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Review

# Livestock waste-to-bioenergy generation opportunities

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ABSTRACT

The use of biological and thermochemical conversion (TCC) technologies in livestock waste-to-bioenergy treatments can provide livestock operators with multiple value-added, renewable energy products. These products can meet heating and power needs or serve as transportation fuels. The primary objective of this work is to present established and emerging energy conversion opportunities that can transform the treatment of livestock waste from a liability to a profit center. While biological production of methanol and hydrogen are in early research stages, anaerobic digestion is an established method of generating between 0.1 to 1.3 $m^3\ m^{-3}\ d^{-1}$ of methane-rich biogas. The TCC processes of pyrolysis, direct liquefaction, and gasification can convert waste into gaseous fuels, combustible oils, and charcoal. Integration of biological and thermal-based conversion technologies in a farm-scale hybrid design by combining an algal $CO_2$-fixation treatment requiring less than 27,000 $m^2$ of treatment area with the energy recovery component of wet gasification can drastically reduce $CO_2$ emissions and efficiently recycle nutrients. These designs have the potential to make future large scale confined animal feeding operations sustainable and environmentally benign while generating on-farm renewable energy.

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## 1. Introduction

With the massive consolidation of confined animal feeding operations (CAFOs) over the past decades, there is a need for new, state-of-the-art waste management systems that make animal operations economically viable and environmentally benign. In addition to the potential environmental threat traditional waste management systems pose (McNab et al., 2007; Stone et al., 1998; Szogi et al., 2006), there are rising energy prices and concerns over petroleum supplies. Thus, there is expanded interest in on-site biofuel production. Bringing biofuel production to the farm-scale provides an opportunity for the agricultural sector to reduce their reliance on imported fossil fuels while improving the soil, water, and air quality (Muller et al., 2007). Currently, animal production annually provides 35 million dry tons of sustainable biomass/manure feedstock that comprises 18% of the total available sustainable biomass from the US agricultural lands (Perlack et al., 2005; Ro et al., 2007). The use of animal manure and other organic-based waste products as bioenergy feedstocks for waste-to-bioenergy conversion processes would allow farmers to take advantage of new markets for traditional waste products. In effect, livestock waste-to-bioenergy treatments have the potential to convert the treatment of livestock waste from a liability or cost component into a profit center that can: (1) generate annual revenues; (2) moderate the impacts of commodity prices; and (3) diversify farm income.

Two basic platforms exist for converting organic biomass – the biochemical (biological) and thermochemical platforms (Fig. 1). Within these platforms are treatment processes that can be designed to solve odor problems, reduce volume, recover inherent nutrients, decrease pollution potential, as well as recover energy from the manure. As discussed by McKendry, 2002a,b, when selecting a conversion process, economics and both the available feedstock's quantity and characteristics are important factors. In most instances, the desired energy form of the final end-product is the overriding factor. The end-products from each conversion process can be placed into three main groups: heat and power generation; transportation fuels; and chemical intermediates (Cantrell et al., 2007; McKendry, 2002a,b).

Biochemical conversion processes are defined by the US Department of Energy as the use of living organisms or their products to convert organic material to fuels (USDOE, 2002). These conversion processes can be realized by both anaerobic and photosynthetic microorganisms to produce gaseous and liquid fuels. Many times, the solid/slurry-phase residual by-product from these processes is nutrient-rich and can serve as an alternative fertilizer. The thermochemical platform is a physical conversion of biomass using high temperatures to break the bonds of organic matter and reform these intermediates into synthesis gas, hydrocarbon fuels, and/or a charcoal residual (Bridgwater, 2003; Cantrell et al., 2007; McKendry, 2002a,b). While the biological-based conversion processes require an extended amount of reaction time (days, weeks or even

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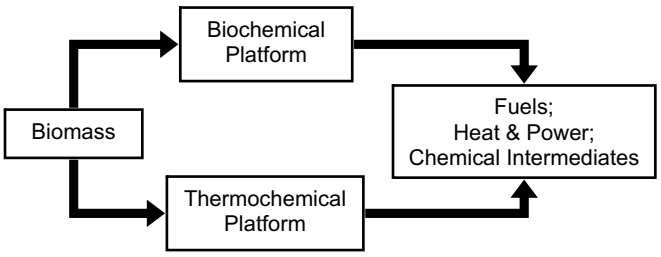


**Fig. 1.** Conversion platforms for livestock waste-to-bioenergy conversion.

months), thermochemical conversion processes (TCC) can quickly (seconds or minutes) yield multiple complex end-products (Bridgwater, 2006). Consequently, the short residence time requirement of TCC drastically reduces the footprint requirements. Thermochemical conversion processes include combustion, pyrolysis, gasification, and liquefaction. Combustion converts manure's energy into heat; however, this method does not provide a way to store the energy until it is needed. Additionally, the ash product from combustion has yet to find a suitable recycle use. As such, pyrolysis and gasification have received the most attention because they have more versatility.

In this paper, we reviewed currently available biological and thermochemical conversion technologies that can be applied to produce bioenergy while treating livestock wastes. We also suggested a biological–thermal hybrid system concept that appears to treat livestock wastes while at the same time reduce greenhouse gas emissions and produce bioenergy.

## 2. Biological conversion

This section intends to examine several biochemical conversion processes that are either established or emerging technologies. Waste-to-bioenergy technologies involving biological treatment of livestock waste have been dominated by anaerobic digestion with full-scale production of combustible biogas. Less known and reported at laboratory-scale has been the use of photobiologic microorganisms like algae and fermentative processes for production of bio-hydrogen. Even less known is the biological production of methanol through the enzymatic conversion of carbon dioxide and methane; both of these gases are produced by anaerobic digestion. These research efforts are in the early stages of development and implementation.

### *2.1. Anaerobic digestion*

Anaerobic digestion has seen a resurgence of interest due to its potential for manure stabilization, sludge reduction, odor control, and energy production. According to the AgSTAR Digest Winter 2006 Issue (USEPA, 2006), installation of anaerobic digesters between 2004 and 2006 has more than doubled the total operating units. Since 2006, the AgSTAR Guide to Operational Systems reports 100 digesters operating at steady state with 22 of those coming on-line (USEPA, 2007).

Anaerobic digestion (AD) involves the breakdown of complex organic wastes and produces biogas chiefly methane ($CH_4$) and carbon dioxide ($CO_2$) by a community of anaerobic microorganisms. The AD process occurs in three main stages – hydrolysis, fermentation, and methanogenesis. During hydrolysis the complex compounds are broken down into soluble components. Thus, they are readily available for fermentative bacteria (acidogenic and acetogenic) to convert into alcohols, acetic acid, other volatile fatty acids (VFAs), and off-gas containing $H_2$ and $CO_2$. These intermediate products are metabolized into primarily $CH_4$ (60–70%), $CO_2$ (30–40%) and other associated gases by methanogens. This methanogenic biogas production rate is sensitive to changes in influent materials, pH, temperature, organic loading rate (OLR), and hydraulic retention time (HRT). As such, these variables must be controlled in order to maximize methanogenic biogas production.

For instance, with methanogens being pH sensitive, and gross VFA production reducing the AD's pH, when the pH falls below 6.3, the likely result is methanogenic population destruction (Chen et al., 2002). Thus, for effective anaerobic digestion operation for biogas production, a balance among the acidogens/acetogens and methanogens is crucial. Temperature also affects the metabolic activities of the microorganisms that, in turn, affect the rate of digestion and methane production. Methane production can occur at temperatures as low as 4 °C with dramatic increases seen within the temperature range of 4–25 °C (Safley and Westerman, 1992b; Umetsu et al., 2005). There are three common temperature ranges for anaerobic digestion: (1) low temperature ranges (<20 °C) is referred to as psychrophilic (Kashyap et al., 2003; Safley and Westerman, 1992b); (2) digestion temperatures within 20–45 °C is mesophilic; and (3) a temperature range of 45–60 °C is termed thermophilic.

The organic loading rate (OLR) is defined as the amount of volatile solids (VS) or chemical oxygen demanding (COD) components fed per day per unit digester volume, and higher loading rates can reduce both the digester's size and consequently, the capital cost. However, enough time should be permitted for the microflora to break down the organic material and convert it to gas. Thus, the need arises to control the hydraulic retention time (HRT). A digester's HRT-value is the average time the liquid is held in the digestion process and is calculated as the ratio of the digester volume to the effluent's volumetric flow rate. If manure is passing through a digester too quickly, then the microorganisms do not proliferate fast enough; leading to digestion failure.

