

# High-Temperature Pyrolysis of Blended Animal Manures for Producing Renewable Energy and Value-Added Biochar

Kyoung S. Ro, Keri B. Cantrell, and Patrick G. Hunt

USDA-ARS, Coastal Plains Soil, Water & Plant Research Center; 2611 W. Lucas Street, Florence, South Carolina 29501

In this study, we used a commercial pilot-scale pyrolysis reactor system to produce combustible gas and biochar at 620 °C from three sources (chicken litter, swine solids, mixture of swine solids with rye grass). Pyrolysis of swine solids produced gas with the greatest higher heating value (HHV) followed by the mixture of swine solids with rye grass and chicken litter. Relatively high S-containing gases were produced; dimethyl sulfide and methyl mercaptan concentrations were higher than the OSHA PEL limits. Biochar yield ranged from 43 to 49% based on dry weight with about 53% of carbon recovery. Whereas the HHV of the chicken litter biochar was slightly below that of low rank coals, swine-based biochars had HHVs between high and low rank coals. Approximately 50% of the feedstock energy was retained in biochar and 25% in produced gases. Manure biochars contained higher concentrations of P and K than that of original manure feedstocks. Consequently, these could be used as a low-grade fertilizer to improve soil fertility and crop yields. Extremely high energy (232.3 MJ/kg) was required to make 1 kg of biochar from wet swine manure with 97% MC. However, dewatering of the wet swine manure to 75% MC substantially reduced the external energy requirement by 19 folds. Mixing of dried biomass such as rye grass with the dewatered swine solids almost eliminated the need for external energy. If one can copyrolyze wet animal wastes with additional feedstock that are drier and more energy dense than rye grass such as waste plastic pellets, it may be possible to produce both valuable biochar and extra power.

## Introduction

Currently, animal production annually provides 35 million dry tons of sustainable biomass/manure feedstock that can be converted to various forms of renewable biomass energy.<sup>1</sup> The annual renewable energy content of the 35 million dry tons of manure is approximately equivalent to 0.43 EJ, about 14% of the total renewable biomass energy consumed in the U.S.<sup>2</sup> This manure comes from a few, large livestock operations. This concentration of waste challenges the use of traditional land application methods.<sup>3–5</sup> This situation can potentially be synergistically mitigated by thermochemical conversion (TCC) technologies. They can convert the surplus manures to produce energy-rich and value-added end productions: such as combustible gases, biooils, and charcoals (hereafter called biochar). These TCC technologies such as gasification and pyrolysis only require treatment times in the span of minutes to hours. The TCC technologies can also quickly destroy pathogens. These are major advantages relative biochemical technologies such as anaerobic digestion.<sup>6–9</sup> Moreover, the TCC technologies do not leave substantial amounts of nonbiodegradable sludge and supernatant that require further treatment and disposal. In TCC conversion, the end-products depend on factors such as the feedstock, operating temperature, pressure, heating rate, and residence time.<sup>10</sup> The TCC products can be used as energy intermediates for combined heat and power generation (CHP) or feedstock for downstream catalytic conversion processes to produce higher value products such as liquid transportation fuels.

Although there is an abundance of literature on gasification and pyrolysis of plant biomass and coals, the literature on TCC technologies for animal manures is rather limited. Furthermore, most of the pyrolysis studies with animal manures were conducted with either laboratory-scale batch reactors or microscale thermogravimetric analyzers (TGAs).<sup>11–18,3,19–25</sup> These small-scale studies provide preliminary information on animal

manure pyrolysis; however, a pilot-scale study was needed to generate design information for full-scale implementation. In this study, we used a commercial pilot-scale skid-mounted pyrolysis reactor system. It was used previously for design of full-scale pyrolysis systems to generate power from municipal solid wastes (MSW) and auto shredder residuals (ASM). The objectives of this study were to 1) assess the thermal decomposition patterns, 2) characterize produced gas and biochar, and 3) evaluate the energetics of pyrolyzing animal manures/blend. To accomplish these objectives, both a TGA-mass spectrometry and a skid-mounted pyrolysis system were used.

