chapter

THERMOCHEMICAL CONVERSION TECHNOLOGIES FOR PRODUCTION OF RENEWABLE ENERGY AND VALUE-ADDED CHAR FROM ANIMAL MANURES

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ABSTRACT

Confined animal feeding operations (CAFOs) in the USA and many other countries have undergone extensive expansions and consolidations for the last few decades. This shift in animal production agriculture toward fewer, but larger operations has created serious environmental concerns in recycling and disposing surplus animal manures because the animal manure production often exceeds assimilative capacity of local land. The surplus animal manures become the main component of livestock wastes. Thermochemical conversion technologies can be used to transform livestock wastes into value-added products and renewable energy. The synthesis gas produced from gasifying livestock wastes can be combusted to provide space heating and the power required for livestock operation. It can also be converted into transportation fuels using downstream catalytic conversion technologies. The char produced from pyrolyzing livestock wastes can be used to build up soil quality and reduce greenhouse gas emission. It can also be activated to be used as an adsorbent for pollution control. This chapter reviews presently established and emerging thermochemical energy conversion technologies that can be used for livestock waste-to-renewable energy production.

4.1 INTRODUCTION

Over the last few decades, confined animal feeding operations (CAFOs) in the USA and many other countries have undergone extensive expansions and consolidations (Gollehon et al., 2001). This shift of animal production agriculture toward fewer, but larger operations, has created environmental concerns in recycling and disposing of surplus animal manure (Stone et al., 1995). Traditional manure management systems may not adequately dispose/recycle the surplus animal manure and pose potential environmental threat (McNab Jr. et al., 2007; Stone et al., 1998; Szogi et al., 2006). Recent rising energy prices and concerns over petroleum supplies make the matter even worse. Currently, annual animal manure provides 35 million dry tons of sustainable biomass feedstock that comprises 18% of the total currently available sustainable biomass from the U.S. agricultural lands (Perlack et al., 2005; Ro et al., 2009). The use of animal manure and other organic-based waste products as feedstocks for waste-to-renewable energy conversion processes would allow farmers to take advantage of new markets for traditional waste products and stimulate the local economy. In effect, livestock waste-to-renewable energy treatments can convert livestock waste treatment from a liability or cost component into a profit center and diversify farm income (Cantrell et al., 2008).

The most common waste-to-renewable energy conversion technology for animal manure is anaerobic digestion, which stabilizes the manure's organic material via two-stage biological processes. The first stage involves the breakdown of complex organic matter into less complex compounds such as short-chain volatile fatty acids. This step is followed by methanogenic bacteria converting carbon compounds into gases, mainly methane and carbon dioxide. Trace gases such as ammonia, oxygen and hydrogen sulfide can also be found in the biogas. Although the anaerobic digestion technology reduces pathogens and produces energy rich biogas, proper disposal or land application of the digestion sludge is still required. Furthermore, this technology requires long process time and large facilities due to its slow anaerobic digestion process.

While anaerobic digestion requires an extended amount of process time (days, weeks or even months), thermochemical conversion processes (TCC) such as gasification and pyrolysis can quickly process waste feedstock and produce renewable energy and value-added biochar in matter of seconds or minutes to hours (Bridgewater, 2006). The short process time requirement of TCC drastically reduces the footprint requirement. This chapter introduces currently available thermochemical conversion technologies that can be applied to treat livestock wastes while producing renewable energy and biochar. Potential environmental applications for the manure-derived biochar are also discussed.

4.2 THERMOCHEMICAL CONVERSION TECHNOLOGIES SUITABLE FOR TREATING/CONVERTING LIVESTOCK WASTES

Thermochemical conversion (TCC) technology uses heat to break chemical bonds of organic matter, releases chemical bond energy, and reforms the reaction intermediates into gaseous, liquid, and solid products. TCC technology used for livestock waste treatment offers the following benefits and advantages: (1) small footprint; (2) efficient nutrient recovery; (3) no fugitive gas emissions; (4) short processing time on the order of minutes to hours; (5) capability of handling a variety of feedstocks and blends; and (6) high-temperature destruction of pathogens and pharmaceutically active compounds (Cantrell et al., 2007; Ro et al., 2007). After conversion, TCC processing leaves minor residual amounts that require further disposal, resulting in reduced applicable land disposal charges associated with fuel, tipping, and transportation.

There are three main TCC processes that can be used for converting livestock manures into renewable energy and value-added biochar production: pyrolysis, gasification, and hydrothermal processes (Cantrell et al., 2008; Libra et al., 2011; Peterson et al., 2008; Ro et al., 2010; Ro et al., 2009). The composition of end product from each process is dependent on the operating temperature, pressure, heating rate, and residence time and is made of a combination of volatile gases, bio-oil, and solids (Bridgewater and Peacocke, 2000; Bridgwater and Peacocke, 2000; Libra et al., 2011; Peterson et al., 2008). The product gases are a mixture of H_2, CO, CO_2, N_2, water vapor, hydrocarbon gases, and tars. A portion of the gases condense to form a combustible bio-oil. The solid residual, commonly referred to as char is a combination of minerals and carbon with a significant portion as fixed carbon. Once cleaned of tars and particulates, the synthesis gases (i.e., H_2 and CO) from gasification can serve as a fuel gas for combined heat and power generation or feedstock for downstream catalytic processes to produce liquid fuels such as mixed alcohols and hydrocarbons. Bio-oil can be upgraded to transportation fuels by reducing its oxygen content and acidity with hydrogenation process.