Even though anaerobic digestion has high standards of maintenance and management along with high initial capital investment, a properly functioning anaerobic digester can provide numerous benefits at farm, local, and environmental levels. These benefits include: (1) odor control; (2) reduction of nuisance gas emissions; (3) potential pathogen kill; (4) reduction of wastewater strength (oxygen demand); (5) conversion of organic nitrogen into plant available ammonia nitrogen; (6) preservation of plant nutrients (e.g., N, P, K) for use as a high quality fertilizer; and (7) production of a renewable energy source-biogas (Beddoes et al., 2007; Kashyap et al., 2003; Wilkie et al., 2004). The digestate can be sent to a solid–liquid separator with the liquid portion being utilized as a fertilizer. The separated solids can be composted to both stabilize them and convert them into a more useful product (Fig. 2). The biogas can be used to meet on-farm heating needs via combustion in a boiler, heater, or engine. It can also be used to meet electrical demands with the excess electricity having the potential to be sold to a local utility company. Unfortunately, in most instances of full-scale anaerobic digestion, the energy savings and potential revenue (i.e., current selling price of electricity) are not enough to provide a positive cash-flow. Thus, producers often explore the use of cost-share, grant monies, or other subsidiary support to off-set a portion of the capital and installation costs (Beddoes et al., 2007; Lazarus and Rudstrom, 2007). Consequently, lab-scale, AD studies have been numerous. Yet, there are limited reports on full-scale AD performance related to biogas generation systems. This is likely to change rapidly with green energy requirements, oil and gas prices, and carbon credits. Carbon credits may have significant economic impact on AD profitability for the coming decades as the US and other global economies use emerging greenhouse gas (GHG) offset markets (Hasselknippe, 2003; Johnson and Heinen, 2004; Schneider and McCarl, 2006). Additional income from carbon credits has already been reported for two US

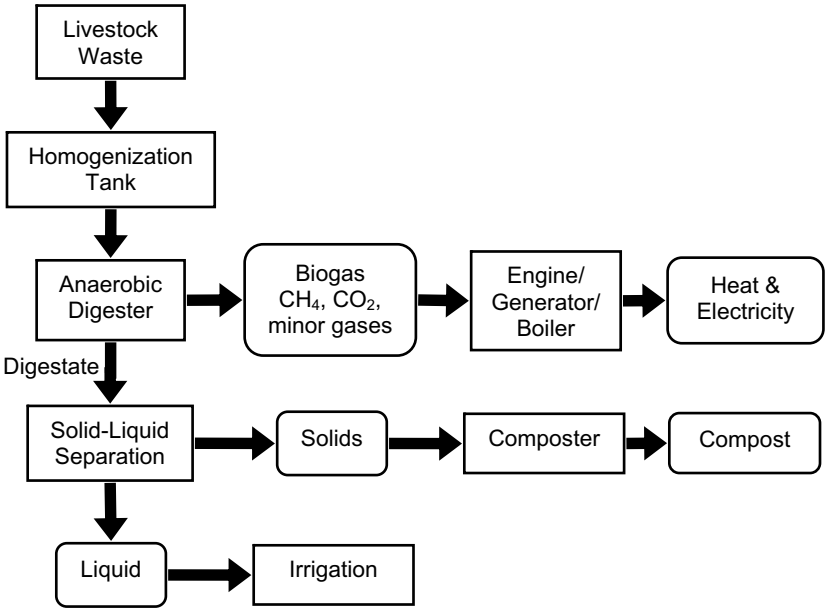


**Fig. 2.** Flow diagram of anaerobic digestion process and end points of products.

dairy farms using anaerobic digestion that prevented the release of over 720 tons of $CH_4$ (USEPA, 2006).

*2.1.1. Covered lagoon digesters*

Open-air, anaerobic lagoons are the most trouble-free, low maintenance systems available for swine and dairy wastewater treatment, and this form of waste treatment has been utilized by a large number of these animal production systems to successfully store and process livestock manure (CAST, 1996; Humenik et al., 1981). Unfortunately, in maintaining these lagoons, sludge storage management is often underestimated leading to a reduced anaerobic treatment volume and incomplete digestion. Open-air design also results in emission of GHGs such as $CO_2$, $CH_4$, and other odorous intermediate products (like hydrogen sulfides, ammonia, phenols, etc.). Reduction of GHGs and air pollutants brought on the need to cover lagoons and harvest the biogas through the use of a floating, impermeable cover (DeSutter and Ham, 2005; Safley and Westerman, 1992a; Safley and Westerman, 1992b).

Anaerobic lagoons operated in this manner are termed covered lagoon digesters (CLD). Today, CLD are typically an earthen structure with the gas covers constructed out of geosynthetic materials – high-density polyethylene (HDPE), polypropelyene (PP), reinforced polyethylene (RPE), etc. The biogas is collected and moved through pipes to their intended use. This gas can be used to fuel both boilers and engines for electricity generation, cleaned and injected into the natural gas pipeline grid, or simply flared. Along with being economical for animal production facilities using hydraulic flushing systems, CLDs can handle a wide range of manure characteristics. Excessive amounts of water from these flushing systems dilute the manure and reduce the OLR between 0.05 and 0.2 kg COD $m^{-3}$ $d^{-1}$. This low concentrated waste stream remains in the CLD anywhere from 60 days to a year (Beddoes et al., 2007). Adding to the disadvantage of an extended HRT, are solid settling issues. Solid removal by CLD occurs both because of settling of the nondegraded matter to form sludge and microbial degradation of the organic matter into biogas. These CLD systems are generally not heated and the digestion temperature follows ambient, seasonal temperatures. Consequently, methane productivity varies seasonally. Unfortunately, the large land area requirement, continual cover maintenance, and groundwater contamination potential are deterrents for establishing CLD common use (Funk et al., 2004; McNab et al., 2007).

While reports on key variables such as loading rate, digester temperatures, and effluent VS and COD concentrations are lacking, a summary of early studies of several swine and dairy operations using CLDs provided indicated swine producers loaded CLDs with 0.04–0.36 kg VS $m^{-3}$ $d^{-1}$ for biogas production per treatment volume ranging between 0.03 and 0.15 $m^3$ $m^{-3}$ $d^{-1}$ (Chastain and Linvill, 1999). Dairy producers loaded CLDs with 0.02–0.12 kg VS $m^{-3}$ $d^{-1}$ to generate biogas at a rate between 0.03 and 0.23 $m^3$ $m^{-3}$ $d^{-1}$ (Chastain and Linvill, 1999). In a detailed study by Safley and Westerman, 1992a, a 2060 $m^3$ CLD with a flexible ethylene interpolymer alloy treating flushed dairy manure had an average OLR of 0.12 kg VS $m^{-3}$ $d^{-1}$. This CLD reduced the average influent concentrations of 8.13 kg $m^{-3}$ of VS and 12.8 kg $m^{-3}$ of COD by roughly 70%. In doing so, it generated 0.061 $m^3$ $m^{-3}$ $d^{-1}$ of biogas with an average concentration of 68.9% $CH_4$. The biogas was used as a fuel in a natural gas boiler to produce hot water. The $CH_4$ yield over the two-year, test period was 0.39 $m^3$ $CH_4$ per kg VS added or 0.53 $m^3$ $CH_4$ per kg VS destroyed. When compared to systems with no additional thermal input, heating the settled sludge during the cold months to an average temperature of 12.5 °C increased $CH_4$ production by 33% from 0.033 to 0.043 $m^3$ $m^{-3}$ $d^{-1}$.

More recently at a 4000-sow swine farm in North Carolina, a 24,480 $m^3$, ambient temperature CLD installed with a HDPE cover and a mean OLR of 0.07 kg VS $m^{-3}$ $d^{-1}$ and 3.80 kg COD $m^{-3}$ $d^{-1}$ reduced the concentration of VS and COD in the effluent by 88.0% and 92.6%, respectively (Cheng et al., 2004). Despite biogas production being seasonal varying from 0.0194 $m^3$ $m^{-3}$ $d^{-1}$ in the winter to 0.0388 $m^3$ $m^{-3}$ $d^{-1}$ during the summer, $CH_4$-composition remained consistent at 63.7%. The biogas was utilized on-farm to generate electricity with waste heat being recovered to heat farrow houses.

