in the gas phase. Instead, the ammonia reacts with the solid with specific stoichiometry. Hence the equilibrium absorption of ammonia in the solid salts used here is much more like formation of a hydrated salt than the dissolution of carbon dioxide in an amorphous polymer like PDMS.[14]

Due to the time constraints involved with reaching equilibrium in practice, it is expected that the amount of ammonia actually held in the solid is always less than the maximum amount which could be held at thermodynamic equilibrium. Instead, because of the oscillating concentration outside the particle during the cycle of absorption and desorption, the actual amount deep within the particle is defined by the time averaged concentration of ammonia available over many cycles. Of course, at the surface of the solid absorbent, the ammonia concentration varies widely, from a high value in the gas discharged by the reactor to near zero when the absorbent bed is being regenerated. In the case of absorbent regeneration, the concentration outside of the solid is small, much smaller than the other concentrations involved. Near the end of the regeneration, this concentration may approach zero. However, the ammonia concentration far within the solid approaches a steady-state value after many cycles, a value greater than zero, but significantly less than the limit which thermodynamics dictates. Similar situations occur often, for example, in fluid mechanics.[15] Even though the stability of the absorbent over several cycles may potentially be an issue, our previous results indicate that the absorbent is stable.[12,13]

We will often track these concentrations not as the total amount present in the absorbent, but as the concentration which would be locally present in a hypothetical gas which is in equilibrium with the absorbent. These concentrations are shown schematically on the upper part of Figure 2 and described in Table 1. The highest actual concentration of the ammonia-salt complex – the ammine -- which is thermodynamically possible is c_s^+, a constant fixed by stoichiometry of the metal ammine salt at the temperature and pressure of the system. The total concentration of ammonia as ammine actually present far within the solid is c_s. This concentration varies with position and time. The hypothetical gas concentration which would exist in the gas which was in equilibrium with absorbent and complex at c_g^+ . Note that c_g^+ does not vary with position, because it is fixed by the equilibrium at a given temperature between the solid absorbent and the solid absorbent-gas complex, both of which have an activity of 1. The concentration of ammonia outside of the solid in the surrounding gas is c_g. In desorption, ammonia is diffusing from a source of complexed ammine through a layer of uncomplexed salt to the surrounding gas – this form of ammonia is shown with a dotted line. It is within the solid but is not a complex with the solid because it is simply providing a means of transport.

Table 1: Summary of ammonia concentrations as depicted in Figure 2 and used in Eqns (1)-(14).

Symbol	Meaning
C_s^+	Equilibrium concentration in the salt, as can be described as either 0 or a stoichiometric ratio of ammonia to salt
C_s	Actual concentration of ammonia in the salt, as can be described as the fraction of salt ammoniated
C_g^+	Equilibrium concentration of ammonia in the gas for a salt at a given temperature
C_g	Actual concentration of ammonia in the gas
C^*	Equilibrium concentration of ammonia during reaction
C	Concentration of ammonia leaving the reactor

The detailed concentration profiles within the solid depend on the rate controlling step of the desorption. Under many of the conditions studied to date, this step appears to be diffusion in the solid, from a core at c_g^+ to the surface at c_g, and across a layer of solid which contains a concentration of ammonia less than that required for reaction but greater than zero. The thickness of this layer ℓ is zero at the beginning of absorbent regeneration, and it grows with time. As a first approximation, the flux j across this layer is assumed to be approximately the steady state value:[16,17]

$$j = \frac{D}{\ell}\left(c_g - c_g^+\right) \tag{1}$$

in which D is the diffusion coefficient of ammonia in the solid. By combining this flux with a mass balance of ammonia in the solid, we find that the flux out of the absorbent at time t is given by

$$j_i = \sqrt{\frac{D\left(c_g - c_g^+\right)c_s}{2t}} \tag{2}$$

The rate of desorption in the absorber containing a volume of absorbent V_A is $j_1 a V_A$, in which a is the surface area per volume of absorbent. The total desorbed m_D over the regeneration time t_R is

$$m_D = aV_A\sqrt{D\left(c_g - c_g^+\right)c_s t_R} \tag{3}$$

The prediction that the total amount desorbed is proportional to the square root of time is consistent with the assumption that the desorption is controlled by diffusion. This prediction, observed experimentally, describes the regeneration of absorbent at constant temperature. Further details of the derivation of Eqn (1)-(3) can be found in the literature.[16,17]

Reaction and Absorption at Constant Pressure We turn next to the entire reactor-absorber process shown on the right of Figure 1, where the ammonia produced by the reaction is separated by absorption. The reactor normally operates around 400 °C, and the absorber is loaded at 180 °C. This reaction and loading take place at constant pressure, as high as 100 bar in this study and potentially higher in practice. Normally, the absorber is a packed bed, which can carry out a more complete separation than a condenser. During loading, the bed keeps capturing ammonia until the ammonia concentration of the gas exiting the bed suddenly rises: i.e. it 'breaks through.' The time at which breakthrough occurs has been found to be a reliable, reproducible measure of the capacity of the bed. When the bed is full, it is disconnected from the reactor, and regenerated at around 350 °C. The pressure during regeneration is much less than 100bar but is not as low at atmospheric pressure.

The reaction rate *r(N₂)* in mole N_2 per time for a magnetite-based iron catalyst was described in detail by Nielsen *et al.,* and Sehested *et al.*:[18-20]

$$r(N_2) = \frac{kM_{cat}\left(p_{N_2} - \dfrac{p_{NH_3}^2}{K_{eq}p_{H_2}^3}\right)}{\left(1 + \dfrac{p_{NH_3}}{K_a p_{H_2}^{\frac{3}{2}}} + \dfrac{p_{H_2}^{\frac{1}{2}}}{K_b}\right)^2} \tag{4}$$

in which k is a reaction rate constant per gram pf catalyst, p_i is the vapor pressure of species "*i*", K_{eq} is the equilibrium constant of the ammonia reaction, and K_a and K_b are constants associated with adsorption and dissociation on the catalyst surface. It should be noted that wustite- based iron catalyst has largely replaced magnetite-based iron catalyst, but the lack of a rate equation for wustite iron necessitates the use of the rate equation for magnetite. By expanding the Sehested et al. equation as a Taylor series at small ammonia concentrations, we find the reaction rate for making ammonia in mole NH_3 per time r:

$$r = k_{cat}M_{cat}(c^* - c) \tag{5}$$

in which c^* is the ammonia concentration at equilibrium, c is the ammonia concentration leaving the reactor, and M_{cat} is the mass of catalyst. The reaction rate constant k_{cat} can be estimated from the more complete expression:

$$k_{cat} = \frac{2kc^*}{RTK_{eg}c_{H2}^3} \tag{6}$$

The use of this pseudo-first order rate constant, which is evaluated at the average conditions in the reaction, is a significant approximation, but considers at least qualitatively the combined effects of reaction and absorption.