4.2.1 Pyrolysis

Pyrolysis thermochemically decomposes and converts the animal manure into a mixture of char and gases by heating in the absence of oxygen. The gases contain both noncondensable gases and condensable vapors which form a combustible pyrolytic oil or bio-oil (Bridgewater and Peacocke, 2000; Mohan et al., 2006). Despite numerous published findings and reviews for pyrolytic oil from biomass (Agblevor et al., 2010; Boateng et al., 2007b; Boateng et al., 2007a; 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 combustible gas and char providing farmers with potential economic benefits due to energy production and carbon credits generated from carbon sequestration. The potential of pyrolyzing animal manure was evaluated using a commercial pilot-scale skid-mounted pyrolysis reactor system that had been used to generate power from municipal solid wastes and autoshredder residuals (Ro et al., 2010). Eight to 19 L of dried chicken litter, swine manure, and a mixture of swine manure and rye (29% rye and 71% swine manure, w/w) were pyrolyzed at 893K for two hours. Devolatilized gas was scrubbed in a venture scrubber, compressed, and fed into a gas storage tank for later use. The scrubbing water was chilled and recirculated for continual scrubbing.

In order to better understand the pyrolysis process of animal manures, thermogravimetric analyses were performed using He as a carrier gas. Pyrolytic degradation of these animal manures started at about 500 K and reached its maximal devolatilization rate at slightly below 600 K. Assuming one-step global pyrolytic decomposition kinetic model, Ro et al. (2009) reported that the swine manure thermogravimetric data fitted Arrhenius equation well with the following kinetic parameters.

$$\frac{d\alpha}{\left(1-\alpha\right)^n}=\frac{A}{\beta}\exp\left(-E/RT\right)dT \text{ 4-1.} \qquad (2)$$

where, A = pre-exponential factor (10^8 min^{-1}),
E = activation energy (92.7 kJ mol^{-1}),
R = gas constant (8.314 J mol^{-1} k^{-1}),
T = temperature (K),
t = time (min),
n = 3.7 = order of reaction,
$\alpha = \frac{m_o - m_T}{m_o - m_f}$ = fraction of conversion
m_T = mass at temperature T (g),
m_f = final residual mass (g),
β = constant heating rate or *dT/dt* (10 K min^{-1}).

While the swine manure decomposition reaction order was higher than that for cellulosic pyrolysis reactions, predominantly first order (Antal Jr and Gronli, 2003; Mok and ANtal, 1983), it was lower than that for the wastewater sludge decomposition reaction orders with n ranging from 4.1 to 7.95 (Chu et al., 2001).

Although the distribution of major noncondensable gases such as CO, CO_2, H_2, and CH_4 from pyrolyzing animal manures at different pyrolysis temperatures has not been reported in the literature, one can get a rough estimate of such distribution by calculating thermochemical equilibriums at each pyrolysis temperature (Yan et al., 2005). Thermochemical equilibrium calculations have traditionally been made through the use of equilibrium constants of well-known reactions such as water-gas-shift and methane formation reactions (Jarungthammachote and Dutta, 2007; Zainal et al., 2001). However, when the system becomes as complex as in animal manure pyrolysis reactions, the equilibrium composition can be better estimated by the direct minimization of the total Gibbs free energy function of the system. The total Gibbs free energy of the system (G^T) is defined as:

$$G^T = \sum_{i=1}^{N} n_i \mu_i \qquad \text{4-2.}$$

where n_i = number of moles of species i,
μ_i = chemical potential of species i (kJ mol^{-1}).

By simultaneously solving the total Gibbs free energy minimization and mass balance of the system, thermochemical equilibrium distribution of the gaseous species at different pyrolysis temperatures can be estimated. Using the HSC-Chemistry 6.0 software (Roine, 2006) along with elemental compositions of each animal manure, equilibrium distributions of the major noncondensable gases were estimated (Figure 4.1). For all three animal manure feedstocks, CH_4 and CO_2 production decreased with temperature; however, H_2 and CO production increased with temperature. At a typical gasification temperature of 850 ^{o}C, predominant gases should be hydrogen and carbon monoxide, the major constituents for synthesis gas. The major pyrolysis gas compositions are shown in Table 4.1. Actual gas compositions from pyrolyzing these animal manure feedstocks taken at 620 ^{o}C were more complex than the simplified thermochemical equilibrium compositions. The main produced gases were CO, CO_2, H_2, CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, and higher C hydrocarbons. Most of NH_3 was lost to scrubbing water due to its high solubility. The main gas composition did not vary much for different animal manure feedstocks except for energy rich $C_{>2}$ hydrocarbons. The swine manure pyrolysis gas contained more than twice of the $C_{>2}$ hydrocarbons than that from chicken manure. Consequently swine manure produced pyrolysis gas with the higher heating value (HHV) of 29.5 MJ/S m^3, nearly twice of that of chicken litter pyrolysis gas.

Animal manure pyrolysis gas also contained relatively high sulfur content, which is of concern not only for odor and health but also for downstream catalytic conversion or combustion processes (Ro et al., 2010). Sulfur containing synthesis gas interferes with downstream catalytic conversion processes by poisoning metal catalysts and produces acid rain forming SO_x from combustion. Other S gases such as H_2S, dimethyl sulfide, and methyl mercaptan produced from pyrolyzing animal manures raise health and environmental concerns. Accordingly, animal manure pyrolysis facilities must be able to control the emission of the S-containing gases and prevent the exposure to workers.