## Materials and Methods

**USIG Skid-Mounted Pyrolysis System.** The skid-mounted pyrolysis system by the US Innovation Group, Inc. (USIG, Indianapolis, IN) is a proprietary thermochemical conversion testing system that can be used to produce combustible gases from various carbon wastes such as ASM, sewage sludge, or MSW.<sup>26</sup> The process flow diagram of the skid mounted system is shown in Figure 1. Eight to 19 L of dried swine solids, chicken litter, and blended swine solids (29% rye and 71% swine solids, w/w) were heated at a rate of 13 °C/min and pyrolyzed in the reactor at 620 °C (893 K) for two hours. Devolatilized gas was scrubbed by water with a venturi scrubber, compressed, and fed into the gas storage tank. After removing tarry oil at the top of water surface, the scrubbing water was returned back to the recirculation tank for continual scrubbing. Gas, liquid, and solid end products from the USIG pyrolysis reactor system were collected and subsequently analyzed for their chemical and thermal properties.

**Feedstock Characteristics.** The swine solids were obtained from a solid–liquid separation system treating flushed manure from a 5600-head finishing swine operation in North Carolina. Once collected, these separated solids underwent solar drying

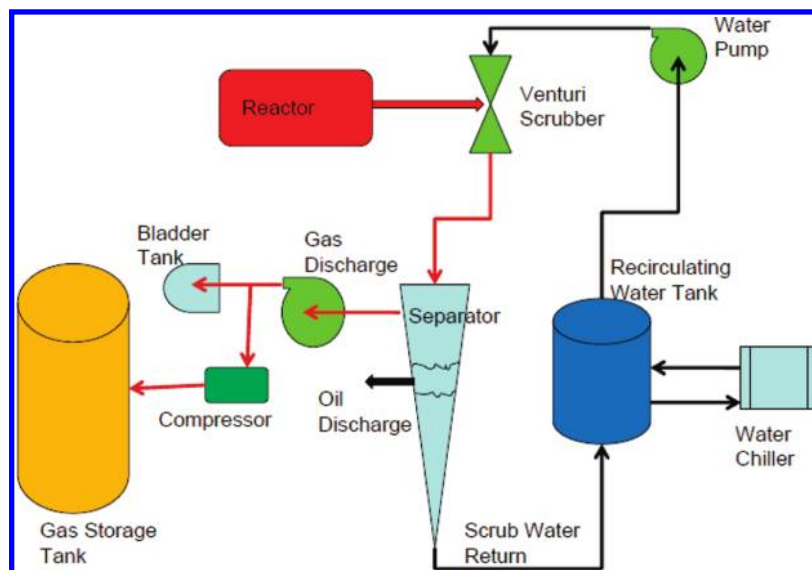


Figure 1. Flow diagram of the USIG skid-mounted pyrolysis system.

Table 1. Proximate and Ultimate Analyses of Individual Feedstocks

parameters	chicken litter	swine solids (dried)	rye grass	blended <sup>d</sup>
Proximate Analyses <sup>2</sup>				
moisture as pyrolyzed (%)	10.2 ± 0.07	12.8 ± 0.3	6.2 ± 0.5	10.9 ± 0.6
volatile matter (% <sub>db</sub> ) <sup>a</sup>	51.1 ± 0.5	60.6 ± 1.1	76.0 ± 1.1	65.1 ± 1.6
fixed C (% <sub>db</sub> ) <sup>c</sup>	8.2 ± 0.5	8.1 ± 0.6	14.8 ± 0.8	10.1 ± 1.0
ash (% <sub>db</sub> ) <sup>b</sup>	30.6 ± 0.5	18.5 ± 0.2	3.2 ± 0.2	14.0 ± 0.3
HHV (MJ/kg)	13.0 ± 0.3	19.5 ± 0.2	18.6 ± 0.0	19.3 ± 0.1
Ultimate Analyses <sup>c</sup>				
H (% <sub>db</sub> )	4.1 ± 0.07	5.9 ± 0.1	5.7 ± 0.1	5.9 ± 0.2
C (% <sub>db</sub> )	34.4 ± 0.5	47.3 ± 0.2	49.8 ± 0.4	48.0 ± 0.4
O (% <sub>db</sub> )	23.4 ± 0.1	20.1 ± 0.4	40.6 ± 0.3	26.1 ± 0.5
N (% <sub>db</sub> )	3.27 ± 0.03	4.58 ± 0.13	0.41 ± 0.05	3.36 ± 0.14
S (% <sub>db</sub> )	0.81 ± 0.10	0.93 ± 0.04	0.04 ± 0.02	0.67 ± 0.04