The gases leaving the reactor at ammonia concentration c next enter the absorber. The maximum concentration thermodynamically possible in the absorbent is still c_s^+, but because this is now at the low temperature for absorption, it is much greater than that at the high temperature at which desorption takes place. The concentration of ammonia deep within the solid is again c_s, which is less than the equilibrium value c_s^+. The concentration of ammonia in the solid where absorption is occurring, again expressed as a hypothetical gas concentration in equilibrium with the partially saturated solid, is the virtual concentration c_g^+; and the gas concentration at the interface between gas and solid is c_g, now larger than c_g^+. Since we always operate the packed bed absorber before breakthrough, the ammonia concentration exiting the absorber is near c_g^+. The relative values of these concentrations are shown on the lower part of Figure 2, a contrast with the concentrations for desorption on the upper part of this figure. In desorption, the concentration in solution c_g was less than that far within the solid; in absorption, c_g is greater than that deep within the solid. In absorption, ammonia is quickly diffusing into the solid across a layer of ammine, that is, salt reacted with ammonia, to react at the interface located at ℓ.

As before, the flux of ammonia into the absorbent is approximated by a pseudo-steady state analysis of the region near the boundary between the gas and the solid. Experimentally and surprisingly, the rate limiting step is now not diffusion within the solid, but the absorption-reaction between ammonia and the solid.[13] While a detailed mechanism for absorption is not known, kinetic experiments conducted previously[13] allow the fitting of an analytical equation:

$$r_{abs} = k_{a1} e^{k_{a2}(P_{NH3} - P_{NH}^{+}\ )}\ when\ (P_{NH3} - P_{NH3}^{+}) < 1\ bar$$

$$r_{abs} = k_{a3}(P_{NH3} - P_{NH3}^{+})^2\ \ when\ (P_{NH3} - P_{NH}^{+}\ ) > 1\ bar \tag{7}$$

where r_{abs} is the rate in micromoles per second per gram absorbent, $k_{a1\text{-}a3}$ are experimentally determined constants, P_{NH3} is the pressure of ammonia in kPa, and P_{NH3}^+ is the equilibrium pressure of ammonia at a given temperature in kPa. The experimental results which form the basis for these equations are shown in the supplemental information. The exponential form of the equation at pressures close to equilibrium suggests the possibility of a nucleation reaction similar to recrystallization under super saturation, but this is very uncertain. At pressures far from equilibrium, the trend in rate appears to shift, perhaps because the highly exothermic nature of absorption causes the process to be heat transfer controlled. It is important to note that this equation implicitly assumes a given surface area per volume for the absorbent; and the magnitude and/or structure of the equation could be significantly different if the surface area is increased. In a similar way to the reaction equation, the absorption equation can be linearized for illustrative purposes, and because the process is in steady state, the rate of absorption is the same as the rate of reaction r:

$$r = k_{abs} a V_{abs}(c - c_g^{+}) \tag{8}$$

where k_{abs} is an absorption rate constant, V_{abs} is the volume of absorbent, and a is its area per volume.

Finally, we must include the effect of the recycle, which alters the concentrations entering and leaving the reactor. As shown in Figure 1, the recycle takes unreacted nitrogen and hydrogen and a small amount of ammonia, adds nitrogen and hydrogen at a rate $2r$ to replace those consumed by the reaction, and sends this combined stream back into the reactor. If the volumetric flow in the recycle stream is m and the ammonia concentration in the recycle stream is c_g^+, then the ammonia concentration entering the reactor is $(c_g^+m)/(mc+2r)$; that exiting the reactor is

$$c = \frac{(c_g^+ m + r)}{cm + r} \tag{9}$$

where r is again the overall rate of ammonia production, that is, the moles of ammonia made per time. Equations 5, 8, and 9 can now be combined to eliminate the unknown intermediate concentration c and find r:

$$r = \frac{\beta}{2}\left(\sqrt{1 + \frac{4\gamma}{\beta^2}} - 1\right) \tag{10}$$

where

$$\beta = mk_{cat}M_{cat}\left(\frac{1}{k_{cat}M_{cat}} + \frac{1}{k_{abs}V_{abs}} + \frac{1 - c_g^+/c}{m}\right) \tag{11}$$

and

$$\gamma = mk_{cat}M_{cat}(c^* - c_g^+) \tag{12}$$

It is useful to consider two limits which can clarify the physical significance of the result. First, when $\gamma/\beta^2 << 1$, the ammonia synthesis rate r is:

$$r = \frac{\gamma}{\beta} = \frac{c^* - c_g^+}{\frac{1}{k_{cat}M_{cat}} + \frac{1}{k_{abs}M_{abs}} + \frac{1 - c_g^+/c}{m}} \tag{13}$$

The numerator of this reassuringly familiar result is the driving force of the process $(c^*-c_g^+)$, and the denominator is the sum of the resistances due to the reactor, the absorber, and the recycle, respectively.[8, 16, 17] In the second limit of infinite recycle where the reaction is controlling, $\gamma/\beta^2 >> 1$ and:

$$r = \gamma^{\frac{1}{2}} = \sqrt{mk_{cat}M_{cat}(c^* - c_g^+)} \tag{14}$$

These results are the key to most of this paper. Before discussing them in detail, we turn to the possibility of combining reaction and absorption in one vessel, operated not at varying temperature and constant pressure, but at constant temperature and varying pressure.

Unsteady State Process at Constant Temperature We now switch from the pseudo-steady state process shown in Figure 1 to the definitely unsteady process shown schematically in Figure 3. Like the process on the right-hand side of Figure 1, the new process in Figure 3 uses absorption, not condensation, to separate the ammonia which has been synthesized. Unlike the more standard processes in Figure 1, that in Figure 3 has the reaction and the absorption at one temperature in the same piece of process equipment.

The configuration combining reaction and separation in the same vessel is unusual. While this configuration is often discussed as a route to process intensification,[21] it is often dismissed because it prohibits separately optimizing process conditions for the reaction and for the separation. In particular, for the pseudo-steady state processes discussed above, the reaction runs best hot, and the separation by absorption is better cold. Instead, in Figure 3, the reactor and the absorber operate at the nearly same temperature. To be sure, releasing the pressure for regeneration does cause a temperature drop in the gas phase, but the thermal inertia of the solid catalyst and absorbent is much greater than the thermal inertia of the gas, so the temperature of the solid is about constant.

