



# REVIEW OF EMERGING NUTRIENT RECOVERY TECHNOLOGIES FOR FARM-BASED ANAEROBIC DIGESTERS AND OTHER RENEWABLE ENERGY SYSTEMS

*PREPARED FOR INNOVATION CENTER FOR US DAIRY*

*November 6<sup>th</sup>, 2013*

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## BACKGROUND

### CHAPTER ONE

#### An Advanced Bio-refinery Business Model for U.S. Dairies

A new business model has the potential to transform the U.S. (US) dairy industry. This model incorporates advanced technology to treat both dairy manure and off-farm food wastes using a core anaerobic digestion (AD) technology, with associated nutrient recovery (NR), as outlined by the Innovation Center for United States Dairy (ICUSD) in their 2013 report, 'National Market Value of Anaerobic Digester Products,' (ICUSD, 2013). This technology platform would produce renewable energy and other valuable co-products, while also mitigating dairy environmental concerns. It has been estimated that a mature industry based on AD on large U.S. dairy farms could create an estimated \$3 billion bio-economy that complements the production of milk and dairy products (Figure 1.1).

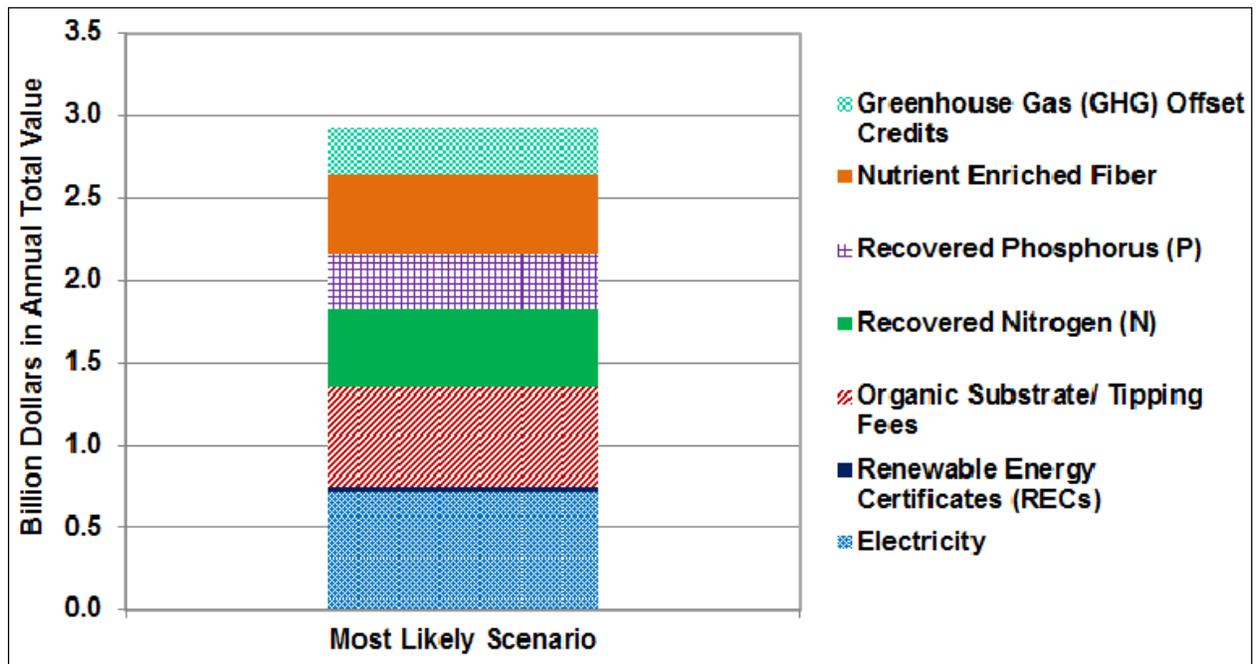


Figure 1.1: Revenue potential for aspects of most likely business scenario (ICUSD, 2013)

While dairy producers have long seen AD as an important option for recovering electricity from manure, it is important to note that almost 70% of the total estimated value from this new bio-economy resides in additional products and credits (Figure 1.1). Development of additional co-products requires implementation of emerging NR technologies, as the AD unit alone does not generate the full range of products described above. While NR technologies for phosphorus (P) and nitrogen (N) exist and are fully commercialized in the municipal and industrial sectors, a moderate amount of continuing research and development (R&D) is still needed to successfully implement these technologies within the dairy sector.

To be successful, ongoing R&D efforts will need to address a number of key challenges. As with any increase in technical complexity, successful implementation of this advanced business model

will require high levels of integration to reduce overall costs and produce high quality products. Adding to the challenges is utilization of manure, a biologically complex and highly variable material. And all processes must be achieved in a farm-based environment, at cost structures affordable to agricultural-based enterprises. Fortunately, ongoing R&D focused on solving these challenges continues to take place, and numerous technologies have already been proven at an advanced pilot or commercial demonstration scale.

### **Anaerobic Digestion with Co-Digestion**

This new business plan is built on a core anaerobic digester that incorporates co-digestion. AD creates an environment without oxygen (anaerobic) in which naturally occurring microorganisms convert complex organic materials in manure and other feedstock to methane-rich biogas, a source of renewable energy (US-EPA, 2006). In the process, it reduces greenhouse gas emissions, diminishes odors, stabilizes waste, and decreases pathogen counts (Martin and Roos, 2007; US-EPA, 2004; US-EPA, 2005; US-EPA, 2008). Co-digestion, in the case of dairies, is the practice of simultaneously digesting a base load of dairy manure with other organic material brought to the farm gate. Co-digestion has the ability to significantly enhance AD project economics through additional biogas production with many common off-farm substrates having two to four times the biogas potential of dairy manure (Alatrisme-Mondragon et al., 2006; Braun et al., 2003). Tipping fees may also be received by the dairy farm for accepting the organic wastes. An economic analysis of an AD facility installed on a 700-cow dairy in Northwest Washington State showed that co-digestion with just 16% organic wastes more than doubled biogas production and almost quadrupled annual digester revenues compared to a manure-only baseline, with 72% of all receipts directly attributable to the addition of organic wastes (Bishop and Shumway, 2009; Frear et al., 2011a).

Organic materials are most often obtained currently from food processing facilities and other industrial sites. However, on a national scale, perhaps the single most promising source is from residential and commercial food scraps. Food scraps are a large category of waste. In the US, Buzby and Hyman (2012) estimated that 30% of all food was lost at the retail and consumer levels. Food waste now represents the largest category of discarded municipal solid waste in the U.S., with only 3.9% recovered via composting or other methods (US-EPA, 2013).

Current landfilling of food waste is costly and unsustainable compared to AD, composting, or other processing strategies, though impacts depend on method of processing, distance of facilities from waste generation sites, and other factors. Using a life cycle analysis, Kim and Kim (2010) demonstrated that AD, composting, or animal feed diversion of food scraps reduced the cradle to grave global warming potential nearly eight fold compared to landfill disposal. And diversion of food scraps from landfills to composting has also reduced costs in some areas of the country, though it can also raise costs somewhat in areas where composting sites are very distant from collection areas (Bloom, 2011; Houssaye and White, 2008).

Because of these benefits, diversion of food scraps from landfills is gaining momentum in the US. The number of municipalities with source separated food scrap collection has grown from 24 in 2005 to a total of 183 in 2012, now serving 2.55 million households (Yepsen, 2013). Evidence suggests that the number of programs will continue to increase, generating an increasing supply of source separated food scraps in need of alternative disposal, preferably through AD (Yepsen, 2013;

Ma, 2013). While there may be regulatory issues that need to be overcome in some states in order for dairies to accept post-consumer food scraps (e.g. Yorgey et al., 2011), this represents a large potential source of energy-intensive materials for dairy-based AD.

In order for large numbers of dairies to access organic wastes and benefit from the operational and economic benefits of AD with co-digestion, dairy nutrient management concerns will need to be addressed. The organic wastes imported onto farms for co-digestion contain nutrients, which need to be managed alongside the nutrients already existing in manure. Case study evidence from Frear et al. (2011a) showed that a mere 16% volumetric addition of pre-consumer food wastes to the manure flow from a 700 cow dairy increased N loading to the farm by 57% while also showing smaller increases in ammonia and P (Figure 1.2).

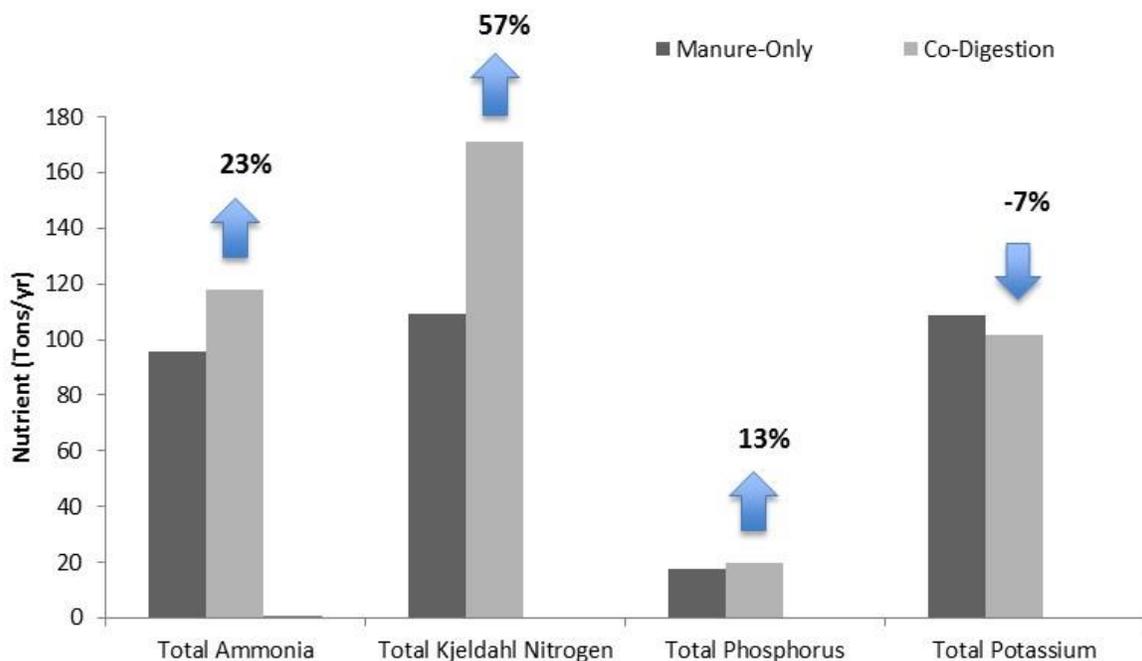


Figure 1.2: Effect of co-digestion on nutrient loads to dairy farm, case study (Frear et al., 2011a)

Farm-based AD systems now operate at 176 sites across the US, with the majority of those installations actively practicing a certain degree of co-digestion and benefitting from the powerful economics of such a model (US-EPA, 2011). Outputs from these combined installations include 541 million kWh of electrical power, 1.2 MMT of CO<sub>2e</sub> destruction through methane capture, 301,000 MT CO<sub>2e</sub> avoidance through fossil fuel displacement, and value-added production of digested fibrous solids for use as animal bedding and as a soil amendment (US-EPA, 2011). In addition, the digestion process produces a manure wastewater, vastly reduced in odor (Powers et al., 1999) and pathogen indicators (Frear et al., 2011a), but containing most of N and P from the manure and any co-digested food scraps, albeit with higher ratios of inorganic to organic forms (Frear et al., 2011a).

