

Integrated Ammonia Recovery Technology in Conjunction with Dairy Anaerobic Digestion

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Introduction

With approximately 696 million tons of animal manure produced yearly in the United States, and 46% of that being generated on concentrated animal feeding operations (CAFOs) (Ribaudo et al., 2003), animal waste management is becoming an important environmental concern. It causes air and water quality concerns and climate impacts. In addition, many CAFOs generate more waste than can be disposed of without causing localized nutrient buildup. Although anaerobic digestion (AD) has been widely used in animal manure management for methane entrapment, reduction of volatile organics, solids reduction, chemical oxygen demand, vector reduction and pathogen removal, it does not reduce or recover nutrients. In fact, AD can make ammonia emissions even more problematic as it partially converts organic nitrogen to the ammonia form.

Nitrogen recovery, whether from animal manure or from animal-manure AD effluent, poses a few problems. As such, to date, no nitrogen removal/recovery technologies have been applied at a commercial scale on operating CAFOs, with or without AD. In the U.S. Barriers include farm economics and the high solids concentration within manure wastewaters which preclude the use of the technologies commonly used in industrial and municipal wastewater settings. Thus, any existing or new technology developed for farm use must be able to simplify the recovery operation and minimize costs while also economically managing the solids. As discussed in the previous chapter, solids removal is intimately linked with phosphorous recovery. Therefore, nitrogen recovery should be combined with phosphorous recovery, allowing for mitigation of two nutrient concerns in one combined technology. Lastly, from both an economic and sustainability standpoint, final recovered products must have a valued market so that farmers can offset capital and operating expenditures.

Biological ammonia and phosphorous removal technologies exist. However, the high concentration of ammonia, phosphorous, and solids in the animal manure AD effluent make it difficult for biological treatment. Although conventional nitrification and denitrification can be applied to animal wastewater for nitrogen removal without AD (Choi et al., 2005; Tilche et al., 2001; Vanotti, 2005), it cannot work with AD effluent because of insufficient biodegradable carbon. Biological phosphorous removal also needs readily biodegradable carbon (Metcalf and Eddy, 2003), and therefore is not possible. A recently developed process, “anammox” does not need biodegradable carbon for nitrogen removal (Mulder et al., 1995), but anammox bacteria’s slow growth rate (Strous et al., 1999) makes it easily out-competed by other organisms, leading to poor kinetics and performance alongside process instability.

Other researchers (Bolan et al., 2004; Bonmatí and Flotats, 2003; Guo et al., 2008; Liao et al., 1995; Vanotti, 2005) have opted for physical-chemical processes for nitrogen removal, including ion exchange and ammonia stripping. Ion exchange can be excluded for AD applications because it requires low solids concentrations (< 1%) which are unattainable even with effective prior solids/phosphorous removal technology implementation. However, ammonia stripping has some potential, as shown through studies on landfill leachate (Cheung et al., 1997), digester supernatant of a municipal wastewater treatment plant (Katehis et al., 1998), and digester supernatant from slaughterhouse waste (Siegrist et al., 2005). It tolerates a certain level of solids, has low energy requirements and involves relatively simple and low capital cost equipment. Ammonia stripping has already been successfully applied to municipal wastewater AD supernatant landfill leachate, and industrial wastewater at commercial scale (Janus and vanderRoest, 1997; Meyer and Wilderer, 2004; Thorndahl, 1993). It was also successfully tested under laboratory conditions for swine manure wastewater (Bonmatí and Flotats, 2003; Liao et al., 1995) and digested dilute dairy manure supernatant (Zeng et al., 2005; Zeng et al., 2006). In addition, ammonia stripping can be easily integrated with acid absorption to recover ammonia as a nitrogen fertilizer. Although ammonia stripping has proven to be technically feasible for digested dairy manure, its economic feasibility has not been studied, nor has it been studied at scale utilizing concentrated scrape manure.

Although a strong potential candidate for economical recovery of nitrogen from dairy farms, ammonia stripping is not without its concerns. First, effective performance is highly dependent on temperature (US-EPA, 2000); however, the mesophilic (35°C) or thermophilic temperatures (55°C) of AD effluent can be used to overcome this concern. More problematic is the fact that in order to strip ammonia from a wastewater, ammonia in its ionic form must first be liberated as free ammonia. The ionic/free ammonia equilibrium is dependent upon pH with increases in pH (9.5-11) favoring the free ammonia form. Potential drawbacks of the required pH adjustment include chemical input costs and production of a resulting ammonia-removed wastewater that is high in pH and unsuitable for lagoon storage and/or field application. Fortunately, the other product of AD, biogas, contains about 25-50% of CO₂ and smaller amounts of H₂S, both which are unwanted acidic impurities that can be used, via bubble absorption, to neutralize the ammonia stripping effluent to a more desirable storage and application-friendly pH. The absorption of H₂S and CO₂ by the ammonia stripping effluent can also increase the quality of biogas and thereby enhance combined heat and power CHP operation or facilitate in the production of a compressed fuel.

Integration of the aforementioned phosphorous and ammonia removal technologies into a combined nutrient recovery process is depicted in Figure 8.1 (Jiang et al., 2008). Ammonia stripping and absorption can take advantage of the elevated liquid temperature and increased ammonia concentration after AD, as well as the prior solid removal for phosphorus recovery. Although capital, chemical, and energy inputs are required for the integrated process, multiple nutrient-rich products that can be marketed off of the farm have the potential to offset costs. Importantly, the

pH readjustment of the ammonia stripping via the AD biogas can eliminate additional chemical costs that otherwise would be required for pH re-adjustment while also generating operation and maintenance cost offsets due to the enhanced purification of the biogas.