*2.1.2. Complete-mixed*

Biogas production performance of AD is primarily affected by the retention time and the degree of contact between the substrate particles and viable bacterial population (Karim et al., 2005). While mixing the contents adds to the capital and operational costs of digesters, it helps to transfer heat and keep the

solids in suspension. This in turn creates a more homogeneous manure/bacteria mixture (Karim et al., 2005).

Completely mixed digestion is often used in heated, aboveground or belowground tanks to treat dairy or swine manure with a 3% to 10% TS concentration (Beddoes et al., 2007). From the case studies presented by Lusk (1998), mixing a digester's content can drastically decrease the HRT from months to between 10 and 20 days. This mixing also significantly improves biogas production to between 1.0 and 1.45 $m^3\ m^{-3}\ d^{-1}$. In most instances, when compared to CLD biogas production, the increase is over 10-fold (Fig. 3).

While mixing the contents of a digester improves biogas production, the co-digestion with lignocellulosic crops and food waste can increase production even more. Full-scale, co-digestion of swine manure with maize, rye, and wheat crop components destroyed roughly 83% of VS and had a biogas productivity of 1.50 $m^3\ m^{-3}\ d^{-1}$ (Lindorfer et al., 2007). When the OLR doubled from 2.11 to 4.25 kg VS $m^{-3}\ d^{-1}$, biogas productivity nearly doubled to 2.91 $m^3\ m^{-3}\ d^{-1}$ (Lindorfer et al., 2007). When compared to the mixed digesters reported by Lusk (1998), co-digestion of manure and food waste can more than triple the biogas productivity. This is likely due to more digestible forms of VS available to AD organisms (Wright et al., 2004). Another example is a completely mixed digester with an HRT of 21 days and a flexible, impermeable cover that was installed on a 675 milking cow farm to digest a mixture of manure (TS = 12.5 wt%) and food waste. This food waste consisted of grape, milk, and fish stick wastes from processing plants. While reducing VS and COD by roughly 67%, this digester produced 3.25 $m^3$ of biogas daily per treatment volume ($m^3$) at 70% methane (Wright et al., 2004).

### 2.1.3. Fixed film

Anaerobic treatment with fixed-film technology is capable of recovering waste's energy with much shorter residence times on the order of one to six days. This technology helps to off-set the unfavorable economics prevalent when treating dilute and low-strength animal waste streams. This fixed-film digestion uses a tank packed with an inert media for which the anaerobic microorganisms can attach and grow to form a biofilm. This biofilm remains in contact with the substrate as it flows past in either an upflow or downflow configuration. Due to the organisms immobilizing themselves on this media, potential washout is prevented, microbial biomass concentration increases, and consequently, biomass retention becomes independent of HRT. This gives the fixed-film digestion the advantages of higher conversion efficiency, shorter HRT, and smaller footprint (Powers et al., 1997; Wilkie et al., 2004).

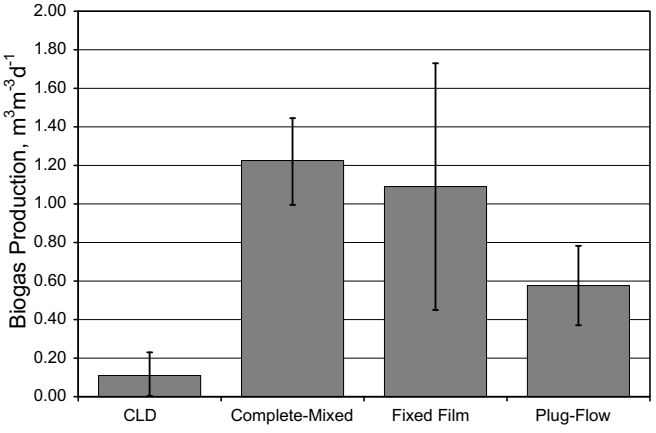


**Fig. 3.** Biogas production from four different types of anaerobic digester designs. Error bars represent range of reported values.

Fixed-film digesters treat manure with a medium to high OLR between 5 and 10 kg COD $m^{-3}\ d^{-1}$ and require a low influent TS content, typically less than 1%. They are used in conjunction with physical separation of both suspended and bulk fibrous solids. Removal of these components helps to avoid clogging and impairing biofilm activity. Separation tends to remove the non-degradable portion of VS leaving the more degradable VS and COD fractions in the wastewater for biological conversion into biogas (Wilkie, 2003). Of the remaining VS and COD fractions, fixed-film anaerobic digestion has been reported to reduce VS by 40% and COD by 48% (Wilkie et al., 2004). A Florida-based, demonstration-scale, fixed-film digester treating flushed dairy manure waste, with VS and COD levels of 2210 and 3530 kg $m^{-3}$, respectively, operates at ambient temperature (27 °C) with an HRT-value of three to five days with a stable biogas production of 0.45 $m^3\ m^{-3}\ d^{-1}$ with an 80% $CH_4$ content (Wilkie, 2003; Wilkie et al., 2004). This biogas is currently being used on-site to fuel water heaters. Largely due to its maintained 37 °C digester temperature, a smaller, fixed-film digester on a 100-cow, tie stall dairy in New York treating 6.1 $m^3\ d^{-1}$ of separated manure with a TS of 5.1 wt% was reported to generate biogas at a rate of 1.73 $m^3\ m^{-3}\ d^{-1}$ (Wright et al., 2004).

### 2.1.4. Plug-flow

Accounting for 51% of all installed AD designs (USEPA, 2007), plug-flow digesters have the highest success rate (Lusk, 1998). These plug-flow anaerobic digesters prevent GHG emissions by capturing biogas under an expandable top. The biogas is produced from belowground, rectangular digesters heated by hot water running through pipes inside the digester to maintain mesophilic temperatures. Plug-flow digesters are unmixed systems operating semi-continuously by regularly receiving a new, untreated "plug" of manure while ejecting digested waste out the other digester end. The digesters have a normal HRT between 20 and 30 days. In order to avoid mixing and separation of the manure, plug-flow designs are appropriate for manure with a high solid content in the range of 11–14%TS. Accordingly, these digesters have an OLR between 1 and 6 kg COD $m^{-3}\ d^{-1}$ (Beddoes et al., 2007). Plug-flow designs are incompatible with manure containing sand and other wood-based bedding materials (Beddoes et al., 2007). As such, prior to digestion, there is a need for removal of these materials. As reported by Wright et al. (2004), plug-flow digesters on dairy operations with HRT-value ranging from 21 to 40 days removed a quarter of the total solids and a third of the influent volatile solids. These authors report that daily, farm-scale biogas production ranged between 0.367 to 0.786 $m^3\ m^{-3}\ d^{-1}$. This biogas had an average $CH_4$ content of 64%. Most product biogas was sent to engine generator systems for electricity production with one dairy generating 0.786 $m^3\ m^{-3}\ d^{-1}$ of biogas producing an average of 4.23 GJ of electricity per 1000 $m^3$ of biogas utilized (Martin and Roos, 2007; Wright et al., 2004).

## 2.2. Bio-hydrogen production

Several experts have predicted that $H_2$ will replace fossil fuels as the next generation of energy sources (Hoffmann, 2001; Rocha et al., 2001). This is, in part, based on the green nature of $H_2$ combustion, which results in water formation. Unlike the mature technology of methanogenesis via anaerobic digestion, biological production of hydrogen (bio-$H_2$) is a relatively new area of scientific research that can currently be divided into three primary processes: (1) photosynthetically by algae in a two-stage photosynthesis and $H_2$ production process, (2) photobiologically by photo-fermentative bacteria, and (3) fermentatively using anaerobic fermentative bacteria in a process commonly referred to as "dark fermentation."

While implementation of bio-$H_2$ production is still in its infancy, a variety of reviews examined the bio-$H_2$ production from waste materials (Angenent et al., 2004; Kapdan and Kargi, 2006; Li and Fang, 2007). These reviews examined over 100 cases of fermentative hydrogen production, and the most productive systems were those which were typically rich in carbohydrates. These reviews also highlight that currently, untreated animal waste is not one of the preferable feedstocks. One review suggested that biohydrogen production be utilized as a pre-treatment step with the resultant effluent being utilized as a feedstock for a value-added product (Angenent et al., 2004). All reviews come to the conclusion that with continual research, development, and technological advancements, these technologies will eventually mature and become reliable $H_2$ sources.