The United States (US) dairy industry has set a goal to reduce its climate impact by 25% by the year 2020. In order to meet this goal, adoption rates for AD technologies need to increase substantially above the current rate of roughly 15 units per year (US-EPA, 2011). Achieving this goal will most likely come from exploiting the full potential of the existing co-digestion model, and pairing it with NR technologies that can alleviate nutrient management concerns within a positive business model. Important outcomes of developing projects with such a systems approach include: (1) generation of ecosystem benefits that go well beyond the odor, greenhouse gas and renewable energy aspects of stand-alone AD; (2) production of saleable, concentrated forms of biologically-based fertilizers for affordable export of nutrients off of impacted farms and out of watersheds; and (3) provision of manure management systems that meet not only the renewable energy desires of project developers, but also the nutrient management plans of dairymen.

### **Report Overview**

To support industry knowledge and decision-making, this report provides an overview of emerging technologies for recovery of P, N, and salts from dairy manure. The bulk of the review focuses on NR technologies that work in concert with AD—based on the enhanced environmental benefits that this combination provides. However, the report also discusses NR technologies that can be used on manure that has not been digested.

The review focused on information from pilot and commercial demonstration of NR technologies, with sources including literature, pilot reports, company literature, project feasibility studies, and interviews. These technologies are rapidly evolving. Because of this, and because no review can ever be truly comprehensive, we do not attempt to identify specific companies or products that could be purchased by dairies. Instead, this review attempts to identify broad approaches, identify strengths and weaknesses of those approaches, as well as specific situations where each might be most appropriate. Individual case studies have been included so as to offer more detailed information about representative technologies.

As part of the review, the authors attempted to estimate a range of performance and cost achievements for each of these broad approaches to NR. Ranges are not necessarily indicative of individual technologies but rather represent an approximate average based on best available data in conjunction with some assumptions. Several factors made these performance and cost estimates challenging. In some cases, technologies are already operating in the dairy sector at commercial scale. In many cases, technologies are operating at a pre-commercial scale, or are used commercially in other sectors such as wastewater treatment facilities. This required assumptions to be made based on informed estimates. Also, because technologies are often applied within a single manure management system, it is often clear that costs would vary significantly if applied in other situations. For example, an NR technology that operates well on dilute flush manure would likely require pretreatment at additional cost if applied to scraped manure. Finally, limited data were available, particularly in regard to costs. This is mostly due to proprietary concerns or unwillingness to cite specific costs due to rapidly changing technologies. These factors mean that performance and cost ranges should be viewed as “best estimates” based on the data currently available to researchers. It is meant to provide a broad view of the industry as a whole, and should not be used for individual technology purchase or investment decisions.

This report is divided into six chapters. These chapters cover:

- The background and rationale for dairy industry NR (this chapter)
- P and P recovery technologies (Chapter 2)
- N and combined N/P recovery technologies (Chapter 3)
- Salt recovery and clean water (Chapter 4)
- Non-AD thermal nutrient recovery technologies (Chapter 5)
- Conclusion (Chapter 6)

# PHOSPHORUS AND PHOSPHORUS RECOVERY TECHNOLOGY

## CHAPTER TWO

### Background

Phosphorus is an important non-substitutable macronutrient, necessary to our diets and food production. Modern, intensive agriculture is the primary user of commercially produced P from rock phosphates, accounting for 90% of total demand for inorganic P fertilizers. Total annual global production is currently 20 million tons of P, derived from approximately 140 million tons of rock concentrates (IFA, 2002; Rockstrom et al., 2009). Nearly all the P used globally is mined from a relatively small number of finite, commercially-exploitable deposits, and it has been estimated that given projected increases in demand (50-100% by 2050), global P reserves may last only 50-100 years (Cordell et al., 2009). Recent price spikes have occurred due to tight supply and increased demand (Figures 2.1; Vaccari, 2009 and Cordell et al., 2009).

One strategy that could lengthen the life of the world's P resources is P recovery and recycling from food systems (Cordell et al., 2009; FAO, 2006). This would occur at identified P 'hot spots' including cities (in industrialized countries) and concentrated animal feeding operations (CAFOs). These hot spots occur because nearly 100% of human ingested P is excreted to wastewater treatment facilities (Jonsson et al., 2004) and about 50% of animal-ingested is excreted to manure systems (Smil, 2000). Efficient recovery and recycle of P from animal and human wastes could simultaneously provide environmental benefits by reducing the amounts of excess P lost to soils and waterways.

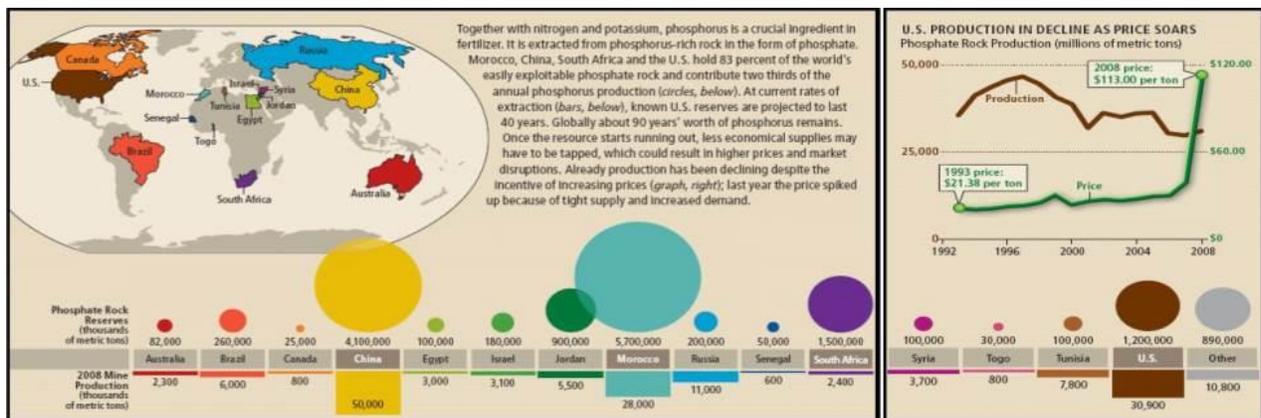


Figure 2.1: Phosphorus pricing (Cordell et al., 2009)

### Forms of Phosphorus in Dairy Manure

The form of P in undigested and digested dairy manure is an important determinant of appropriate P-extraction and recovery technologies. Importantly, the majority of the inorganic P is particulate-bound (Gerritse and Vriesema, 1984; Zhang et al., 2010). Several studies show that the particulates are predominantly Ca-P and Mg-P (Chapuis-Lardy et al., 2004; Gungor and Karthikeyan, 2005a; Gungor and Karthikeyan, 2005b) that result from the high Ca:P molar ratio (1.66-2.43) of a dairy cow's diet. Gungor and Karthikeyan (2008) reported that total dissolved P constituted about 12% of TP in the undigested dairy manure (prior to AD). By inference, then, the majority of P in dairy

manure is not dissolved. Rather, it is suspended, in the form of small, colloidal non-crystalline particles attached to calcium or magnesium (Zhang et al., 2010). Available data indicate that the form of P does not change drastically following AD. Güngör and Karthikeyan (2008) reported that total dissolved P constituted about 7% of TP in the effluent liquid from AD, somewhat less than in the influent. As Figure 2.1 indicates, digested dairy manure has suspended solids roughly evenly distributed across particle sizes of 600-20 microns, with a bulk of P found preferentially between 74-0.5 microns. Notably, fibrous solids separation occurs using screens with 3,000 microns pore-size, resulting in little impact to P reduction.

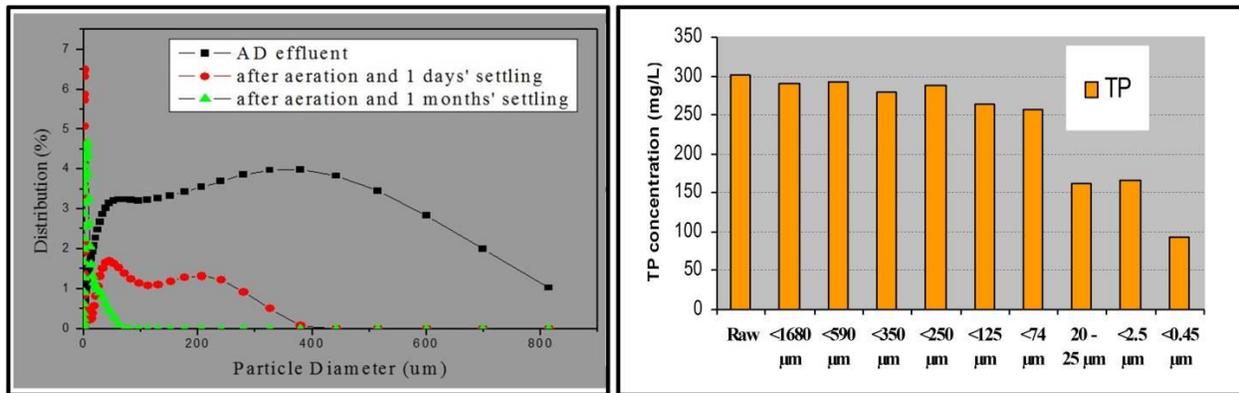


Figure 2.2: Size distribution of suspended solids (left) and phosphorus (right) in digested manure (Zhao et al., unpublished)

The implications are that in order to recover the majority of P, small, suspended solids must be removed. By definition, this means that the screens currently used by the dairy industry to recover fibrous solids will not be sufficient.

### Phosphorus Removal Technologies

As the above discussion suggests, the majority of technical approaches utilize various forms of mechanical screening operations with increasing complexity aimed at enhancing removal efficiency—albeit usually at the expense of added capital and operating costs. The exceptions to these screen-based approaches are struvite crystallization and enhanced biological P removal. In short the suite of available P technologies can be sub-divided into five classes, with the first four of these to be further discussed as individual case studies:

- Primary and secondary sequential screening for fibrous and fine solids
- Sequential screening plus advanced systems not-utilizing chemicals
- Sequential screening plus advanced systems utilizing chemicals
- Struvite crystallization
- Enhanced biological P removal

#### Primary and Secondary Sequential Screening for Fibrous and Fine Solids

Primary and secondary screening systems for AD effluent, with sequential removal of fibrous solids followed by finer solids, is increasingly becoming an industry standard for AD. Various types of screens and screw presses can be used within this general categorical approach, with or without additional mechanical aids (dewatering augurs, roller presses, vibrating screens,

automated cleaning systems, etc.). The main reasons for the sequential approach are to (1) produce a separate fibrous product from the finer solids as the fibrous product has known high value markets while the fine product is still in need of market development and (2) to reduce the risk of blinding within the much finer secondary screen, by removing larger fibrous solids first.