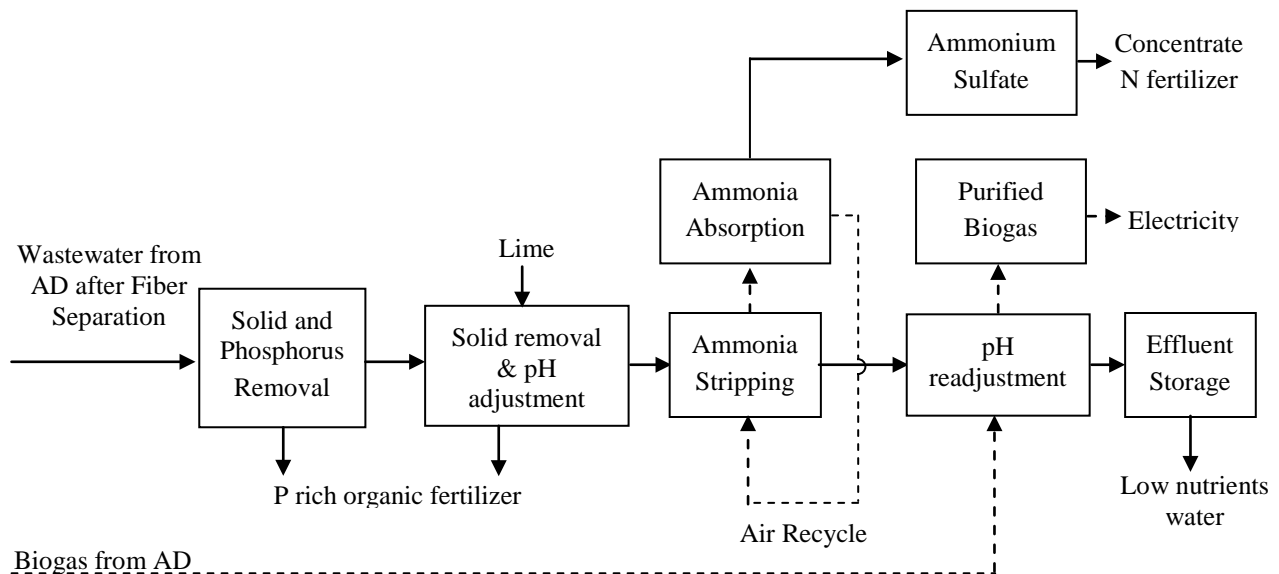


Figure 8.1: Schematic flowchart of suggested process.

Particular objectives of this research project were to study: (1) the ammonia stripping efficiencies of different AD dairy wastewaters; 2) the acid absorption efficiency of the stripped ammonia; 3) the possibility of using the biogas for pH readjustment and the resulting composition change of the biogas; and 4) the techno-economics of the integrated system. Experimentation occurred at both bench and pilot scales, with pilot scale data used for eventual commercial demonstration.

Materials and Methods

Bench-Scale and Pilot Testing

Both flush (wastewater #1) and scrape AD (wastewater #2) dairy wastewater were evaluated in the bench study (Table 8.1). The flush wastewater was taken from the flush manure handling system at the Washington State University (WSU) Dairy Center (Pullman, WA). The flush wastewater was produced by hydraulically flushing alley-scraped fresh manure with lagoon stored wastewater twice a day and then removing solids by using a screen separator with 0.5 cm opening followed by a high solids settling pond. Gravity overflow from the high solids settling pond was used as stored flush wastewater. Sampling for the wastewater occurred at the gravity overflow point. AD effluent resulting from a commercial digester and scrape dairy in Washington State (Lynden, WA) was used as the second wastewater. The

commercial dairy scraped fresh manure to an underground pit three times a day. Manure was then sent to a mixing pit, where it was combined with outside food processing wastes used in co-digestion (16% v/v food substrates). The resulting mixture was fed every two hours to an axial-mixed plug-flow, mesophilic digester (GHD Inc, Chilton, WI). Coarse fibrous solids were separated with a 0.3 cm slope screen (US Farms, Tulare, CA) while the supernatant flowed into a storage lagoon. Sampling occurred at the lagoon entry pipe. The samples of wastewaters used in our experiments were stored at room temperature for at most two weeks before experimentation.

Table 8.1: Characteristics of dairy wastewaters.

Source	TS (mg/L)	VS (mg/L)	TAN (mg/L)	TP (mg/L)	Note
Flush	7530~8054	4723~5109	602~662	7.6~8.52	Wastewater #1
Scrape AD	28545~33400	19065~22800	2271~2729	385~425	Wastewater #2

TS=total solids; VS=volatile solids; TAN=total ammonia nitrogen; TP=total phosphorous

The experimental system consisted of three parts: 1) a lime reaction and settling system; 2) an ammonia stripping system; and 3) a biogas pH readjustment system (Figure 8.2). The lab-scale experimental system was operated within a temperature controlled hot room (35°C).

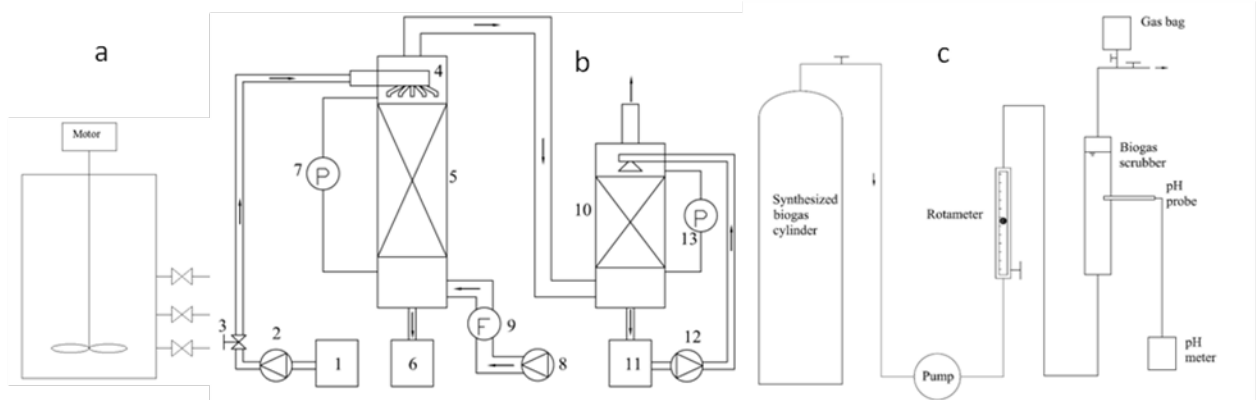


Figure 8.2: The experimental system used to treat test wastewaters, including (a) the lime reaction and settling system (b) schematic flow chart of the ammonia stripping system with parts 1. Supernatant feeding tank; 2. Centrifugal pump; 3. Valve; 4. Nine-tube liquid distributor; 5. Ammonia stripping column; 6. Stripping effluent storage tank; 7. Pressure difference meter; 8. Blower; 9. Rotameter; 10. Ammonia absorption column; 11. Acid tank; 12. Pump; and 13. Pressure difference meter); and (c) biogas purification and pH readjustment.

