Role of Thermochemical Conversion in Livestock Waste-to-Energy Treatments: Obstacles and Opportunities

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Integrating thermochemical conversion (TCC) technologies with current animal waste treatment practices can treat and reduce quantities of manure from consolidated animal feeding operations. Additionally, TCC technologies can produce value-added, renewable energy products. These products can meet heating and power needs or be catalytically converted into liquid fuels. The primary objectives of this study were to assess opportunities and obstacles in the treatment and energy conversion using currently available TCC processes. Both dry and wet livestock manures were assessed. Dry wastes like poultry litter and feedlot manures can be processed directly via pyrolysis and air/steam gasification technology. The solids in the aqueous waste streams from dairy and swine operations can undergo wet gasification or direct liquefaction processes. Alternatively, these solids can be separated and dried before conversion. Due to high ash and sulfur contents, pretreatment of manure is necessary to prevent catalyst poisoning and promote effective unit operation. While the energy input requirements for a conceptual wet gasification manure treatment system of a model swine farm is larger than a traditional anaerobic digestion operation, there are many significant advantages in implementing TCC technology including the following: compact design; faster treatment times; reduction of odors, BOD, and pharmaceutically activated compounds; and elimination of sludge.

Introduction

Over the past decades, the United States animal production industry has seen a massive consolidation of concentrated animal feeding operations (CAFOs). This change to fewer, but larger operations not only significantly increased the number of animals per facility but concentrated large quantities of manure, wastewater, and bedding materials.[1,2] Traditional manure management practices have recycled plant nutrients through land application. Unfortunately, manure production from CAFOs is often greater than local crop and proximal pastureland nutrient demands. Overapplication of the animal manure can result in the following: (1) spread pathogens; (2) emit ammonia, greenhouse gases, and odorous compounds; (3) release hormones and other pharmaceutically active compounds; and last (4) enrich surface and groundwaters with nitrogen and phosphorus compounds leading to eutrophication.[2−4]

In order to reduce the environmental impact of CAFOs, animal manure treatment practices commonly incorporate biological processes such as composting and anaerobic digestion. Drier animal manures like poultry litter and feedlot waste, with a total solids (TS) content ranging from 60 to 80 wt %[5,6] have traditionally been treated with composting. Aqueous waste streams from dairy and swine facilities (0.70−7.0 wt % TS[7,8]) are typically discharged into open-air, anaerobic lagoons.[9,10] Both practices reduce pathogens and produce a more uniform fertilizer. Unfortunately, these practices involve large facility footprints and long process times, on the order of days to months, due to their associated slow microbial degradation processes.[11] These practices are a potential source of contamination to groundwaters or surface waters and even still require proper land disposal of the residual product to control ammonia and other greenhouse gas emissions.[9]

Alternative, environmentally acceptable means of manure treatment lie with introducing current manure treatment practices to more efficient energy conversion processes. These waste-to-energy conversion treatment processes have dual functions: (1) remove large amounts of oxygen-demanding, organic wastes and (2) produce energy-dense, alternative fuels. One category of waste-to-energy conversion processes includes thermochemical conversion (TCC), where high-temperature chemical reforming processes break the bonds of organic matter and reform these intermediates into synthesis gas and hydrocarbon fuels. The minor, unreacted, residual is a combination of minerals and fixed carbon, commonly referred to as char. The quantity and quality of each end product are dependent on the reactor system used and feedstock characteristics.

In addition to being a mass consumer of its organic feedstock, TCC processing of animal manure has a number of advantages when compared to common biological treatments: (1) thermochemical reactors can be sized to suit the intended application making them more compact; (2) the conversion processes take place in a matter of minutes; (3) the high process temperatures destroy pathogens and most pharmaceutically active compounds; (4) the process can use a variety of blended on-farm seasonal crop residues and animal manure feedstocks; (5) the process generates no fugitive gas emissions; and (6) more efficient nutrient recovery is achievable. In concentrating the plant nutrients (e.g., P and K) into a nutrient-dense, residual solid, application of TCC technologies reduces applicable land disposal charges associated with fuel, tipping, and transportation.

The objectives of this paper are to (1) introduce various scenarios integrating TCC technologies with existing livestock waste management practices; (2) perform a preliminary energetic

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10.1021/ie0616895 CCC: $37.00

Table 1. Characteristics of Various Animal Wastes

	dry wastes			wet wastes	
	poultry litter[14]	soil surfaced feedlot manure[6]	paved surfaced feedlot manure[6]	pit-recharge liquid swine manure	flushed dairy manure
total solids (TS) (%)	92.5	80.2	79.7	2.0[15]	3.82[16]
volatile solids (% of TS)	40.3	33.8	64.6	68.7	83.8
ash (% of TS)	43.9	58.7	20.2	31.3[a]	16.2[a]
fixed carbon (% of TS)[b]	15.8	7.5	15.2	na[c]	na
composition (% dry basis)					
C	22.0	21.7	43.1	45.717	44.718
H	3.8	2.62	5.22	6.45	5.85
N	2.6	1.94	3.11	3.45	2.05
S	0.7	0.42	0.67	0.38	0.31
O[d]	27.1	14.6	27.7	31.4	38.2
HHV (kJ/kg $TS_{\text{dry basis}}$)	9240	7861	16810	17170	18220

[a] Reported as fixed solid content (FS), which is a combination of ash and fixed carbon (TS = VS + FS). [b] Calculated by difference (TS = VS + ash + fixed carbon). [c] na, not available. [d] Calculated by difference among C, H, N, S, and ash content.

evaluation of a model swine farm using two wastewater treatment scenarios: (a) a combined biothermochemical wastewater treatment process and (b) wet gasification as sole treatment; and (3) identify the potential challenges and limiting factors using animal manure feedstocks in TCC operations.