*2.2.1. Algal photosynthetic $H_2$ production*

Photobiological hydrogen production is well understood. During photosynthesis, algae convert water molecules into hydrogen ions ($H^+$) and oxygen; these hydrogen ions are subsequently converted into $H_2$ by hydrogenase enzymes. Because hydrogenase activity is repressed by oxygen, algal cultures for bio-$H_2$ production must be subjected to anaerobic conditions (Ghirardi et al., 2000; Melis et al., 2000). Providing an anaerobic environment results in a "two-stage photosynthesis and $H_2$ production" process. In the first aerobic stage, algae are grown photosynthetically. During the second anaerobic stage the algae are deprived of sulfur thereby stimulating $H_2$ production (Melis and Happe, 2001). Melis and Happe indicate that the theoretical maximum of $H_2$ production by green algae treated via this method is ~80 kg $H_2$ $acre^{-1}$ $d^{-1}$ (Melis and Happe, 2001). Ghirardi et al. (2000) report $H_2$ accumulations of ~25 ml $H_2$ $h^{-1}$ for the first 25–35 h using sulfur deprivation, an equivalent of 7 mmol $H_2$ (mol chlorophyll)$^{-1}$ $s^{-1}$. In order to easily cycle between growth and $H_2$ productivity modes, Hahn et al. (2007) developed a two-stage process bioreactor with immobilized algal cells. While there are currently technical limitations to the photosynthetic bio-$H_2$ processes, they represent future avenues for bio-$H_2$ sources given proper research and development (Benemann, 1997; Levin et al., 2004).

*2.2.2. Photo-fermentative $H_2$ production*

For photo-fermentation, a number of bacteria are capable of converting organic acids such as acetic, butyric, and lactic acid into $H_2$ and $CO_2$. This conversion is done in the presence of light and under anaerobic conditions. A number of studies have been performed using a variety of bacteria and different organic acids to evaluate hydrogen production rates and yields (Barbosa et al., 2001; Fang et al., 2005; He et al., 2005; Koku et al., 2002; Maeda et al., 2003; Oh et al., 2004). While some photo-fermentative systems have been shown to produce more $H_2$ than their dark fermentation counterparts (Koku et al., 2003; Oh et al., 2004), their production is linked directly to the illumination conditions. Unless cost-effective solid–liquid separation methods can be utilized, photo-fermentative systems are at a major disadvantage for livestock waste $H_2$ production making the only viable option dark fermentation.

*2.2.3. Dark fermentation*

Dark fermentation utilizes principles similar to anaerobic digestion. However, methanogens, which would otherwise consume $H_2$ during the $CH_4$ formation, are inhibited. This methane inhibition can be undertaken in a variety of ways (Kraemer and Bagley, 2007) including: (1) heat treatment for selection of hydrogen-producing bacteria (Lay et al., 1999; Mu et al., 2007); (2) changes of the reactor pH to that outside of the optimal methanogenisis range (below 6.3 or above 7.8) (Chen et al., 2002); (3) forced aeration of the sludge (Ueno et al., 1995; Ueno et al., 1996); and (4) chemical addition such as 2-bromoethanesulfonate (BES) (Wang et al., 2003), acetylene (Sparling et al., 1997; Sprott et al., 1982), or chloroform (Liang et al., 2002). Another option for bio-$H_2$ production is to carefully control the digestion process such that both hydrogen and methane can be produced. This has been accomplished and demonstrated with two-stage reactors (Kyazze et al., 2007; Ueno et al., 2007; Zhu et al., 2007).

Laboratory-scale, dark fermentation has been shown to produce bio-$H_2$ from filtered municipal waste (Wang et al., 2003). At mesophilic temperatures, the fermentation of the filtrate was able to produce between 5 and 15 mg $H_2$ $g^{-1}$ COD with peak production between 16 and 30 h. The authors also reported utilizing the separated biosolids to produce methane; therefore, it appears feasible that solid separation followed by pre-treatment of the filtrate to reduce ammonia could provide an influent that would be conducive to bio-$H_2$ production.

With either mode of fermentative hydrogen production from animal waste, an area of concern is the level of ammonia (Kapdan and Kargi, 2006). Animal wastewaters typically contain high concentrations of ammonia, which inhibits microbial fermentative hydrogen production (Koku et al., 2003; Salerno et al., 2006). Prior to fermentation it will therefore be necessary to pre-treat animal waste to reduce ammonia concentrations. Fortunately, there are advances in this area (Sumino et al., 2006; Szogi et al., 2007; Vanotti and Hunt, 2000).

*2.3. Bio-methanol production*

The need for renewable MeOH is great. Ninety percent of the current worldwide demand for MeOH, some twenty nine million tonnes, is derived from methane in natural gas (Olah et al., 2006). A possible new source may be found in the biological production of MeOH. This process could be performed at ambient temperature and pressure. From the standpoint of biological production of MeOH from animal waste, there are two pathways which lend themselves to consideration. Both pathways are dependent upon the generation of either $CO_2$ or $CH_4$.

*2.3.1. Methane-derived methanol*

The conversion to MeOH from $CH_4$ involves a single step process whereby $CH_4$ is oxidized by the enzyme methane monooxygenase (MMO) according to the following reaction (Furuto et al., 1999):

$$CH_4 + O_2 + 2e^- + 2H^+ \rightarrow CH_3OH + H_2O \quad (1)$$

Methane monooxygenase is found in two forms, a soluble MMO (sMMO) and a membrane-bound or particulate MMO (pMMO) (Hakemian and Rosenzweig, 2007). With one or both enzymatic systems found in methanotrophs, these microorganisms can utilize $CH_4$ as their sole source for carbon and energy (Dalton, 2005). Unfortunately, the caveat to this one-step conversion process, MeOH is an unstable product that is quickly oxidized by MeOH dehydrogenase (MDH) to formate. Therefore, the need for MDH inhibition presents itself. Studies using *Methylosinus trichosporium* have revealed phosphate inhibition of MDH allows the culture to accumulate MeOH in micromolar amounts – 6 μmol $mg^{-1}$ $h^{-1}$ (Mehta et al., 1987). This same group later demonstrated similar results using the chelator ethylene-diamine-tetra-acetic acid (EDTA) (Mehta et al., 1991). Likewise, another group reported a semi-continuous process operated over 6 h involving the addition of cyclopropanol, an MDH inhibitor, resulted in the production of 36.1 μmol MeOH at an hourly stationary rate of 3.17 μmol per mg dry cell (Furuto et al., 1999). While the MeOH yield of the previous study is micro-scale, two more recent works with *M. trischosporium* have demonstrated increased MeOH productivity. One study revealed that incubation of *M. trischosporium* (5 ml with dry cell

density of 0.6 mg $ml^{-1}$) in a phosphate buffer mixed with sodium formate for NADH regeneration and sodium chloride as an MDH inhibitor resulted in the 36-h accumulation of 7.7 mM MeOH (equivalent to a nominal accumulation rate of 71.3 μmol $mg^{-1}$ $h^{-1}$) (Sang et al., 2004). Another study demonstrated regulation of $CO_2$ concentrations in a 100 ml continuous flow (6.67 ml $h^{-1}$) bioreactor for MeOH production at a rate of 0.13 μmol $h^{-1}$ (Xin et al., 2004).