The lime reaction and settling system with a total volume of 20 L had a mixer and three liquid discharge openings placed at increasing heights (12, 15, and 17.5 L of

supernatant). The stripping and absorbance towers within the ammonia stripping system were packing columns, each with an Internal Diameter (ID) of 0.1 m and packing heights of 1.5 and 0.8 m, respectively. Both towers were packed with 25.4 mm plastic Pall rings with a surface area of $210 \text{ m}^2\text{m}^{-3}$ (Jaeger Products, Houston TX). The ammonia stripping column was equipped with nine tube-distributors with ID of 3 mm for distribution of liquid to the packing material. The absorbing column was equipped with a sprayer for liquid distribution. U-tubes were installed in both towers to measure the air pressure drop. The supernatant feeding tank was continually mixed during the experiment in order to keep the feeding homogeneous. Temperature was measured at the stripping column inlet with a thermocouple. Wastewater was pumped to the ammonia stripping tower by a centrifuge pump and acid solution was pumped to the absorption tower with a peristaltic pump. A blower was used to supply the air and the air flow was measured by a rotameter. The wastewater flow rate was measured by the effluent volume and the operation time. During the experiment period, the air flow rate was fixed at $0.85 \text{ m}^3\text{min}^{-1}$. Wastewater flow rates were tested at various levels from 0.13 to 0.35 L min^{-1} .

Lime powder (CaO: JT Baker Chemical Co., Phillipsburg, NJ) was directly added into the lime reaction and settling tank. The quantity of lime added was determined by titration with 1N NaOH. The settling tank was covered to minimize ammonia loss during pretreatment and pH adjustment. The stirrer was kept on for two hours for lime reaction at which point it was turned off and settling was allowed to occur for four hours. The supernatant (85-93% volume during the experiment) was applied to the ammonia stripping tower after fine pH adjustment by 3N NaOH and 10% H_2SO_4 (w/w). Temperature was adjusted with a Heat-O-Matic Immersion Heater (Cole Parmer, Chicago, IL).

Pilot System Experimental Set-up

A 1.5 gpm pilot facility (Figure 8.3) was established at a dairy in Lynden WA that is currently operating with a commercial mixed plug-flow anaerobic digester. Effluent from the digester was accessed after fibrous solids separation using a slope



screen (US Farm, Tulare CA) with a 0.30 cm pore size. This primary screen effluent was then treated for additional solids and phosphorous removal using a decanting centrifuge (SWECO, Florence, KY). The effluent was then adjusted to a range of higher pH (9.5-11) using lime dosing.

Prior to entry into the ammonia stripping column, immersion heaters were used to re-establish the preferred 30-35°C temperatures that normally would be used in an envisioned commercial application. The immersion heaters were necessary in this pilot study as the various solids testing processes as well as use of slip streams within a working farm protocol caused the time between removal of the digester effluent and its entry into the stripping column to be abnormally long, allowing the effluent temperature to drop considerably. After ammonia stripping, the manure waste stream was sent to an acid chamber to recover the ammonia from the air, producing a solution of ammonia sulfate. The resulting effluent from the entire process, now at elevated pH (10-10.5) was then batch tested for pH adjustment via the biogas scrubbing.

The majority of testing and analysis procedures used within the bench studies were used in the pilot studies. The major technology change being evaluated in the pilot studies was the use of tray towers instead of packing material within the stripping tower. The tray towers were evaluated for their potential to minimize concerns regarding solids accumulation within the tower.

Optimization of Ammonia Stripping Operation

Ammonia stripping performance and optimization experiments at the bench and pilot scales evaluated dairy wastewater ammonia stripping performance while varying conditions including temperature (25°-40°C) and pH (9.5-11.0). Together with the regression of alkali titration results, economically optimized parameters of pH and temperature were obtained. By measuring the solids content of the influent and effluent of the ammonia stripping system, the effect of solids accumulation within the stripping tower was investigated. In the bench-scale experiments, the total ammonia nitrogen (TAN) concentration of the lime settling supernatant for wastewater #1 was adjusted to 1500-2000 mgL⁻¹ through addition of 10% ammonium hydroxide. No ammonium hydroxide was added to wastewater #2. Temperature and pH were adjusted for both wastewaters prior to stripping experimentation. Final pH adjustment was accomplished by using 3N KOH and 10% H₂SO₄ (w/w). Temperature adjustment was accomplished with an immersion heater. Four levels of TAN concentrations for wastewater #1 with three replicates were also studied, to determine the effect of ammonia concentration.

Ammonium Sulfate Recovery

Sulfuric acid was used for ammonia absorption in both the bench and pilot scales. The acid solution was stored in batch tanks and circulated via pump during several weeks of ammonia stripping but tested for ammonia concentration after each run. Known volumes of concentrated sulfuric acid were added to lower the pH to less

than 1.0 whenever the pH of the acid solution rose above 2.0. Data available during runs assisted in determining the maximum ammonia sulfate concentration that could be achieved and this value was compared against the theoretical value as determined by solubility (~40% w/w).

Biogas Purification and pH Readjustment

Synthesized biogas was used for pH readjustment. The synthetic biogas was made to mimic a typical gas composition leaving the commercial digester, namely 62.1% CH₄, 37.7% CO₂, and 2,000 ppm H₂S. The system utilized a peristaltic pump for biogas dosing and a rotameter for flow rate measurement. The biogas flow rate was calibrated with water displacement method with acidic water (pH=0.8). The biogas flowed into the wastewater column using a tube with an inner diameter (ID) of 3 mm. The wastewater column had an ID of 50 mm and height of 400 mm with a working volume of 700 mL. Ten 7-hole-honeycomb packing with outer diameter 17 mm and length of 1 cm were put in the column for biogas bubble splitting in order to enhance the mass transfer.