### Case Study 1— Double A Dairy, Jerome, ID (Primary and Secondary Sequential Screening for Fibrous and Fine Solids) (Andgar, 2013)

The Double A Dairy in Jerome, Idaho, has a primary and secondary screening operation as part of their 12,500 cow digester. Figure 2.3 (top) shows the system during construction with (1) three primary fibrous solid screens utilizing a slope screen connected to two roller presses, (2) two secondary vibrating screens with tighter mesh screens for production of fine solids, and (3) separate collection and processing areas for the respective solids. The lower part of the image shows the system with completed buildings, covers and staging areas.



Figure 2.3: Screening operation at Double A, Jerome ID

Performance and costs were as follows as of fall 2013:

- The system produced 350 yards of wet fiber product day<sup>-1</sup> as well as fines.
- Solid recovery resulted in 35-40% reduction in total solids (TS), 15-20% reduction in total N and 12-18% reduction in total P.
- Approximate capital costs for complete solids recovery operation were \$35-40 cow<sup>-1</sup>. This included all screens/machinery, pumps, electrical work, and building/excavation.
- Approximate operating costs for solids recovery operation were \$5-6 cow<sup>-1</sup> year<sup>-1</sup>, including labor, electricity, spare parts, chemical wash, and contingency.
- Some additional treatment of both the fibrous and fine solids would be required to achieve high value markets. In the case of the fine solids, drying and even pelletizing could be required, adding thermal and cost pressures to the system.

### Sequential Screening plus Advanced Systems, Not Utilizing Chemicals

In order to recover increasingly small particles associated with P, NR systems can incorporate more advanced components to work in series with the initial screening operations. Given blinding limitations associated with extremely small pore-size screens, advanced components usually rely on rotational gravitational enhancements via rotating screens, low-g centrifuge screens, or decanting centrifuges. The result is greater TS and P removal through recovery of ever-smaller sized particles.

#### Case Study 2— Big Sky Dairy, Jerome, ID (Sequential Screening Plus Advanced Systems Not Utilizing Chemicals) (Andgar, 2013)

While several sites utilize various decanting centrifuges with AD, many of these add polymer/coagulant chemicals. Thus, the only available case study for a non-chemical process was a pilot study completed by one of the authors at Big Sky Dairy in Jerome, Idaho (Figure 2.4). The pilot study was completed using screened effluent run at a flow rate of 45 gallons minute<sup>-1</sup>, about 2/3 the flow rate for the 3,000 wet cow equivalent dairy.



Figure 2.4: Pilot centrifuge, Big Sky Dairy, Jerome ID

Performance and costs were as follows as of 2013:

- TS removal of 30-35% was achieved from the centrifuge alone, giving a system TS removal rate of 55-60%.
- Total N reduction was on order of 10-15%, giving a system N removal rate of 25-30%.
- Total P reduction was 40-50%, giving a system P removal rate of 50-65%.
- The separated solids were about 23% solids, still requiring extensive drying for value-added sales and marketing.
- Costs, based on the pilot study as well as interviews (DVO, 2013) were assumed to be approximately \$25-50 cow<sup>-1</sup> year<sup>-1</sup> in operating costs and \$57-136 cow<sup>-1</sup> for capital costs for the combined screening and centrifuge system.

### **Sequential Screening plus Advanced Systems Utilizing Chemicals**

As can be seen from the above case study, even the enhanced g-forces of centrifugation, on their own, have limited ability to recover very small, colloidal P-associated solids. As a result, most existing systems that use enhanced mechanical separation add chemicals to induce flocculation.

Flocculation is the process by which small, suspended particles clump together. The process is dictated by the behavior of colloids in water, which in turn is strongly influenced by particles' electro-kinetic charge. Each colloidal particle carries a like charge, most often negative. Because of a force known as electrostatic repulsion, the particles repel each other and therefore tend to remain discrete, dispersed, and in suspension. If the charge is significantly reduced or eliminated, then the colloids will gather together, forming small groups of particles, then larger aggregates and finally visible floc particles which settle rapidly.

Three chemical species are generally used in other sectors for the recovery of colloids containing P, either alone or in combination. In water treatment, flocculation is accomplished by adding cationic flocculants (also known as coagulants) such as Alum or Ferric Chloride to reduce the surface charge. Polymers may also be used. These are long, branched, high-molecular weight chemicals that trap small, coagulated particles and intensify flocculation. Beyond enmeshing particles, some polymers are charged, in which case they may serve a dual role as a surface charge neutralizer. Lastly, there are binders. Binders are chemicals or natural species within the wastewater (i.e. fibrous solids) that can assist coagulants and polymers in accumulating flocs of appropriate size.

The key to successful chemical flocculation is developing a combination of inputs that successfully treats the waste stream while minimizing the required chemical inputs. This is because chemical inputs strongly impact process economics and the quality of the final product. Some initial systems for anaerobically digested dairy manure have utilized the digested fibrous solids as binders but in doing so remove the possibility of recovering such fibers as a source of additional revenue to the project. Other early systems utilized considerable amounts of both coagulants and polymers, causing costs to be exorbitantly high. This strategy also produced treated wastewater and solids high in chemical content, particularly aluminum, which can be toxic to crops in high concentrations (Chen, 2008). More recently, experience and R&D have allowed for more refined systems that have drastically reduced the chemical input, costs and impact on products, with that refinement still continuing today (DVO, 2013; Kemira, 2011).

Beyond chemical inputs, these systems require companion operations to cost-effectively recover (settle, float, skim, etc.) and dewater (g-forces such as centrifuges, mixing tanks, belts, dissolved air floatation, etc.) the P solids. This is done not only to maximize recovery, but also to produce a more valued form of product. While varying systems exist, all successful systems must cost-effectively collect the recovered solids and dewater to a practical value. Note that, as with the sequential screening, additional dewatering and product formulation (pellets, blending, etc.) are still required to achieve high value sales. These steps will require additional infrastructure and heat, raising costs.

### Case Study 3— Bio-Town AD facility, Reynolds, IN (Sequential Screening with Advanced Systems Utilizing Chemicals) (DVO, 2013)

Full-scale demonstration of a combined sequential screening and dissolved air flotation (DAF) system utilizing polymer dosing has been installed at the 6,000 wet cow equivalent plus co-digestion Bio-Town AD facility (Figure 2.5). Primary screening removes the fibrous product, while secondary screening removes an additional portion of fine suspended solids. Lastly, a DAF system with organic polymer inputs is used to flocculate and raise flocs to the surface where they are skimmed and partially dewatered with an auger screw press.



Figure 2.5: Sequential DAF, Bio-Town IN

Data from system operation documented the following performance and costs as of fall 2013:

- TS and total suspended solids (TSS) were reduced by 75-80% and 95-97%, respectively, for the full system.
- Total N reduced by 50-55% for the full system.
- Total P reduced by 85-95% for the full system.
- Operating and capital costs were estimated at \$25-30  $\text{cow}^{-1} \text{ year}^{-1}$  and \$130-150  $\text{cow}^{-1}$ , respectively.

### Struvite Crystallization

P can also be recovered by crystallization in the form of struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) (Battistoni et al., 2006; Jeong and Hwang, 2005). Effective performance has been seen in large-scale studies while treating swine manure (~80% TP removal; Bowers and Westerman, 2005). However, several factors can affect struvite precipitation, including pH, super-saturation of the three ions in the solution, and the presence of impurities (e.g., calcium), which can cause the formation of calcium-P precipitates (Le Corre et al., 2005). As dairy manure contains these calcium-P precipitates, poor performance has been observed when using dairy manure, particularly digested dairy manure

(~15% TP removal) (Zhang et al., 2010). However, modifications to the struvite crystallization process have allowed for enhanced removal efficiency (~75% TP removal) (Zhang et al., 2010).

#### Case Study 4— Qualco Digester, Monroe, WA (Struvite Crystallization) (MFH, 2013)

A pilot-scale struvite crystallizer (Figure 2.6) with process modifications required for treatment of a portion of the digested dairy manure has been operating at the 1,400 wet cow equivalent plus co-digestion Qualco digester in Monroe, WA. The system can be operated either on non-AD wastewater or post- AD wastewater (after fiber has been separated).



Figure 2.6: Struvite crystallizer, Qualco, Monroe WA

Performance and costs were as follows as of fall 2013:

- Removal efficiencies from fiber-separated AD effluent were 75% for total P and 10% for total N. Total system performance was roughly 85-90% total P and 25-35% total N.
- Operating costs were estimated at \$80-100  $\text{cow}^{-1} \text{ year}^{-1}$  while capital costs were in the range of \$75-125  $\text{cow}^{-1}$ . These costs were for the struvite crystallizer, excluding fibrous screening.
- Relatively high operating costs were due to the chemical additions.
- Product is quite dry and in pelletized form that allows for easy storage, transportation, and application with existing fertilizer systems.
- Both digested and un-digested manures can be treated.

#### Advanced Biological Nutrient Removal Approaches

While not yet implemented at the commercial scale on dairies, two biological nutrient removal approaches are worth discussion: enhanced biological P removal (EBPR) and algae systems for integrated wastewater treatment-fuel production.

### ***Enhanced Biological Phosphorus Removal***

Enhanced biological P removal is a biological process where P is consumed by bacteria that are subjected to alternating anaerobic and aerobic conditions (Ahn, 2007). The alternating anaerobic and aerobic conditions give a selective advantage to a specific microbial population known as P-accumulating organisms (PAOs), over other heterotrophic bacteria in the system (Mino et al., 1998). PAOs are able to store P in greater quantities than needed for their own cell components. Typically the anaerobic process is performed first. During the anaerobic phase, volatile fatty acids (VFA's), mainly acetate, contained within the wastewater are consumed by PAOs. Simultaneously, PAOs release phosphate out of their cells through the hydrolyzation of intracellular phosphate (Ahn, 2007). VFA's are converted to poly- $\beta$ -hydroxyalanoates (PHA) during this process using a reducing power generated from oxidation of intracellular glycogen (Mino et al., 1998). When aerobic conditions are imposed, dissolved oxygen becomes available and PAOs grow using the previously stored PHA for energy. During metabolism, phosphate is taken up by PAOs (Wentzel et al., 1991; Yanosek, 2002). Due to microbial growth, more  $\text{PO}_4\text{-P}$  is taken up in the aerobic environment than is released in the anaerobic environment, thus concentrating the  $\text{PO}_4\text{-P}$  in the biomass and creating a sink for P. Although P is removed from the liquid fraction of the wastewater, it remains in the biomass solids, and these require separation (Yanosek, 2002).