<sup>a</sup> ASTM D3175–07. <sup>b</sup> ASTM D3172. <sup>c</sup> ASTM D3176–02. <sup>d</sup> Calculated based on 2.9/7.1 mass ratio of swine solids and rye grass. <sup>e</sup> Calculated as 100-Volatile Matter – Ash.

in a greenhouse. Chicken litter was obtained from a 52 000-bird broiler farm in South Carolina. Rye grass sample was obtained from the Clemson University Pee Dee Research and Education Center, Florence, SC. Table 1 shows proximate and ultimate analyses of the individual fuels along with heating values. The hybrid feedstock was produced by blending 2.9/7.1 (kg/kg) ratio of rye grass and swine solids.

## Analytical Methods

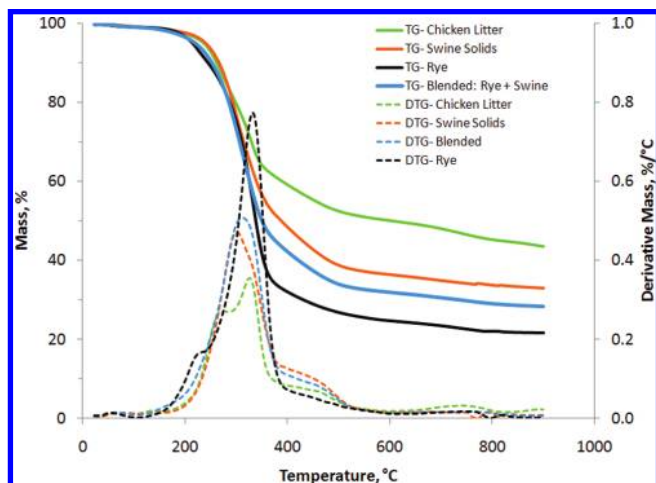
Duplicate samples of produces gases from pyrolyzing animal manures were analyzed by Midwest Analytical Services, Inc. (Ferndale, MI) for major hydrocarbons, sulfur containing gases, and higher heating values (ASTM D1945/D1946, D6228–98, D3588–98). Proximate and ultimate analyses (ASTM D3172 and 3176) along with higher heating values (HHV) of triplicate samples of feedstock and duplicate samples of biochar were performed by Hazen Research Inc. (Golden, CO). Duplicate biochar samples were also analyzed for the total elemental composition by the Arizona Laboratory for Emerging Contaminants.<sup>27</sup> The biochar samples were digested using the EPA method 3052 microwave-assisted acid digestion method.<sup>28</sup> The elemental P and K concentrations of the biochar samples were measured using an Elan DRC-II (PerkinElmer, Shelton, CT) inductively coupled plasma (ICP) mass spectrometer.

**Thermogravimetric Analyses.** The three feedstocks and an additional sample of rye grass were dried and ground with a Wiley Mill to pass through a 60 mesh screen (250  $\mu$ m). Samples

were then subjected to thermogravimetric analysis runs (TGA) using a TGA-DTA analyzer (TGA/SDTA851e, Mettler Toledo International Inc., Columbus, OH). Immediately prior to He pyrolysis runs, samples underwent a drying step using the TGA as described by Cantrell et al.<sup>29</sup> to allow for subsequent TGA runs to be determined on a dry-basis. All samples were placed in open top Al<sub>2</sub>O<sub>3</sub> 70  $\mu$ L crucibles and were pyrolyzed with ultrahigh purity He as both the carrier and protective cell gas under the following conditions: hold at 25 °C for 7 min with a He carrier flow rate of 60 mL min<sup>-1</sup>; temperature ramp from 25 to 900 °C with constant heating rate of 30 °C min<sup>-1</sup> and He carrier flow rate of 10 mL min<sup>-1</sup>. The TGA unit interfaced via a heated capillary line (200 °C) with a Pfeiffer-Vacuum Thermostar mass spectrometer (MS). The MS had the following settings: emission current was 0.99 mA; the filament current was 2.80 A; the tune voltage was set to 1.94 V. The MS continuously sampled the evolved gases producing a time based MS spectrum while scanning for mass-to-charge ratio ( $m/z$ ) up to 44 (dwelling for 50 ms). This time-based spectrum was converted to coincide with the TGA's temperature based mass profile. For this investigation, only qualitative inferences were drawn from these mass profiles.