Table 4.1 Major noncondensable gases produced from pyrolysis up to 620oC (Modified from Table 2 of Ro et al., 2010)

Parameters	v/v % Chicken Litter	v/v % Swine	v/v % Blended
H2	17.2 ± 4.1	15.7 ± 0.0	12.6 ± 5.4
CO2	27.5 ± 0.2	21.5 ± 2.3	21.6 ± 1.8
N2	18.0 ± 0.8	10.0 ± 0.2	18.1 ± 6.2
CO	16.1 ± 1.9	10.7 ± 0.4	13.0 ± 1.0
CH4	10.9 ± 0.6	19.9 ± 0.8	16.9 ± 1.2

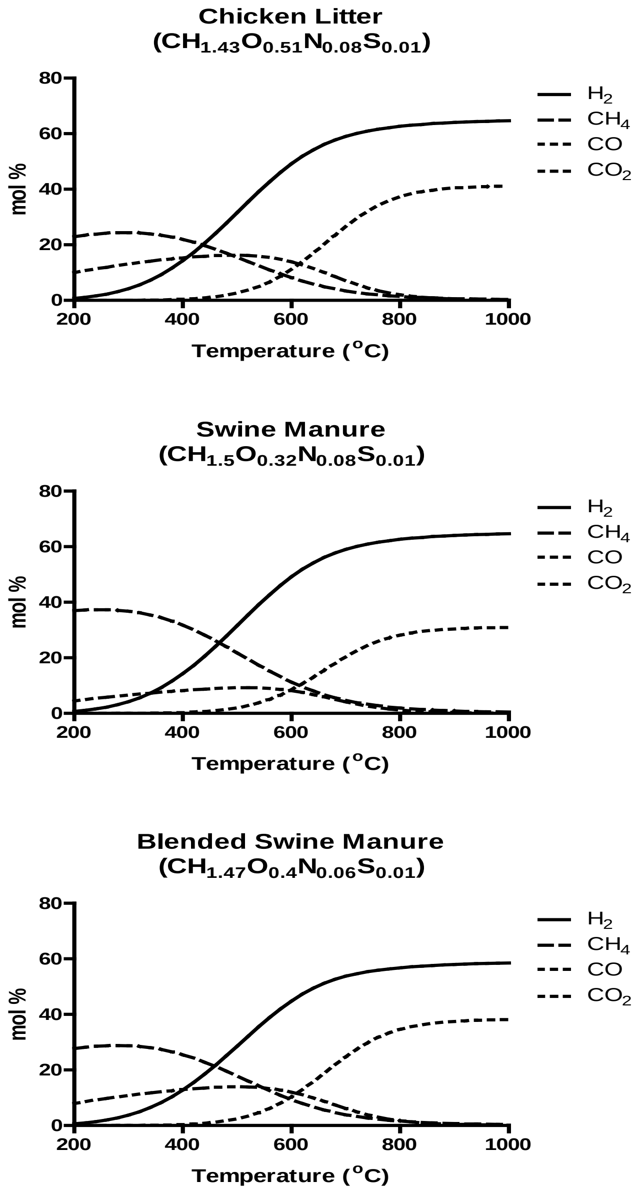

Figure 4.1 Gas distribution of animal manure pyrolysis calculated using HSC software

Pyrolysis of animal manures at 620 °C produced chars with yields ranging from 43 to 49% based on dry weight (Ro et al., 2010). These chars showed general reductions of H/C ratios, indicating an increase in aromaticity due to losing aliphatic and carboxylate portions of manures during pyrolysis (Cao et al., 2011; Novak et al., 2009; Rutherford et al., 2005). This increase in aromaticity also increased the fixed carbon yields of chars. About 48 to 56% of feedstock carbon was recovered in char during pyrolysis. The heating value of the chicken litter char was slightly below that of low rank coals; swine-based char had heating values between high and low rank coals. Approximately 50% of the animal manure feedstock energy was retained in the char and 25% in the produced gas. System efficiencies will increase if some of the remaining 25% of feedstock energy in the tar/scrubbing water component is captured and reused. In addition, one can produce both char and extra power from combustible gas by co-pyrolyzing wet animal wastes such as dewatered swine solid with drier and more energy dense feedstocks such as waste plastic pellets. Furthermore, because the manure-based chars retained most of P and K, these can be used to improve soil fertility. The characteristics and the potential use of manure-based char as a soil amendment and adsorbent material will be discussed later this chapter.

5.2.2. Gasification

Gasification uses an oxidizing atmosphere by addition of air, oxygen, or steam as a reaction medium to convert the organic portion of a feedstock into the minor by-product char and primarily noncondensable, permanent gases, CO, CO_2, H_2, and low molecular weight hydrocarbon gases (Bridgewater, 2003; McKendry, 2002). Gasification uses preheated oxidizers (800-1300°C) at atmospheric pressure to convert the dry biomass to char and synthesis gas. The principle stages in gasification are drying, pyrolysis, reduction, and oxidation (Bridgewater, 2003; McKendry, 2002; 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.