Economic Analysis

Economic analysis included major chemical and power costs only. Lime, sulfuric acid, and ammonium sulfate prices were obtained from the Chemical Market Reporter (2009). The prices of the lime, sulfuric acid, and ammonium sulfate were \$70, \$87, and \$165/ton respectively. The electricity price was assumed to be \$0.07/kWh (EIA, 2009). Major power consumption arose from the use of blowers and pumps. Economic evaluation the integrated process incorporating primary solids separation and secondary solids separation for phosphorous recovery, as well as the ammonia stripping operation, ammonia sulfate recovery, and effluent pH adjustment.

Results and Discussion

Solids Interception of the Ammonia Stripping System

As noted before, solids content in the wastewater is a concern for the ammonia stripping process, particularly when using packing material as, over time, solids may clog the system, reducing performance in some cases causing failure. The bench-scale stripping tower utilizing packing material was therefore evaluated for its susceptibility to solids accumulation. During continued operation with dilute flush manure (<1% TS), eighteen pairs of ammonia stripping influent and effluent samples were randomly taken so as to determine whether solids were intercepted by the packing material (indicating solids accumulation). The mean TS of the influent and effluent samples were 9149 ± 990 and 8650 ± 579 mgL⁻¹ respectively. Although the paired T-test had a p-value of 0.0594 (just short of the 0.05 desired to give 95% confidence), it appeared that some solids interception was occurring. The relatively large range of values may be due to periodic solids accumulation and sloughing, indicating a dynamic equilibrium as is sometimes seen with trickling filters for wastewater treatment. Thus, application of ammonia stripping to animal

wastewater may need to consider more efficient solids removal or use of a stripping column that can deal with more solids (i.e. larger packing material or trays). Notably, the size of the packing for the experimental unit, 25.4 mm Pall ring, is relatively large compared to the ammonia stripping column which had ID of 100 mm. A larger scale column could use larger packing such as 51 mm or 76 mm Pall rings.

Subsequent testing of a tray tower approach during pilot-study unfortunately led to the conclusion that use of tray towers can still lead to solids accumulation concerns (particularly through the retention of foam and solids along the sides of the trays) while introducing an additional concern of large pressure drops which require increases in blower energy compared to the packing material.

Thus, pilot results indicate that a future commercial design will likely need to utilize packing material or develop an improved tray design to keep energy costs down, but efforts such as use of larger packing rings, increased air/liquid flow ratios, and built-in clean-outs, etc. must also be incorporated to more satisfactorily deal with solids present within the wastewater.

Lime Dosing

As noted earlier, in order to obtain the high fraction of free ammonia necessary for ammonia stripping, pH or temperature needs to be raised. Figure 8.3 summarizes the equilibrium kinetics under various temperature and pH regimes. From the figure it can be seen that pH is a greater determinant in free ammonia than temperature with a minimum pH of 9.5 needed to be on the side of the titration curve favoring significant free ammonia concentration. The necessary pH elevation can be accomplished through the addition of various alkali agents including sodium hydroxide, which is readily soluble in solution, and lime, which is less soluble but lower cost.

A titration curve, developed from the results of experimentation, shows the effect of alkali dosing on pH and potentially indicates an economically advantageous pH that allows for effective free ammonia release with a minimum of required chemical input. Figure 8.4 below is a titration curve based upon lime addition completed at pilot scale. Two curves are represented, one using AD effluent pretreated with primary screening and secondary centrifuge and the other pretreated with primary screening and aeration/gravity settling. From Figure 8.4 it is clear that the mass and cost of lime necessary for appropriate stripping is strongly affected by both the pH target and the pretreatment method. The alkali needed to increase pH to 12 is significantly higher than that needed to achieve a range near 10. This is because of the abundance of HCO_3^- present in the dairy manure, which has a pKa of 10.25 at 25°C. However, the equilibrium kinetics (Figure 8.3) indicate that at 35°C, the critical pH will be about 10.0. Gains in amount of free ammonia are not considerable beyond that point (Katehis et al., 1998), and thus, 10.0 represents the target pH for lime dosing of mesophilic AD effluent.

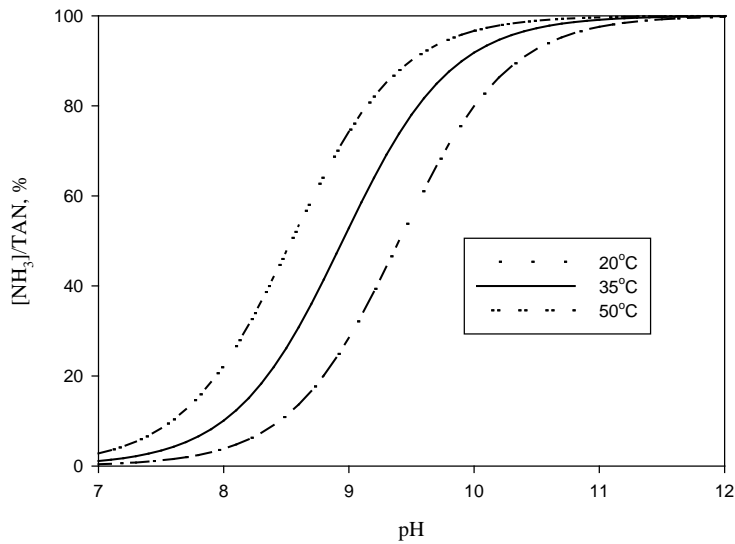


Figure 8.3: Relationship between TAN and pH and temperature.