Animal Manure Characteristics

Feedstock characteristics have a significant effect on the conversion efficiency of TCC processes. For instance, important parameters such as the TS, volatile solids (VS), and ash contents vary depending on source (Table 1). The characteristic TS concentration influences the type of conversion process as well as the necessary pretreatments of drying or dewatering. The VS provides a measure of the ease with which the feedstock can be utilized as an energy source. The ash represents the nondegradable portion in the feedstock; this includes the alkali metal content consisting of salts like sodium, potassium, calcium, and magnesium.

Poultry and feedlot operations collect a mixture containing manure, bedding, waste feed, and, in some instances, underlying soil. These mixtures are generally dry. When collection incorporates soil, the ash content is high. Furthermore, both the VS and carbon content of soil-containing manure decrease; this negatively affects the higher heating value (HHV).

Dairy and swine feeding operations typically produce a dilute solids waste stream composed primarily of discharged wash water but also manure, urine, and undigested feed. Discharged swine and dairy manure characteristics are highly dependent on the following: growth stage of the animals; the type of manure handling and collection system (flush, pull-plug, or pit-recharge); and the amount of added water.[12] Compared to the poultry- and cattle-based manures, dairy and swine manure VS is a significant portion of the TS (69−84%) meaning more organic material is available for conversion contributing to a greater HHV. In a preliminary wet gasification analysis, Ro et al. reported that, among five major types of animal manure, swine manure as a feedstock would produce product gases with the highest energy per kilogram of dry TS.[13]

Livestock Waste-to-Energy Scenarios

There are three main TCC processes that can be easily incorporated with existing manure management practices for converting livestock manures into a value-added, renewable energy product: pyrolysis, gasification, and direct liquefaction. Dependent on temperature, pressure, heating rate, and residence time,[19,20] each process generates some combination of volatile gases, bio-oil, and solids. The volatile gases are a mixture of H_2, CO, N_2, water vapor, hydrocarbon gases, and tars. A portion of the volatile gases, namely the tars, condense to form a combustible bio-oil.

The end use of these products can be placed into three main groups: heat and power generation; transportation fuels; and chemical feedstocks.[21] The products intended for heat and power generation or transportation fuels should be cleaned prior to use as they contain tars, metals, water, organic acids, and dust; all these materials are corrosive to construction materials and detrimental to the engine's operation. Additionally, these fuels may also contain nitrogen and sulfur compounds that will contribute to NO_x and SO_2 emissions when burned.[20,22] Through downstream processing and catalytic techniques, TCC products can serve as chemical intermediates and be upgraded to more energy dense and useable forms. Steam reforming of the hydrocarbons can yield synthesis gas (H_2 and CO) for conversion to methanol, higher alcohols, or Fischer−Tropsch fuels.[23,24]

Dry Animal Wastes Scenario: Poultry and Feedlot Manures. Waste-to-energy systems using dry manure feedstocks: namely, poultry litter and feedlot manure produce gases, bio-oils, and char that can be cleaned and used for combined heating and power (CHP) requirements or catalytically converted into liquid fuels and mixed alcohols (Figure 1). The TCC processes of pyrolysis and gasification are more easily applicable since the overall drying requirements would be far less to bring these wastes to within the generally recommended TS of 90 wt %.[14]

Pyrolysis. Destructive distillation of wood to produce "wood alcohol" has historical significance. The wood alcohol (mainly methanol) is ancient technology but not energy efficient, and the modern day version of this process is pyrolysis. In the absence of oxygen, pyrolysis converts the organic portion of the feedstock into a mixture of char and volatile gases containing noncondensable vapors and condensable tars (oxygenated hydrocarbons), which form a pyrolytic oil or bio-oil.[19] The individual contribution of char, pyrolytic oils, and gases to the overall final product composition is dependent on heating rate, reactor temperature, and residence time. With slow pyrolysis, low reactor temperatures (400 °C) and long vapor residence times (>20 s) promote char production. When higher temperatures (500 °C) and short residence times (∼1 s) are used, fast pyrolysis converts biomass mainly to a liquid product (60−75 wt %).[25] While no pyrolysis of animal manure has been demonstrated, early pyrolysis experiments focused on oils from woody feedstocks. However, oil production from alternative feedstocks has expanded to include agricultural residues and microalgae. Most wood-based oils have a heating value in the range of 20−25 MJ/kg. Agricultural residues, like sugarcane and olive bagasse, can provide pyrolytic oils with heating values as high as 35 MJ/kg; algae-based pyrolytic oils offer 30−40 MJ/kg of heat.[19,20,25]

Dry Gasification. Gasification uses air, oxygen, or steam as a reaction medium to convert the organic portion of a dry or wet feedstock to noncondensable, permanent gases, CO, CO_2, H_2, and low molecular weight hydrocarbon gases. This process leaves behind a char byproduct. The permanent gases are produced through a variety of heterogeneous and homogeneous reactions involving the remaining char (mostly fixed carbon) and product gases (Table 2). The first three reactions involving

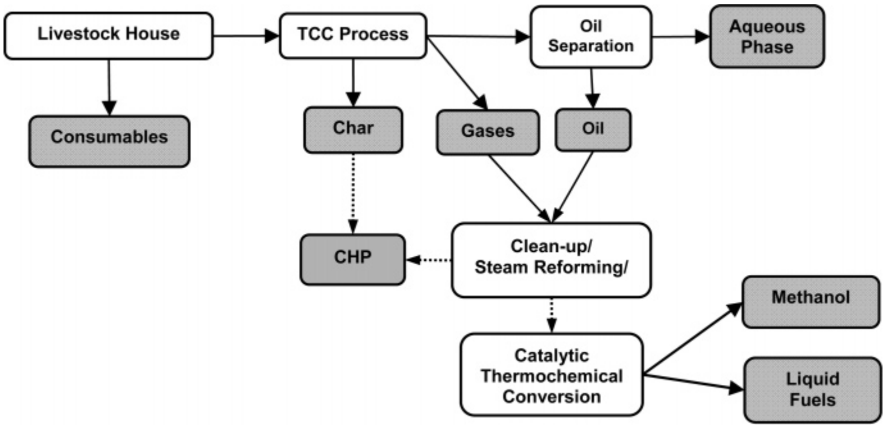

Figure 1. Dry manure feedstock waste-to-energy treatment system.

