OVERVIEW OF NITROGEN REMOVAL TECHNOLOGIES AND APPLICATION/USE OF ASSOCIATED END PRODUCTS

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SUMMARY

Anaerobic digestion of manure produces a liquid with moderate to high concentrations of ammonia. The concentrations vary with farm practices and strongly with the source of manure. It is shown in this paper that recovery of ammonia by flash distillation (such as the Ammonia Recovery Process) or hot gas stripping will produce financial benefits to farms or organic waste digesters of sufficient size. Emphasis is on dairy farms and model calculations indicate that dairies with at least 2000 cows can profitably recover ammonia fertilizer. Farms accepting organic waste for co-digestion will likely produce additional ammonia and therefore be able to profitably recover ammonia with smaller herds.

Ammonia recovery with ammonia separation effectively reduces potential losses during manure storage and normal field application. These methods produce a nitrogen fertilizer that is stable and can be sold or applied by the farmer when and in quantities beneficial to the crop, without added P which may otherwise not be necessary

Historically, ammonia has been recovered with sulfuric acid to produce ammonium sulfate. It is shown in this paper that both in terms of net revenue and requirements for storage of the product, nitric acid will in most cases be preferable to sulfuric acid as a medium for ammonia capture.

INTRODUCTION

Wastewater streams rich in the nutrients nitrogen (N) and phosphorus (P) are produced by municipal, industrial, and agricultural processes. These are present in various forms: partially bound to solids and not immediately available to the ambient air and water, and also present in water soluble form (phosphate, nitrate, ammonia, organic nitrogen), and in the case of ammonia in a volatile form. All three forms are present in anaerobic digestion (AD) effluent known as digestate. The soluble and volatile forms of these elements are particularly prone to loss pathways and pose a variety of environmental and human health threats.

Both N and P can be transferred to surface waters through runoff and erosion processes, leached into ground water or intercepted by subsurface drainage systems and released directly to surface waters, and N as ammonia can be volatilized and add to air pollution. On the other hand both N and P are essential nutrients for plants and animals, and have been added to increase the productivity of soil for millennia through the direct placement of manure. Preventing fugitive losses through capture and reuse of nutrients can increase overall nutrient use efficiency, partially replace chemical N and P fertilizers and reduce manufactured N and stretch P mineral resources, while also reducing adverse environmental impacts.

Pollution control and recovery of value of these elements from agricultural or other organic waste can be accomplished for both P and N. Work presented in this paper focuses on ammonia-nitrogen recovery from animal manure. While manure is the generic term for urinary and fecal excreta of domestic farm animals, the source of the manure (dairy, swine, poultry and others) and the conditions of both its generation and treatment vary greatly.

METHODS OF AMMONIA CAPTURE FROM MANURE

Potential public concerns and especially the aesthetic impact (odor) of raw manure favor its treatment prior to land application as a crop fertilizer and soil conditioner. Anaerobic digestion greatly reduces these adverse qualities of manure. The combined benefits for manure management and potential revenue generation from energy, fertilizer and other products have promoted the growing use of AD technologies. USEPA/AgStar (2012) states that 176 digesters were operating on animal manure by the end of 2011 (over 80% dairy), and there is an annual increase of 16 digesters/yr. This has created the coupled problem and opportunity of ammonia in the digestate. Several methods for recovery of this ammonia are described in this section.

Much of the ammonia can be captured for reuse by filtration of the digestate if the process includes ultrafiltration and reverse osmosis. This captures both soluble and solids nitrogen, but the product has critical characteristics of raw digestate that decrease its utility relative to chemical fertilizer.

1. Nitrogen is recovered daily and remains relatively unstable, while crop utilization occurs seasonally. This requires either storage or export of the material, both costly due to the space required for these low nitrogen content products.
2. Managing N in its various forms can be challenging, especially in low nutrient density materials encountered in manure related products. Often, N losses to both the air and ground water and transformations make high efficiency recovery by crops in the field difficult, resulting in reduced N effectiveness.
3. Since N:P ratios of these materials are generally fixed, more P may be applied than needed to deliver enough N to high N-utilizing crops like field corn.