*2.3.2. $CO_2$-derived methanol*

Unlike the single step conversion process of $CH_4$ to MeOH (Eq. (1)), the conversion of $CO_2$ to MeOH involves a three step reaction process (Eq. (2)). Carbon dioxide is reduced to formate by formate dehydrogenase ($F_{ate}DH$). The formate is converted to formaldehyde by formaldehyde dehydrogenase ($F_{ald}DH$). The final step is formaldehyde conversion to MeOH by alcohol dehydrogenase (ADH). For each reaction reduced nicotinamide adenine dinucleotide (NADH) acts as a terminal electron donor for a ratio of NADH to $CO_2$ or MeOH as 3:1:

$$CO_2 \xrightarrow[F_{ate}DH]{NADH} HCOOH \xrightarrow[F_{ald}DH]{NADH} HCHO \xrightarrow[ADH]{NADH} CH_3OH \quad (2)$$

Each of the enzymes, $F_{ate}DH$, $F_{ald}DH$, ADH, can be obtained from a variety of bacteria and yeast. Based on this principle, Obert and Dave (1999) reported the conversion of $CO_2$ to MeOH in a silica sol–gel matrix. The silica sol–gel matrix has previously been shown to assist in maintaining stable enzymatic activity (Ellerby et al., 1992). Based on the 3:1 ratio of NADH to MeOH (i.e., 3 mol of NADH is consumed per each mole of MeOH generated), low levels of NADH addition (50 μmol) resulted in a MeOH yield of 91.2% (15.2 μmol) (Obert and Dave, 1999). Yield was defined as the percentage ratio of mol of MeOH to one third the moles of NADH added. When compared to the enzymes in solution (1.3 μmol MeOH generated), this was over an 11-fold increase. Based on the work of Obert and Dave, Wu et al. (2004) successfully worked on increasing the enzymatic activities of sol–gel mediated conversion of $CO_2$ to MeOH using polyethylene glycol (PEG). Subsequently, it was demonstrated that use of an alginate–silica hybrid gel resulted in MeOH yields as high as 98.1%; but yield declined to 76.2% after 53 days of storage. After repetitive use, this hybrid gel had MeOH yields of 78.5% (Xu et al., 2006).

While reaction conditions for $CH_4$ and $CO_2$-derived MeOH processes need to be improved to maximize MeOH yields, these studies lay the groundwork for the biological production of MeOH at ambient temperatures and pressures. This is an advance that should eventually allow for a more cost-effective MeOH source.

## 3. Thermochemical conversion (TCC)

Thermochemical conversion (TCC) is a high-temperature chemical reforming process that breaks apart the bonds of organic matter and reforms these intermediates into char, synthesis gas and highly oxygenated bio-oil. In addition to TCC being a mass consumer of a manure's organic portion that extracts all available energy, TCC processing has a number of other benefits and advantages: (1) small footprint; (2) efficient nutrient recovery; (3) no fugitive gas emissions; (4) short processing time on the order of minutes; (5) capability of handling a variety feedstocks and blends; and (6) high-temperature elimination of pathogens and pharmaceutically active compounds (Cantrell et al., 2007; Ro et al., 2007). After conversion, TCC processing leaves minor residual amounts requiring disposal that results in reduced disposal charges associated with fuel, tipping, and transportation.

There are three main TCC processes identified for converting livestock manures into a value-added renewable energy product: pyrolysis, gasification, and direct liquefaction (Cantrell et al., 2007; He et al., 2000; Priyadarsan et al., 2004). Some of these processes have been tested with livestock manure as a feedstock (Table 1). For each process, the end-product is dependent on the operating temperature, pressure, heating rate, and residence time and is some combination of volatile gases, bio-oil, and solids (Bridgwater and Peacocke, 2000). The volatile gases are a mixture of $H_2$, CO, $CO_2$, $N_2$, water vapor, hydrocarbon gases, and tars. A portion of the volatile gases, namely tars, condense to form a combustible bio-oil. The unreacted, solid residual is a combination of minerals and fixed carbon, commonly referred to as char. As indicated in Fig. 4, all of these intermediate products have multiple end uses. Once cleaned of dust, tars, metals, water, and organic acids the synthesis gases from gasification and pyrolysis can serve as a fuel gas or bioenergy feedstock. Bio-oil also has combustible qualities allowing it to be utilized as a fuel source or bioenergy feedstock.

### 3.1. Pyrolysis and bio-char production

Pyrolysis uses heat and a non-oxygen atmosphere to convert the organic portion of a feedstock into a mixture of char and volatile gases containing both noncondensable vapors and condensable tars (oxygenated hydrocarbons), which form a combustible pyrolytic oil or bio-oil (Bridgwater and Peacocke, 2000; Mohan et al., 2006). Despite numerous published findings and reviews for pyrolytic oil from biomass (Boateng et al., 2007a,b; Bridgwater and Peacocke, 2000; Mohan et al., 2006; Yaman, 2004), little research to date has investigated bio-oil production from livestock waste. Slow pyrolysis converts animal wastes into char, providing farmers with potential economic benefits due to energy production and carbon credits generated from carbon sequestration. Char can be used as a feedstock ("green coal") for existing coal combustion and gasification plants. Char can also be applied to soil as a soil amendment to improve fertility (Antal and Grønli, 2003). Char produced from animal waste can become a source of activated carbon (Bridgwater, 2003; Dominguez et al., 2003; Koutcheiko et al., 2007; Lima and Marshall, 2005a; Sanchez et al., 2007). Poultry and turkey litter and cake was pyrolyzed at 700 °C and 800 °C, respectively, using nitrogen and then steam-activated the char (Lima and Marshall, 2005a,b). When compared to commercial granular activated carbon, the poultry and turkey-based chars had greater copper ion adsorption showing promise in potential metal ion removal applications.

### 3.2. Direct liquefaction

Direct liquefaction (DL) hydrolyzes the lignocellulosic components in biomass and converts the biomass into lighter organic oils (bio-oils). It is hypothesized that the metal salts naturally present in the waste catalyze the hydrolysis reactions (He et al., 2000). When compared to pyrolysis, direct liquefaction proceeds in a pressurized environment (5–20 MPa) and typically occurs at lower temperatures (250–350 °C). A University of Illinois research group investigated batch and continuous liquefaction experiments on swine manure (TS 20–27 wt%) (He et al., 2001a,b; He et al., 2000; Ocfemia et al., 2006a,b). In batch studies under a CO atmosphere and reactor temperatures ranging 285–350 °C, volatile solid conversion to oil was as high as 76.2%. This swine bio-oil product was energy dense with an average heating value of 36.4 MJ $kg^{-1}$. Additional processing of the oils is necessary due to the presence of nitrogen and sulfur. Continuous operation ($T$ = 305 °C and $P$ = 10.3 MPa) resulted in slight decreases for both the maximum oil yield, down to 70.4%, and the oil's heating value, ranging between 25.2 and 31.1 MJ $kg^{-1}$ (Ocfemia et al., 2006a,b). As a waste treatment alternative, DL did reduce the initial swine waste stream's COD by 64.5%. Unfortunately, reductions in the nitrogen, phosphate, and potassium of the post-processed stream were not

**Table 1**
Summary results of tested thermochemical conversion (TCC) processes using livestock manure as a feedstock

| TCC Process | Feedstock | Conditions | Primary product | Major constituent | HHV | Reference |
|---|---|---|---|---|---|---|
| Direct liquefaction | Swine manure | $T$ = 305 °C; $P$ = 10.3 MPa | Bio-oil | | 31.1 MJ kg$^{-1}$ | (Ocfemia et al., 2006a,b) |
| Dry gasification | Poultry litter | $T$ = 816 °C; $P$ = 0.1 MPa* | Gas | 28.3% CO | 4.5 MJ m$^{-3}$ | (Priyadarsan et al., 2004) |
| | Feedlot manure | $T$ = 816 °C; $P$ = 0.1 MPa* | Gas | 29.2% CO | 4.1 MJ m$^{-3}$ | (Priyadarsan et al., 2004) |
| Pyrolysis/gasification | Anaerobically digested sewage sludge | $T$ = 1000 °C; $P$ = NA | Gas | 39.3% $H_2$ | 6.9 MJ m$^{-3}$ | (Dominguez et al., 2006) |
| Wet gasification | Dairy manure | $T$ = 350 °C; $P$ = 21 MPa | Gas | 56% $CH_4$ | 25.1 MJ m$^{-3}$ | (Elliott et al., 2004) |

* Indicates an approximation to atmospheric pressures; NA indicated information not available.