Table 2. Heterogeneous Reactions Involved in Gasification

	heterogeneous chemical reaction	rxn	$\Delta H_{rxn,298}$ (kJ/mol of C)[a]
carbon−steam	$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$	(1)	131.3
	$C(s) + 2H_2O(g) \rightarrow CO_2(g) + 2H_2(g)$	(2)	90.1
Boudouard	$C(s) + CO_2(g) \rightarrow 2CO(g)$	(3)	172.5
hydrogasification	$C(s) + 2H_2(g) \rightarrow CH_4(g)$	(4)	−74.8
water−gas shift	$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$	(5)	−41.5
methanation	$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$	(6a)	−206.1

[a] Heat of reaction based on heat of formation at 298 K.

the char, carbon−steam, and Boudouard are endothermic and favored at high reactor temperatures. Hydrogasification (eq 4) and the homogeneous gas-phase reactions are exothermic. The quantity of end products from these reactions is dependent on the process temperature, pressure, and feedstock characteristics.

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. In the drying stage, moisture is evaporated 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. Here, oxidation of the volatile compounds consumes all oxygen, leaving the steam and CO_2 to oxidize the char in carbon−steam and Boudouard reactions (eqs 1−3), and releases 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.[14] 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.[26] The remaining char was between 14 and 25% of the original input while tar production was less than 2%.

Steam can be used in gasification systems as the oxidizing agent to increase H_2 production due to steam's involvement in the carbon−steam reactions (eqs 1 and 2) and more importantly the water−gas shift reaction (WGS; eq 5). Hydrogen production can further improve with an increase in steam's temperature; this rise in operational temperature can increase feedstock carbon to gas conversion improving gas yield while decreasing char and tar production. For instance, early work by Corella's group[27] was able to: maximize sawdust carbon conversion to gas up to 80%, generate a product gas containing more than 50% H_2, and decrease char yield from 22% to 8%.

To promote greater gas production and diminish the production of tar, catalytic steam gasification processes utilize a heterogeneous catalyst, such as nickel. Depending on the process reactor temperature, this catalyst can operate either concurrent or in series with the gasification process to increase the reaction rate of carbon−steam reactions and the WGS; thereby the process generates a higher quality synthesis gas. When compared to the lack of a catalyst, using a Ni−Al catalyst during steam gasification of pine sawdust can double the gas yield as well as increase the H_2 to CO ratio four to five times.[28] 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. 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. Researchers at the University of Tennessee Space Institute (UTSI) investigated catalytic steam gasification of pyrolyzed poultry litter char (fixed carbon, 54.7%) with and without the addition of potassium carbonate and langbeinite ($K_2Mg_2(SO_4)_3$) as catalysts.[29−31] 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.[29]

Wet Animal Wastes: Swine and Dairy Manures. In a wet waste-to-energy treatment system (Figure 2), swine and dairy manures contain excess water that can serve as the carrier fluid and reaction medium for direct liquefaction, aqueous-phase gasification technologies, and combined pyrolysis/gasification process. If these water-based TCC systems are used on wet slurry biomass such as animal manure and sewage sludge, the wet feedstock does not have to be dried. This drastically reduces the need for feedstock pretreatments processes like thickening,

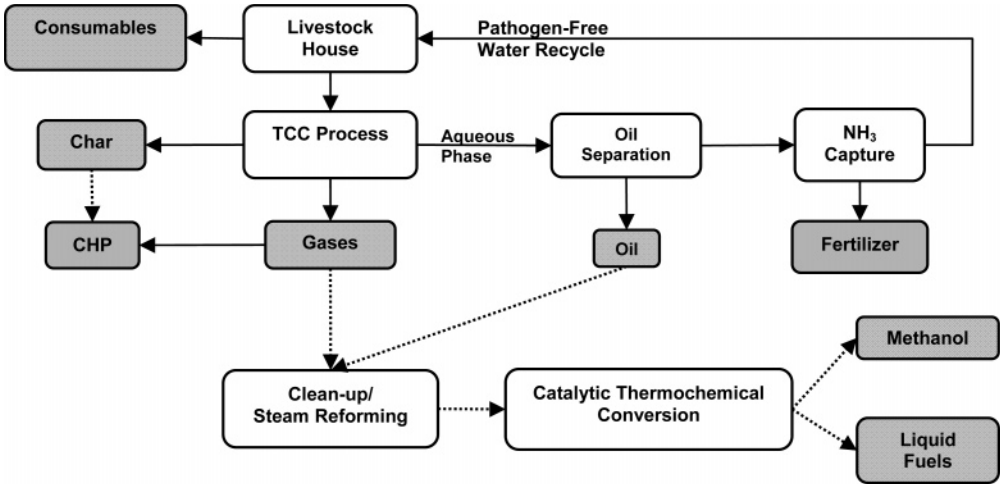

Figure 2. Wet feedstock waste-to-energy treatment system.

dewatering, and drying. Application of these water-based systems also provides a means to clean and purify potable water for livestock house reuse. Prior to recycling, ammonia captured and concentrated from the aqueous stream via stripping or membrane separation can serve as a nitrogen-fertilizer source. As with poultry and feedlot manure treatment systems, the end use of the char, bio-oil, and gases remain the same—CHP or catalytic conversion to liquid fuels.