In contrast to manure, as well as digestate and digestate solids; chemical fertilizer is available in many forms and ratios, is more concentrated, more easily managed, and in the case of N, is more easily stabilized. These features allow greater latitude for the farmer to apply fertilizer close to the time of highest crop need, and the proportion of nutrients can usually be better balanced to suit the crop and soil. The same advantages exist for methods of ammonia recovery that separate ammonia from the digestate. Ammonia recovery with ammonia separation effectively reduces potential losses during manure storage and normal field application. These methods produce a nitrogen fertilizer that is stable and can be sold or applied by the farmer when and in quantities beneficial to the crop, without added P which may otherwise not be necessary.

The following section surveys four available methods for recovery of ammonia and focuses on the two major techniques for separation of the ammonia from digestate in a form equivalent to chemical fertilizer: air stripping and flash distillation. *Struvite is a slow release P fertilizer than can be crystallized from digestate. Since struvite is an ammonium salt, some ammonia is also recovered with the P. However this is generally no more than 20% of the free ammonia in the digestate and is therefore not considered as an ammonia recovery technology in this paper.*

Costs and Benefits of Ammonia Recovery Methods

Methods of recovery of the fertilizer value of ammonia in digestate vary in efficacy and in costs. The quantitative evaluation of these methods is specific to the manure or food waste treated, site-specific factors and the choice of method of ammonia recovery. Quantitative economics are presented for ammonia recovery from dairy manure in later sections of this paper. . If the NH3-N is recovered as liquid fertilizer, it is shown that a five year payback period could be conservatively estimated for the preferred method of ammonia recovery.

1. Application of digestate as a source of nitrogen fertilizer is the least efficacious of the available methods, since the NH3-N is dilute (@0.1%) and the ammonia is both soluble and volatile so that a fraction is lost in storage and after application to soil depending on placement and timing of applications and ensuing weather conditions.
2. Capture of NH3-N with the post-digestion solids incurs capital and operating costs for separation of water from dissolved as well as suspended solids, but increases both concentration and stability of the NH3-N. The fertilizer content is dilute with concomitant requirements for storage and transport of the material.
3. Stripping of ammonia from digestate produces the advantages of chemical fertilizers in terms of purity, predictability and concentration. The concentrated fertilizer requires least space for storage, and can be exported easily or used on-farm to offset fertilizer purchases. Hot gas stripping requires large power input and large contacting vessels to provide the gas/liquid contact to achieve recovery of the ammonia from the digestate. The gas is stripped of ammonia with an acid scrubber and the ammonia recovered as the ammonium salt of the acid.
4. Flash distillation of the digestate uses pH/temperature control to achieve transfer of ammonia from the digestate to the vapor phase. Heat is required to liberate the ammonia/water mixture. Vapor is condensed and the ammonia captured as described for the hot air stripper.

Each of the above could be selected for a specific application. However, consideration of the criteria of: cost for storage and transport, N-capture efficiency, and both capital and operating cost; the last two technologies will be preferred for applications sufficiently large to produce economic quantities of fertilizer. They will be discussed in detail in this paper.

Both hot gas stripping and flash distillation involve four steps in going from ammonium ion in digestate to a useful liquid fertilizer.

1. Conversion of ammonium ion to dissolved ammonia gas.
2. Movement of ammonia out of the digestate into the vapor phase
3. Capture of the ammonia in a clean liquid phase
4. Concentration of the ammonia to a useful level.

Definition of a useful level of concentration depends on the use of the product. For example, if the ammonia will be stored in a lagoon and applied with irrigation water, the ammonia would be captured in acid solution and no further concentration might be needed. If the ammonium were used as a commercial fertilizer or industrial chemical then the solution after ammonia capture would be concentrated to saturation in order to minimize storage and transportation or field-application costs. In a large-scale application the product might be dried and pelletized for commercial distribution.

Advantages of Nitric Acid for Ammonia Recovery on a Farm

The common method for step 3 is to strip ammonia from the vapor phase with sulfuric acid. Sulfuric acid is readily available and is the least-cost acid. Ammonium sulfate is a commercial fertilizer and for soils that require added sulfur, it would be the preferred N-fertilizer. Ammonium sulfate is also a relatively low-N concentration salt and therefore is less used as N-fertilizer than are various solutions of ammonium nitrate, USDA, ERS, (2011).