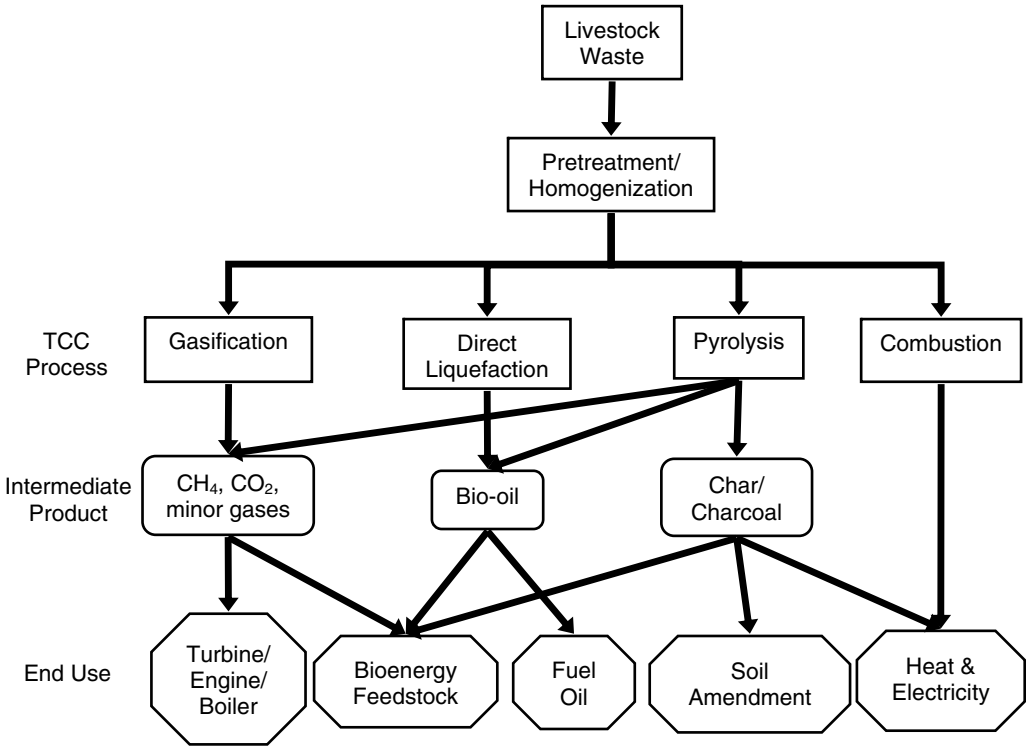


**Fig. 4.** Main thermochemical conversion processes, their intermediate products, and suggested end use.

realized. The authors concluded that further treatment of this water is necessary before discharging into a wastewater stream.

### 3.3. Dry gasification

Gasification uses air, oxygen, or steam as a reaction medium to convert the organic portion of a dry or wet feedstock into the minor by-product char and primarily noncondensable, permanent gases, CO, $CO_2$, $H_2$, and low molecular weight hydrocarbon gases (Bridgwater, 2003; McKendry, 2002a,b). Dry gasification uses preheated oxidizers (800–1300 °C) at atmospheric pressure to convert the dry biomass to chars and a low-Btu gas. The principle stages in dry gasification are drying, pyrolysis, reduction, and oxidation (Bridgwater, 2003; Cantrell et al., 2007; McKendry, 2002a,b; Priyadarsan et al., 2004). In the drying stage, water evaporates using the heat generated by the later stages. Starting around 250 °C, the dried biomass then undergoes pyrolysis reactions to release volatile compounds and char, which are then subjected to oxidative and reductive reactions. Oxidation of the volatile compounds consumes all oxygen, leaving the steam and $CO_2$ to oxidize the char and release a mixture of $H_2$ and CO.

Current testing of the dry feedstocks of poultry litter and feedlot manure have been limited to dry gasification systems (Priyadarsan et al., 2004). Using air as the oxidizing agent, fixed-bed gasification yielded a low-Btu gas with an average HHV of 4.5 MJ m$^{-3}$ for poultry litter (TS = 92.5 wt%) and 4.1 MJ m$^{-3}$ for feedlot manure (TS = 92.4 wt%). The product gases contained a combustible portion consisting on average of 5.8% $H_2$, 27.6% CO, and 1.0% $CH_4$. Unfortunately, the product gases were severely diluted with nitrogen, thus decreasing the potential HHV by roughly 60%. No mention was made of the final proportion of ash or char. Similar to the animal waste feedstocks, sewage sludge (TS = 88.3 wt%) has been tested in a throated downdraft gasification unit to generate, again, a low-Btu gas with a HHV of 3.8 MJ m$^{-3}$ (Dogru et al., 2002). The remaining char was between 14% and 25% of the original input while tar production was less than 2%.

### 3.4. Enhancing dry gasification

Even though it has not been tested with livestock waste, steam can be used in gasification systems as the oxidizing agent to increase $H_2$ production from the solid-phase carbon residual. This is due to steam's important role in the water–gas shift reaction (WGS). With an increase in steam's temperature, hydrogen production can further improve. This rise in operational temperature can increase feedstock carbon to gas conversion improving gas yield while char and tar production decrease.

Even greater synthesis gas production can be achieved through catalytic steam gasification processes that utilize a heterogeneous catalyst, such as nickel. They can operate either concurrent or in

series with the gasification process to promote higher quality synthesis gas and diminish tar production. Even though heterogeneous catalytic steam gasification could potentially improve synthesis gas from animal wastes, there is an associated increase in both the capital cost of a system and additional pretreatment of the feedstock to avoid ash and sulfur catalytic poisoning (Cantrell et al., 2007). Thus, this is an area of potentially high impact research and development.

Animal manures naturally contain potassium and alkali salts thought to have catalytic properties. Catalytic steam gasification of pyrolyzed poultry litter char (fixed carbon, 54.7%) has been tested with and without the addition of potassium carbonate and langbeinite ($K_2Mg_2(SO_4)_3$) as catalysts (Jones and Sheth, 1999; Sheth and Bagchi, 2005; Sheth and Turner, 2002). These catalysts were selected due to their common use in the fertilizer industry, making them a less expensive alternative to expensive Co and Ni catalysts. For gasification at 700 °C and 1000 kPa, the addition of langbeinite to the char increased the gasification rate by 35% while the addition of potassium carbonate increased the gasification rate by nearly 130%. These studies reported complete fixed carbon conversion was possible while providing a fuel gas with less than 50 mol% $CO_2$. Preliminary tests suggest the phosphorus remains in the gasified char while 20–60% of the nitrogen would be released into the gas as ammonia, which could be trapped for recycled use (Jones and Sheth, 1999).

### 3.5. Combined pyrolysis and gasification

Using a single reactor treatment process, a system that integrated drying, pyrolysis, and gasification converted the organic portion of biomass primarily to the gas phase with oil and chars as the lesser by-products (Dominguez et al., 2005; Dominguez et al., 2006a,b; Menendez et al., 2005). By implementing elevated temperatures, long gas residence times, high heating rates, and no additional catalyst, this system maximized gas production. For this integrated unit process, microwave heating ovens provide the necessary high heating rate and temperatures. By turning the excess water into steam, three functions are achieved: (1) drying of the sludge; (2) gasification of the remaining solids; and (3) steam reforming of the organic vapors. The long gas residence time increases the reaction of the steam with the char and organic vapors further promoting formation of synthesis gas (Dominguez et al., 2006a,b).

Using helium as the carrier gas, this batch treatment was successfully applied to aerobically digested sewage sludge (TS = 29 wt%) to generate four fractions: 10.1 wt% char, 60.7 wt% aqueous stream, 3.0 wt% oil, and the remaining as gas (Menendez et al., 2005). The composition of the product gas was 33% $H_2$, 30.1% CO, 8.0% $CO_2$, 6.4% $CH_4$, 16.9% $N_2$, and 5.6% as higher carbon-chain compounds. This process separated the energy density of the sewage sludge from an initial 16,680 kJ $kg^{-1}$ into 5576 kJ $kg^{-1}$ for char; 8500 kJ $m^{-3}$ for the gas, and 36,800 kJ $kg^{-1}$ for the bio-oil. In addition to producing the product streams, this process was effective in treating the sewage sludge; combined pyrolysis/gasification of the sewage sludge removed all measurable biological oxygen demand ($BOD_5$) and 95% of the initial chemical oxygen demand (COD). Since this system was effective in treating sewage sludge, the same success can be inferred for livestock waste treatment.