Poultry litter and feedlot manure was gasified using air as the oxidizing agent, and 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%) (Priyadarsan et al., 2004). The product gases were severely diluted with inert nitrogen gas and contained a combustible portion consisting on average of 5.8% H_2, 27.6% CO, and 1.0% CH_4. Potassium and alkali salts in animal manure can enhance gasification due to their catalytic properties. Pyrolyzed poultry litter char (fixed carbon, 54.7%) gasified with steam has been tested without the addition of low-cost catalysts, potassium carbonate and langbeinite ($K_2Mg_2(SO_4)_3$) (Jones and Sheth, 1999; Sheth and Turner, 2002; Sheth and Bagchi, 2005). These catalysts were selected due to their common use in the fertilizer industry, making them a less expensive alternative to 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%. Preliminary tests suggest the phosphorus remains in the gasified char while 20 to 60% of the nitrogen would be released into the gas as ammonia, which could be trapped for recycled use (Jones and Sheth, 1999).

4.2.3 Hydrothermal Processes

In hydrothermal processes, the solid biomass is surrounded by water at temperature above 200 ^oC and at pressures sufficient to keep the water in either a liquid or supercritical state (Peterson et al., 2008). The critical temperature and pressure of pure water is 374 ^oC and 22.1 MPa, respectively. As in pyrolysis and gasification, the reaction temperature and its corresponding autogenic pressure determine the product distribution (Libra et al., 2011). Hydrothermal carbonization, liquefaction, and hydrothermal gasification are three most common hydrothermal processes that can be applied to livestock wastes. In hydrothermal carbonization (HTC) processes, the process temperatures increase up to about 250 ^oC and corresponding autogenic pressures to about 5 MPa: Most organics remain as or transformed into solids with very litter gas (1-5%) production. In liquefaction process with temperatures of up to about 400 ^oC, more oil and gas are produced. If the temperature and pressure are increased further to supercritical state of water, the primary reaction product is gas. This is called hydrothermal gasification. One of main advantages of the hydrothermal processing is that the energy-consuming drying stage is avoided when converting wet feedstocks such as swine and dairy manures. The energy required to dry these wet manures is much larger than that for pyrolysis (Ro et al., 2010).

4.2.3.1 Hydrothermal Carbonization (or Wet Pyrolysis)

Similar reaction pathways occur during both pyrolysis and HTC of biomass (Berge et al., 2011; Libra et al., 2011). Pyrolysis of biomass at temperatures between 200 and 500 ^{o}C in the absence of oxygen leads to thermal degradation of biomacromolecules without oxidation except by the oxygen already contained in the feedstock. In hydrothermal carbonization, biomass is heated in subcritical water to between 150 to 250 ^{o}C at autogenic pressures for reaction times typically greater than 1 hr. Feedstock is decomposed by reaction mechanisms similar to those in pyrolysis, which include hydrolysis, dehydration, decarboxylation, aromatization, and recondensation (Libra et al., 2011). In contrast to pyrolysis, hydrothermal degradation of biomass is initiated by hydrolysis, exhibiting lower activation energy than most of the pyrolytic decomposition reactions (Mok et al., 1992). As a result, the principle biomass components are less stable under hydrothermal conditions leading to lower decomposition temperatures than that for pyrolysis. Compared to pyrolysis, HTC produces higher solid yields, more water soluble organic compounds and mainly CO_2. Furthermore, the chemical structure of the solid products, hereafter referred to as hydrochar (or HTC coal), more closely resembles natural coals than pyrolysis char (Libra et al., 2011; Schuhmacher et al., 1960). The unique carbonaceous structure of the hydrochar is attributed to the diversity of its potential applications as discussed in the later section of this chapter.

4.2.3.2 Liquefaction

Liquefaction process typically occurs at temperatures between about 200 to 370 ^{o}C and pressures between about 4 to 20 MPa, sufficient to keep the water in liquid phase. It hydrolyzes the lignocellulosic components of animal manure and converts the manure into oil. He et al. (2000) hypothesized that the metal salts naturally present in the waste catalyze the hydrolysis reactions (He et al., 2000). A research group in the University of Illinois investigated batch and continuous liquefaction of swine manure (TS 20 – 27 wt%) (He et al., 2000; He et al., 2001a; 2001b; Ocfemia et al., 2006). In batch studies with CO as a reducing agent and reactor temperatures ranging from 285 to 350°C, volatile solid conversion to oil was as high as 76.2%. This swine-manure-based bio-oil was more energy dense than most wood-based pyrolytic oils, with an average heating value of 36.4 MJ kg^{-1}. 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., 2006). The impact of liquefaction temperature and retention time on swine-manure-based biooil was investigated by NC AandT State University researchers (Xiu et al., 2011a; 2011b). Oil yield, carbon content, and heating vale of the oil increased with temperature ranging from 260 ^{o}C to 340 ^{o}C. Retention time affected the extent of the liquefaction process and the oil yield rather than the quality of oil. Interestingly adding crude glycerol as a co-substrate dramatically increased oil yield, but decreased the carbon content and heating value of oil.