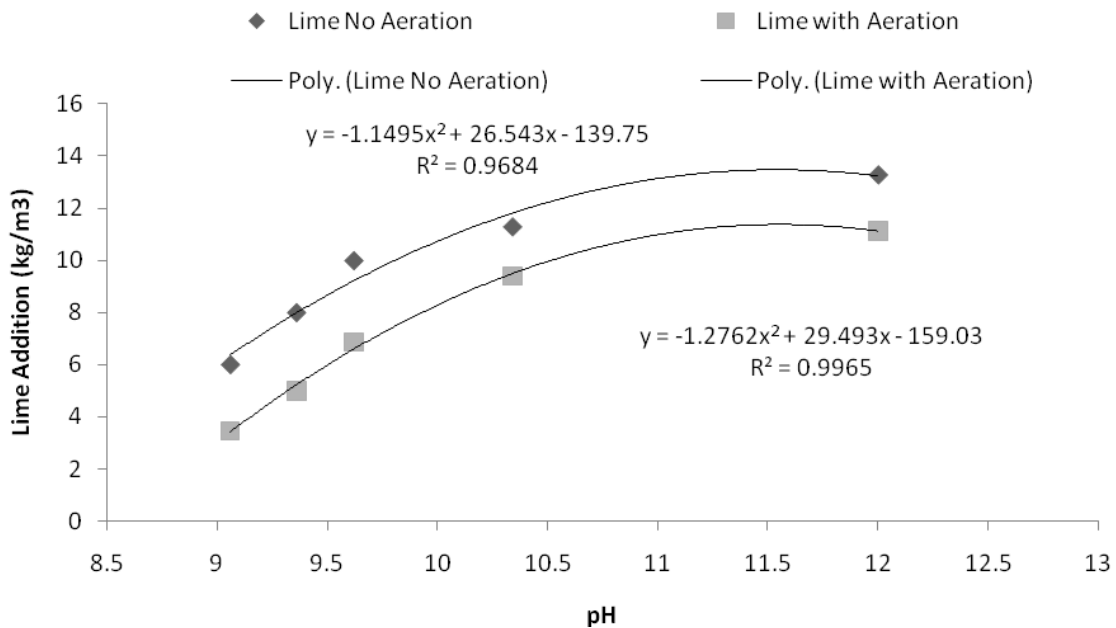


Figure 8.4: Pilot scale results for lime dosing requirement against pH and solids treatment method.

Results also indicated that pretreatment could impact the amount of lime needed. When AD effluent was pretreated with primary and secondary centrifuge solids removal, approximately 6-12 kg lime m⁻³ was required for pH adjustment. When secondary solids and phosphorous removal utilized aeration (1 hour of aeration

with 24 hours of subsequent settling), the pH rose due to carbon dioxide release. The higher pH simultaneously led to improved settling and solids/phosphorous removal and a lower lime requirement ($3.5\text{-}9\text{ kg lime m}^{-3}$) to achieve the desired pH. The lime dosing required after pretreatment with aeration was reduced by nearly 40%. At an assumed price of \$70/ton for delivered lime (ICIS, 2009), this dosing concentration amounts to roughly $30\text{-}90\text{¢ m}^{-3}$ or less than $0.033\text{¢ gallon}^{-1}$ of treated effluent which is a quite low chemical cost when compared to commercial flocculent/polymer solids and phosphorous removal technologies that aim to achieve about a 1¢ per gallon cost for economic viability on large dairy CAFOs. Finally, many dairies already purchase large supplies of lime for addition to their bedding, thus creating a purchasing situation that can intensify bulk sales and further reduce costs.

Ammonia Stripping Performance

The results of ammonia stripping at different TAN concentrations are given in Table 8.2. Statistical analysis showed that there is no significant difference between any of the TAN concentration levels at $\alpha=0.05$ ($p=0.3593$).

Table 8.2: Ammonia stripping efficiency at different TAN concentrations

Replicate	pH	Temperature	TAN in, mg/L	Ammonia removal
1	9.99	34.8	488	47.5%
2	9.99	34.6	480	46.7%
3	10.01	34.5	464	44.8%
1	10.02	33.8	1163	48.2%
2	10.02	34.5	1079	46.2%
3	10.03	34.2	1147	47.3%
1	10.02	34.3	1505	47.5%
2	10.02	34.5	1491	48.4%
3	10.01	34.1	1470	47.9%
1	10.01	34.2	817	46.8%
2	10.01	34.2	836	50.6%
3	10.01	33.9	811	48.3%

This result is confirmed by the Onda correlation (Onda et al., 1968), an ammonia stripping model that does not include pH as a parameter, since pH only affects the free ammonia ratio of the model. Accordingly, ammonia stripping efficiencies can be analyzed without consideration for changes in initial TAN concentration and thus conclusions resulting from bench and pilot-scale testing of this particular manure and farm are quite applicable to numerous farms and projected projects.

Figure 8.5 summarizes the ammonia removal efficiencies experienced during the pilot scale studies across the previously determined optimal pH range. As can be seen from the graph, at an approximate pH of 10.0-10.20, the level of ammonia

removal achieved begins to level off, showing that removal efficiencies of nearly 70-80% can be achieved within this pH range while minimizing chemical input needed.

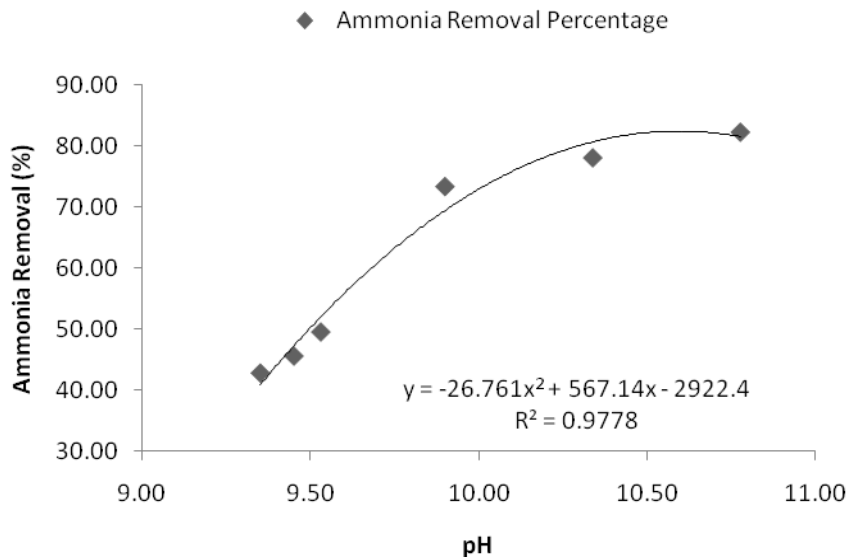


Figure 8.5: Ammonia stripping performance against pH.