### 3.6. Wet gasification

Wet gasification or hydrogasification utilizes unique water properties that only exist in the vicinity of its critical region. The concept of wet gasification was first introduced by Modell and his co-workers (Modell, 1985; Modell et al., 1978) where they were able to demonstrate that glucose and cellulose could be converted to $H_2$, $CO_2$, carbon monoxide, and other trace gases in supercritical water without producing char. Later, Elliott and co-workers at the US DOE Pacific Northwest National Laboratory (PNNL) developed sub-critical (250–360 °C, up to 22 MPa), metallic catalytic-based water gasification technology (Elliott et al., 2004; Elliott et al., 1997; Sealock et al., 1988; Sealock et al., 1997). Bench and pilot-scale testing of sub-critical water gasification of dairy manure and other agricultural wastes using Ruthenium (Ru) catalysts provided almost complete conversion of the carbon in waste into a gas mixture averaging 40% $CO_2$ and 57% $CH_4$ (Elliott et al., 2006; Elliott et al., 2004). Recently, Ro et al. (2007) evaluated the feasibility of wet gasifying various agricultural and municipal wastes using the PNNL technology and reported that swine waste generated the highest positive net energy. The threshold total solids concentration for wet gasification of livestock wastes was 8%. This was the net energy break even point. It considered all process energy requirements like pumping and heat loss. Above this point the process is a net energy generator. Although the high costs of Ru catalysts and auxiliary processes for preserving catalytic activities poses the major obstacle, the PNNL wet gasification technology offers significant environmental benefits over existing treatment technologies. With technical advances and cost reductions, this technology offers potential for agricultural and municipal wastes treatment.

### 3.7. Heat recovery

Since all of the TCC processes are heat intensive, heat recovery is an essential component to make these processes energy feasible. If a significant portion of the product gas or liquid streams' heat could be recycled to heat the incoming feedstock, these TCC systems would quickly become net energy positive. In fact, Elliott et al. (1997) developed a double-tube heat exchanger that could recycle up to 90% of the energy used to raise the headstock temperature. From this assumption, Ro et al. (2007) estimated that wet gasification systems treating livestock waste streams with a TS as low as 2 wt% could become net energy positive. In an energetic evaluation of a model 5000-sow swine farm, Cantrell et al. (2007) estimated that in order for a wet gasification system to become energy neutral the heat recovery could be as low as 50%.

## 4. Bio-thermochemical opportunities

Carbon dioxide is a major component in the product gases from anaerobic digestion and thermochemical conversion processes. Since an increased atmospheric concentration of $CO_2$ is considered one of the main causes of global warming (Schneider, 1989), it is important to recover $CO_2$ to limit short-term release. By naturally fixing atmospheric $CO_2$ via photosynthesis ten times more efficiently than terrestrial plants (Usui and Ikenouchi, 1997), algae can rapidly generate both algal biomass and intracellular oil (Miao and Wu, 2006; Miao et al., 2004). These algal products can then be harvested and converted into multiple value-added products.

### 4.1. Algal $CO_2$-removal

Algae's $CO_2$-fixation efficiency is highly variable with reported numbers as low as 0.26 mg $CO_2$ $m^{-3}$ $h^{-1}$ (Cheng et al., 2006) to high removals upwards of 1.33 g $CO_2$ $m^{-3}$ $h^{-1}$ (Hirata et al., 1996). Algae's ability to remove $CO_2$ as a biological treatment for combusted gases has been reported numerous times. Chlorella vulgaris was shown to fix $CO_2$ from a flue-gas stream with a $CO_2$ concentration of 15% at an estimated 26.0 g $m^{-3}$ $h^{-1}$ (Yun et al., 1997).

Using the flue-gas from a small power plant, microalgae were grown in a pilot-scale photo-bioreactor. This system had a reported $CO_2$-removal efficiency of 50.1% on cloudy days, and on sunny days the efficiency was 82.3% (Vunjak-Novakovic et al., 2005).

At the industrial-scale level, an Australian consortium in conjunction with GreenFuel Technologies plan to use microalgae grown in photo-bioreactors to sequester $CO_2$ from gases generated from a coal-fired electric power plant (Bullock, 2006). Similar $CO_2$-removal systems should be feasible for the sequestration of $CO_2$ generated from either TCC processes or anaerobic digestion. Indeed, Doucha et al. (2005) have proposed such a system for anaerobically digested animal waste. The resulting biogas would be combusted, and the flue-gas containing $CO_2$ would be utilized to produce algal biomass for animal feed.

### 4.2. Algal waste treatment

In addition to light and $CO_2$ requirements, algae require water and plant nutrients. All of these components are generally found in treated or untreated livestock wastewater, and they can be recycled to conserve resources as well as reduce algal culture medium cost (Ayala and Vargas, 1987). Consequently, a number of groups have demonstrated the ability of various algae to utilize animal waste as a growth medium (Ayala and Bravo, 1984; Barlow et al., 1975; Chiu et al., 1980; Olguín et al., 1994; Wilkie and Mulbry, 2002; Yang and Duerr, 1987). Recently, Kebede-Westhead et al. (2006) reported the use of an algal turf scrubber colonized with freshwater, filamentous algae for the treatment of raw swine manure. This report demonstrated that loading rates of 0.40 L $m^{-2}$ $d^{-1}$ resulted in an harvestable algal biomass of an average of 9.4 g $m^{-2}$ $d^{-1}$ with the concurrent removal of 95% N removal and a P removal of 77% (Kebede-Westhead et al., 2006). This same group has reported the treatment of anaerobically digested, flushed dairy manure effluent with a similar system, with loading rates of 9 L $m^{-2}$ $d^{-1}$ and harvestable biomass of 17.7 g $m^{-2}$ $d^{-1}$ with 68% N and 73% P removal (Kebede-Westhead et al., 2003). Table 2 shows several reported algal treatment systems, their biomass yields as well as their rates of nutrient removal. In addition to N and P removal, other studies have also reported the successful use of algae to remove heavy metals from wastewaters (Mallick, 2002; Mallick, 2003; Mallick et al., 1996; Priya et al., 2007; Romera et al., 2007; Singh et al., 2007).

### 4.3. Algal bio-fuels

Unlike the biological processes for generation of gases such as $H_2$ or $CH_4$, the traditional utilization of algae for bioenergy purposes does not typically result in an immediate source of fuel. Rather, the growth of algae serves the role of providing biomass, which could then lend itself to various energy generating processes. When compared to other sources of biomass, algae provide several benefits including: rapid generation rates with biomass harvesting of up to 50 metric tons $acre^{-1}$ $yr^{-1}$ (Demirbas, 2001); the accumulation of large amounts of fatty acids and hydrocarbons; as well as the ability to play a role in waste treatment.

As a biomass feedstock for the energy generation, algae have seen several applications. An extensive review covered algal-based biodiesel (Chisti, 2007). The microalgae *C. vulgaris* has been proposed for direct incorporation as an additive for emulsion fuels (Scragg et al., 2003). Immobilized cultures of the microalgae *Botryococcus braunii* have been cultured to recover long-chain, unsaturated hydrocarbons via solvent extraction (Frenz et al., 1989a,b). Gasification of 1 g of Spirulina with a heating value of 17.0 $kJg^{-1}$ would theoretically yield 0.64 g MeOH; this yield is comparable to methanol yields from woody biomass (Hirano et al., 1998).

With regards to thermochemical conversion processes, microalgae was subjected to fast pyrolysis at 500 °C with a heating rate of 600 °C $s^{-1}$ in a nitrogen atmosphere to generate a high quality bio-oil comprising between 18 and 24 wt% of end-product composition. This bio-oil had a low-oxygen content and a higher heating value (HHV) of 29 MJ $kg^{-1}$, a density of 1160 kg $m^{-3}$, and a viscosity of 0.10 Pa s (Miao et al., 2004). In later research through manipulation of the metabolic pathway of the heterotrophic Chlorella proto-thecoides, the yield of bio-oil increased to roughly 58 wt% of end-product and improved the bio-oil quality by decreasing both the density (920 kg $m^{-3}$) and viscosity (0.02 Pa s) and increasing the HHV by 30% to 41 MJ $kg^{-1}$. Compared to wood-based pyrolytic oils, these algal bio-oils are richer in carbon and hydrogen and provide more energy per unit mass (Mohan et al., 2006).

In order to avoid expensive feedstock drying techniques, which are required for several thermochemical processes, researchers examined the possibility of utilizing the high moisture content of algae to produce low molecular weight liquid fuels in thermochemical liquefaction (Yang et al., 2004). Under experimental conditions (340 °C, 30 min holding time, 5 wt% catalyst dosage), Yang et al. (2004) demonstrated a 33% oil yield; the oil had a heating value of 31 MJ $kg^{-1}$. In an earlier study, direct liquefaction of *Botryococcus braunii* produced more of a hexane-soluble lipid product than algae alone (Sawayama et al., 1995). In addition to these studies, several other groups have looked at liquefaction of algae, either in a co-liquefaction process with coal (Ikenaga et al., 2001), or individually (Dote et al., 1994; Inoue et al., 1994; Matsui et al., 1997; Sawayama et al., 1995; Sawayama et al., 1999).