4.2.3.3 Hydrothermal Gasification

Hydrogasification or wet gasification, utilizes unique water properties that 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) of MIT, who demonstrated 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 U.S. DOE Pacific Northwest National Laboratory (PNNL) developed sub-critical (250-360°C, up to 22 MPa), catalytic-based wet gasification technology (Elliott et al., 1997; 2004; Sealock Jr et al., 1988; Sealock et al., 1997). Bench and pilot-scale testing of sub-critical wet gasification of dairy manure and other agricultural wastes using Ruthenium 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). Later Ro *et al.* (2007) evaluated the feasibility of wet gasifying various agricultural and municipal wastes using the PNNL technology. Chemical elemental balances of the wet gasification reactions of these residuals are shown in Table 4.2. For all feedstocks examined, about half of the carbon was converted to CH_4 and the other half to CO_2. Energetics of these reactions showed that the threshold solid concentration for these feedstocks was about 8%. The threshold concentration is an energetically breakeven point, above which the wet gasification process yields a net positive energy, when considering all process requirements such as pumping and heat loss. If a significant portion of produced gas stream heat can be recycled to heat the incoming feedstock, the threshold concentration would crease to low values. The PNNL researchers were able to develop a double-tube heat exchanger system that could recycle up to 90% of the energy needed to raise the feedstock temperature to the operating temperature (Elliott et al., 1999). If the wet gasification system is equipped with the 90% heat recovery system, all feedstocks would generate positive net energy at solid concentrations above 2% as shown in Figure 4.2.

The economics of utilizing a wet gasification swine manure management system for a model swine farm (4400-head, feeder-to-finishing) were evaluated using the spreadsheet model developed by the PNNL for the technology (Ro et al., 2007). In this proposed system, the flushed swine manure was directly treated with the wet gasification system. The product gas could be used as space heating or further processed in downstream catalytic thermochemical processes to produce liquid fuels. The ammonia in the product water stream could be recovered via stripping or membrane separation. The rest of the water could be recycled back to the swine farm as drinking water for pigs after minimal treatment. The installed capital cost of the farm-scale wet gasification unit for the 4400-head model swine farm was $991,000 with an annual operating cost of $218,359. The product gas would generate a net positive cash flow of $47,006/yr. When annualized costs of the wet gasification system were compared with that of conventional anaerobic animal lagoon system, the capital and operating costs of the wet gasification system ($375 per animal unit) were significantly higher than that of the lagoon system ($85-$95 per animal unit). Although the high capital cost and the cost of Ru catalysts and auxiliary processes for preventing poisoning of catalysts pose the major obstacle, the PNNL wet gasification technology offers significant environmental benefits over existing treatment technologies. With technical advances and cost reductions in the near future, this technology offers significant potential for agricultural and municipal wastes treatment.