Wet Gasification Utilizing Subcritical, Critical, or Supercritical Water. Wet gasification utilizes unique water properties that only exist in the vicinity of the critical region. The supercritical water (SCW) refers to the water at temperatures above its critical point (i.e., 374 °C and 22.1 MPa) with its density varying from 0.2 to 0.7 g/cm^3. As the SCW density decreases considerably from that of normal liquid water, hydrogen bonds between water molecules significantly weaken resulting in very low values of dielectric constant, comparable to those polar organic solvents. The loss of polarity of the SCW reduces the solubility of normally water-soluble salts but enhances the solubility of organic compounds. As a result, SCW becomes an excellent solvent for biomass organic compounds such as cellulose that are normally not soluble in room temperature.

Model and his co-workers[32,33] at MIT first introduced the wet gasification concept, utilizing the water with temperature and pressure conditions essentially at its critical point. They were able to demonstrate that glucose and cellulose could be converted to hydrogen, carbon dioxide, carbon monoxide, and other trace gases in supercritical water without producing char. However, the feedstock material must be brought up to the critical conditions rapidly without significant time exposure to the subcritical temperatures in which char formation is favored. Since then, numerous researchers investigated the wet gasification of biomass and organic wastes at near or supercritical water conditions. Researchers at the University of Hawaii at Manoa utilized various activated carbons as catalysts in SCW gasification of glucose, sewage sludge, and other waste materials.[34,35] Using coconut shell-derived activated carbon catalyst at 2.8 wt % feed, SCW gasification achieved near-complete gasification with a very low unconverted total organic carbon value of 0.28 g/L.[34] The product gas contained 1.1, 1.4, and 0.13 mol/g of feed of H_2, CO_2, and CO, respectively.

Elliott and co-workers at the U.S. DOE Pacific Northwest National Laboratory (PNNL) developed subcritical (250−360 °C, up to 22 MPa) water gasification technology through the use of various metallic catalysts.[36−39] Subcritical water gasification of dairy manure and other agricultural wastes was almost completely converted to CO_2 and CH_4 in bench- and pilot-scale reactor systems using Ru catalysts.[40] Just recently, Ro et al. evaluated the feasibility of wet gasifying various agricultural and municipal wastes using the PNNL technology.[13] Although the PNNL wet gasification technology offers significant environmental benefits over existing treatment technologies, the high costs of Ru catalysts and auxiliary processes for preserving catalytic activities poses the major obstacle for this technology to be implemented for agricultural and municipal wastes treatment applications in the near future.

Supercritical water partial oxidation (SWPO) is the latest development in the wet gasification technology utilizing SCW. Unlike the previously discussed wet gasification processes, SWPO utilizes the heat from the partial oxidation of feedstock with oxygen or air. The heat generated by in situ partial oxidation reactions of the feedstock results in rapid heating of the gasification medium, reduction in char formation, and enhanced hydrogen production. The extent of the partial oxidation is controlled by introducing less than stoichiometric quantities of oxygen. General Atomics is currently conducting a 9-year program developing a SWPO process for efficient and environmentally attractive gasification and hydrogen production using sewage sludge, municipal solid wastes, and other low-grade biomass materials as feedstocks.[41] In order to offset the high disposal costs many municipalities face today, one aspect of the program is focused on the use of biosolids, or treated sewage sludge, as a primary feedstock. However, successful implementation of SWPO using biosolids as feedstock will have to overcome the low heating value of the biosolid and the need for an auxiliary fuel to help attain gasifier operating temperatures higher than 650 °C.

Combined Pyrolysis and Wet Gasification. Using a single reactor treatment process, Menendez and co-workers at Spain's INCAR combined drying, pyrolysis, and gasification.[42−44] This integrated system converts the organic portion primarily to the gas phase with oil and chars as the lesser byproducts. By using elevated temperatures, long gas residence times, high heating rates, and no additional catalyst, this group maximized gas production. 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. However, both the excess steam and exothermic nature of the water−gas shift reaction promote CO_2 formation at the expense of CO.[45]

For this integrated unit process, microwave heating ovens provide the high heating rate and temperatures necessary. 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.[42] 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 into 5576 kJ/kg for char; 8500 kJ/m^3 for the gas, and 36 800 kJ/kg for the bio-oil. In addition to producing the product streams, this process was effective in treating the sewage sludge: combined pyrolysis/gasification removed all measurable biological oxygen demand and 95% of the initial chemical oxygen demand (COD) in the sewage sludge.

Direct Liquefaction (DL). With little to no char byproduct formation, 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.[17] 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 %).[17,46−48] 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%. Compared to most wood-based pyrolytic oils, this swine bio-oil product was more energy dense with an average heating value of 36.4 MJ/kg. 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.[48] 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 postprocessed stream were not realized. The authors concluded that further treatment of this water is necessary before discharging into a wastewater stream. However, recovery of these components would be ideal to meet fertilizer needs.

Downstream Processing

Synthesis Gas Processing. In order to maintain efficient operation of direct gas utilization technologies or liquid fuel conversions, synthesis gas cleanup would require the following: (1) the removal of water, dust, particulates, and condensable tars; and (2) mitigation of nitrogen-, sulfur-, and chlorine-containing compounds, for example H_2S, HCN, and HCl. Following gas cleanup, gas conditioning would include the following: (1) CO_2 removal; (2) H_2/CO ratio adjustment; and (3) light hydrocarbon catalytic reforming.