Table 1. ERS Sale of N Fertilizers, tons/year

	Ammonia		Ammonium		
Year ending June 30	Anhydrous	Aqua	Nitrate	Sulfate	Nitrogen solutions
2010 :	4,045,433	415,049	719,380	1,310,407	11,460,172

The high N-concentration of ammonium nitrate makes it a higher value product in most areas of the United States. The “ammonium sulfate” and “ammonium nitrate” tabulated by ERS are the solid products, which are economical to produce only in large volumes. The ammonium nitrate is sufficiently high in N that it has substantial value as liquid fertilizer, often blended with urea to form UAN, USDA, National Agricultural Statistics Service (2011).

Table 2. USDA NASS Prices Paid for Fertilizer – United States: March 2011

Fertilizer	$/ton
Ammonium nitrate	479
Anhydrous ammonia	749
Aqua ammonia	249
Nitrogen solutions	
28% N	369
30% N	351
32% N .	403
Sulfate of ammonia .	423

In most cases, ammonium nitrate would be the higher value product of ammonia recovery. As noted above, the preferred product depends both on the final use of the product and the relative value of S and N if the use is as fertilizer. Fertilizer prices vary significantly over time and with region of the United States. Recent prices average about $0.70/#N for N-fertilizer. Where industrial demand for the product exists, the value of the product could be substantially higher.

The decision as to the form in which the ammonia is recovered is independent of whether the method for recovery is stripping or flash distillation. In the comparison of the two methods in the next section, it is assumed that ammonia is captured with sulfuric acid because the published study for hot gas stripping employed sulfuric acid.

The following sections will show that the 5000 cow herd would produce about 1970 dry tons/year of ammonium sulfate if ammonia is captured in sulfuric acid, and about 2400 dry tons/year of ammonium nitrate if nitric acid were used to capture ammonia. If these were stored as saturated solutions this would be 967,000 gallons per year of liquid ammonium sulfate fertilizer per year or 690,000 gallons per year of liquid ammonium nitrate fertilizer. The lower volume of stored liquid fertilizer is another reason to prefer nitric acid over sulfuric acid.

Comparison of stripping and flash distillation

Hot gas stripping of ammonia depends on contact of the gas with digestate. Generally a high ratio of gas to digestate is required to maintain the driving force for ammonia transfer. While this provides an effective recovery of ammonia, it both requires a large vessel to allow the large flow of gas and extended contact time to affect the transfer from the liquid to vapor phase. There is also a large demand for energy to force the hot gas through the liquid in the vessel. Flash distillation accomplishes the same function in a smaller vessel by forcing the liquid to form small drops that rapidly transfer water and ammonia to the head space. In this case energy is required to pump the digestate through a mechanism to provide the small droplets.

In order to estimate the cost of removing ammonia with these two methods, calculations were performed for examples of each. An integrated system for recovery of both N and P has recently been patented by Washington State University, and reported in an AgStAR publication, Frear, et al, 2011. They report cost estimates based on field pilot testing of the system, and include a separation of costs for the nitrogen reduction (NR) portion for both capital and operating expenses. ThermoEnergy Corporation has done extensive pilot testing with their Ammonia Recovery Process (ARP) at commercial scale, and also developed cost estimates not previously reported. The ARP system has been described in conference proceedings, Orentlicher, et al., 2009.

Both systems were analyzed for a typical AD application with dairy manure with 2200 ppm of NH3-N reduced to 400 ppm in the treated digestate, for which excess heat is available. Stripper and flash distillation operation is at 80C without caustic addition. The O&M cost was estimated in both cases at 2% of installed cost. Since neither system has a commercial operation history, this rule of thumb estimate was required. Washington State results were reported on a “cow year” basis, while ARP results were calculated on “#N” recovered basis.

The dominant difference in cost between the two systems is in the electrical energy required by each. The electrical energy for moving the hot gas through the digestate is about 6x that needed to circulate liquid through the flash distillation unit. This causes the operating cost to be higher for gas stripping than for flash distillation, about $0.6/#N for hot gas stripping and about $0.4/#N recovered with ARP. This operating cost is about $2/gallon of manure treated, with no credit for the fertilizer produced. The much larger gas system is estimated to also require a higher capital cost than the flash distillation system at the same capacity of ammonia removal. The capital cost is about $2.50/#N/yr of NH3-N removal, or about $10/gpd of digestate treated.

The preceding cost analysis is for the nitrogen recovery operations only.