## Results and Discussion

**Thermal Decomposition of Manures/Blend.** The mass (TG) and derivative of TG curves (DTG) of the manure feedstocks (Figure 2) exhibited typical pyrolytic degradation profiles of

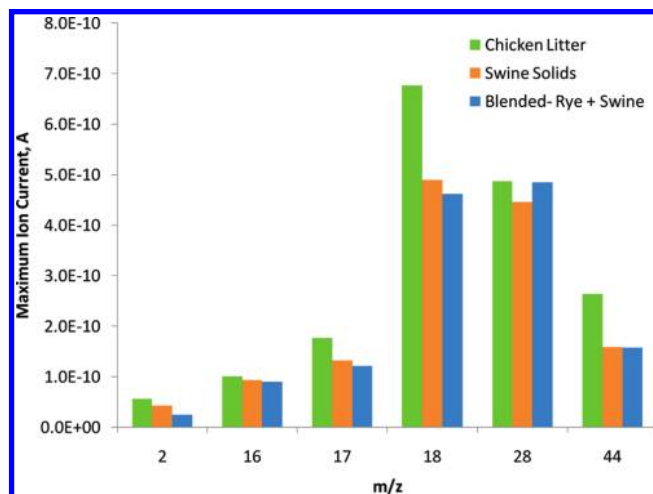


**Figure 2.** Mass (TG) and derivative mass curves (DTG) curves for chicken litter, separated swine solids, rye grass, and blend of rye grass and swine solids during He pyrolysis: 25 – 900 °C, 30 °C min<sup>-1</sup>; mass (%) is the percentage of actual weight to initial dry sample weight.

other biomass materials and manures<sup>30–32</sup> with a primary devolatilization stage (as indicated by the peaks). The onset temperature of this stage ( $T_{on}$ ) was determined as the weight loss of 5% respect to the final dry-basis weight loss. Once the bulk of biomass was devolatilized, the next stage was a slow and continuous weight loss often attributed to degradation of heavier chemical structures.<sup>33</sup> In accordance with Table 1, chicken litter had the greatest residual, and rye grass had the least amount of residual. Blending swine manure with rye grass decreased the residual. A final temperature of primary devolatilization ( $T_f$ ) was defined on the DTG curve as the temperature corresponding to the intersection of tangent lines in both devolatilization stages.

For this current study,  $T_{on}$  was 219, 226, 236, and 241 °C for rye, blended rye, chicken litter, and swine solids, respectively. Temperature at maximum devolatilization,  $T_{max}$ , decreased from rye grass at 329 °C to swine solids at 302 °C with the blended feedstock exhibiting a  $T_{max}$  of 305 °C. For chicken litter, there were two overlapping, yet distinct, max temperatures. One at 273 °C and then other at 336 °C. This phenomenon could be attributed to the heterogeneous nature of chicken litter, which is a combination of spent feed, bedding, and manure, giving rise to compositional stratifications with respect to the proteins and carbohydrates of celluloses and hemicelluloses. For example, Bernhart and Fasina<sup>34</sup> effectively superimposed the overall devolatilization of chicken litter with devolatilization curves from lignin, protein, cellulose, and hemicellulose. This dual peak phenomenon may not have been seen in the blended feedstock due to the increased heating rate. Increasing the heating rate has been documented to increase both  $T_{on}$  and  $T_{max}$ .<sup>31</sup> The greatest temperature range of devolatilization, 153 °C, occurred for rye grass with a  $T_f$  of 372 °C. The manures' devolatilization temperature range was similar ranging 122 °C ending between 357 and 364 °C. The blended feedstock devolatilized within the smallest temperature range, 111 °C, completing the primary stage at 366 °C.