Conditions must be monitored to ensure that the process is not hampered by biological competitors. Specifically, glycogen-consuming organisms (GAOs) are believed to compete with PAOs for VFA during the aerobic process. On top of that, the EBPR is influenced by several environmental and operational factors, including pH (Filipe et al., 2001), temperature (Whang, 2002), organic loading rate (OLR) (Ahn, 2007) and anaerobic-aerobic contact time (Wang 2001). External disturbances can also reduce P removal during the EBPR process, with disruptions ranging from excessive rainfall to shortage of potassium (K) (Brdjanovic et al., 1996), excessive aeration (Brdjanovic et al., 1998), or high nitrate loading to the anaerobic zone (Kuba et al., 1994).

Most importantly, the system requires readily biodegradable carbon, thereby diminishing its likelihood of being used successfully on anaerobically digested wastewater. In AD, the organisms in the digester have already destroyed the readily biodegradable carbon and generated biogas. For this reason, as well as its complexity and susceptibility to biological contamination, the authors have not included it as a technology of focus. In addition, while commercial systems do exist within municipal wastewater facilities, to the authors' knowledge there are no active pilot or commercial-scale systems within dairies. A thesis by Yanosek (2002) evaluated the use of EBPR on an 805 dairy cow farm without AD. Estimated costs, on a per cow basis were  $\$300 \text{ cow}^{-1} \text{ year}^{-1}$  and  $\$160 \text{ cow}^{-1}$  for operating and capital costs, respectively. Clearly, such costs would also present a significant barrier to commercialization, in addition to the above concerns, especially when no renewable energy is produced concurrent to its use.

### ***Algae Systems***

Similar to EBPR, integrated algae systems for wastewater treatment and bioenergy production depend on microorganisms to remove nutrients. In these systems, microalgae consume nutrients for growth. Afterwards, microalgae are harvested for their entrained lipids. Lipids can then be processed into several potential biofuel or bioenergy product options, including *trans*-esterified

biodiesel (Chisti, 2007; Scott et al., 2010), fermented bioethanol (Bush and Hall, 2006), photo-biological hydrogen (Ghirardi et al., 2000; Melis and Happe, 2001), hydrocarbon biofuels for drop-in replacements of gasoline, diesel, and jet fuel (Jones and Mayfield, 2012; Regalbuto, 2009), or anaerobically generated methane (Sialve et al., 2009; Uellendahl and Ahring, 2010).

Production of methane from either whole cells or algal residues would likely be most appropriate for application in a dairy setting. This strategy has been regarded with general interest by both the research and commercial communities, though there has been more focus on the potential production of drop-in fuels. During methane production on dairies, whole cells or algal residues would most likely be co-digested along with manure in the existing digester. From a whole-cell perspective, microalgae blooms cultivated from wastewater for treatment and environmental protection purposes are typically low in lipid content, warranting this lower-value use and simpler processing approach (Sialve et al., 2009).

Existing concerns associated with microalgae treatment of dairy waste include the opacity of the manure, leading to light penetration issues and limiting algal growth. They also include the potential for biological contamination, difficulty of separating the nutrient-absorbed algae, and of course questions concerning scale-up and economic viability of a full system (Wang, 2010). However, early pilot operations across a wide range of wastewaters including dairy AD effluent showed excellent nutrient removal efficiencies—on the order of 90-100% TSS, 90-100% total P, and 80-100% total N (Algeolve, 2013). In the opinion of the reviewers, considerable additional R&D is required before commercial demonstration or application is warranted. However, continued but cautious observation of ongoing developments is justified, due to the demonstrated removal efficiencies and potential for integration with existing AD operations.

### **Conclusion**

Because of the form of P in dairy manure, particularly digested dairy manure, methods for solids and P removal are linked. Thus, increasing P removal efficiencies are achieved mainly by increasing separation of fine solids. As a result of this linkage, commercial applications are at this time focused on mechanical separation processes that use chemicals to flocculate very fine, colloidal solids that are associated with the majority of P. Given the existing business plans for AD, of capitalizing on high value sales of digested and separated fibrous solids, these systems are sequential in nature. Fiber (and its associated N/P content) is removed first, followed by removal of smaller solids with the majority of the P.

This approach produces a stackable but quite wet product. Thus, drying and form modulation will be required before high value markets can be realized. This would add to the thermal and economic costs. Importantly, development of these processes should be designed with explicit consideration of organic certification, particularly as the product could supply a generally balanced fertilizer product with numerous macro and micronutrients. Organic certification may be important to developing product markets, as organic producers have access to more limited types of fertilizers, and therefore may be more willing to pay a price premium or purchase products in less-than ideal forms.

Two other P recovery approaches of note are struvite crystallization and advanced biological nutrient removal processes. Struvite is notable for its production of a preferred product that is

already pelleted, mostly dry and quite balanced in fertilizer property. As a consequence, it is easily spread using existing fertilizer application methods. The costs for this process may be comparable to, or slightly higher than, the combined mechanical-chemical processes. Among biological P recovery processes, EPBR is well known in municipal wastewater processes, but is problematic for incorporation into an AD operation on farms. Algae systems, another biological approach, represent a relatively undeveloped concept but one that has potential due to its nutrient absorbance efficiencies. Refinement of the system and cost reductions in algae separation processes will be key to advancement of this concept.

Figure 2.7 summarizes the five main classes of approaches to P recovery. Estimated performance and costs ranges are color-coded red (low relative performance or high relative cost) yellow (medium performance or cost) or green (high performance, low cost). In general, as P removal improves, costs also increase. Also, while large pore size screening leads only to limited removal (15-30%), methods that allow for recovery or absorption of small particle sizes achieve near-maximum recovery of P (75-90%).

Key Technology Primarily P	Performance	Operating Cost /cow/year	Capital Cost /cow	Scale
1' and 2' Mechanical Screens	TN 15-30%, TP 15-25%	\$5-6	\$32-36	Commercial
Sequential Screening + Advanced Non-Chemical	TN 24-30%, TP 50-65%	\$25-50	\$57-136	Commercial
Sequential Screening + Advanced Chemical	TN 45-55%, TP 75-90%	\$25-75	\$130-150	Commercial
Struvite Crystallization	TN 30%, TP 75%	\$90-110	\$100-150	Commercial
Enhanced Biological Phosphorus	TP 42-91%	\$150-170	\$275-300	Pilot

Figure 2.7: Summary of performance and cost estimates with partial list of concerns and scale tested for representative class of P recovery approaches

While various methods can be utilized for P recovery, it is clear from full-scale demonstrations that the following performance can be achieved:

*45-55% N and 75-90% P removal at roughly a cost of \$25-75 cow<sup>-1</sup> year<sup>-1</sup> in operating costs and \$130-150 cow<sup>-1</sup> for capital costs, while also separating a valued fibrous product.*

P recovery is the most commercially advanced area of NR on dairy farms, with a handful of dairy operations throughout the US actively utilizing systems with various technologies. Ongoing R&D efforts continue, aimed primarily at reducing costs and developing markets for the resulting nutrient products.

# NITROGEN AND COMBINED NITROGEN/PHOSPHORUS RECOVERY TECHNOLOGY

## CHAPTER THREE

### Background

Nitrogen recovery is of increasing interest across the world, as concern rises about N eutrophication, nitrate leaching, nitrous oxide greenhouse gas emissions, and ammonia particulates. At their core, these problems are driven by the cycle of large N losses in agricultural systems and subsequent fossil-based synthetic N replenishment. An estimated 85% of reactive N (forms other than di-nitrogen gas, N<sub>2</sub>) is lost to the environment (waterways, atmosphere, etc.) during food production. Meanwhile the vast majority (95%) of the remaining 15% that enters human mouths is excreted and eventually lost to those same waterways and atmosphere (Galloway et al., 2004). To replace N lost from agricultural systems, industry converts non-reactive N<sub>2</sub> to synthetic N fertilizer via the economical, but energy-intensive and environmentally harsh Haber-Bosch process (12 Kwh kg N<sup>-1</sup>; Sutton et al., 2009) (1.4-2.6 kg CO<sub>2e</sub> kg N<sup>-1</sup>; Wood and Cowie, 2004). The result is an unsustainable N cycle that consumes limited fossil fuel resources and contributes to environmental threats.

### Forms of Nitrogen in Dairy Manure

Due in part to the high-energy diet formulations fed to modern dairy cows, dairy wastes contain a considerable concentration of N (~0.6% on a wet basis and 5% on a dry basis). Of that N, roughly half is in an organic form while the other half is soluble (dissolved) ammonia (Frear et al., 2011a). During AD, microorganisms convert a portion (25-40%; Frear et al., 2011a) of the organic N to ammonia, thereby increasing the overall concentration of ammonia in the manure, and producing a wastewater with N that is more readily available for plant uptake. As noted earlier, co-digestion, utilizing various pre and post-consumer food processing or waste products, can significantly increase this N loading (Frear et al., 2011a).

### Combined Nitrogen and Phosphorus Recovery Technologies

Recovering N at concentrated N 'hot spots' could reduce losses of N to the environment while diminishing demand for synthetic fertilizers. As with P, important hot spots include human and CAFO wastewater treatment facilities, prior to dilution within waterways, soils or the atmosphere. As Figure 3.1 indicates, there are three general approaches to recovering N from wastewater or waste solids. The first two recover N in a variety of forms while the last method, highlighted in a different color, disposes of N as non-reactive N<sub>2</sub> gas into the atmosphere. As in Chapter 2, each of these classes of removal will be discussed. When possible, case studies identifying performance and cost are included.