The removal efficiencies were considerably higher than what was experienced in earlier laboratory studies due to the use of higher stripping column and air/liquid ratios. The target pH for ammonia stripping efficiency matched the approximate pH range where lime input leveled off (Figure 8.4). Thus, from the pilot data it can be seen that AD treated dairy effluent after primary and secondary screening of solids is optimally treated by pre-treatment with aeration, dosing with lime to a pH range of 10.0-10.2 and stripping at the targeted 35°C temperature. Under these conditions, 70-80% ammonia removal can be achieved.

The results of the study also suggested several other strategies that might be used to achieve higher efficiencies in future applications. Higher air/liquid ratios than used for this pilot study could allow for higher removal efficiencies but at a slightly higher energy cost due to the increased pressures needed to sustain the higher ratio. Use of a larger packing column would also better accommodate higher air/liquid ratios than what were used in this pilot study because of the minimal drop in pressures associated with packing columns. Finally, it is quite conceivable that with some dairy digesters, particularly those practicing co-digestion, the available waste heat would be high enough to warrant use of thermophilic temperatures further increasing ammonia removal efficiencies.

Even without these improvements, though, pilot data have shown that it is possible to achieve 70-80% ammonia removal with limited chemical input of about 10 kg lime m^{-3} effluent, which amounts to roughly 0.3¢gallon $^{-1}$ treated effluent.

Ammonium Sulfate Recovery

Solubility curve calculations show that the theoretical maximum achievable concentration of ammonium sulfate within the slurry is 40% by weight, but tests were needed to determine whether a percentage near this theoretical limit could be attained in practice. Validation of this point is important in regard to overall project mass balances, techno-economic assessment of project feasibility. It is also important to determining if and when crystallization of the product will be so that concerns regarding clogging of the recovery column could be avoided.

Figure 8.6 shows the running total for both total N and ammonia sulfate percentage as reaction time increased during a single batch production of the fertilizer product. Results are not shown after 47-50 hours, as additional reaction time led to no further increase in yields with an assumed crystallization of product occurring within the absorbance column. Results show that at the air temperatures present during the pilot study and using the acid dosing protocol in batch production processing, a 30% ammonia sulfate and 6.4% nitrogen solution is attainable. Given these results, three possible products are possible. First, ammonia sulfate slurry could be directly marketed at low pH. Second, with subsequent drying and/or fractional crystallization with a chiller (representing an additional cost), a crystallized ammonia sulfate product could be sold. Third, the excess primary screened fibers (already produced by the AD process) could be mixed with the P-rich solids and the ammonia sulfate slurry to make one saleable fertilizer product.

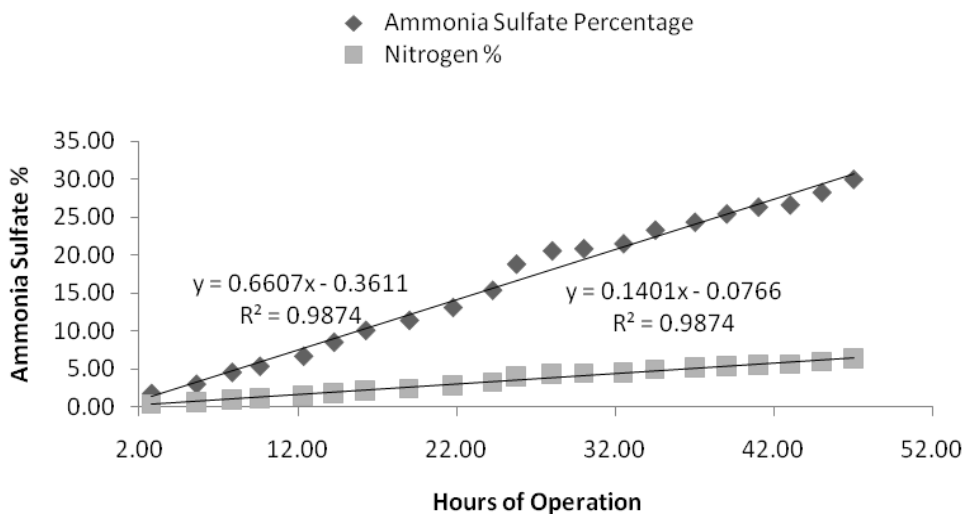


Figure 8.6: Maximum ammonium sulfate and nitrogen content of liquid fertilizer product

Biogas Purification and pH Readjustment

The effluent produced from the stripping and absorbance process is at a higher pH than preferred for land application. To remedy this, we tested (in batch mode) the concept of using the AD biogas and its acidic gaseous components (H_2S and CO_2) as a means for simultaneously purifying the biogas and re-adjusting effluent pH. Since the biogas from the commercial AD unit was difficult to access without significant infrastructure changes to the AD unit and it was variable in gas component composition, bottled and pressurized synthetic biogas was utilized as the biogas source for the experiments. The synthetic biogas was made to mimic a typical gas composition for dairy AD biogas, namely 62.1% CH_4 , 37.7% CO_2 , and 2,000 ppm H_2S . At the various biogas flow rates (low, medium, high) and gas/liquid ratios (5-25) tested, the effluent pH was quite easily and readily re-adjusted from its approximate pH of 10.0 back to a near neutral pH (~8.0-8.5) (Figure 8.7).

Unfortunately, at typical gas/liquid production rates of co-digestion digesters (~25-30:1), the amount of acidic gaseous compounds needed to reduce the pH are low in comparison to the total mass of biogas generated. In short, at high gas/liquid bubbling ratios, removal rates of the acidic compounds are not nearly as high as hoped for. Notably, though, H_2S , the more problematic impurity in biogas, is preferentially scrubbed during this process (Figure 8.8). At low gas/liquid bubbling ratios, the percentage of H_2S scrubbed is quite impressive. In this study, a 2,000 ppm H_2S percentage was used as that is typical of many co-digestion digesters in operation, though some yielding concentrations as high as 4,000 ppm. New proprietary technologies utilizing O_2 dosing and subsequent bacterial oxidation of the H_2S , though, are allowing digesters to cost-effectively control these concentrations to near 500 or below. As such, this scrubbing/pH re-adjustment technique might well serve as a polishing step, capable of reducing the H_2S to near zero even at high gas/liquid ratios.