The combined process does not run at anything like steady state, but has the two steps shown in the figure. In the first, high pressure step, the reaction makes ammonia, which is absorbed once the pressure of ammonia is above the absorption equilibrium pressure. In the second, low pressure step, the absorbent desorbs the ammonia, which is removed from the process before it can undergo the reverse, catalysed reaction. This reverse reaction is inhibited because the rate-controlling steps for absorption and desorption are different. During absorption, chemical synthesis is faster than absorption, which is limited by the reaction of ammonia at the interface within the absorbent where the complex is being formed. Thus the ammonia pressure between particles of catalyst and absorbent may be high, at least as high as several bar. During desorption, the rate is controlled by diffusion of ammonia from the internal interface between the ammonia complex and the uncomplexed salt to the surrounding solution. Because diffusion across this uncomplexed region is slow, the pressure of ammonia between particles is low, ideally below atmospheric, and the reverse reaction is still slower. Thus the kinetics of absorption and desorption conspire to aid ammonia synthesis. More details of this process are given in the following paragraphs.

We first return to the different ammonia concentrations in Figure 2 detailed in the discussion above, and specifically to those that would exist during desorption shown on the right-hand side of Figure 3. The virtual concentration of ammonia deep within the solid is c_g^+, a hypothetical concentration in equilibrium with the ammonia complexes within the solid. This time-averaged concentration c_s, less than the saturated value c_s^+ dictated by thermodynamics, is constant from deep within the solid to the edge of the complex-containing zone, near the surface of the solid. From this edge, the concentration of ammonia drops from c_g^+ to the low value c_g in the gas at the solid-gas interface. During the part of desorption when the ammonia is being harvested, the concentration c_g is much lower than that in the gas when the ammonia is being synthesized. Hence during desorption, the reverse reaction converting ammonia back into nitrogen and hydrogen is small. The mass desorbed in this step is that given in Equation 3.

With regard to the reaction plus absorption step shown on the left-hand side of Figure 3, this process is described by the same reaction plus absorption process detailed earlier in this paper. However, there is the major simplification that the reactor and absorber are at the same temperature. Equation 8 still applies, but with this simplification.

Now we must face a similar question to that we had to face for the more conventional constant pressure process: how do we choose the temperature and pressure at which we plan to operate? While an exact answer must again consider the total cost, including capital and operating expenses, we can illustrate the compromises involved by considering the relative magnitude of the times and resistances of the various steps. How this estimation proceeds is shown in the following paragraphs both for the process at the right of Figure 1 and for the process in Figure 3.

Methods

To analyse the implementation of an ammonia absorption process with the synthesis reaction, the thermodynamics of each first need to be established. The basic reaction and the reaction equilibrium for ammonia synthesis are described as:[2]

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \Leftrightarrow NH_3 \tag{15}$$

$$c^* = c_{NH_3} = K_{rxn} c_{N_2}^{\frac{1}{2}} c_{H_2}^{\frac{3}{2}} \tag{16}$$

Because the reaction is exothermic, the equilibrium constant K_{rxn} for the reaction drops with increasing temperature. The reactions and equilibria for the absorption are similar;[22-25] for example, ammonia reacts with magnesium chloride in three steps,

$$\begin{gathered} NH_3 + MgCl_2 \Leftrightarrow MgCl_2 \cdot NH_3 \\ NH_3 + MgCl_2 \cdot NH_3 \Leftrightarrow MgCl_2 \cdot (NH_3)_2 \\ 4NH_3 + MgCl_2 \cdot (NH_3)_2 \Leftrightarrow MgCl_2 \cdot (NH_3)_6 \end{gathered} \tag{17}$$

Because both the salt and the ammine are solids and hence have unit activity,[14] the equilibrium between ammonia gas at concentration for c_g^+, for example, the complex $MgCl_2 \cdot NH_3$ is:

$$c_g^+ = \frac{1}{K_{complex}(0 \rightarrow 1)} \tag{18}$$

where $K_{complex}$ is an equilibrium constant for this reaction, which has a specific, pressure-independent value for each temperature. This means that an isotherm for absorption for this type of material is not anything like the familiar Langmuir form. Instead, the isotherm is just the value of $K_{complex}$, a constant at a given temperature until a new stoichiometry is reached, when it jumps to a new value. An isotherm for this type of absorbent can look like a step; for different stoichiometries, it can look like a staircase.

Finding the optimal conditions for either the process in Figure 1 or Figure 3 requires consideration of economic and operational factors which are beyond the scope of this paper. Rather, we have used equations (4) and (7) to look at the effect of temperature, pressure, unit size, and recycle rate on ammonia synthesis. In utilizing these equations, the reaction rate parameters are from the literature[19] and the absorption rate parameters are from experiments,[13] as detailed in Table 2.

Table 2: Parameters used in equations (4) and (7). The temperature dependences of the rate constants for reaction were acquired from literature and the rate constants for absorption were experimental fits shown in the supplemental information.

Rate Constants for Reaction	Rate Constants for Absorption
$k = 7.79E^3 \exp\left(\frac{-6.6}{8.314E^{-3} * T(K)}\right) \frac{\mu mol}{sec * g * bar}$	$k_{a1} = 1.6E^{-4} \frac{\mu mol}{sec * g}$
$K_A = 2.7E^{-2} \exp\left(\frac{-27.1}{8.314E^{-3} * T(K)}\right) bar^{-1/2}$	$k_{a2} = 9.0E^{-2}\ kPa^{-1}$
$K_B = 2.16E^{-3} \exp\left(\frac{-48}{8.314E^{-3} * T(K)}\right) bar^{1/2}$	$k_{a3} = 3.8E^{-6} \frac{\mu mol}{sec * g * kPa^2}$

$$K_{eq} = 2.03E^{-12} \exp\left(\frac{101.6}{8.314E^{-3} * T(K)}\right) bar^{-2}$$

The linearized forms of the reaction and absorption equations were not utilized to improve accuracy. Any linearized equation will only be satisfactory in a limited range, and the goal of this work is to examine the effect of changing operating conditions over a large range. Nevertheless, the linearized forms create a crucial conceptual framework for examining the system and explaining the results of the full equations, as will be discussed later. The analysis of a system that combines reaction and absorption must start with the rates of reaction and absorption being equal to create a pseudo-steady state. While there are additional degrees of freedom with the mass of absorbent and mass of catalyst, in many cases we found an equal mass basis assumption to be useful in analysing the fundamental relationship between catalyst and absorbent. This is true either when there are different ammonia concentrations and temperatures in the absorbent and catalyst beds, such as in the case of the process in Figure 1, or when the absorbent and catalyst are under homogeneous conditions, such as in the case of the process in Figure 3. In the first case, a computer code is necessary to discretize both the reactor and absorber to calculate the transient ammonia concentration down each bed. The pseudo-steady state is found by repeating the calculation for the reactor and absorber sequentially until the concentration at any point in the cycle no longer changes. In the second case, the method is simply to find the ammonia concentration at which the two rates are equal. While this could be done analytically, we choose to solve these equations numerically through a code which will scan through ammonia concentrations until the two equations are equal within a small margin. The details of this code can be found in the supplemental information.