**Produced Gas Characteristics from Slow Pyrolysis up to 620 °C.** The major pyrolytic thermal decomposition of feedstocks occurred in the temperature range from 225 to 375 °C (Figure 2). With primary reactions being those related to dehydration, decarboxylation, and methanation, the major gas produced in this temperature range would be water vapor, CO<sub>2</sub>, and CH<sub>4</sub>.<sup>30,35</sup> As temperature increased to 620 °C, thermodynamic equilibrium shifts toward production of H<sub>2</sub> and CO.<sup>36</sup>



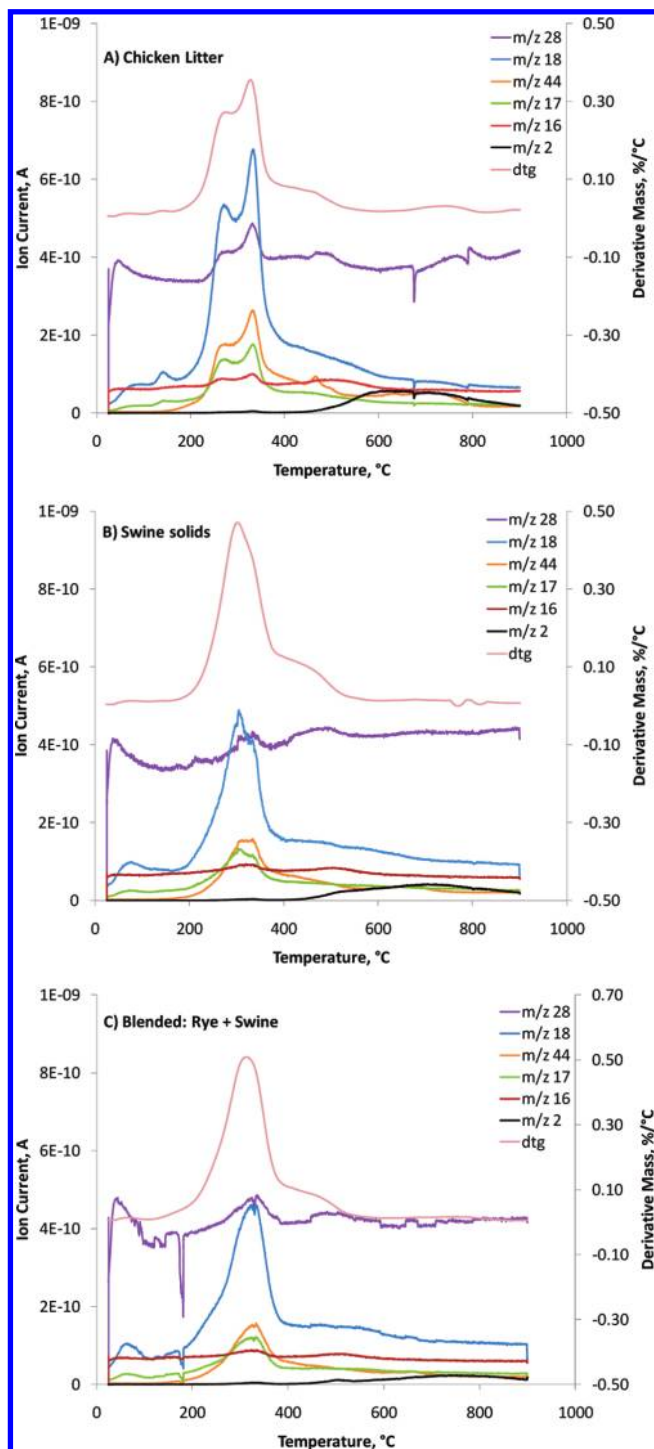
**Figure 3.** Maximum ion current of select  $m/z$  ratios during He pyrolysis of chicken litter, swine solids, and blend of rye grass and swine solids.