This chapter focuses on N-stripping and conversion to non-reactive N<sub>2</sub> gas. Solids separation has already been discussed in detail in Chapter 2. For review, solids separation, represented by primary screening for fibrous solids, secondary screening for manure fine solids, and chemical flocculation (DAF, centrifuge, belt press, etc.) currently allows for *45-55% N and 75-90% P recovery at operating and capital costs of \$25-75 cow<sup>-1</sup> year<sup>-1</sup> and \$130-150 cow<sup>-1</sup>.*

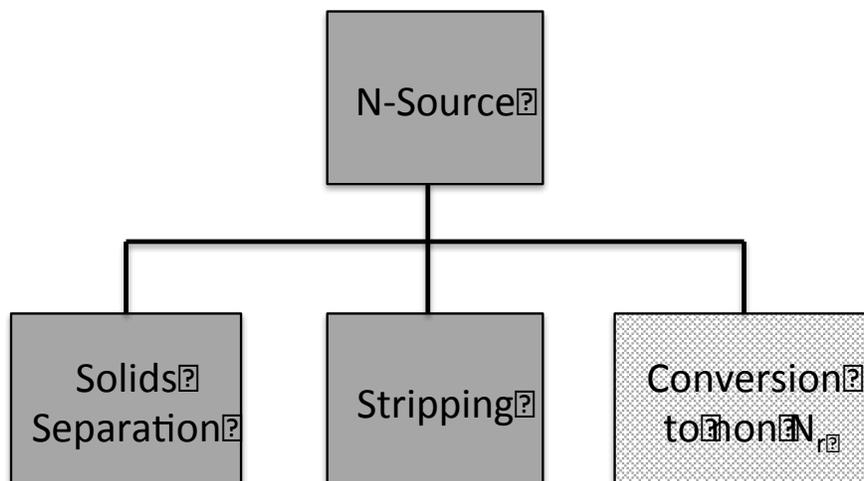


Figure 3.1: Schematic of N recovery approaches to wastewater and waste solids

For both N-stripping and conversion to  $N_2$  gas, this chapter emphasizes a combined N/P approach as opposed to stand-alone N recovery. Because N is present in both solids-associated organic forms and soluble forms, N recovery technologies are most successful and cost-effective when recovery of solids (P and some N) is combined with targeted N recovery. Solids separation recovers largely organic forms, while N-stripping or conversion to  $N_2$  gas focuses mainly on soluble ammonia, though sometimes also on organic forms.

### Ammonia Stripping in Conjunction with Solids Separation

Ammonia N-stripping is a known recovery technology, with commercial application within industry and some wastewater system, that takes advantage of the fact that soluble ammonia tends to become gaseous at certain temperature and pH ranges (Jiang et al., 2013; Guo et al., 2008; Lei et al., 2007; Zeng et al., 2006; Bolan et al., 2004; Bonmati and Flotats, 2003). Achievement of the appropriate temperature and pH ranges and the subsequent stripping of ammonia gas can be accomplished through a variety of techniques including chemical air stripping, non-chemical air stripping, vacuum stripping, and steam stripping (Eekert et al., 2012). The approach is a natural fit with AD, as the AD process increases the proportion of N in the ammonia form, and raises pH part of the way to the required range. AD also produces excess heat that can be used for the stripping process.

Unfortunately, even with these synergies, many existing approaches are expensive. Chemical air stripping requires additions of alkali chemical to elevate the pH and release the gaseous ammonia ( $\sim 10\text{-}11$  kg lime  $m^{-3}$  at a cost of  $\$1$   $m^{-3}$ ; Jiang et al., 2013; Lei et al., 2007). Non-chemical air stripping and vacuum systems reduce required chemical inputs but require additional electrical draw. And ammonia steam stripping requires thermal inputs often above that available from AD projects, thus requiring the purchase of expensive outside energy inputs (Liao et al., 1995). Additionally, traditional tower systems utilizing packing media or tray towers are prone to clogging when used on dairy AD effluent. This occurs because even after primary separation, AD effluent contains  $\sim 3\text{-}5\%$  TS (Frear et al., 2011b). However, several creative approaches to ammonia N stripping have been and are continuing to be developed (Zhao et al., 2012; Spindler et al., 2011; Pedros et al., 2013). These new technologies, associated patents, and commercial

systems are lowering project costs to a more realistic range. Once the soluble ammonia has been stripped to its gaseous form, several approaches can be used to recover, store and market the ammonia in a solution or crystalline form. Typically, concentrated inorganic acids, organic acids, or rock salts are allowed to come into contact with the ammonia gas, producing saleable fertilizers such as ammonium sulfate, ammonium nitrate, or ammonium citrate. Some of these fertilizers are in a form that could be organically certifiable.

#### Case Study 5— Wenning Poultry, Fort Recovery OH (Ammonia-N stripping in conjunction with solids separation) (DVO, 2013)

Dry poultry manure from a 1.5 M layer poultry operation is mixed with digested, treated effluent and then anaerobically digested (Figure 3.3). After AD, effluent is treated by air stripping with a non-chemical methodology. Gaseous ammonia is then contacted with sulfuric acid to make ammonium sulfate solution. The resulting effluent is sent through a dissolved air flotation (DAF) solids separation process to remove solids and P and produce mixing water for the front end of the process.



Figure 3.3: Sequential AD, NR and DAF operation at Wenning Poultry

Performance and costs for the NR system were as follows as of fall 2013:

- 70-75% and 93-97% reductions in TS and TSS, respectively.
- 80-90% reduction in total P and 55-65% reduction in total N.
- 10-12 tons of ammonium sulfate solution (8:0:0:10) day<sup>-1</sup> (4-5 tons day<sup>-1</sup> if crystallized).
- Dried, digested chicken solids (4:6:3 nitrogen-phosphorus-potassium (NPK)).
- Approximate operating costs were \$100-160 cow<sup>-1</sup> year<sup>-1</sup> (not including AD). This included labor, electricity, spare parts, chemicals, and contingency (conversion to cow numbers from flows treated).
- Approximate capital costs were \$400-500 cow<sup>-1</sup> (conversion to cow numbers from flows).

Many of the initial commercial demonstrations for ammonia N stripping have taken place on poultry or other mixed feedstock facilities that have relatively high ammonia-N concentration in their wastewaters (~4-5 g N/L as compared to 1-2 g N/L for dairy wastewater). This is because the higher ammonia concentrations can significantly improve project economics. In addition, these facilities often require some degree of process water return for dilution of high solids before entry to a slurry-based digester, giving added incentive to removing ammonia, an agent known to inhibit AD microorganisms.

These technologies may be currently less applicable to dairy manure, given its lower ammonia and already dilute nature (except at dry lot dairies). However, if further cost reductions can be achieved, and N product markets formalized, ammonia stripping may be of increased interest in the future, with several demonstration projects already operating on dairies (DVO, 2103).

The various forms of ammonia N stripping can achieve 60-95% ammonia N release and recovery. This implies roughly 40-60% total N recovery when it is assumed that AD effluent has a total N composed of approximately 65% ammonia-N and only ammonia N stripping is practiced. As ammonia N stripping traditionally works more efficiently with reduced levels of settled and suspended solids, most systems will utilize a sequential approach to remove solids (with associated P and some N) prior to ammonia N treatment. Given that recovery of solids has been shown to recover 44-55% of total N, the combined, total N removal capabilities of solids and P screening with ammonia N stripping is approximately 65-85%.

### **Biological Conversion to Non-Reactive Nitrogen**

There are several methods for converting organic or ammonia N to non-reactive N. For each of these approaches, commercialized versions have been applied to large-scale municipal wastewater treatment facilities across the US and world (Eekert, 2012). In short, these processes are:

- *Conventional nitrification-denitrification*—This form of biological N removal involves two sequential steps, carried out in different reactors: nitrification followed by denitrification. During nitrification, ammonium oxidizers oxidize ammonium in wastewater to nitrite and then to nitrate. During denitrification, nitrate is converted to N<sub>2</sub> gas under anaerobic condition (Wiesmann, 1994). The first step of this process requires oxygen and the second step requires carbon. This makes this process the most expensive biological N removal process (Ahn, 2006) and difficult to use in conjunction with AD, as AD removes the needed carbon source.
- *Simultaneous nitrification-denitrification (SND)*—The oxidation of ammonium to N<sub>2</sub> gas can also be achieved in a single vessel. In SND, ammonium oxidizers and denitrifying bacteria are accommodated in one reactor with strict control of dissolved oxygen (Zhu et al., 2008). Typically, this process has slower ammonia and nitrate utilization rates as compared to two reactor designs because only a fraction of the total biomass is participating in either the nitrification or the denitrification steps.
- *Shortcut biological nitrogen removal (SBNR)*—In this process, ammonium is oxidized to nitrite by ammonium-oxidizing bacteria but not further to nitrate. Nitrite is reduced to N<sub>2</sub> gas by denitrifying bacteria under anaerobic conditions with an electron donor.

- *Anaerobic ammonium oxidation (Anammox)*—Anammox involves the oxidation of ammonia with nitrite as the electron acceptor to yield  $N_2$  gas. The organisms that carry out this reaction grow with carbon dioxide as the sole carbon source and use nitrite as the electron donor to produce cellular material (Vlaeminck et al., 2012). Anammox is typically used for wastewater with high concentrations of ammonia. Importantly, the system does not need organic carbon and thus can work well alongside AD.

**Case Study 6— Watson Dairy, Trenton FL (Solids Separation, Conventional Nitrification/De-nitrification with Polymer Clarification and Sludge Settling) (FPPC, 2007)**

Pilot demonstration of an integrated nitrification/de-nitrification system to dairy manure has been carried out on an 800 wet cow equivalent dairy (Figure 3.4). In this system, in order to maintain the necessary carbon for the process, AD is omitted. Fibrous solids are separated prior to treatment. The remaining liquid undergoes a semi-batch nitrification and de-nitrification process in dedicated basins utilizing some recycle of sludge for maintenance of bacterial populations. The effluent from the basin is clarified using polymers and then additional solids and P removal is accomplished in sludge drying basins.



Figure 3.4: Nitrification/De-nitrification system at Watson Dairy

Performance and costs for NR system as of fall 2007 were as follows:

- Within the liquid fraction, 88% and 67% reductions in total N and total P were achieved, respectively.
- Estimated operating costs from pilot data and scale-up were \$80-104  $cow^{-1} year^{-1}$ .
- Estimated capital costs from pilot data and scale-up assumptions were \$438-563  $cow^{-1}$ .
- Additional solids were being produced from the mechanical screening as well as the sludge drying, giving additional P and N removal if solids are exported off of the farm.

While considerable commercial interest in various N<sub>2</sub> gas conversion technologies exists within the larger municipal wastewater industry, less interest has been demonstrated by the farm sector, particularly dairies. One concern is the high cost of the semi-batch basins and required associated aeration. This is of particular concern given that the technology produces N<sub>2</sub> gas rather than a salable form of N. As with the aforementioned ammonia N stripping process, technology advancements are underway, which hold potential for reducing costs and applying the approach to farms and in combination with AD. For example, single reactor non-nitrification/de-nitrification systems can reduce capital and operating costs while also reducing the need for reactive carbon—opening up their potential use with AD.

While requiring further R&D to move from idea to reality, one intriguing concept is the use of a biological N<sub>2</sub> conversion technology with operation of a Haber-Bosch system to produce biologically based N fertilizers, using AD as a methane (energy) and hydrogen gas source. Further refinement and demonstration will be needed before it is clear whether this concept would be achievable within a farm-scale system, or whether it may only be appropriate within a larger scale wastewater treatment setting.