- Pre-treatment of digestate may be necessary and would be specific to the manure source and the AD used.
- Storage requirements would depend on whether the product was exported or used on site, and on the product properties: sulfate vs. nitrate, solid vs. saturated liquid.

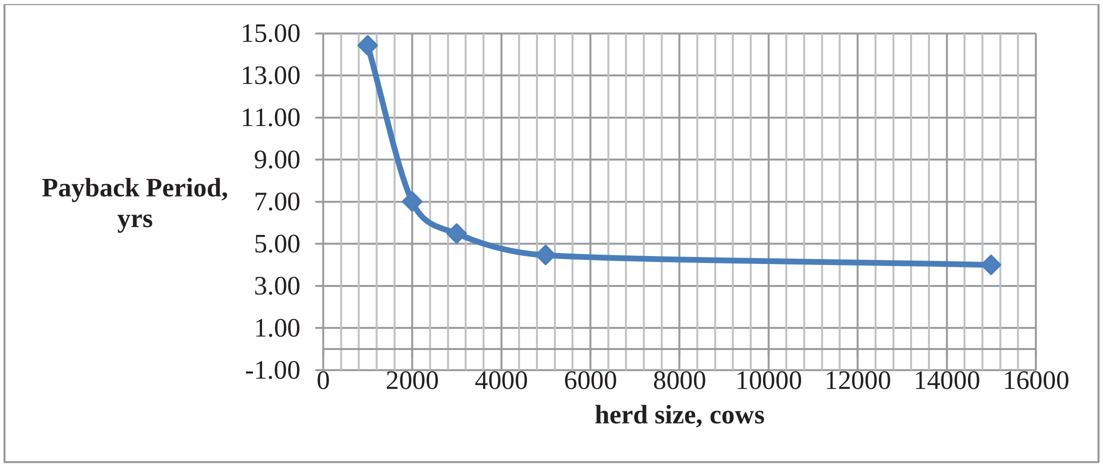
Economics of Ammonia Recovery from Manure and Scale of Operation

When the ammonia reduction is required for compliance with regulations (Nutrient Management Plans, planned EPA air emissions regulations), the operation is viewed as a cost center for the farm. However for *AD operation of a sufficient size and producing sufficient concentration of ammonia; this operation can be a source of revenue for the farm.* These conditions could be achieved due to the number of animals (different criteria for dairy, swine, and poultry) or due to organic waste co-digested with the manure. Pre-treatment and storage costs will be case specific, so this analysis only considers the direct costs of removing ammonia from digestate and producing a concentrated product.

Sulfuric acid is more familiar and lower cost than nitric acid and most ammonia stripping has been done with sulfuric acid. However for fertilizer production, there are distinct advantages when using nitric acid. Since in most cases the nitrate product will be of higher value, the analysis assumes capture with nitric acid. Pricing is as in the previous analysis with two exceptions: product is priced at $0.7/#N, acid is nitric acid at $400/ton.

The conclusion of the economic analysis is that the Ammonia Recovery Process can be a source of revenue for farms treating manure with anaerobic digestion, if they produce sufficient ammonia. For dairy herds, that requires about 2000 cows to achieve a five year payback in the absence of co-digestion. As shown in the following figure, economics are not attractive for smaller herds, and the Payback Period is slightly better than five years for herds of 5000 cows or greater.

Figure 1. Payback Period and herd size, digestion of cow manure



Ammonia recovery as a concentrated liquid product would be beneficial for dairies with less than 2000 cows under two conditions: aggregation of digestate in a community digestion plan, or importation of organic waste in a co-digestion operation. Tipping fees and increased energy production are major financial benefits of co-digestion with organic waste, but there could also be a substantial increase in ammonia recovery and in revenue from the liquid fertilizer produced.

THE AMMONIA RECOVERY PROCESS

The preceding narrative has demonstrated that separation and concentration of ammonia from digestate has the potential for revenue production when associated with digesters of sufficient size. Since commercial operation is not yet achieved for the technologies that produce the equivalent of chemical fertilizer, this demonstration is still speculative. Performance of ammonia separation technology to accomplish production of the fertilizer has been proven. Some detail is provided in this section regarding the Ammonia Recovery Process of ThermoEnergy Corporation and pilot data with dairy digestate.