Comparison of the maximum relative ion current during the He pyrolytic runs indicated that the greatest fluctuations in evolved gases were predominately with the signals  $m/z$  of 2, 16, 17, 18, 28, and 44 (Figure 3). The signal  $m/z = 28$  is commonly associated with N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and CO evolution. However, the signal at  $m/z = 28$  along with  $m/z = 16$  (CH<sub>4</sub>) were complicated with very high background noises. The major signals at  $m/z$  17 (NH<sub>3</sub>), 18 (H<sub>2</sub>O), and 44 (CO<sub>2</sub>) resembled those of their respective DTG curves (Figure 4). During major breakdown of the feedstocks in the temperature range from 225 to 375 °C, these signals indicated that dehydration, decarboxylation, and deammonification reactions contributed to the formation of these gases. Propane, C<sub>3</sub>H<sub>8</sub>, also has a signal  $m/z$  of 44; with the small concentrations detected in the produced gas (Table 2). However, CO<sub>2</sub> was the predominate influence with concentrations 20 folds greater. For the case of H<sub>2</sub> ( $m/z$  2), initial spikes of H<sub>2</sub> were detected at  $T_{max}$ . However, primary H<sub>2</sub> production began for all feedstocks around 440 °C and peaked respectively for chicken litter, swine solids, and the blend at 654, 705, and 741 °C (Figure 5). Thus, operation of the skid-mounted unit at 620 °C would be expected to generate H<sub>2</sub>. Formation of C<sub>2</sub>H<sub>6</sub> ( $m/z$  30) was found to peak initially for all feedstocks at the same temperature as H<sub>2</sub>O formation. A second formation peak of these compounds occurred later close to 480 °C (Figure 5).

The average compositions and HHV of noncondensable produced gases are summarized in Table 2 from pyrolyzing the three feedstocks in the skid-mounted unit. The main products were CO<sub>2</sub>, H<sub>2</sub>, CO, N<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, and high C hydrocarbons. At higher temperature as in gasification, heavy molecular weight compounds should break down to CO<sub>2</sub>, H<sub>2</sub>, CO, and CH<sub>4</sub> by cracking and reactions with gasifying agents. Gas analyses showed less than 10 ppmv NH<sub>3</sub> for both the swine solids and rye-blend and none for chicken litter; most of NH<sub>3</sub> was assumed to be lost to scrubbing water. The main gas compositions did not vary much for different fuels except for C<sub>2</sub> hydrocarbons. The concentrations of C<sub>2</sub> hydrocarbon from swine solid pyrolysis were more than twice that from chicken litter pyrolysis. As a result, swine solid produced gas with the HHV of 29.5 MJ/S m<sup>3</sup>, slightly below that of methane.

The produced gases from pyrolyzing animal manures contained relatively high sulfur content from several compounds as shown in Table 3. Sulfur in the produced gas is of concern not only for odor but also for downstream catalytic conversion or combustion processes. It will interfere with downstream





**Figure 4.** Overlay of DTG during He pyrolysis with selected major MS current measurements. ( $m/z$  ratio: 28 -  $N_2$ , CO,  $C_2H_4$ ; 18 -  $H_2O$ ; 44 -  $CO_2$ ,  $C_3H_8$ ; 17 -  $NH_3^+$ ; 16 -  $CH_4$ ; 2 -  $H_2$ ).

catalytic conversion processes by poisoning metal catalysts. It will also form  $SO_x$  during combustion, a major acid rain forming pollutant. Although the concentration of the toxic  $H_2S$  gas is well below the OSHA Permissible Exposure Limit (PEL) for a ceiling concentration of 20 ppm, concentrations of dimethyl sulfide from all three feedstocks and methyl mercaptan from chicken litter were more than twice of the PEL limit of 10 ppm. Among other S-containing gases, carbonyl sulfide concentrations were an order of magnitude higher than the rest of gases. Although OSHA PEL limit is not established for carbonyl sulfide, it may be metabolized to hydrogen sulfide, which is