**Conclusions**

While combined N/P recovery technologies are not as developed as P recovery technologies, several of these strategies are being demonstrated or practiced at commercial scale. One important class, ammonia-N stripping, takes advantage of the fact that the AD process raises pH (though not as far as needed for N-stripping), provides excess thermal energy and increases the proportion of ammonia N. Various manifestations of ammonia-N stripping exist, with all approaches having made strides over the years in reducing chemical, electrical and thermal inputs, while maintaining effective N removal. Contact of the stripped free ammonia with acids allows for production of ammonia salt fertilizers, which could generate revenue to offset costs, though markets for these products are not yet developed.

Another class of approaches involves biological conversion of reactive forms of N within the manure (digested or undigested) to non-reactive N<sub>2</sub> gas. Specific processes within this class include nitrification-denitrification, partial nitrifications and Anammox. Current interest and deployment is active in larger municipal operations, but still limited within farm projects, although swine lagoons in particular have several demonstration projects. Figure 3.5 summarizes the current performance capabilities and cost structures of these two integrated systems.

Key Technology N & P Combined	Performance	Op Cost /cow/year	Capital Cost /cow	Scale
Integrated Ammonia Stripping	TN 65-85%, TP 85-90%	\$100-190	\$450-650	Commercial
Conversion to non Nr + Chemical P	TN 80-90%, TP 65-85%	\$80-180	\$425-575	Pilot

Figure 3.5: Performance and cost ranges for integrated ammonia N stripping and conversion to non-reactive N technologies

From a cost and performance perspective, the completed review shows that integrated systems that allow for recovery of value-added fibrous solids as well as effective removal of both P and N are

feasible and now emerging within the commercial setting. Performance and costs for the integrated systems are in the following general range:

*65-85% N and 75-90% P removal at roughly a cost of \$100-200 cow<sup>-1</sup> year<sup>-1</sup> in operating costs and \$400-600 cow<sup>-1</sup> for capital costs, while also separating a valued fibrous product and in some cases N/P fertilizer products.*

Notably costs, both capital and operating are considerable. Ongoing work on both these classes of technologies may clarify whether further improvements in performance, reductions in costs, or development of NR product markets will facilitate their adoption on dairies in the coming years.

## SALT RECOVERY AND CLEAN WATER

### CHAPTER FOUR

#### **Salts Extraction and Moving Towards Clean Water**

While the review has thus far focused on the recovery of P and N, several other wastewater treatment options relevant for dairy merit mention, in particular because of their ability to recover salts and move towards clean water. Within the U.S. these technologies are not yet being demonstrated or implemented at the commercial scale on farms. However, ongoing R&D has the potential to make these technologies relevant to the dairy industry in the coming years.

During N and P recovery, most of the salts remain dissolved within the wastewaters. This complicates land application of post-treatment wastewater, and also limits the opportunities for re-use of water. In order for salts to be recovered, more advanced membrane technologies would need to be incorporated within the systems already discussed. These membrane systems are designed to remove extremely small, suspended solids and dissolved solids such as salts. Importantly, they could also be used to remove ammonia N, so could be used in place of the N recovery technologies discussed in the previous chapter.

In general, membrane filtration removes particulate matter from water by forcing the water through a semi-permeable film (membrane) with a driving force (Mulder, 2000). The driving force can be a difference in pressure, concentration, temperature or electric potential. Most membrane processes are pressure-driven. Electricity is used to generate the pressure differential, and this means they could require a significant fraction of electricity generated by an associated AD system. The separation range of membrane processes is shown in Figure 4.1, with the more common classes briefly described below.

- *Microfiltration (MF)*—MF filters have a pore size that generally spans 0.1 micron to 1 micron. MF is a low-pressure process, which can separate large solids.
- *Ultrafiltration (UF)*—UF uses membranes with pore sizes in the range of 0.1 to 0.001 micron. Typically, UF membranes will remove high molecular-weight substances, colloidal materials, and organic and inorganic polymeric molecules. Neither MF nor UF can remove dissolved substances unless they are first adsorbed (with activated carbon) or coagulated (with alum or iron salts).
- *Reverse osmosis (RO)*—RO filters have a pore size around 0.0001 microns. After water passes through a RO filter, it is essentially pure water. In addition to removing all organic molecules and viruses, RO also removes most dissolved minerals and salts that are present in the water. RO also removes monovalent ions, which means that it desalinates the water.

RO is the class of membrane filtration system capable of removing the bulk of the salts and producing clean water. However, as previously mentioned, the high solids and heterogeneous nature of manure requires extensive sequential treatment in order for the entire process to be operational and not overwhelm systems from blinding. The important question facing technology developers is the extent and particular form this sequential treatment must take in order to be

successfully treat dairy manure (i.e. the specific sequence of primary, secondary screening followed by one or more membranes and/or RO).

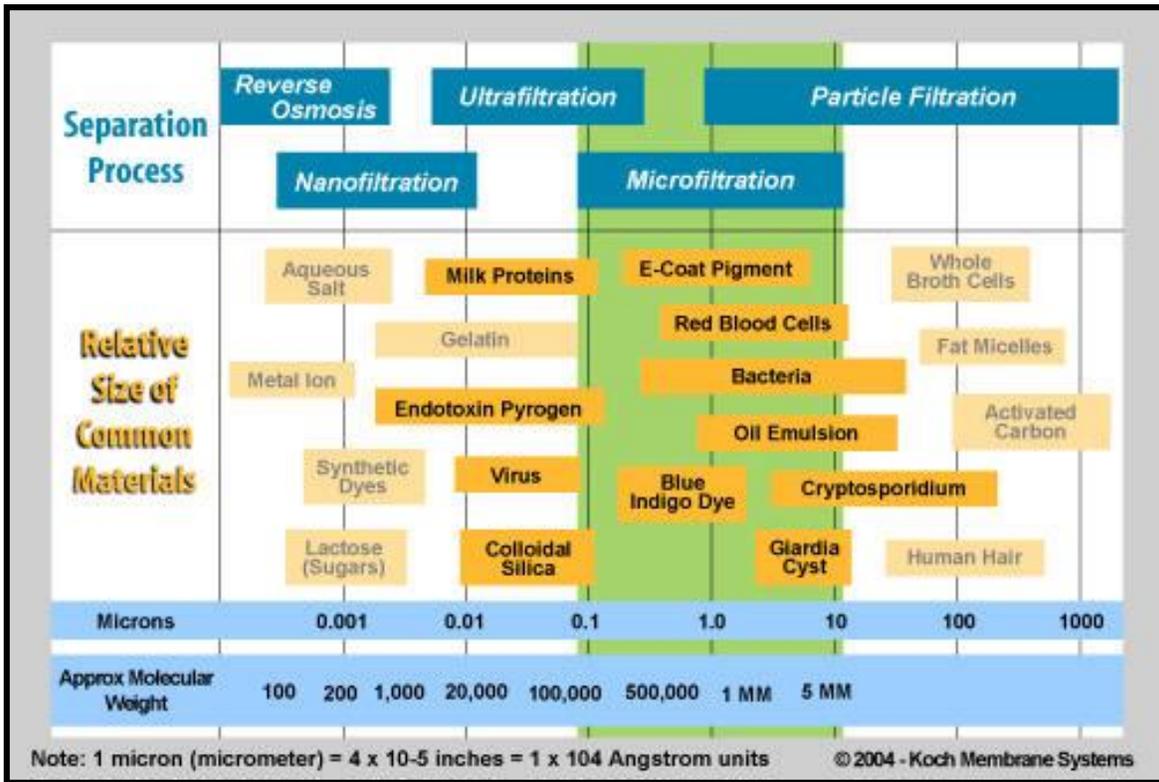


Figure 4.1: Schematic of various membrane approaches and their application (Koch membranes, [www.kochmembrane.com](http://www.kochmembrane.com))

Membrane systems produce both a final processed wastewater, and a reject stream. In order to keep costs down, it is important to be able to recycle or utilize reject streams. Ultimately, the reject stream from a final RO step is a concentrated salt solution (sodium, K, ammonium, etc.) with fertilizer revenue potential while the processed wastewater is useable for animal drinking water or stream discharge. Both of these potential uses could conceivably be used to generate both revenue (bio-based fertilizers) and valuable offsets (i.e. reduced water costs in dry areas).

While the developments in membrane technology during the last decades have significantly decreased membrane costs and energy requirements (Churchouse, 1999) they are still relatively expensive for farm-based wastewater treatment. A main limitation of membrane systems remains the aforementioned membrane fouling, requiring the use of sequential removal to achieve relatively low suspended solids levels prior to their use (Peter-Varbanets et al., 2009). Additionally, membrane systems tend to have high electrical costs due to the pressure-induced process, and periodic replacement of membranes also adds to costs.

### Case Study 7—Poultry Pilot (Sequential Solids Separation plus Reverse Osmosis for Clean Water)

Halpern (2013) discusses a membrane process and estimates costs using both piloted and calculated scaled-up assumptions. Following AD (Figure 4.2) fibrous solids are separated through primary screening and chemically assisted solids and P separation. Afterwards, ultrafiltration with membranes produces reject slurry containing the bulk of the larger organic N solids, and a liquid stream. The reject slurry can be used as a product or returned to AD for additional biogas production and organic N conversion. After appropriate pH adjustment, the processed liquid stream is sent to a RO operation, producing both processed clean water and a concentrated salt reject solution containing dissolved nutrients that can be further concentrated by a vacuum evaporator.

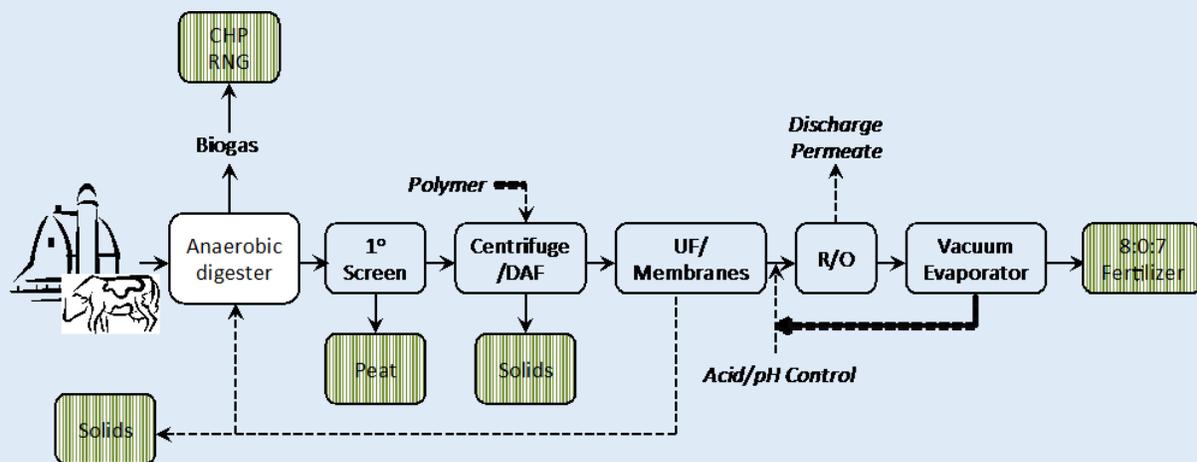


Figure 4.2: Clean water system and salts recovery

Estimated performance and costs for the system were as follows:

- Near complete removal of N, P, and K.
- Approximate operating costs were \$900-1,000 cow<sup>-1</sup> year<sup>-1</sup>, which is quite high due to the complex operation (conversion to cow numbers from flows treated).
- Approximate capital costs were not released, although also assumed to be quite high due to the complexity of the operation.
- Potential for increased biogas production, multiple product streams, the addressing of salt concerns, and potential sales to organic markets.
- Near clean water release from the process.