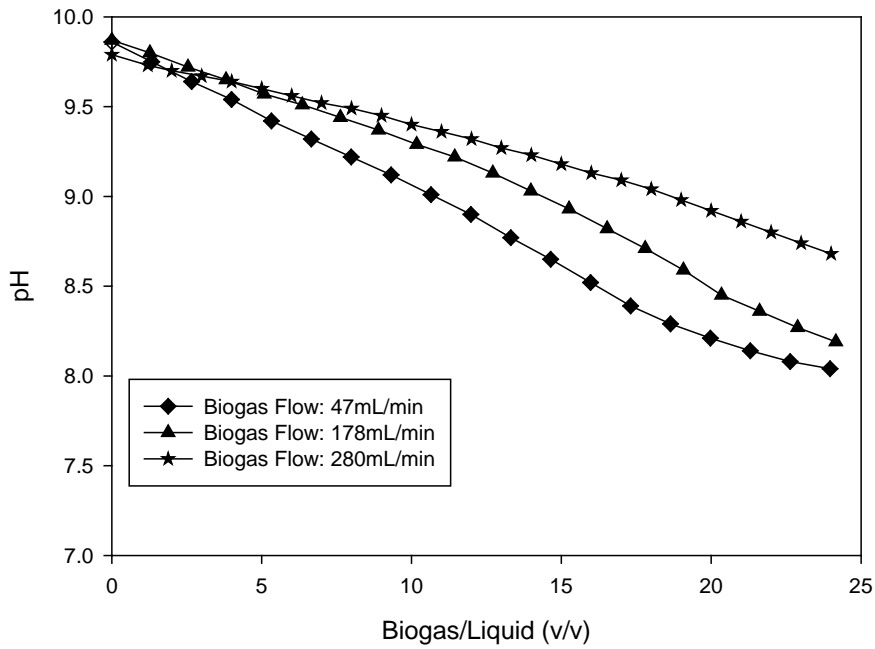


Figure 8.7: Effluent pH re-adjustment via biogas bubbling.

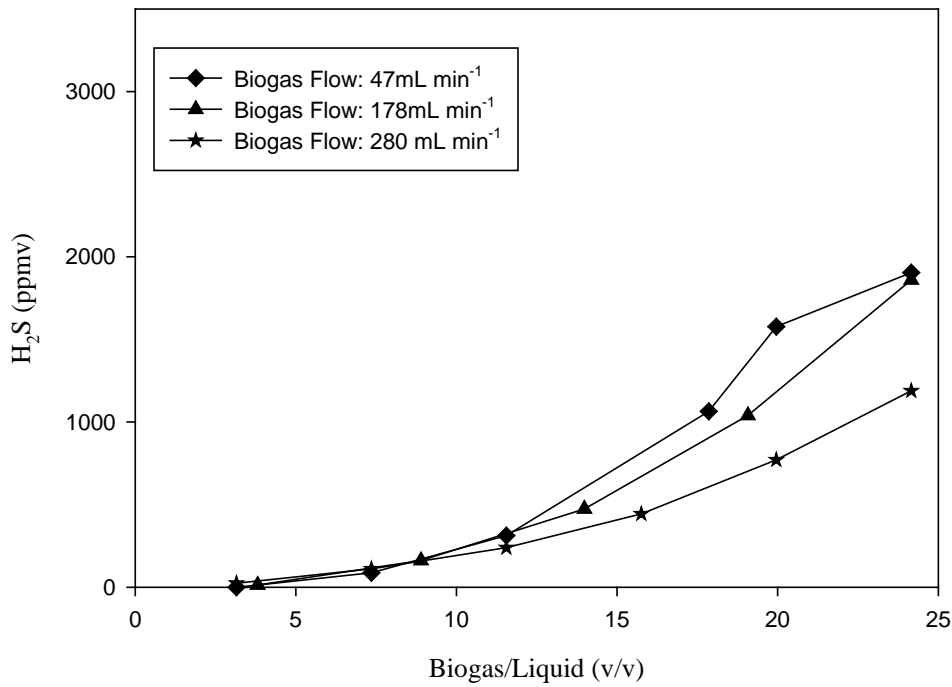


Figure 8.8: H₂S reductions at various gas/liquid ratios and biogas flow rates.

Economic Analysis

The preliminary results from the pilot testing are promising from a techno-economic standpoint with the following capabilities confirmed:

- Primary and secondary screening/separation of solids and phosphorous are attainable using a wide variety of potential technologies. These techniques are capable of removing nearly 75% of total phosphorous and a considerable fraction of solids, thus minimizing the risk of clogging or solids accumulation in down-stream ammonia stripping steps.
- At the relatively low pH and gas/liquid ratios tested, using only a 4.3 m stripping tower, ammonia removal rates of 70-80% were shown to be practical—removal efficiencies will only improve if higher temperatures, taller towers, and higher gas/liquid ratios are utilized.
- Assuming the ability to operate at 35°C temperature with no additional external heating (through waste heat or thermophilic operation to overcome heat losses), attaining the 10-10.2 operating pH requires lime dosing for the ammonium stripping operation that are not excessive. At an assumed bulk price of \$70ton⁻¹, lime dosing costs no more than \$0.80m⁻³ effluent treated (~0.3¢gallon⁻¹ treated). Preliminary estimations of electricity costs using a packing column (7.6 m column) approach are expected to be no higher than 0.20 kWhm⁻³ effluent treated which at an assumed electrical pricing of \$0.09kWh⁻¹ amounts to \$0.02m⁻³ treated.
- Acid absorbance studies showed that batch production of a 30% by weight ammonia sulfate product is achievable through an efficient sulfuric acid dosing protocol. Pilot results show a dosing rate of 0.03 L concentrated sulfuric acidgallon⁻¹ of ammonia sulfate product which at \$105ton⁻¹ (\$0.21L⁻¹ solution) bulk pricing of concentrated sulfuric acid (ICIS, 2009) amounts to \$0.0063gallon⁻¹ of ammonia sulfate (30% w/w) product. At a pilot production rate of 1 gallon product/0.15 m³ effluent this amounts to an acid input cost of \$0.04m⁻³ effluent treated.
- Total chemical operating costs (lime + sulfuric acid) are thus expected to be less than \$0.85m⁻³ effluent treated and total operating costs including stripping blower and associated pumps, etc. to be below \$1m⁻³ effluent treated or less than ½¢gallon⁻¹ effluent treated.
- Biogas scrubbing testing shows that the biogas can be used to easily re-adjust effluent pH to near 8.0 and in the process acidic compounds within the biogas are removed. Removal percentages with an assumed starting concentration of 2,000 ppm and a gas/liquid ratio of 25-30:1 is quite minimal but may still be operationally significant if lower gas/liquid ratios are utilized and/or starting concentrations of H₂S are considerably lower.