Once CO_2 is removed to decrease inert gas concentrations, the synthesis gas generated from animal waste primarily contains CH_4, CO, and H_2. Adjustment of the H_2/CO ratio through methane reforming allows for customization of the syngas to better suit the desired downstream liquid fuel production. Two methane reforming methods are available: Partial oxidation (POX) and steam−methane reforming (SMR). For POX, methane reacts with O_2 to yield a 2:1 ratio of H_2/CO. The SMR process is a commercial technology receiving much attention as a method to produce pure H_2 gas (>99.99%) in order to drive the "hydrogen economy".[49] The overall SMR process is a multistep involving a reverse methanation reaction of methane and steam reacting at 750−800 °C to produce synthesis gas that further undergoes the WGS reaction (eqs 5 and 6b):

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g) \qquad \Delta H_{298} = 206.1\ \text{kJ/mol} \quad (6b)$$

The WGS reaction occurs in two stages: high-temperature shift at 350 °C and low-temperature shift at 190−210 °C. With an overall process efficiency between 65% and 75%, the endothermic SMR process involves both a prestep for feedstock purification to remove chloride and sulfur impurities that extends the catalyst's life and a poststep to remove all the CO_2 produced in the WGS via the pressure swing absorption method. Upon production, synthesis gas is available to synthesize clean fuels via Fischer−Tropsch technology.

Catalytic Thermochemical Conversion. Liquid fuels such as methanol and hydrocarbons can be produced from the animal waste-derived synthesis gas via catalytic processes. If the synthesis gas contains a significant amount of CH_4, the SMR process can be used to convert methane to a mixture of H_2/CO. Common downstream processes for biofuel synthesis utilize Fischer−Tropsch and methanol synthesis reactions. These processes typically use metal catalysts to lower the activation energy, and the reactions take place at much lower temperatures than previous TCC processes. The following sections briefly review the SMR and the downstream processes for producing liquid fuels from the animal waste-derived synthesis gas.

Fischer−Tropsch (F−T) Synthesis. The F−T catalytic synthesis pathway is one of the leading gas-to-liquid options that converts natural gas to hydrocarbon-based liquid fuels that are low in sulfur and chloride impurities. The F−T reaction involves catalytic hydrogenation of CO to hydrocarbon products that range from undesirable methane to high molecular weight waxes (eq 7):[50]

$$nCO + 2nH_2 \rightarrow (CH_2)_n + nH_2O \qquad \Delta H_{298} = -165\ \text{kJ/mol} \quad (7)$$

where the $-CH_2$ moiety is a repeating n-length unit that represents hydrocarbons. Equation 7 is written for synthesis gas with an H_2/CO of 2. Unfortunately, under typical F−T synthesis conditions, CO_2 unequivocally appears in the product gas due to facile WGS reaction.[50−53] The hydrocarbon product distribution can be approximated by the Anderson−Schulz−Flory model that contains the probability of carbon-chain growth term, α.

In addition to the expensive and selective Ru-based catalysts, iron- and cobalt-based catalysts are sometimes used.[49,51] The original German F−T commercial plants from the 1930s used coal as a feedstock and Fe-based catalysts as do current operations by Sasol in South Africa.[50,52] The last three decades have seen modifications to the F−T process utilizing natural gas as a feedstock. The natural gas-based F−T-process uses the more expensive Co-based catalyst to produce waxes. These waxes can undergo further cracking to yield diesel fuel. The overall process efficiency is still compromised by low space−time yield, catalyst attrition, and product selectivity.

Progress toward cleaner fuel production has been made in both biomass gasification technologies and downstream processing via F−T.[54−56] A technical feasibility and economics study using commercially available gasification characteristics analyzed the biomass integrated gasification−Fischer−Tropsch (BIG-FT) process for production of 5-carbon chain and higher

Table 3. Model Swine Farm Waste Stream and Anaerobic Digester Effluent Characteristics[61]

	swine waste stream	anaerobic digester effluent
volumetric flow rate (L/d)	52320	52320
TS (mg/L)	47181	21161 (55.1)[a]
VS[b] (mg/L)	30858	11114 (64.0)
sulfur (mg/L)	579	363 (37.3)
total Kjeldahl nitrogen (mg/L)	4504	4276 (nsd)
ammonia nitrogen (mg/L)	3244	3423 (nsd)
organic nitrogen (mg/L)	1260	853 (32.3)
pH	8.0	8.4

[a] Numbers in parentheses represent concentration reduction (%) with nsd symbolizing a nonsignificant difference. [b] FS content can be calculated using, TS = VS + FS.

liquid fuels.[56] Using the modeling tool, Aspen^{plus}, Tijmensen et al. reported overall energy efficiencies in the range of 33−50% depending on the type of dry gasification technique used. The authors also identified areas of improvement including the following: cleaning of the gasifier product gas prior to F−T conversion; tailoring the gasifier product gas to better suit the desired end F−T liquid fuel; and development of large-scale systems to lower operation costs.

Methanol Synthesis. Livestock waste-to-energy treatment system with solid separated feedstock would include both methanol and liquid fuel production options (F−T fuels are included in liquid fuels). Though the F−T route is gaining popularity due to the hydrocarbon product slate, especially diesel production, an attractive alternative is to synthesize methanol from the syngas produced (eq 8):

$$CO + 2H_2 \rightarrow CH_3OH \quad \Delta H_{298} = -129\ \text{kJ/mol} \qquad (8)$$

Methanol is presently manufactured from synthesis gas, primarily produced from natural gas, using a supported Cu/ZnO heterogeneous catalyst at 250−300 °C and between 5 and 10 MPa operating pressure.[57] However, the methanol synthesis reaction is exothermic and that poses thermodynamic limitation, which together with poor process heat control limits gas conversion to <20% per pass during commercial synthesis.