### Conclusion

Salts are an important environmental concern in many key dairy regions, particularly in California and other western states. To remove a large percentage of salts from the wastewater, AD integrated NR must involve RO membrane filtration, likely in combination with other membrane classes. Operation and capital costs are significantly higher than the cost increases identified for P and N recovery. While extremely costly and still in need of full-scale demonstration on farms, the outputs are considerable and not just from an environmental or regulatory viewpoint. Organically

certifiable fertilizer products as well as relatively clean water are both produced from such systems, offering the potential for high value sales and important offsets.

On the downside, energy requirements are so high that such projects potentially cease to be renewable energy projects but fertilizer/clean water projects, as a significant percentage of the produced renewable energy would be utilized within the processing, forcing project economics to rely on the sales and offsets from the NR process.

Current limited data suggests that membrane systems could achieve performance and costs in the following general range:

***85-95% N and 85-95% P removal at roughly a cost of \$900-1,000 cow<sup>-1</sup> year<sup>-1</sup> in operating costs and \$1,500-1,800 cow<sup>-1</sup> for capital costs, while also separating a valued fibrous product, concentrated nutrient/salt fertilizer and clean water.***

Despite the current high costs, the need for future process improvements, and the necessity for scaled demonstrations, clean-water approaches should be quite exciting to the dairy industry. They meet emerging salting concerns on valuable soils (Chang et al., 2005), while offering the potential for a future where dairies do not have to store or land-apply wastewater. If successful, these technologies would allow direct discharge of dairy water, or the production of animal drinking water, a valuable product in drought-prone dairy regions.

## NON-AD THERMAL NUTRIENT RECOVERY TECHNOLOGIES

### CHAPTER FIVE

#### Thermal Processes for Un-digested Manure Streams

While the focus of this review is primarily on NR technologies that work in concert with AD, there are notable NR processes that are appropriate for undigested manure. Thermal processes, which produce energy and/or fuels through thermal (heat-driven) processes, include combustion, pyrolysis/torrefaction, direct liquefaction, and gasification—each with their own processing steps, advantages and disadvantages, and products (Cantrell et al., 2008; Bridgwater, 2003; McKendry, 2002) (Figure 5.1). While these processes are generally of most interest for their ability to produce energy, non-volatile nutrients like P and K are also concentrated and dried into char or ash form. Meanwhile, volatiles such as some of the C and N leave as gases, some of which can be problematic to air quality (e.g., NO<sub>x</sub>) (Di Nola et al., 2009).

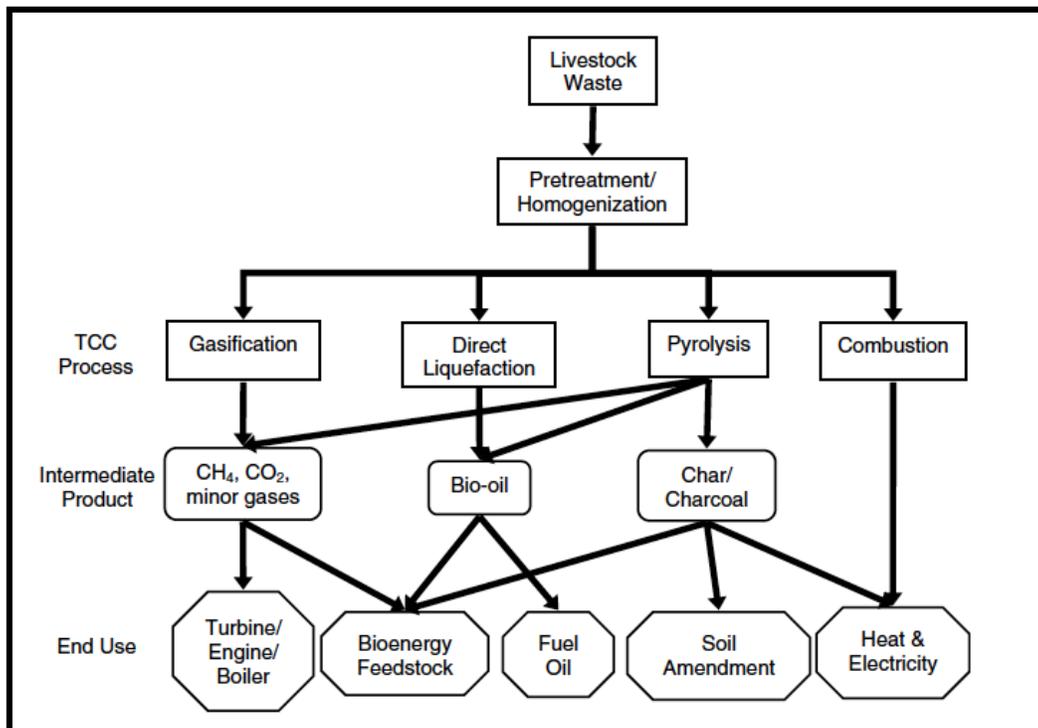


Figure 5.1: Schematic of thermal processing options for livestock waste (Cantrell et al., 2008)

Combustion has already been applied commercially across Europe and the US to treat high solids poultry litters (Font-Palma, 2012). These systems produce heat, generally used to produce combined heat and power (CHP). They also generate an ash byproduct concentrated in P, K, and metals, which research suggests has value as a soil amendment (Codling et al., 2002).

Pyrolysis and torrefaction are two other thermal technologies of potential interest. Pyrolysis and torrefaction convert lignocellulosic wastes into a number of products, including heat, bio-oil (an energy product) and biochar (a charcoal product that can be used for a variety of purposes). The

two processes operate at different temperatures, with torrefaction at lower temperatures, and focus on different final products. While considerable research has been conducted on pyrolysis and torrefaction of forestry and field residues, particularly for production of bio-oils (Boateng et al., 2007), notably less research has been conducted on pyrolysis of manures or biosolids (Domínguez et al., 2006; Lima and Marshall, 2005). This has been particularly true for slow pyrolysis and its production of heat and char—a process and products most likely more suitable in the near term for farm-based projects (Garcia-Perez, 2010; Cantrell et al., 2008).

Gasification of manures to generate carbon monoxide, hydrogen and carbon dioxide has also received considerable research attention. Several gasification approaches are currently moving through pilot demonstration and towards commercialization (Wu et al., 2012; Gordillo and Annamalai, 2010; Priyadarsan et al., 2004; Young and Pian, 2003).

**Case Study 8—IEUA Dairy, Chino, CA (Non-AD, centrifuge with polymer for production of solids that are gasified and converted to CHP and/or fuel) (FPPC, 2010)**

A pilot test was completed for a thermal gasification of manure solids at a 700 wet cow equivalent flush dairy treating mixed feedstocks. A centrifuge and polymer system is used to separate solids from the liquid waste stream, and solids are subsequently gasified for electricity or optionally treated through a Fischer-Tropsch system to liquid fuel.

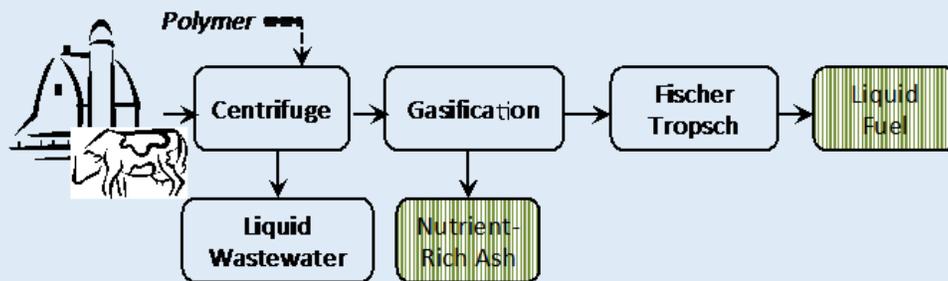


Figure 4.2: AWS thermal system

Performance and costs for the system were as follows as of fall 2010:

- Centrifuge/polymer treatment reduced liquid stream in N, P, and K by 67%, 90% and 40%, respectively.
- Most of P and K remained with ash, which was produced at 17 mass% of processed solids with 11% N content within produced gases.
- With a 21% BTU parasitic need for drying of 60-70% moisture solids, system could net produce 7.9 ft<sup>3</sup> syngas per dry pound solids.
- Approximate operating costs were \$60-80 cow<sup>-1</sup> year<sup>-1</sup>, which is quite high due to the complex operation (conversion to cow numbers from flows treated).
- Approximate capital costs were estimated at \$1,200-1,400 cow<sup>-1</sup>. This compared to typical AD costs of 1,500-2,000 cow<sup>-1</sup> plus additional 25-30% for nutrient recovery add-on.
- System proved viable on mixed feedstock, including very wet flush dairy manure.
- Greater electrical output than a typical anaerobic digester with biogas engine and generator, due to enhanced efficiency.

## Conclusion

Thermal processes offer intriguing business and sustainability capabilities. While historically focused on dry manures such as poultry litter, newer applications such as those described above use effective solids and P separation to successfully treat very dilute flush manures as well as a wide variety and even mixture of feedstock. Similar to the earlier discussed membrane technologies, thermal processes provide mechanisms to harness and collect salts within products that have value-added potential (ash, chars). Air quality concerns associated with thermal processes must be closely monitored, as a portion of the N can be released during processing. The performance and cost summaries are difficult to compare with other technologies, as these are not merely NR unit operations but combined thermal and NR systems. However, the included case study indicates that effective performance can be achieved at relatively modest operating costs and capital costs nearing or below AD, if additional liquid fuel components are not included. Nonetheless, further demonstration is required to solidify performance, economics and application to scale. Existing data suggests that performance and cost are within the following range:

*60-80% N and 80-90% P removal at roughly \$60-80 cow<sup>-1</sup> year<sup>-1</sup> in operating costs and \$1,200-1,400 cow<sup>-1</sup> for capital costs for the entire system, while also producing renewable energy (additional costs to produce liquid fuel).*

An intriguing option for both AD and thermal processes is the potential for moving beyond CHP systems and towards fuel production systems that make compressed natural gas (CNG), syngas to fuels, or other products. While they do increase complexity, these strategies are particularly appealing as received electrical prices continue to drop across the nation due in part to production of new found fossil-based natural gas (Coppedge et al., 2012). An additional area of exploration that is of potential technical importance but to date is still largely un-explored is the fusion of thermal and biological processes (e.g. pyrolysis/torrefaction and AD) within an integrated environment for process cost savings and production of multiple co-products (Garcia-Perez, 2012).