Process Description of Ammonia Recovery Process

Anaerobic Digestion (AD) is a primary tool for recovery of value from organic waste, whether manure, industrial waste or food waste. If the organic waste requires pre-processing; that will frequently require water addition prior to the AD. The output of the AD will produce a solid and a liquid effluent. The latter can be the source of ammonia suitable for production of commercial grade fertilizer. This is shown schematically below.

Figure 2. Ammonia Recovery following Anaerobic Digestion of Organic Waste

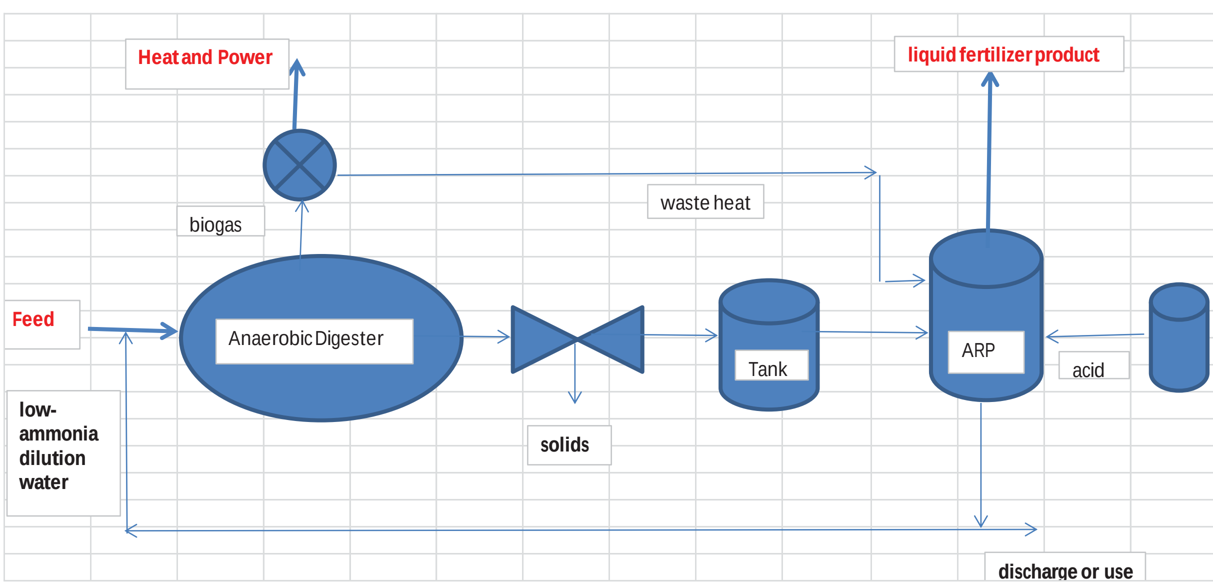


Figure 3. Central Component of Ammonia Recovery Process: RCAST System for Flash Distillation.