Bio-Oil Cleanup for Processing. Direct pyrolysis of low bulk density carbonaceous materials to higher density bio-oil makes for an attractive option for use in CHP units, upgrading to transportation fuels, or as a gasifier feedstock.[58,59] Disadvantages making pyrolysis energy inefficient include both the nonreproducible product and the extensive upgrading, which requires cleanup. The bio-oil is a heterogeneous mixture of hydrocarbons, both neat and oxygenated, whose upgrading requires lowering the oxygen content. This bio-oil may contain undesirable impurities such as fixed S, fixed N, and alkalis that must be removed. Additional issues with subsequent bio-oil use include the oil's corrosive nature, phase separation, thermal instability, and aging compositional changes.[58,60] While source-specific cleanup technologies are available, the biomass or agriculture waste to pyrolysis oil conversion option is still under development.[19,20,25,60]

Energetic Evaluation of Model Swine Farm

Reports on full-scale application of waste-to-energy systems using animal manures as feedstocks have not been forthcoming. The subsequent analyses were based for a 5000-sow, farrow-to-wean model swine farm using a pull-plug pit manure collection system generating swine waste (TS = 47.2 g/L) at 52 320 L/d (Table 3). Two conceptual waste-to-energy treatment systems are considered: (1) wet gasification treating swine manure directly (Figure 3); and (2) combined biological−thermochemical conversion waste treatment using anaerobic digestion followed by wet gasification (Figure 4).

When using wet gasification as the sole treatment, the swine manure is homogenized and passed through a wet gasification reactor at 350 °C and 20MPa. The product gases, mostly CH_4, CO_2, and H_2, can eventually be used in a CHP unit or further processed thermocatalytically to produce liquid fuels. As presented previously, the aqueous-phase ammonia-nitrogen can be recovered and sold on the market or used on-farm as fertilizer. After stripping, the pathogen-free water can be recycled back to the house for drinking and cleaning needs.

Based on the elemental composition for swine manure in Table 1, the chemical empirical formula for wet gasification of the VS portion of swine manure is estimated as

$$CH_{1.70}N_{0.065}O_{0.515}S_{0.003}(s) + 0.385H_2O(l) \rightarrow 0.55CH_4(g) + 0.45CO_2(g) + 0.003H_2S(g) + 0.065NH_3(aq) + 0.0345H_2(g) \qquad (9)$$

Approximately half the carbon is converted to CH_4 and the other half as CO_2. All the nitrogen is assumed to be converted to aqueous NH_3.[62] Sulfur is assumed to transform into H_2S with hydrogen production balancing the equation.

The wet gasification reaction energy, E_{rxn}, can be estimated using both the swine manure's HHV of 451.3 kJ/mol reactive manure and the products' heat of combustion ($\Delta H_{c,298}$). The resulting reaction energy balance is a slightly exothermic reaction: −72.5 kJ per mol of manure VS or −3160 kJ kg of VS_{in}^{-1} d^{-1} (Table 4). An estimate of the shaft work necessary (E_{Ws}) can come from the enthalpies of water; it is assumed swine manure is exiting the house at ambient conditions and being pressurized and heated to 20 MPa and 350 °C. The net energy (E_{Total}) from gasifying swine waste is estimated as the summation of E_{rxn}, E_{Ws}, and the energy value of product gas (E_{Gas}). Without heat recovery, this model scheme is highly endothermic requiring ∼40 300 MJ/day. This process could become energy neutral if at least 50% of E_{Ws} could be captured and recycled by using the heat from the product gas and the treated aqueous streams to raise the influent's temperature. In order to raise the influent temperature using internal system heat, Elliott et al.[38] developed a double-tube heat exchanger capable of recycling up to 90% of the heat energy. If 90% heat recovery was possible, wet gasification of the swine manure would generate 32 240 MJ/d.

In a biothermochemical waste-to-energy design, anaerobic digestion is coupled with wet gasification to produce an additional CH_4-rich biogas product that can be used in a CHP unit or further processed with gasification gases to produce liquid fuels (Figure 4). With this design, the wet gasification step converts the residual volatile solids thus providing the additional purpose of a disposal method for the digested effluent and accumulating sludge. Within an anaerobic digester, TS and VS reductions (Table 3) are due to the following: (1) microbial conversion of the organic matter into biogas and (2) settling of the nondegraded matter to form sludge. Microbial biogas production from anaerobic digestion typically contains 30−45% CO_2 and 55−70% CH_4[5] with the stoichiometric degradation represented as[63]

$$CH_{1.70}N_{0.065}O_{0.515}S_{0.003}(s) + 0.366H_2O(l) \rightarrow 0.559CH_4(g) + 0.441CO_2(g) + 0.003H_2S(g) + 0.065NH_3(aq) \qquad (10)$$

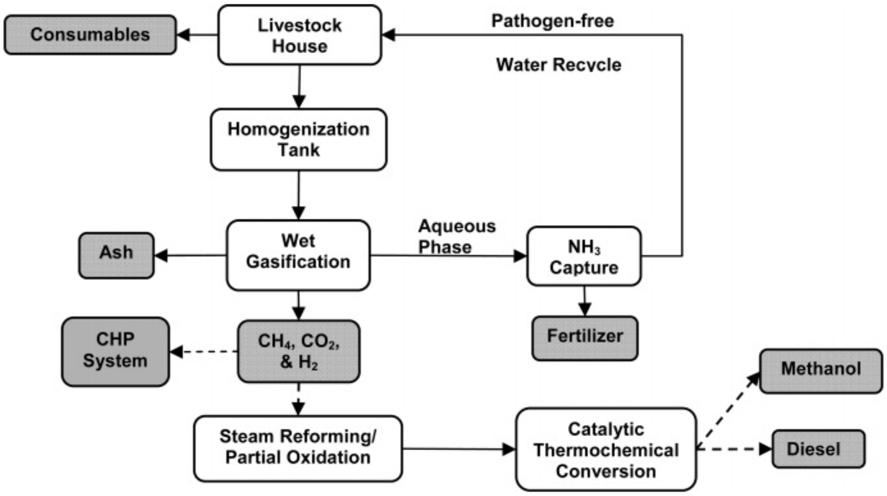

Figure 3. Thermochemical, swine manure waste-to-energy treatment system via wet gasification.