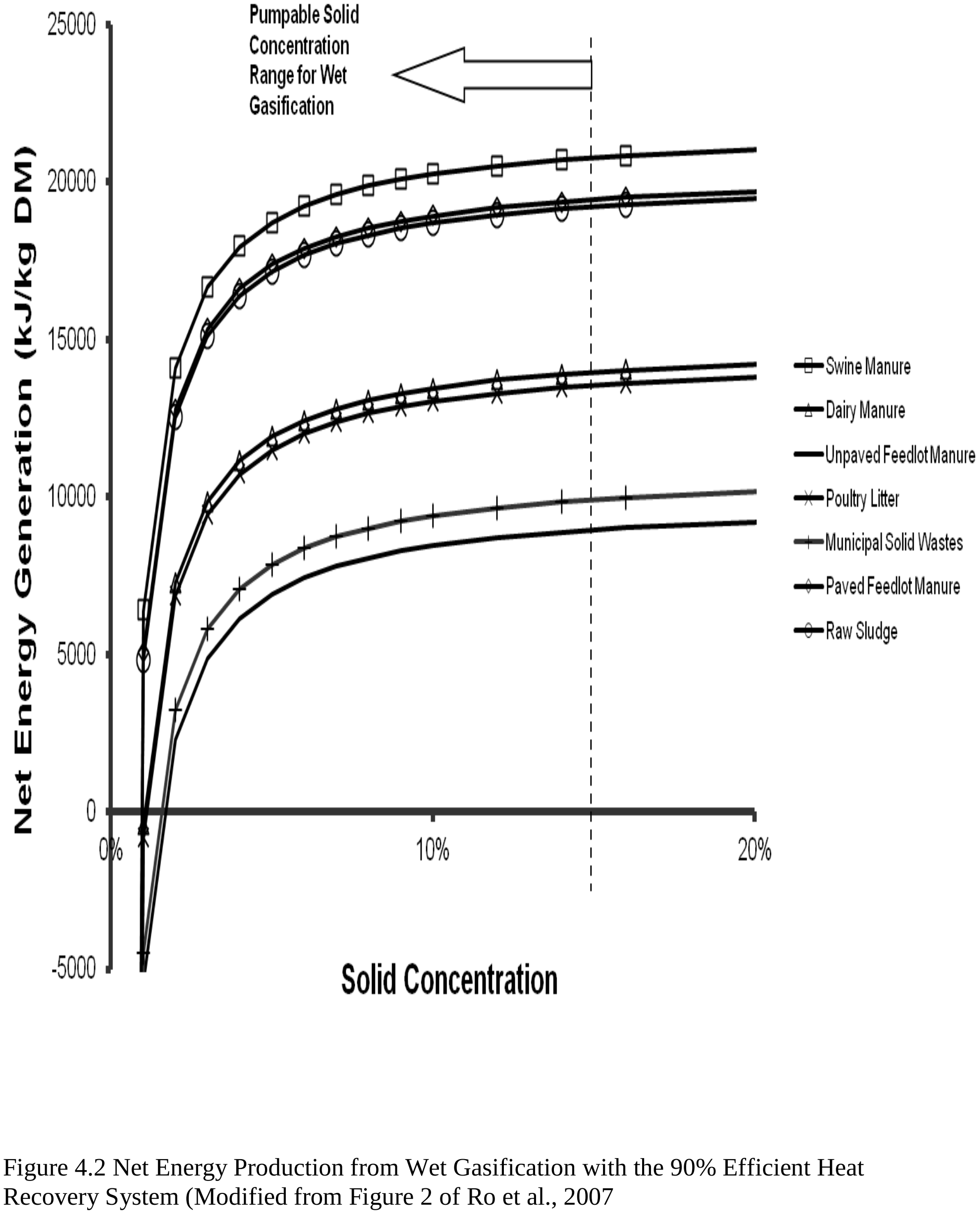

Figure 4.2 Net Energy Production from Wet Gasification with the 90% Efficient Heat Recovery System (Modified from Figure 2 of Ro et al., 2007

Table 4.2 Wet Gasification Reactions of Various Animal and Municipal Wastes (Modified from Table 1 of Ro et al., 2007)

Materials		Wet Gasification Reaction
WetMane	Swine Manure	$CH_{1.69}N_{0.06}O_{0.51}$ (s) + 0.39 H_2O (l) → 0.55 CH_4 (g) + 0.45 CO_2 (g) + 0.063 NH_3 (aq) + 0.01 H_2 (g) 4-3.
	Dairy Manure	$CH_{1.57}N_{0.04}O_{0.64}$ (s) + 0.32 H_2O (l) → 0.52 CH_4 (g) + 0.48 CO_2 (g) + 0.04 NH_3 (aq) + 0.01 H_2 (g) 4-4.
DryManue	Poultry Litter	$CH_{1.45}N_{0.07}O_{0.56}$(s) + 0.12 H_2O (l) → 0.48 CH_4 (g) + 0.52 CO_2 (g) + 0.07 NH_3 (aq) + 0.08 H_2 (g) 4-5.
	Unpaved Feedlot Manure	$CH_{1.45}N_{0.08}O_{0.5}$ (g) + 0.48 H_2O (l) → 0.51 CH_4 (g) + 0.49 CO_2 (g) + 0.08 NH_3 (aq)+ 0.07 H_2 (g) 4-6.
	Paved Feedlot Manure	$CH_{1.45}N_{0.06}O_{0.47}$ (s) + 0.59 H_2O (l) → 0.47 CH_4 (g) + 0.53 CO_2 (g) + 0.06 NH_3 (aq) + 0.28 H_2 (g) 4-7.
Municipal	Primary Sludge	$CH_{2.07}N_{0.06}O_{0.57}$ (s) + 0.43 H_2O (l) ☐ 0.5 CH_4 (g 4-8.
	MSW	$CH_{1.56}N_{0.03}O_{0.55}$ (s) + 0.39 H_2O (l) → 0.53 CH_4 (g) + 0.47 CO_2 (g) + 0.03 NH_3 (aq) + 0.07 H_2 (g) 4-9.

4.2.4 Downstream Processing for Biofuel Synthesis

Liquid fuels such as hydrocarbons and methanol can be produced from animal manure derived synthesis gas via downstream catalytic processes. Synthesis gas, mainly H_2 and CO, can be produced from gasification of animal manures or steam-methane reforming (SMR) of methane produced from animal manure digestion process (van Kempen, 2003). Common downstream processes for biofuel synthesis utilize Fischer-Tropsch (F-T) and methanol synthesis reactions using metal catalysts to lower the activation energy. The F-T reaction converts CO and H_2 of the synthesis gas to hydrocarbon products ranging from undesirable methane to high molecular weight waxes (Dry, 1981).

$$nCO + 2nH_2 \rightarrow (-CH_2-)_n + nH_2O \qquad \Delta H_{298} = -165 \text{ kJ/mol} \quad 4\text{-}10.$$

where the $-CH_2$ moiety is a repeating n-length unit of hydrocharbons. The original German F-T commercial plants from the 1930s and current operations by Sasol in South Africa used coal as a feedstock and Fe-based catalysts. The F-T process has been modified for the last three decades to use natural gas as a feedstock. Though F-T route is gaining popularity, an attractive alternative is to synthesize methanol from the synthesis gas (Mahajan, 2005).

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H_{298} = -129 \text{ kJ/mol} \quad 4\text{-}11.$$

Methanol is presently manufactured from the natural gas derived synthesis gas using a supported Cu/ZnO heterogeneous catalyst at 250-300 ^{o}C and between 5-10 MPa operating pressure (Cantrell et al., 2007). While a typical commercial scale methanol plant is of 2000 tons/d or higher input, potential farm scale application requires plant size of 100 tons/d for centralized animal waste facility. This scale of economy issue along with the stringent requirement to clean animal manure derived synthesis gas with high sulfur compounds must be overcome before the manure-to-liquid fuels can be realized in the future.

4.3 POTENTIAL USE OF MANURE-BASED CHAR

Char produced from pyrolyzing animal manure can be used as a feedstock (“green coal”) for existing coal power plants. Char can also be applied to soil as a soil amendment to improve fertility (Antal Jr and Grønli, 2003; Gaunt and Lehmann, 2008; Lehmann, 2007; Lehmann et al., 2003a; Lehmann et al., 2003b; Libra et al., 2011). Char produced from animal manures can also be activated to remove pollutants in water and air as an adsorbent (Bridgewater, 2003; Dominguez et al., 2003; Koutcheiko et al., 2007; Lima and Marshall, 2005; Sanchez et al., 2007). The following sections briefly review the characteristics and applications of chars made from animal manures.