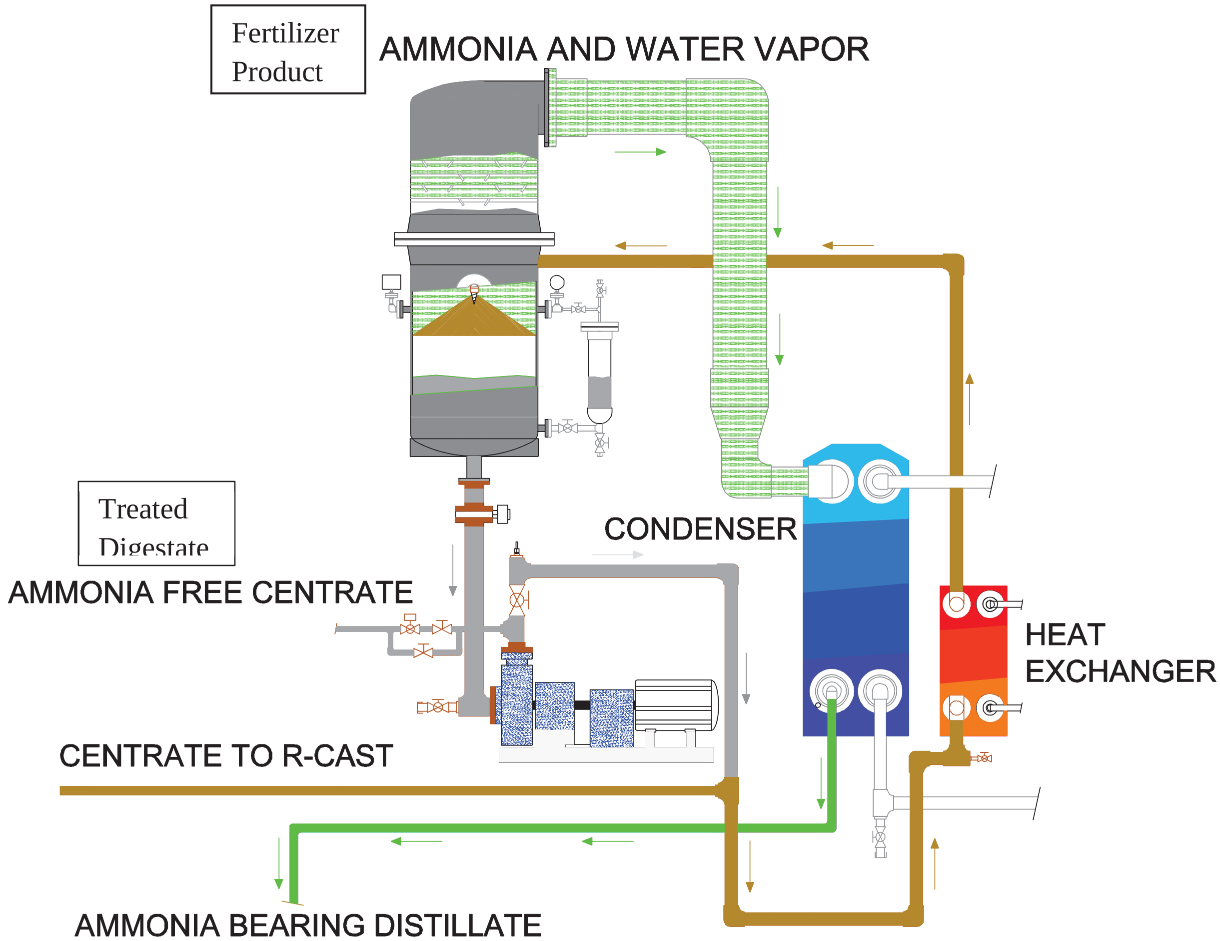


Figure 2 shows the flow of digestate through the AD and ARP to produce the fertilizer product.

- Dairy application of ARP has two products: a low-ammonia liquid that could be discharged to the field or treated for other farm use, and a concentrated nitrogen fertilizer for storage or export for use as needed. Food waste AD requires a low-ammonia source of water that is typically potable water, which would be replaced with the liquid discharge of ARP.
- Waste heat from the combustion of the biogas provides the thermal input required to transfer the ammonia from AD digestate to the vapor phase.

Figure 3 shows some detail of the operation of ARP's system to flash distill ammonia and water from the digestate. Digestate is recirculated through a heat exchanger and sprayed into the RCAST vessel to achieve the first two necessary steps in ammonia recovery.

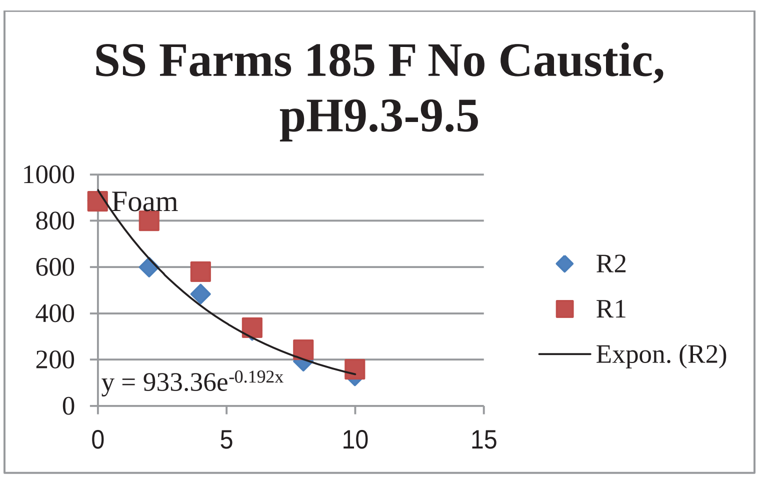
1. Conversion of ammonium ion to dissolved ammonia gas.
2. Movement of ammonia out of the digestate into the vapor phase