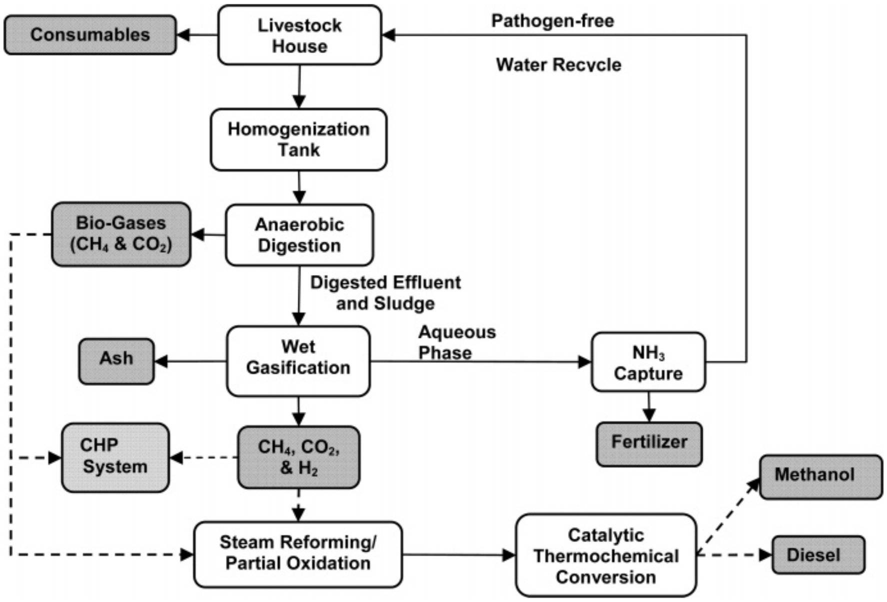

Figure 4. Biothermochemical swine manure waste-to-energy treatment system.

Similar to wet gasification, minor amounts of H_2S and NH_3 appear, and approximately half the carbon is converted into CH_4 and CO_2. Alongside biogas production is settled sludge accumulation. In order to maintain digester operation and restore maximum treatment volume, the settled sludge must be periodically removed and disposed.[64] The digested sludge still contains a residual organic portion, VS, which can serve as a feedstock for the wet TCC technologies.

For a biothermochemical model, swine manure is first introduced into a homogenization tank and then into a mesophillic, intermittently mixed, anaerobic digester. The 2060-m^3 in-ground, concrete digester with a design hydraulic retention time of 40 days is maintained at 35 °C. This digester would operate with a daily batch-loaded, fill and draw reactor with effluent flow occurring in response to influent flow. The digester is equipped a with an overhead, flexible reinforced plastic collection dome to capture biogas. When the biogas is not actively being processed, it would be flared in order to control dome pressure. The associated net energy, E_{Total}, is calculated much in the same manner as before with E_{Ws} estimated from the energies required to heat the ambient waste and maintain the digester at 35 °C.

Compared to the first treatment design, the overall system produces 90% as much volumetric CH_4 and requires triple the energy input. This is largely due to the E_{Ws} (kJ kg of $\mathrm{VS_{in}}^{-1}$ d^{-1}) for wet gasification of the digested effluent being 2.25 greater with 65% less VS than gasification of raw swine manure. In order for this scheme to become energy positive, more than 80% heat recovery would need to occur with energy from the biogas theoretically providing 10%.

In comparing biological conversion of the raw, untreated swine waste to thermochemical conversion, anaerobic digestion produces a biogas with composition of 28% more CH_4 and 35% less CO_2 than wet gasification. This increase in CH_4 leads to a 26% larger energy value (kJ/mol) (Table 4). However, the energy production of gasification's product gas is 89% larger than biogas meaning a better utilization of the organic portion or higher VS conversion efficiency.

Obstacles and Challenges

Animal Manure Conditioning. With most of the waste coming from CAFOs being extremely diverse in particle size, some type of grinding, blending, or pelletizing for uniform

Table 4. Product Gas Composition (%) and Energetic Information from Wet Gasification (WG) and Anaerobic Digestion (AD) of Raw Swine Manure and Digested Effluent

	thermochemical platform			biothermochemical platform				
	$\Delta H_{c,298}$,[a] kJ/mol	WG biogas from raw swine manure		AD biogas from raw swine manure		WG biogas from AD effluent		total system
		kJ/mol[c]	%	kJ/mol[c]	%	kJ/mol[c]	%	%
CH_4(g)	−890.4	−471	52.9	−605	67.9	−471	52.9	60.1
CO_2(g)	0	0	43.2	0	32.1	0	43.2	37.2
H_2(g)	−285.8	−10.3	3.6	0	na	−10.3	3.6	1.7
H_2S(g)	−518.0	−1.5	0.29	−3.0	0.58	−1.5	0.29	0.45
NH_3(aq)	−348.5[b]		0		0		0	
mass of influent VS (kg of VS_{in}^{-1} d^{-1})		1614		1614		581		1614
energy value of product gas[d] (kJ/mol of gas)		481		608		481		
volumetric production of gas[e] (L/d)		1,849,920		775,120		664,970		1,440,090
energy production of gas, E_{Gas} (kJ/kg of VS_{in}^{-1} d^{-1})		−21,810		−11,550		−21,820		−33,370
estimated shaft work, E_{Ws} (kJ/kg of VS_{in}^{-1} d^{-1})		49,940		2960		112,350		115,310
wet gasification reaction energy, E_{Rxn} (kJ/kg of VS_{in}^{-1} d^{-1})		−3160		−		−3160		−3160
net energy,[f] E_{Total} (kJ kg of VS_{in}^{-1} d^{-1})		24,970		−8590		87,370		78,780
heat recovery required to become energy neutral (%E_{Ws})		50		0		78		68