The assumptions made in this analysis are 1) the ratio of N_2: H_2 is stoichiometric, 2) there is no pressure drop across the absorber, 3) there are no temperature gradients in the reactor or absorber, 4) the mass of absorbent is equal to the mass of catalyst unless otherwise noted, and 5) the absorbent bed has such a large capacity that is never reaches saturation. While each of these assumptions is significant, the last is the most major because discounts breakthrough of the absorbent bed. As a result, a situation could arise in which the size of the absorbent bed for a given simulation is too small to be effective because it would need to be cycled very rapidly. However, this assumption allows examination of how the absorbent and catalyst interact at a fundamental level under different conditions.

Results/Discussion

This paper explores the use of selective absorption as a means of separating the ammonia produced by a Haber-Bosch synthesis catalyst. For a given amount of catalyst, we want to compare the ammonia made using absorption with that made by condensation of ammonia liquid. The amount of ammonia made can be greater with separation by absorption than with separation by condensation, even when the operating pressure is lower than that used conventionally.

This exploration begins with a comparison of reaction and separation equilibria expressed as ammonia pressure vs. operating temperature. These equilibria must be supplemented with measured kinetics, because measured concentrations are often well short of those predicted from thermodynamics. We then compare ammonia production at 400 °C using different pressures, absorber temperatures, and recycle ratios. Finally, we identify promising conditions for absorption at high recycle ratios. The results are obtained using the parameters in Table 2, as detailed in the supplementary material.

The way in which the ammonia pressure changes with temperature as the result of these equilibria is shown in Figure 4. The lines of negative slope at the right of the figure are the results of the chemical reaction equilibria at the pressures indicated in the legend. The equilibrium pressure drops as the temperature increases. For example, at temperature of 400 °C and a total pressure of 10 bar, the ammonia concentration expressed as a partial pressure is only about 0.3 bar; at 400 °C and 100 bar total, it is about 20 bar. At the same time, the pressure for condensing liquid ammonia at -20 °C is about 1.9 bar, shown as the horizontal line. (Note this is shown as a reference, and is not a plot vs. temperature on the *x*-axis.) Thus a process with the reaction at 400 °C and 10 bar would not permit separation of any ammonia by condensation, but a process making ammonia at 400 °C and 100 bar would.

The dotted lines of positive slope in Figure 4 trace the ammonia pressure at equilibria over the absorbent $MgCl_2$ as a function of temperature; the dashed lines do the same thing for $CaCl_2$. These lines were calculated using separately measured ammonia TPD results[26] and the Van't Hoff equation. For a given peak temperature during an ammonia TPD with complexed salt, the equilibrium constant at that temperature is unity because the TPD is done in atmospheric pressure. From one equilibrium constant and temperature, the equilibrium constant at any other temperature is calculated using the Van't Hoff equation and the enthalpy of reaction. Our previous equilibrium measurements have shown close similarity to these theoretical values, as shown in the supplemental information. The different lines are for different stoichiometries. For example, at 300 °C, the complex $MgCl_2{\cdot}NH_3$ forms at ammonia pressures of only 0.1 bar; the complex $MgCl_2{\cdot}(NH_3)_2$ forms at 1 bar.

These equilibrium curves indicate that absorption, unlike condensation, allows the separation of ammonia when the reactor is at high temperatures and low pressures. Furthermore, these curves indicate the absorber temperature at which it is no longer performing better than a condenser. For example, above about 240°C, calcium chloride will not be able to separate ammonia more completely than condensation. However, these estimates are based on absorption equilibrium, which almost certainly will not quickly occur. Certainly, adsorption onto solid surfaces can be fast, and approach saturation in many practical situations. Absorption into the bulk of crystalline salts is expected to be much slower, even though it also is expected to be more selective than adsorption, and more stable at higher temperatures. These expectations have merit: absorption *is* slower and more selective than adsorption under many conditions.

While the absorption equilibria are only slowly approached, this is not crippling, as shown in Figure 5, which plots the rates of Equations (4) and (7) vs. ammonia pressure for total pressures of 100 bar (solid line) and 20 bar (dotted line), respectively. The rates are in moles of ammonia made per second per gram of catalyst at 400 °C. The rates, beginning around 100 μmoles per gram of catalyst per second, drop as the ammonia pressure rises. This widely studied drop is due to the reverse reaction, which increases as the ammonia pressure rises. For example, the sharp drop in rate near 2 bar NH_3 and 20 bar total is because that ammonia pressure is near the equilibrium limit under these conditions.

The rates of absorption, shown as the rising dashed curve in Figure 5 for $MgCl_2$ at 250 °C and for $CaCl_2$ at 100 °C, are a contrast. (Accidently, at these temperatures, these two salts give absorption rates which are about equal, even though the chemistries are different.) The rate of absorption is near zero at 0.002 bar ammonia pressure, which is the ammonia pressure at equilibrium for these absorbents. This rate gets faster as the ammonia pressure rises, possibly because of some form of nucleation in the ammine. It eventually slows at high ammonia pressure, probably as heat transfer away from the absorption site becomes the limiting factor. This trend of an exponential increase in rate followed by a slower increase is shown in the experiment data provided in the supplemental material. Importantly, at ammonia pressures around 1 bar, the rates of chemical reaction and of absorption are the same order of magnitude, so that neither rate would dominate an overall process. However, if the absorption is operated hotter, this region of appreciable absorption rate rapidly shifts to higher ammonia pressures. This can be overcome in several ways. For example, making the absorber much larger relative to the reactor with shift the rate curve up. As a second example, supporting the absorbent on an inert like a zeolite may increase the rate of absorption because it increases the surface area of the absorbent.

Condensation or Absorption We next compare the ammonia production rates for processes using absorption with those based on condensation in a heterogeneous system like that shown in Figure 1, using the computer simulation described above. To do so, we assume as a base case a reactor operating at 400 ^{0}C and of a size comparable to the pilot plant in Morris, MN (~15L).[8] After reaction, we assume that the ammonia is removed by condensation at -20 °C, which implies a pressure of 1.9 bar ammonia recycled to the reactor. This process of reaction and condensation involves a recycle and a fresh feed to replace the ammonia removed. Lastly, since conventional ammonia synthesis is typically operated near equilibrium in the reactor outlet, we adjusted the recycle ratio until the outlet of the reactor was within 5% of equilibrium. This implies an outlet ammonia pressure of at least 22.5 and 2 bar at 100 and 25 bar total pressure, respectively, which corresponds to a conversion of 18.3% and 9.1%. This specification does not need to exactly mirror the conditions in any particular conventional process because it is only a base case to analyse the effect of the absorbent.