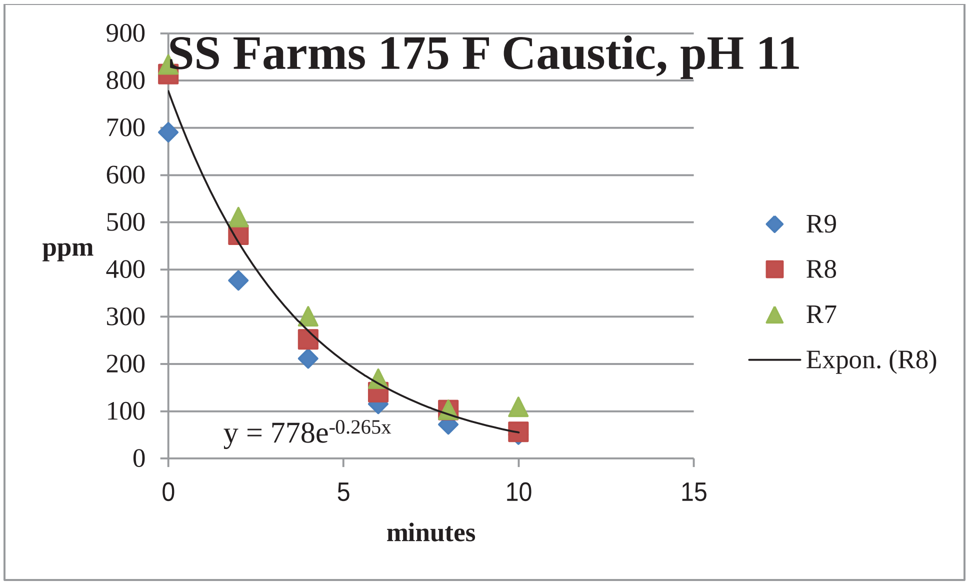
Condensation of the distillate in the condenser achieves the third step and the ammonia-bearing distillate is then concentrated to the desired level, using operations that depend on the form of ammonia desired and the level of concentration desired.

3. Capture of the ammonia in a clean liquid phase
4. Concentration of the ammonia to a useful level.
5.

Success of the ARP depends upon the ability of the RCAST system to remove ammonia from the digestate at a high enough rate to provide the Payback Periods previously shown, This rapid removal was first demonstrated with the municipal digestate known as centrate, Orentlicher, et al, 2009, which was the basis for New York City to contract for the first commercial ARP installation at its 26th Ward wastewater plant. RCAST has been piloted with several dairy digestates, and one series of tests is shown below for a New York State dairy digestate. The dark, opaque liquid was preheated to about 180 F prior to feeding to the vacuum distillation vessel. At a fixed temperature of 175 F, tests in triplicate were conducted for three conditions: no added caustic, 35% of full caustic and full caustic addition.   Results for no-caustic and full caustic addition are shown in Figure 4. Rapid removal of ammonia from the digestate was reproducibly achieved in both cases, but addition of caustic increased the ammonia removal rate. Choice of use of heat alone or heat with caustic will be a farm-specific one, involving a balance of capital and operating costs. The preceding economic analysis was based on no use of caustic.

Figure 4. Ammonia Removal from NYS Dairy Digestate





CONCLUSION

Whether the final product is liquid Ammonium Sulfate or liquid Ammonium Nitrate, the products can be used interchangeably with commercially purchased fertilizer materials. Either material can be used in planters outfitted with liquid application capabilities, and these materials can be mixed with commercial liquid fertilizers (such as 10-34-0 to add P or UAN to increase nutrient density). Ammonium nitrate at 36% N as solid and 25% N as saturated liquid would be equivalent to a 25,0,0 liquid fertilizer. Ammonia recovery from digestate captures significant quantities of N that are normally lost, even under optimal management conditions. A substantial portion of N used in agriculture originates in an ammonia plant that uses significant energy resources, and much of this N is lost to the environment with traditional manure management practices. Therefore, recovery of ammonia from digestate is both an economic value to the farmer and an environmental and energy benefit to society.

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