4.3.1 Characteristics of Manure-Based Chars Made From Various Pyrolysis Processes

Physicochemical and thermal properties of chars made from pyrolyzing swine manure via both pyrolysis and HTC (or wet pyrolysis) processes were evaluated along with their chemical structures via solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy (Cao et al., 2011). Raw swine manure was converted into hydrochar by anaerobically heating the manure solution (20% solid) to 250 ^{o}C under its autogenic pressure for 20 hrs. The swine hydrochar had been washed with acetone to remove mobile compounds adsorbed on hydrochar. Pyrochar was produced by pyrolyzing dried swine manure at 620 ^{o}C for 2 hrs with a heating rate of 13 ^{o}C/min using a proprietary skid-mounted batch reactor system (Ro et al., 2010). The changes in chemical compositions and thermal properties resulting from both dry and wet pyrolysis processes are shown in Table 4.3. Both fixed carbon and ash contents of pyrochar increased dramatically from that of raw swine manure. While C contents in both hydrochar and pyrochar increased slightly, both H and O contents of the pyrochar decreased substantially, indicating the increase in aromaticity due to pyrolysis.

The increase in aromaticity of the pyrochar can be seen clearly by comparing the NMR spectra of these chars to that of raw swine manure (Figure 2 of Cao et~~l~~ al., 2011). HTC-swine W, HTC-AW-swine A, and HTC-AC-swine A are water-washed hydrochar, acid-prewashed hydrochar, and acid-catalyzed hydrochar, respectively. The ^{13}C cross polarization and total suppression of sidebands (CP/TOSS) spectra, serving mainly as reference spectra, show the signals from potentially all carbon sites qualitatively in these samples. Dipolar dephased CP/TOSS and ^{13}C chemical-shift-anisotropy (CSA) filter spectra were employed to select non-protonated carbons and mobile groups, such as OCH_3 and CCH_3, and sp^3-hybridized carbons, respectively.

^{13}C NMR spectra of raw swine manure show the following characteristics; a) strong signals centered around 30 ppm from resonances of alkyl carbons in the region of 0-48 ppm, b) NCH signals between 48-60 ppm, c) signals attributed to the resonances of carbohydrates in the region of 60-112 ppm, d) small signals arising from aromatic/olefinic carbons in the region of 112-165 ppm, and e) appreciable signals from COO/N-C=O groups in the region of 165-190 ppm. Significant signals in the regions of 48-112 ppm and 165-190 ppm indicated that proteins or peptides are one of the major constituents of swine manure along with carbohydrates. When the raw swine manure was carbonized via HTC, the signals from aromatic or olefinic carbons around 130 ppm increased while the signals from COO/N-C=O functionalities decreased. Comparing the spectra of HTC-swine A and W, there was a substantial increase in mobile $–(CH_2)_n$- groups in HTC-swine w char, as indicated by the dominant band around 30 ppm in its dipolar-dephased spectrum. It appeared that the acetone wash removed some mobile $–(CH_2)_n$- groups in the hydrochar.

The pyrochar spectra showed very different functionalities than that of hydrochars. The pyrochar was predominantly aromatic, with only very small peaks in the alkyl region (0-48 ppm). The dipolar-dephased spectrum showed a very pronounced signal from nonprotonated aromatic carbons with signals from the mobile $–(CH_2)_n$- and CCH_3 components. The signals assigned to anomeric O-C-O carbons around 103 ppm completely disappeared in the CSA-filtered spectrum, indicating the absence of carbohydrates in pyrochar. It also did not contain any peptides or proteins, as demonstrated by the lack of NCH signal around 53 ppm and N-C=O signal around 172 ppm.

^{1}H-^{13}C long-range recoupled dipolar dephasing experiments provide information about distances of the aromatic hydrocarbons from protons at the edge of the fused aromatic ring system. The larger the ^{1}H-^{13}C distance, the slower the dephasing of the ^{13}C signal, and the larger the aromatic cluster size. As shown in Figure 4.7, the dephasing times of HTC-swine A ranged from 0.29 to 0.86 ms, while those of pyrochar ranged from 0.29 to 1.43 ms. The dephasing curves of HTC-swine A, pyrochar, and lignin suggested the presence of fused or more substituted aromatic rings in both hydrochar and pyrochar than lignin but a more condensed character of aromatics in pyrochar than hydrochar.