For comparison, we assume a reaction producing ammonia at the same rate, after which the ammonia is removed by absorption at 100°C. The absorber in this base case comparison is sized to be able to remove just as much ammonia as the condenser, as calculated using the kinetics of absorption and discretizing the absorber bed. Such an absorber contains 0.01 g absorbent per g catalyst because in comparing with condensation, the ammonia only needs to be absorbed down to 1.9 bar, and absorption at 100°C occurs very fast with ammonia pressures that high. It is important to emphasize that the breakthrough time of the absorber – which would obviously be too quick to be practically useful - is not considered because the transients of the process are not being analysed. The calculation of relative mass of absorbent per catalyst is not especially meaningful: the catalyst of course does not consist only of active sites, so a more meaningful comparison might be normalized by the number of active sites. In the same way, different samples of an absorbent may behave differently depending on their area per volume, or on the chemistry of any absorbent support. Still, the rate relative to this base case gives one comparison between the two methods of separation.

Some examples of these comparisons are given in Figure 6, as the amount produced vs. the recycle ratio and absorbent mass. All these results are for a reactor at 400 °C and an absorber at 100 °C. The results in Figure 6a, which produce more ammonia, are at a pressure of 100 bar. When the absorbent mass is the base value and the relative recycle ratio is increased fifty times, the ammonia synthesis rate increases slightly. The ammonia synthesis rate can be increased more dramatically if both the absorbent mass and the recycle ratio are increased. Potential increases in ammonia production are investigated further by the results in Figure 6b, for the lower pressure of 25 bar. Now, the standard for comparison is a reactor with 0.005 g absorbent per g catalyst, which gives the same result as one separating ammonia by condensation at this lower total pressure. Even at low recycle, the ammonia production is now more than doubled by increasing the amount of absorbent, as shown by the increased intercepts in the figure. As before, increasing both absorbent amount and recycle ratio increases the ammonia produced, by as much as a factor of six.

Even with only the slower kinetics of bulk magnesium or calcium chloride, we can now use the analysis above to identify conditions of temperature and pressure where absorption seems especially effective. To do this, we can use the idea of resistances in series, where the ammonia synthesis rate is limited by the resistances of the reactor, the absorber, and the recycle. This is the idea made explicit by Equation 13. For example, from Figure 6a, we see that at 100 bar, a reactor at 400 °C, an absorbent mass which is only 0.5% of the catalyst mass (equivalent performance to a condenser), and a recycle ratio of approximately 5, increasing the recycle ratio has little effect on the synthesis rate. This shows that the rate must be largely controlled by the resistances of the absorber and the reactor. If we increase the amount of absorbent 16 times so that it is 8% of the catalyst mass, the synthesis rate increases dramatically, but only if the recycle ratio is also increased significantly from the base case. For example, at a recycle ratio of 150, it is almost ten times larger than that at 0.5% absorbent. In this case, the resistances of absorber and recycle have both been reduced. Similar dependences on the resistances of reactor, absorber, and recycle can be seen at a lower pressure of 25 bar in figure 6b, but with a greater resistance in the absorber.

This shift in resistances at lower pressures can be justified by looking at the equilibrium pressures of ammonia. At 400°C and 100 bar, the equilibrium pressure of ammonia for the reaction is approximately 23 bar and the vapor pressure during condensation is approximately 1.9 bar. Thus the single pass production rate could only be increased by 10% even if the equilibrium pressure in the absorber approached zero. Because the conventional condensation process already removes the vast majority of the ammonia, little advantage is gained from better ammonia removal, as shown in Figure 6a. In contrast, with an equilibrium of 2.1 bar ammonia at 25 bar total, reducing the recycled ammonia pressure below 1.9 bar by increasing the mass of absorbent will substantially increase the production rate, as shown in figure 6b. While it is acknowledged that the same gains in production rate are attainable with an increased recycle for a conventional condensation process, it is significantly easier to increase the recycle rate with an absorbent both because the heating/cooling loads are less and because the condensation process typically has a brief flash after the condensation to release entrained gases.[27] In contrast, while the pressure drop in the absorber may become a problem at very high recycle, we have not found it to be an issue at moderate experimental space velocities.

Reaction and Absorption at High Recycle We can investigate how chemical reaction and absorption interact when the recycle rate is large, so that the ammonia production is affected only by the chemical kinetics and the rates of absorption. We again assume that the reactor is operating at 400 °C, and that the mass of the catalyst and the mass of absorbent are equal. We then use the aforementioned computer code to scan through ammonia pressures in Equations (4) and (7) at a given absorber temperature and overall pressure until the rate of reaction and absorption were equal. Some of the results of this case are shown by the plots of reaction rate vs. absorber temperature in Figure 7. The results for different process pressures for $MgCl_2$ are shown as solid curves, while those for $CaCl_2$ are given as the dashed curves. The results for both salts are qualitatively similar. At low absorber temperatures, the absorption rate is high, and the rate of ammonia synthesis is unaffected by this temperature. At higher absorber temperatures, the absorption slows and the overall synthesis of ammonia also is lower. Similar effects occur at all pressures, though the reductions to overall rates occur at lower temperatures when the process is operating at lower pressure.

Reaction and Absorption at a Single Temperature Finally, we turn to the case of combined reaction and absorption in a single piece of process equipment, as suggested by Figure 3. While we appreciate that in doing this, we sacrifice the chance to optimize reaction and separation independently, we are attracted by the much simpler process. In considering this, we are also checking on the possibility of process integration, currently a popular strategy.

Using the same, experimentally-based expressions used to evaluate more conventional processes shown in the previous figures, the same computer model used previously, and assuming that the mass of absorbent equals the mass of catalyst, we get the results at constant temperature shown in Figure 8. As expected, the reaction rate per gram of catalyst does go through a maximum as the process temperature increases. At temperatures below this maximum, the reaction rate is slow and controls the overall rate. At higher temperatures, the absorption is slow and controls the overall rate. The maxima occur at lower temperatures for $CaCl_2$ than for $MgCl_2$, but the rates of ammonia synthesis are higher for the magnesium salt than for the calcium one. Increasing the relative amount of absorbent will shift the peaks to higher temperatures and increasing the amount of catalyst will shift the peaks to lower temperatures. Nevertheless, equal mass of absorbent and catalyst is a good first approximation because both the absorption and reaction rate are strong functions of temperature compared to a proportional mass dependence. This single pot synthesis remains an interesting possibility, but for the present, we will focus our attention on the process in Figure 1b, where the chance of success seems more immediate.

Conclusions

This paper extends our efforts to evaluate absorption as a means of separating the ammonia produced in a Haber-Bosch synthesis. Earlier experiments suggest that this change may increase the ammonia produced per mass of catalyst used when compared to the conventional process. Some experiments report that the same production rates can be achieved at lower operating pressures. This work begins to provide a roadmap, rather than a complete optimization, for understanding how the production rate should be expected to increase by various amounts under certain conditions based on the fundamental relationships between reaction and absorption/condensation.