## CONCLUSION

### CHAPTER SIX

#### Performance and Cost Review

This review has focused on the status, performance and costs of various technical approaches to NR. In an attempt to distill these findings, Figure 6.1 highlights nine classes of NR approaches, and their current documented achievements with regard to performance and cost. To the authors' knowledge, these classes represent some of the more common emerging approaches that have achieved some level of scale and commercialization, though additional approaches are being pursued.

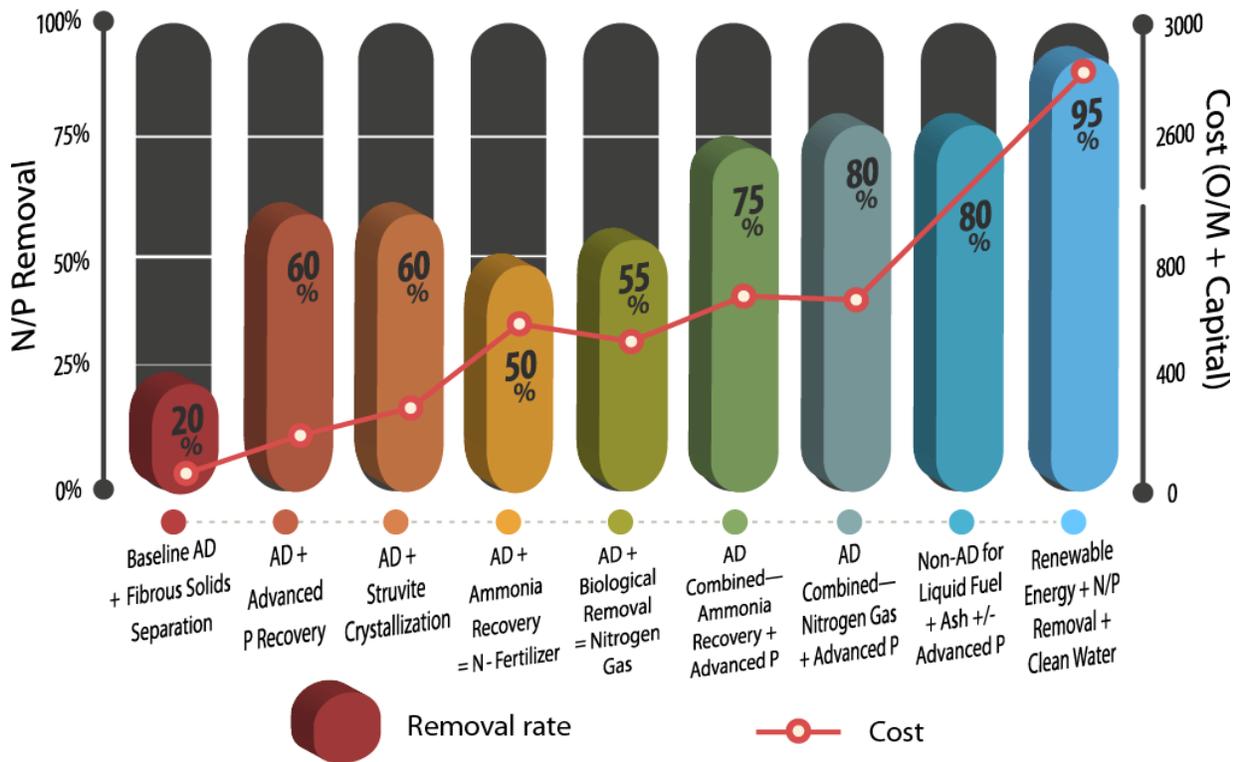


Figure 6.1: Nine general classes of NR approaches on dairies and their comparison in regard to performance (*left axis, bars*) and cost (*right axis, red dots; combined operating and capital*). Notice the break in cost axis scale, due to large cost of clean water systems. (Note: Unable to assign a cost value to thermal system due to inability to separate out NR unit from renewable energy production unit)

As can be seen from the figure, a variety of technological approaches are available, ranging from systems that remove limited fractions of nutrients at relatively low cost, to high performance systems capable of achieving near clean water at vastly increased costs. Note that these estimates of costs do not incorporate any assessment of the potential for cost recovery through sale of recovered nutrient products. Across the spectrum are three clear levels of performance and cost structure:

- Advanced solids and P recovery, typically using a polymer type approach.
- Solids and P recovery plus advanced N recovery.
- Solids and P recovery plus membrane treatment for salts recovery and clean water.

Between the first and second levels, total recovery of N and P goes from 50-60% to 70-80%, but with a three to four-fold increase in combined operating and capital costs. This cost increase implies that without cost decreases or improvements in N product markets, this technology is currently only applicable to areas with severe N or ammonia concerns. Accordingly, given current technologies, it is likely that incentives would need to be in place in order to induce adoption by dairy farms.

Between the second and third levels, total recovery of combined N/P increases to 95%, with additional recovery of salts plus clean water, but with an additional four to five fold increase in operating and capital costs.

If clean water and salt removal are not a priority, then an AD plus NR platform, via several different technical platforms is capable of:

*A combined N/P removal of approximately 50-80% at operating costs of \$50-200 cow<sup>-1</sup> year<sup>-1</sup> and capital costs of \$150-600 cow<sup>-1</sup>, while also separating a valued fibrous product and concentrated nutrient/salt fertilizer.*

If compared to AD operating and capital costs of \$12-24 cow<sup>-1</sup> year<sup>-1</sup> and \$1,500-2,000 cow<sup>-1</sup>, respectively (Andgar, 2013), these values represent a 3- to 11-fold increase in operating costs and 10-35% increase in capital costs for an integrated AD and NR system. Even at the lower end of the range, this increase in operating costs indicates that successful NR technologies most likely will require production of high-value products, emphasizing an industry need to solidify markets for these products.

### **Additional Comments**

In interpreting these summary cost estimates, it is important to remember that they were made based on the data provided in the case studies. They thus represent implementation of a technology in a specific situation, with a specific type of manure. Dairy manure is collected and stored in three distinct forms: flush (1-2% TS), scrape (3-10% TS) and dry lot (15-25% TS) (Frear et al., 2011b). Because each of these wastes has very different characteristics, NR processes that work well with one type of manure will not necessarily work well for others. As an example, a struvite crystallizer is often operated on manure wastes that are very dilute so as to not interfere with the crystallizing process. When it is applied to more concentrated scrape or dry lot manure, pre-treatment is required. This consideration is potentially applicable to many other technical approaches and has significant cost implications. It also means that over time, a number of different technologies will likely become commercially viable for different forms of manure or for other specific situations.

In addition to the performance and cost considerations summarized by Figure 6.1, there are many other important factors that will be important in developing the path forward for the dairy industry with respect to NR. For example, form and function of recovered NR products was briefly

indicated in this review, but was not discussed in depth. Form and function of recovered products are intimately linked to market value, and therefore to the potential for revenues that could offset the costs of NR technologies. As one case in point, ammonia N stripping can produce ammonium sulfate, usually in a solution. Because it is a liquid solution, storage and transportation are relatively expensive, negatively impacting total project economics. In addition, the dilute nature of the nutrients, and the N to S ratio (approximately 1:1), are both less than ideal for integration with existing methods for fertilizer delivery to grain crops. On the other hand, struvite crystals have a dry, pelletized form and a nutrient formulation that acts as a slow-release fertilizer. Both of these features make struvite easy to incorporate with existing fertilization methods for a variety of cropping systems. Ongoing development of dairy NR technologies should therefore aim to develop products that fit seamlessly into existing fertilizer delivery systems while providing a form that meets transportation and market needs, at price points that are competitive with synthetic fertilizers. Development within such a competitive environment requires not only a sustained effort, but also national and capable partners, a lesson that has been identified during development of a market for high-value peat moss replacement from AD. Early lessons from first adopters of NR technology point to similar barriers in regard to sales of biologically based fertilizers (DVO, 2013).

Attention also needs to be paid to the remaining, treated wastewater, if produced during NR. While concerns exist with the current application of untreated dairy wastewaters to agricultural fields, they do have a nutrient content, which is somewhat parallel to plant needs. In some cases this nutrient balance is negatively impacted after NR treatment, for example, when the resulting wastewater has high salt content and low amounts of N and P. Thus it is important to view the entire system with an agronomic eye, educating project developers and crop producers on how best to partition and utilize the various nutrient streams for cost effective and agronomic use.

A look at the bigger picture, using analytical tools such as life cycle analysis, is also important. For example, N recovery approaches can generate outputs ranging from ammonium sulfate solution to non-reactive N gas released to the atmosphere. Comparison of the performance capabilities and costs of these two approaches are one point of comparison, but a more in-depth comparison may also include consideration of resource management and sustainability, including features such as energy balance, greenhouse gases, and eco-system benefits that were not possible within the scope of this review. As the NR field matures, it is imperative that dairy industry leaders and project developers keep a keen eye on total system inputs and outputs and promote discussions of their overall impact on the sustainability of the dairy industry, surrounding communities, and the environment.

## **Conclusion**

Emerging NR technologies have been implemented at the commercial scale on several dairy farms in the US, and have proven capabilities at cost structures that may support more widespread adoption in the future. However, these technologies need to undergo additional development, both technical and product markets, before they can fully deliver on their promise. Current NR technologies range from those in the early stages of commercial adoption, to ideas that still need significant development, adaptation and scaled testing before they are ready for implementation across the industry.

As the NR sector develops, it will be important for industry to continue to keep abreast of, and support, these efforts. In particular, dedicated pilot or full-scale demonstrations will be important to testing how these technologies work in commercial farm settings. Ongoing development is also needed to reduce costs, enhance performance, and generate sustainable and salable nutrient products. In addition to focusing on improvements in existing promising NR technologies, it will be important for the industry to support the development of entirely new NR strategies. Many of the reviewed NR technologies were adapted from technologies designed for the municipal wastewater industry to treat either their very dilute wastewaters or their digested and pressed biosolids. Dairy and other animal manures are quite different in form and structure than these materials, and thus there is a need for investigation of completely new approaches not previously considered or researched by the municipal wastewater industry.

Despite the remaining challenges, significant progress has been made in recent years in making these technologies a reality. With development, these technologies may become an essential tool for enhancing the economic and environmental sustainability of the dairy industry. This vision, though, will not only require researchers, producers, and entrepreneurs, but also support from government and the larger industry. Within this context, it is hoped that this review can help focus the current and future efforts of project developers, industry, and government agencies. This information can also serve as a baseline to the dairy industry as manure management transitions from being an assumed liability to a resource capable of sustainable economics as well as environmental sustainability—as suggested by the ICUSD business model.

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