Table 4.4 shows the quantitative structural compositions of the carbons of the swine chars produced from either pyrolysis or hydrothermal carbonization with and without post processing conditions based on ^{13}C direct polarization/magic-angle spinning NMR (^{13}C DP/MAS NMR) experiments. The dominant structural component in the raw swine manure was alkyl (62.7%), followed by O-alkyl (12.6% excluding O-CH_3), COO/N-C=O (11.0%), and NCH (5.7%) groups, representing lipids, carbohydrates, and protein/peptides. These functionalities decreased while aromatic components increased as the swine manure was carbonized via HTC. This increase in aromatic carbons accompanying the decrease in carbohydrates and proteins/peptides suggested that the carbonization process had taken place to a certain extent. The decrease in O-alkyls, NCH, and COO/N-C=O as well as corresponding increase in aromatic/olefins in HTC-swine A compared to HTC-swine W indicated that acetone washing substantially removed carbohydrates and peptides of the hydrochar. In contrast, pyrochar displayed wholly different structural features. Raw swine manure underwent substantially deeper carbonization during the dry pyrolysis than the HTC processes as indicated by its higher aromatics and low alkyl groups. Aromatic carbons (82.0%) became the predominant components, with the remainder being mostly alkyl hydrocarbons (11.0%). Furthermore, majority of aromatic carbons (about 75% of total aromatic carbons) are not protonated. Substantial loss of peptides/proteins (NCH and COO/N-C=O groups) corresponded well to the 68% N loss observed during swine manure pyrolysis (Ro et al., 2010).

Table 4.3 Proximate and Ultimate Analyses of Raw Swine Manure and Its Chars (Modified from Table 1 of Cao et al., 2011)

parameters	raw swine	swine Hydrochar	swine pyrochar
Proximate Analyses			
moisture (%)	12.8 ± 0.3	3.4 ± 0.8	3.4 ± 0.1
volatile matter (% $_{db}$)	60.6 ± 1.1	59.1 ±1.5	14.1 ± 2.5
fixed C (% $_{db}$)	8.1 ± 0.6	13.1 ±1.3	41.2 ± 1.3
ash (% $_{db}$)	18.5 ± 0.2	27.8 ± 0.3	44.7 ± 1.2
Ultimate Analyses			
H (% $_{db}$)	5.9 ± 0.1	5.7 ± 0.0	1.9 ± 0.3
C(% $_{db}$)	47.3 ± 0.2	49.5 ± 2.8	50.7 ± 0.6
O(% $_{db}$)	20.1 ± 0.4	16.5 ± 6.0	< 0.01
N(% $_{db}$)	4.58 ± 0.13	1.92 ± 0.95	3.26 ± 0.08
S(% $_{db}$)	0.93 ± 0.04	NA	0.66 ± 0.01
P(mg/g dm)	23.7 ± 0.8	47.7	71.5 ± 1.3

Table 4.4 Quantitative structural information of raw swine manure and its chars (Modified from Cao et al., 2011)

Sample	Ppm								
	190-220	165-190	165-145	112-145		112-60	60-48		48-0
	Aldeyde Ketone	COO/ N-C=O	Aromatic C-O	Nonprotonated aromatic/ olefinic C	Protonated aromatic/ olefinic C	O-alkyl C	NCH	O-CH3	Alkyl
Raw swine manure	1.1	11.0	0.5	3.2	1.7	12.6	5.9	1.2	62.7
HTC-swine W	2.1	6.0	4.4	11.5	6.1	6.6	2.6	0.7	59.9
HTC-swine A	1.8	5.6	5.2	14.1	7.0	1.8	1.8	0	62.6
Pyrochar	0.9	2.8	6.4	54.9	20.7	2.2	1.1	0	11.0

4.3.2 Soil Application of Char

In recent years, much research effort has been expended to show that returning char-based carbon to the soil can sequester carbon and increase soil fertility (Antal Jr et al., 2003; Gaunt and Lehmann, 2008; Lehmann, 2007; Novak et al., 2009). Its suitability as a carbon sequestration strategy will depend on the overall carbon balance of the production process and the long-term stability of char in soil. In order to assess the sequestered CO_2 equivalents over the product life cycle with due diligence, reliable and reproducible methods are needed. In addition, the soil, climatic and management conditions may vary widely from location to location, which will significantly influence char stability in soil. Soil application of char may provide multiple beneficial effects on soil physicochemical properties: 1) Enhance the water holding capacity, aeration, and hydraulic conductivity of soils (Glaser et al., 2002; Novak et al., 2009; Oguntunde et al., 2008).; 2) Reduce the tensile strength of hard-setting soils (Chan et al., 2008); 3) Increase the cationic exchange capacity (CEC) of soils, resulting in improved nutrient retention (Novak et al., 2009; Steiner et al., 2008); 4) Stimulate growth, activity and the metabolic efficiency of the microbes (Kolb et al., 2009; Steiner et al., 2008); and 5) Reduce N_2O emissions from soil (Libra et al., 2011). Although crop yield does not always increase with char addition, char application can improve crop yields for degraded, low-fertility, or tropical soils (Libra et al., 2011). More discussion on soil application of animal-manure derived char is discussed in Chapter 8.

4.3.3 Char as an Adsorbent

Chars made from pyrolyzing biomass and animal manures can be activated to increase their sorption capacity. Lima and co-workers produced activated carbon from both poultry and turkey litter (Lima and Marshall, 2005; Lima et al., 2008; Lima et al., 2009). When compared to commercial granular activated carbon for water filtration, the poultry and turkey-based activated chars had greater copper ion adsorption capacity showing promise in potential metal ion removal applications. Sun et al. (Sun et al., 2010) reported that nonactivated hydrochars made from hydrothermal carbonizing chicken litter and swine manure showed high adsorption capacity for endocrine disrupting chemicals (EDCs) such as common estrogenic compounds, bisphenol A (BPA) and 17α-ethinyl estradiol (EE2), and a polycyclic aromatic hydrocarbon, phenanthrene (Phen). This study demonstrated that manure-based hydrochar could adsorb a wide spectrum of both polar and non-polar organic contaminants.

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