Equilibrium ammonia pressures for reaction, absorption, and condensation indicate that absorption is able to separate ammonia at a much lower pressures than condensation, but this is no longer the case if the temperature of the absorbent is increased. This comparison of absorption and condensation becomes more complex when considering the pressure of the reaction, where the suitability of replacing a condenser with an absorber depends on the resistances of the absorber, reactor, and recycle. At higher pressures (100 bar) and a low recycle ratio (5), the resistance of the separator is not limiting the process because nearly all of the ammonia at the reactor equilibrium (23.6 bar) is removed by the condenser (1.9 bar). So increasing the size of the absorber to gigantic proportions will not increase the production rate substantially. However, if the recycle ratio is increased, the absorber is now limiting and increasing the mass can substantially increase the production rate. This is an important adjustment to the previous assumption that replacing a condenser with an absorber in an industrial process will always result in a higher production rate.

At lower pressures (25 bar), the resistance of the separator is more important because the amount recycled (1.9 bar) is significant relative to the amount leaving the reactor (2.1 bar), so increasing the size of the absorber has a substantial effect on the overall production rate. Still, it is not until a larger absorber is combined with a higher recycle ratio that the production rate approaches that of the baseline high pressure process. This does not necessarily mean that the chance of operating a practical process at lower pressure should be dismissed without further thought. To be sure, the rate of reaction will be smaller. However, replacing low temperature liquid ammonia condensation with higher temperature ammonia absorption means that the capital cost of the equipment and for heating and cooling will be smaller. More importantly, the cost of compression, expected to be a major factor in operating expense, will be reduced by using lower pressure. Whether this is enough advantage to make low pressure feasible will not be decided by the science alone, but by the marketplace.

Supporting Information. Included are graphs which shown an equilibrium pressure curve for calcium chloride and half-lives for the rate of absorption in calcium chloride. Also included is an example MATLAB script for the calculation of the reactor – absorber loop.

Acknowledgements

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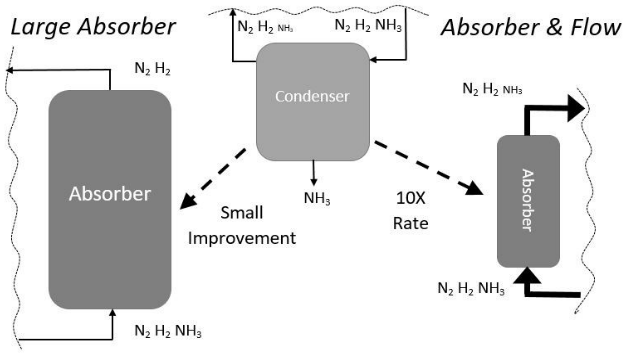

Synopsis

If the condenser in a conventional Haber-Bosch process is replaced with an absorber, the production rate will not be improved – not matter the size of the absorber – if the recycle rate is not increased.

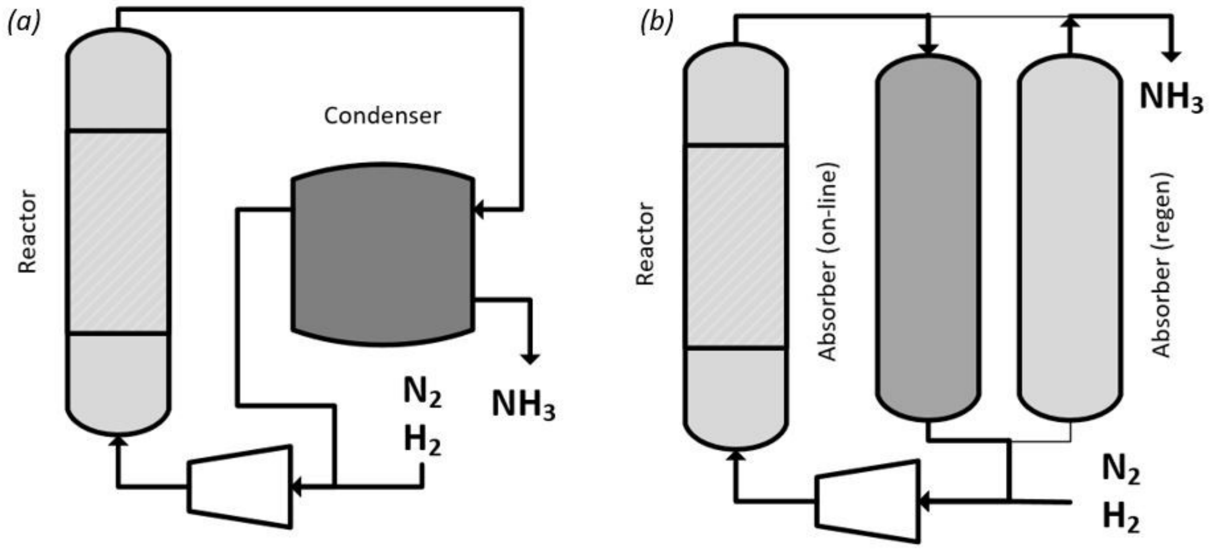

Figure 1. Two Constant Pressure Processes for Synthesizing Ammonia. That in *(a),* the standard Haber-Bosch process, has a reactor and a condenser. That in *(b)* also has a reactor, but replaces the condenser with absorbent beds.

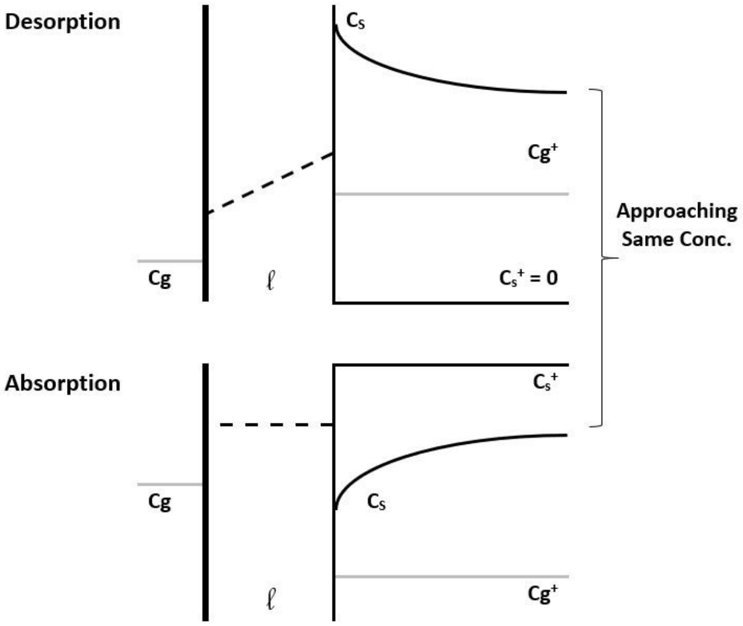

Figure 2. Ammonia Concentrations within the Absorbent. Those at the top occur during desorption; those at the bottom occur during absorption. The concentrations shown are defined as: C_g the concentration in the gas; C_g^+ the concentration in the gas that would be in equilibrium with the solid; C_s the concentration in the solid in complexed form; C_s^+ the thermodynamic limit on ammonia complex concentration in the solid. The dotted lines represent ammonia transporting through the solid in an uncomplexed form to reach either the surface through an uncomplexed shell (desorption) or the core through a complexed shell (absorption).