Estimation of farm mass balances hinge on the type of solids/phosphorous recovery technology utilized. The following mass balance was determined from conditions at the commercial AD co-digestion dairy, with use of a primary slope screen, a secondary solids/phosphorous separation process using aeration and settling, and ammonia stripping/recovery as determined by the pilot operation (Table 8.3). Analysis shows that in order to offset operating costs alone (not considering labor,

maintenance and capital expenditures), the single combined fertilizer product (1.5% P and 2.5% N dry weight), that mixes excess primary screened fiber with the system's P-rich solids and ammonia sulfate slurry would need to sell for a market value of roughly \$15/ton excluding shipping costs.

Table 8.3: Mass Balance (cow/yr)*

Cow/yr	TS kg	TN kg (% TAN)	TP kg	Product	2 nd Product
Digester Influent	3,650	146 (50%)	32	445 kg CH ₄	0.25 kW
Digester Effluent	2,360	146 (65%)	32	817 kg CO ₂	1,225 CO ₂
Fibrous Recovery	1,740	138 (65%)	28.5	1,865 kg Bedding 74% M; 0.3% P	1,865 kg Fiber M; 0.3% P
P Recovery	956	107 (65%)	8.6	3,470 kg P-solids	77% M; 2.5% P; 4.0% N
Ammonia Recovery	956	58 (36%)		816 kg Ammonia Sulfate Slurry (30% AS; 6.4% N)	
<i>Total Recovery</i>	<i>74%</i>	<i>60%</i>	<i>73%</i>	<i>6.15 MT single product w/ 75% M; 1.5% P; 3.5% N</i>	

*Assumed scrape dairy manure only, 20 day HRT plug-flow digester, 0.30 cm primary slope screen, and aeration/lime/settling secondary solids M=moisture content; N= nitrogen content as dry weight; P=phosphorous content as dry weight; AS=ammonia sulfate content as dry weight
MT = metric tons (1 MT = 1 Mg)

Conclusions

The pilot study has shown the viability of integrating AD with traditional primary screening for fibrous solids/bedding with secondary phosphorous solids removal technologies discussed in the previous chapter and the ammonia stripping discussed here. The integration is complementary as chemicals and methods can be co-utilized to diminish costs, reduce negative byproducts such as acidic components of biogas, and generate wastewater that can be land applied or stored without concern.

Results project a significant recovery of nutrients from the AD effluent allowing for a potential income stream as well as the alleviation of multiple farm-level nutrient loading concerns. These effects could improve farm economics and digester adoption rates. Exporting nutrients off-farm through AD nutrient recovery can allow dairy producers to better meet nutrient management plans, even when practicing co-digestion (which imports nutrients onto the farm). Under some scenarios, this process has the potential to reduce the amount of land necessary for application of existing manure. Depending on their circumstances, if this is achieved, dairies may be able to sell current land, avoid purchasing new land, and/or increase their herd size on existing land. Storage and application of nutrient-reduced wastewater could also lead to reductions in odor, gas emissions and fears regarding leaching and runoff. Bio-fertilizer exports could be open to carbon credits and/or Renewable

Energy Credits (REC credits) if protocols are developed. Finally, it is possible that the product could fetch a premium price if organic status could be established.

In regard to climate impacts, combined N and P recovery and subsequent marketing of the fertilizer products could have important implications, as replacement of inorganic-based P and N in the fertilizer industry would generate a global warming potential offset via reductions in climate emissions from P mining and production. Using the earlier assumptions regarding an assumed achievable 40 dairy AD installation operating under co-digestion scenarios (this report), the following mitigation potential could be realized from the sale of N and P recovered from an assumed aeration/lime/settling scenario and ammonia recovery capable of 80% retention of both P and N (Table 8.4).

Table 8.4: Greenhouse credits from combined nutrient recovery under 40 dairy AD scenario ^a

	Nutrient Product MT-P or N/yr ^{b, c}	GWP MT CO ₂ e/MT-P or N ^d	Total Offset MMT CO ₂ e/yr
Bio-phosphorous	500	6.11	0.0031
Bio-nitrogen	5,353	2.638	0.014
Total	5,853	----	0.0171

^a AD adoption scenario is as described in Frear et al. (this report)

^b Assume 0.048 lbs P/cow day and 0.4 kg P/MT food waste (Frear et al., 2009) and an 80% P recovery; 2.65 kg TANm⁻³ (TAN = total ammonia nitrogen) (Frear et al., 2009), 0.12 m³ manurecow⁻¹day⁻¹, and 80% conversion to ammonia product

^c MT = metric tons (1 MT = 1 Mg); MMT = million metric tons (1 MMT = 1 Tg)

^d (Davis and Haglund, 1999)

Key Project References Related to Chapter

The majority of the work presented in this chapter has been previously published as:

- PhD thesis, Anping Jiang, Ammonia recovery from digested dairy manure as nitrogen fertilizer, Washington State University, Department of Biological Systems Engineering, December 2009.
- Jiang, A., Frear, C., Zhang, T., Chen, S., 2008, Combined nutrient recovery and biogas scrubbing system integrated in series with animal manure anaerobic digester, United States Patent and Trade Office, Serial Number 12/132,016, June 3, 2008.

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