### 4.4. Combined algae and wet gasification

While the above thermochemical conversion processes essentially extract the algal oil, no one has yet to investigate the potential of combining an algal $CO_2$-fixation treatment with the algal energy recovery component of wet gasification. The use of algae to clean biogas from anaerobic digestion of distillery waste (molasses from sugar cane) was shown to reduce the initial $CO_2$ concentration of 44–48 vol% to a product gas $CO_2$ concentration between

**Table 2**
Harvestable biomass, Nitrogen (N) and Phosphorous (P) removal characteristics of different algal waste treatment systems

| System | Effluent | Harvestable Biomass g $m^{-2}$ $d^{-1}$ | % N removal | % P removal | Notes | Reference |
|---|---|---|---|---|---|---|
| Algal Turf Scrubber | Swine wastewater | 9.4 | 95 ± 20 | 77 ± 13 | 0.04 L $m^{-2}$ $d^{-1}$ loading rate | Kebede-Westhead et al., (2006) |
| Algal Turf Scrubber | AD effluent (dairy) | 19.1 | 68.2 ± 25.2 | 73.2 ± 24.4 | 9.0 L $m^{-2}$ $d^{-1}$ loading rate, high light | Kebede-Westhead et al., (2003) |
| Outdoor raceway | Sea-Water + AD effluent (swine) | 4.3 to 8.5 | 100 | n.m. | Set 2, temperate climate, Spirulina sp., semi-continuous culture | Olguin et al., (1997) |
| Outdoor Raceway | Sea Water + AD effluent (swine) | 14.4 | 91 ± 7.1 | 87 ± 6.3 | Summer 1999 values, tropical climate, Spirulina sp., semi-continuous culture | Olguin (1996) |

AD – anaerobic digestion, n.m. – Not measured.

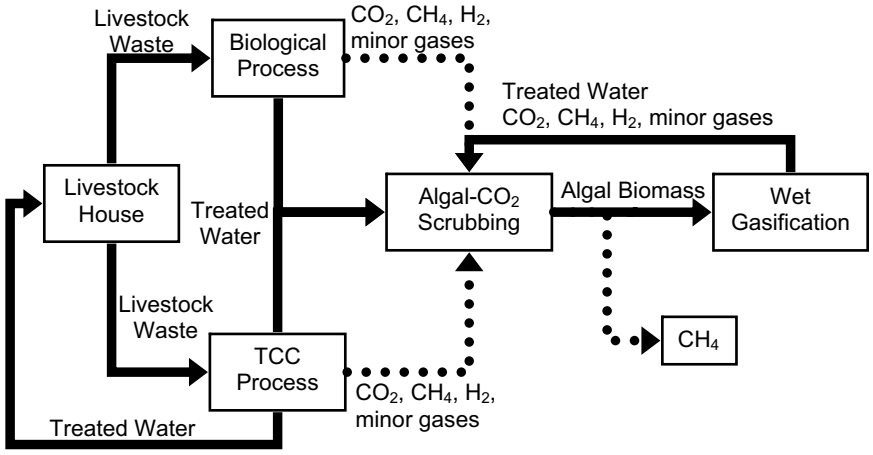


**Fig. 5.** Fully integrated bio-thermochemical waste-to-bioenergy platform with algal $CO_2$ scrubbing and wet gasification.

3 and 11 vol% (Travieso et al., 1993). As shown in conceptual design in Fig. 5, by scrubbing the $CO_2$ from the gas streams from either biological or TCC processes, algae can be grown for feedstock generation purposes. The treated effluents from both these processes contain N and P and can serve as the growth medium. The accumulated algal biomass along with its growth medium can be sent to wet gasification for additional production of minor gases and $CH_4$. The high temperature-treated water can then be recycled back to the livestock house or to the algal $CO_2$ scrubbing system. If a farm were to implement wet gasification as its sole waste-to-bioenergy treatment process, then a mixed feedstock stream of manure and algal biomass could be thermochemically converted (Fig. 6). Either hybrid scenario produces a cleaner $CH_4$ gas product that can be used on-farm.

Based on the model 5000 head sow swine farm Cantrell et al. (2007) describes, anaerobic digestion produces 775,120 L of biogas daily containing 32.1% $CO_2$ – the ambient condition equivalent (20 °C, 1 atm) of 433 kg $CO_2$. As demonstrated by a $CO_2$ mass balance for a photo-bioreactor by Doucha et al. (2005), not all of this $CO_2$ will be available for algae fixation; a large portion of the supplied $CO_2$ is lost during saturation of the growth media leaving the algae cells with 38.7% of the original $CO_2$ (Doucha et al., 2005). For the AD biogas, these losses potentially leave the algae with 168 kg $CO_2$. In order to generate 1 kg of biomass, algae need roughly 1.74 kg $CO_2$ (Doucha et al., 2005); with an 82% algal $CO_2$-fixation efficiency (Vunjak-Novakovic et al., 2005), the $CO_2$ requirement increases to 2.12 kg. At a harvest rate of 9.4 g $m^{-2}$ $d^{-1}$ (Kebede-Westhead et al., 2006), algal growth on this swine farm can be supported with roughly an 8400 $m^2$ (2.1 ac) area.

If this same farm was sending its waste to wet gasification, 1,849,920 L of gas would be generated daily with a $CO_2$ content of 43.2%. In order to fix the 538 kg of available $CO_2$, a larger surface area would be needed: 27,000 $m^2$ (6.7 ac). Both these conceptual designs assume cleaning and conversion to take place during the day; therefore, appropriate nighttime storage facilities need to be available. Additionally, improvements can be made in the net algae productivity. This effectively reduces the area required for growth. Further research is also needed in order to understand the distribution of $CO_2$ in an algal system and design of photo-bioreactors to increase the amount of available $CO_2$. Both of these conceptual designs suggest a livestock waste-to-bioenergy treatment opportunity that drastically reduces $CH_4$ and $CO_2$ emissions and efficiently recycles all nutrients suggesting the potential for future CAFO production to be both sustainable and environmentally benign.

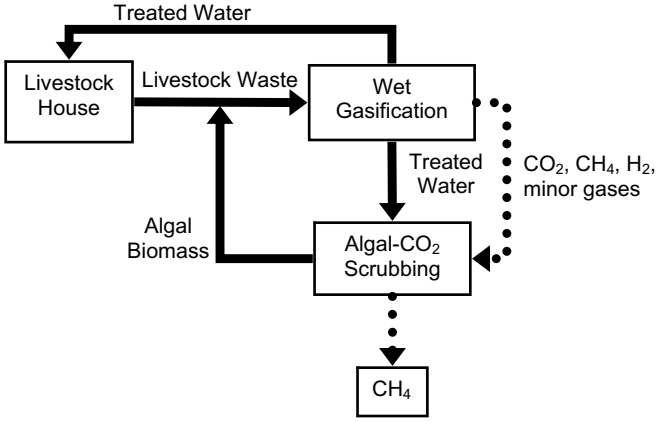


**Fig. 6.** Bio-thermochemical waste-to-bioenergy platform with algal $CO_2$ scrubbing and algal biomass recycling.

## 5. Conclusions

In this paper, we reviewed multiple livestock waste-to-bioenergy processes to help combat rising energy prices and reduce the environmental threats from traditional livestock waste management practices. The biochemical process of anaerobic digestion is an established technology capable of biogas production; however, other biological processes like bio-hydrogen and bio-methanol production are still in early research stages and show promise to become a sustainable, renewable energy resource. Within the thermochemical conversion processes, pyrolysis, direct liquefaction, and gasification, both dry and wet, also have the capabilities of converting livestock waste into value-added products like gaseous fuels and combustible oils. Integration of biological and thermal-based conversion technologies by: (1) recapturing the evolved $CO_2$ to promote algal growth and (2) utilizing wet gasification as the algal energy recovery component holds promise for a highly efficient and resource sustainable waste-to-bioenergy scheme.

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