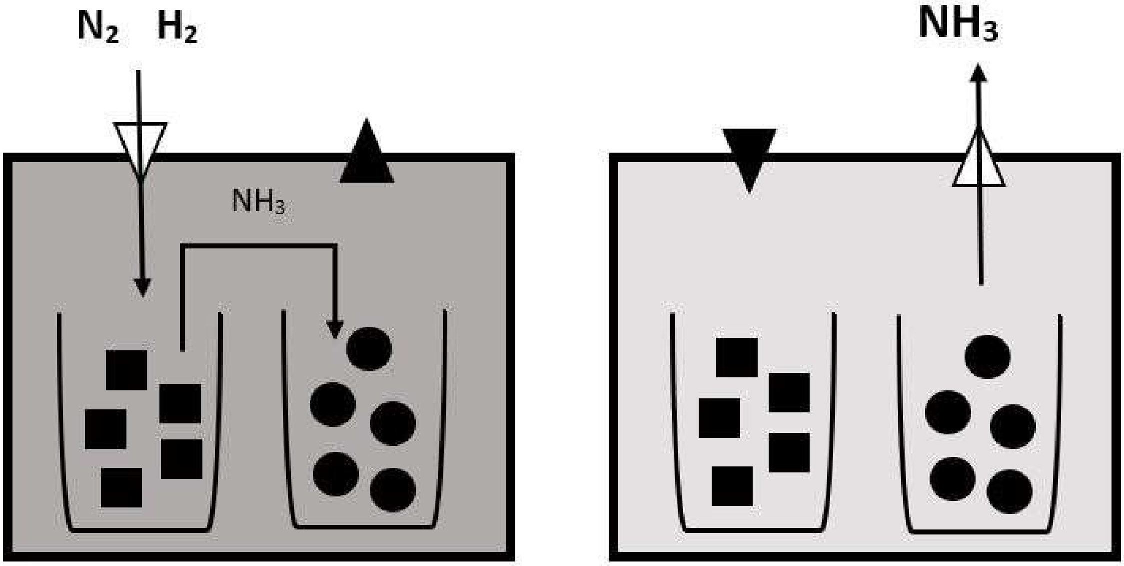

Figure 3. A Constant Temperature Process for Synthesizing Ammonia. In the high-pressure step shown on the left, ammonia synthesized over the catalyst is quickly absorbed by the solid absorbent. After the absorbent is loaded, it is regenerated at low pressure, as shown on the right.

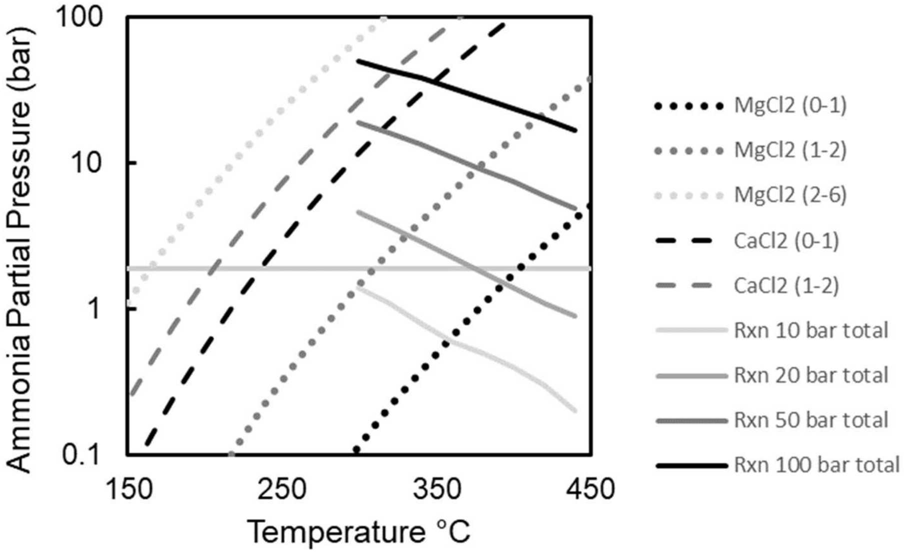

Figure 4. Ammonia Pressure at Equilibrium *vs.* Temperature. The equilibrium pressures of ammonia synthesis reaction, shown as the solid lines, decrease as the temperature rises. The equilibrium pressures of NH_3 over $CaCl_2$ and $MgCl_2$, shown as the dashed and dotted lines, respectively, get bigger as the system gets hotter. The horizontal line depicts the vapour pressure of ammonia at -20C. The bracketed numbers for the salts correspond to the level of ammoniation reaction with the salt – see equation (17).

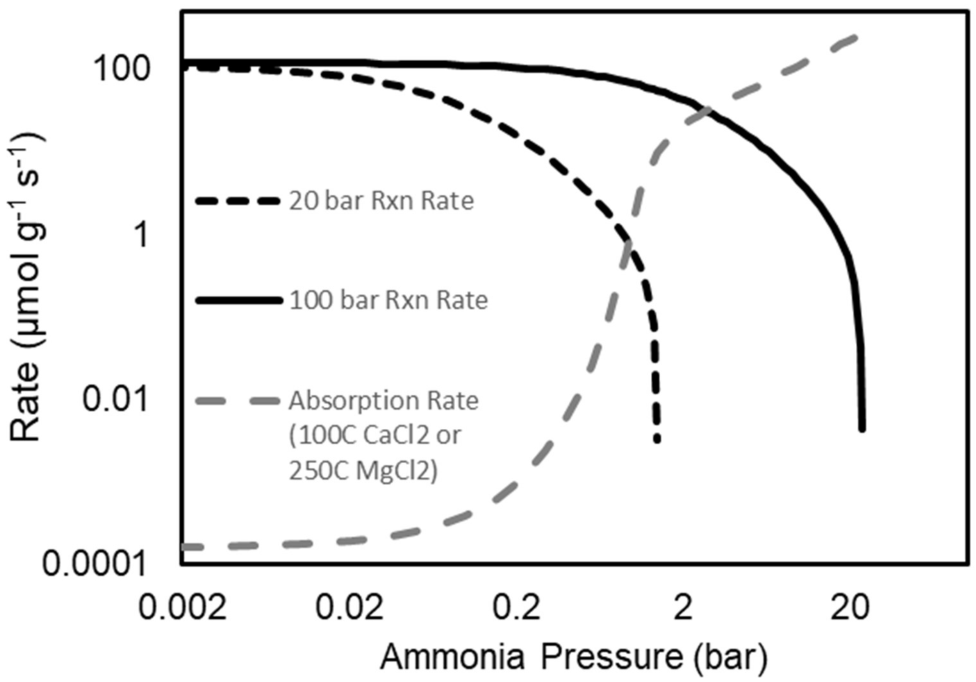

Figure 5. Rates of Reaction or Absorption per gram of Catalyst or Absorbent *vs*. Ammonia Pressure. The chemical reaction rates, as defined by Sehested et. al.[19] and shown at 400°C by the decreasing curves, show that the reaction slows as the ammonia pressure rises. The absorption rates, as defined by experimental fits and shown as the rising curve, are accidentally nearly equal for $MgCl_2$ at 250°C and for $CaCl_2$ at 100°C.