[a] Standard heat of combustion at 298 K for individual constituents. [b] Estimated from $4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(l)$. [c] Estimated standard heat of combustion per mole of product gas. [d] Assumes H_2S removal. [e] Estimated for operating conditions of 35 °C and 1 atm. [f] $E_{Total} = E_{Gas} + E_{Ws} + E_{Rxn}$; positive value for endothermic and negative value for exothermic; assumes no heat recovery.

particle size would be ideal. In the case of dry gasification systems, uniform particle size is important to the peak-temperature propagation rates; smaller particles have a larger surface per unit volume thereby leading to faster burnout and an increase in reactor temperature.[14]

The removal of feedstock contaminants is a prerequisite for these high-temperature conversion systems. In the catalytic-driven gasification systems and downstream processing, sulfur can quickly poison the metal catalysts. The ash portion in manure contains alkali salts and metals that contribute to ineffective operation of TCC systems caused by bed agglomeration and reduced peak temperatures.[65,14] Despite being removed frequently and continuously, ash from gasification of sewage sludge has been found to lead to clinkering that results in blocking fuel flow and decrease in product gas quality.[26] The oxidation temperatures used in most of the dry gasification systems are above the ash melting point. In the case of agricultural residues and soil-rich manures, the melted salts combine with silica to form a sticky mobile phase composed commonly of the tertiary system of $K_2O{-}CaO{-}SiO_2$; this phase plugs streams, block air flow, and coat catalytic sites.[65] The sulfur, chlorine, and nitrogen are readily released to the atmosphere, while phosphorus is thought to remain in the char residue.[65,31]

Process Issues. Much of the reported research is performed batch mode in laboratory-sized reactors. In developing continuous reactors, certain issues will need to be addressed: feedstock delivery to a high-pressure reactor; efficient heat recovery to make the process energy positive; and avoiding depressurization while obtaining products.

Plugging of reactor systems is primarily due to solid formation or carbon and ash buildup. Some researchers have found that routine cleaning by pumping hydrogen peroxide through the system can restore operation. D'Jesus demonstrated continuous operation of a supercritical water gasification system using untreated corn silage (i.e., metals, salts, and other contaminants like silica were not removed) as a feedstock by suppressing solid formation with regular, high water pressure, full-system washings.[66]

The efficiency of the downstream biofuels synthesis processes can be significantly improved by bypassing the highly endothermic SMR step. If the animal waste gasification step and downstream processing of synthesis gas is combined in a single step, it will drastically simplify the overall waste-to-fuel process trains, making an ideal candidate for modular, farm-scale units in the future. The challenge of this approach is to find a compromise temperature and design a robust and inexpensive catalyst.

Economies of Scale. A typical world-scale methanol plant has an output of 2000 tons/day or higher. The process efficiency and economy of scale prohibits the use of present commercial methanol synthesis technology for "fuels on the farm" application that would require plant sizes of the 100 tons/day range for centralized animal waste facility. Work is ongoing at Brookhaven National Laboratory (BNL) to address the specific issues of methanol synthesis for farm applications.[67] The BNL focus is on catalyst design and formulation that can achieve high gas conversion per pass virtually eliminating a need for gas recycle during methanol synthesis. Of the metal systems evaluated, soluble transition metal complexes, such as Ni complexes activated by alkoxide bases, affect homogeneous CO reduction to methanol at low temperatures (80−130 °C) and low pressures (2000−5000 kPa) to achieve CO conversion and methanol selectivity of >90 and >95%, respectively. The associated space−time yield is ∼20% higher than that achieved with the commercial Cu catalyst system. Preliminary process flow sheets based on the BNL catalyst show that a skid-mounted unit could be built to economically process biomass and livestock waste feedstocks.

Conclusions

To help meet on-farm heating and transportation fuel demands, multiple TCC technologies such as pyrolysis, gasification, and direct liquefaction can be used to convert both dry and wet animal manures. These technologies can produce value-added products like gaseous fuels and pyrolytic oils. After conversion, application of downstream processing techniques via catalytic thermochemical conversions can upgrade these products to alcohols and light diesels. With minimal additional treatment and ammonia capture, the post-TCC water can be sent back to the house for drinking and washing needs. Integration of these TCC technologies with animal manure treatment operations results in waste-to-energy schemes capable of processing waste coming directly from an animal house, solid−liquid separator, or anaerobic digester. However, for many of the TCC processes, the removal of animal manure contaminants is a prerequisite. The high ash and sulfur contents can present operational difficulties like plugging and slagging, which can render catalytic-based conversions useless. Even with these challenges, the TCC-based waste-to-energy treatment schemes provide significant environmental improvements for existing manure management practices. Along with a higher VS conversion efficiency, TCC can destroy pathogens, eliminate nuisance compounds, reduce wastewater strength, and lessen the risk of surface water contamination.

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Received for review December 29, 2006
Revised manuscript received September 17, 2007
Accepted September 19, 2007

IE0616895