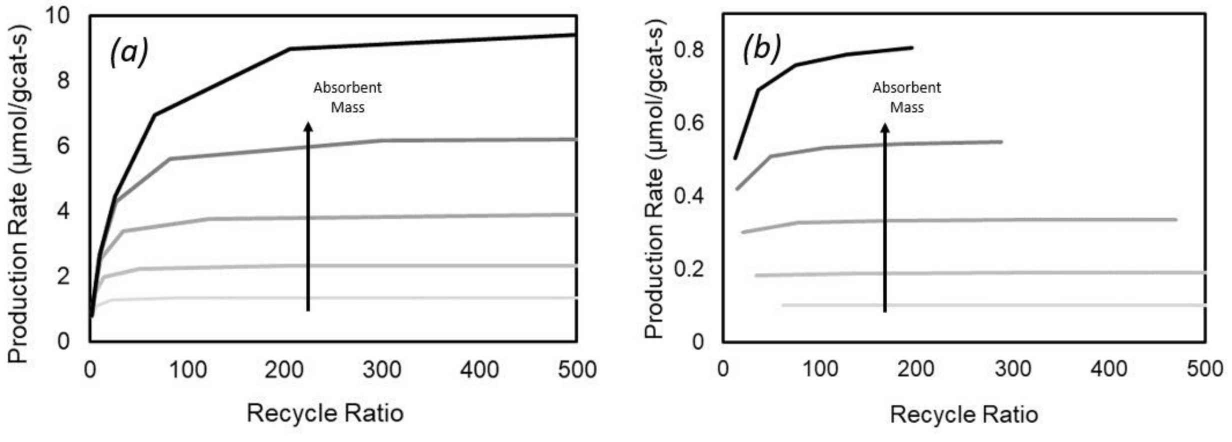

Figure 6. Improving the Reaction Rate with Absorption at (a) 100 bar and (b) 25 bar. The rates shown are for ammonia production by absorption relative to that for condensation at -20C. The base case of a process with condensation is in the bottom left corner of each plot. The reaction is calculated at 400°C using the Sehested et.al. rate equation.[19] Absorption is calculated at 100°C. In (a), reading from bottom to top, the absorbent masses are 0.5, 1, 2, 4, and 8% of the catalyst masses. In (b), they are 1, 2, 4, 8, and 16%.

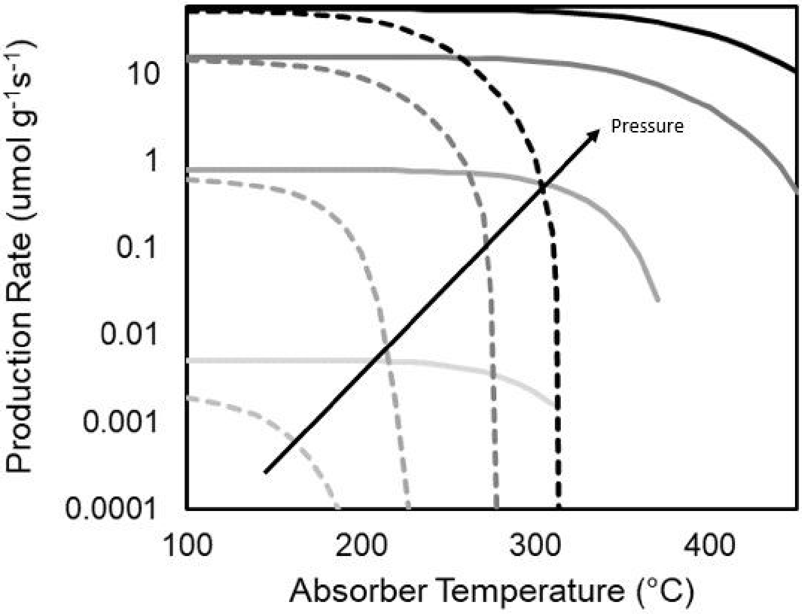

Figure 7. Ammonia Synthesis Rates at Infinite Recycle and Equal Absorbent and Catalyst Mass. The results for $MgCl_2$ and $CaCl_2$ are the solid and dashed lines, respectively. Reading from bottom to top, they are for pressures of 10, 20, 50, and 100 bar. Here, the masses of catalyst and absorber are equal and the reactor temperature is 400°C.

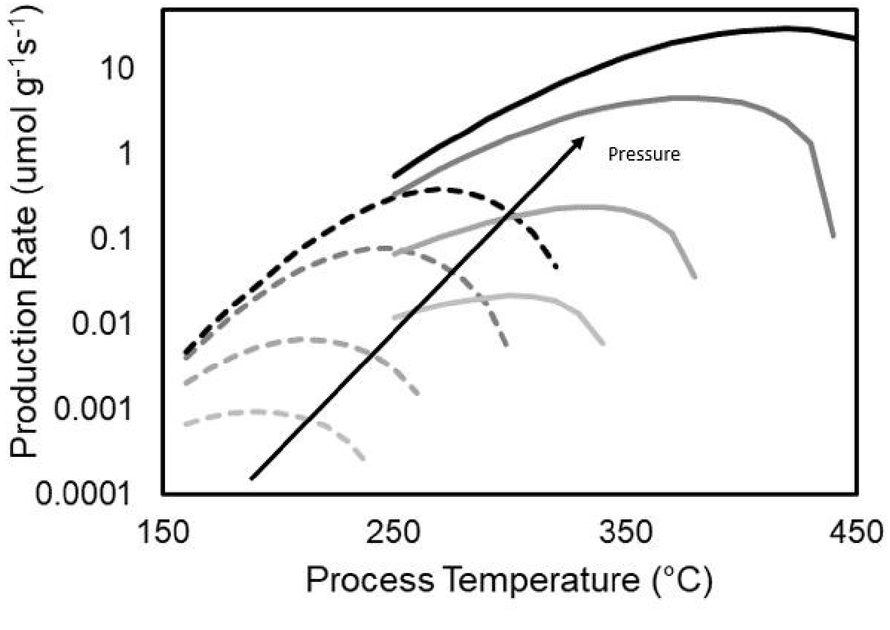

Figure 8. Ammonia Synthesis at Constant Temperature in one Vessel. The solid curves are for $MgCl_2$, and the dashed curves are for $CaCl_2$. Starting from the top, the curves are for total pressures of 100, 50, 20, and 10 bar.