**Table 2. Major Noncondensable Produced Gases from Slow Pyrolysis up to 620 °C**

parameters	mol % chicken litter	mol % swine	mol % blended
$H_2$	$17.2 \pm 4.1$	$15.7 \pm 0.0$	$12.6 \pm 5.4$
$CO_2$	$27.5 \pm 0.2$	$21.5 \pm 2.3$	$21.6 \pm 1.8$
$N_2$	$18.0 \pm 0.8$	$10.0 \pm 0.2$	$18.1 \pm 6.2$
CO	$16.1 \pm 1.9$	$10.7 \pm 0.4$	$13.0 \pm 1.0$
$CH_4$	$10.9 \pm 0.6$	$19.9 \pm 0.8$	$16.9 \pm 1.2$
$C_2H_6$	$1.43 \pm 0.10$	$4.5 \pm 0.3$	$3.14 \pm 0.06$
$C_2H_4$	$0.60 \pm 0.05$	$3.7 \pm 0.3$	$2.54 \pm 0.09$
$C_2H_2$	N/D	N/D	$0.002 \pm 0.000$
$C_3H_8$	$0.45 \pm 0.02$	$1.52 \pm 0.14$	$0.87 \pm 0.12$
$C_3H_6$	$0.62 \pm 0.07$	$3.55 \pm 0.59$	$1.98 \pm 0.47$
higher HC	$2.89 \pm 0.52$	$6.24 \pm 0.63$	$4.94 \pm 0.70$
HHV (MJ/S $m^3$ )	$15.0 \pm 0.6$	$29.5 \pm 2.2$	$23.2 \pm 0.0$

<sup>a</sup> N/D = Not detected; S = S: standard condition at 15.6 °C and 1 atm.

toxic. Implication on downstream processes by this high concentration of carbonyl sulfide other than combustion is not known.

**Biochar Characteristics.** Biochar yield ranged from 43 to 49% based on dry weight. Proximate and ultimate analyses of biochars are shown in Table 4 along with HHV data. As shown in Figure 6, ultimate analyses of manure and blended feedstocks and their corresponding biochars showed general reductions of H/C ratios, indicating an increase in aromaticity due to pyrolysis. The increase in aromaticity is the result of losing aliphatic and carboxylate portions of the manures during pyrolysis.<sup>37,38</sup> This increase in aromaticity also increased the fixed carbon yields of biochars – 201, 157, and 198% increase for swine solids, chicken litter, and mixed solids, respectively.

The blended manure (i.e., swine solid mixed with rye grass) had the greatest fixed carbon followed by swine solids and chicken litter. The heating values of the biochar made from swine solids and the blended manure were in between high (anthracite, 33 MJ/kg) and low (lignite, 16.1 MJ/kg) rank coals.<sup>39</sup> The heating value of the chicken litter biochar was slightly below that of low rank lignite because of high ash content. On the basis of yields and HHVs of feedstocks and biochars, approximately 50% of the feedstock energy was retained in biochar and 25% in produced gases. System efficiencies will increase if some of the remaining 25% of feedstock energy in the tar/scrubbing water component is captured and reused.

On the basis of biochar yield and C contents of feedstocks and biochars, about 56, 48, and 54% of feedstock carbon were recovered in biochar for chicken litter, swine solids, and blended swine solids, respectively. While P and K nutrient contents of the biochars were higher than that of original feedstocks, N and S contents in the biochars were lower (Table 5). It was interesting to note that, whereas 92% of S in chicken litter was recovered in its biochar, this was in contrast to the swine-based biochars with only about 31% recovery. On the other hand, P and K of all three feedstocks were almost completely recovered in biochar as we expected for nonvolatile elements. The increase in biochar P and K nutrient contents along with other potential positive influences on soil properties would suggest that biochar can be used as a low-grade fertilizer to improve soil fertility.<sup>40,37</sup> In fact, the terra preta (darkend earth) of the Amazonian fertile soils are thought to have been created by indigenous tribes mixing charcoals with soil thousands years ago.<sup>41</sup> Amazingly, these soils still retain their high fertility to date. It will be interesting to determine whether the manure-based biochar with higher nutrient content would promote even higher soil fertility than that made from plant biomass. However, it is beyond the scope of this study.

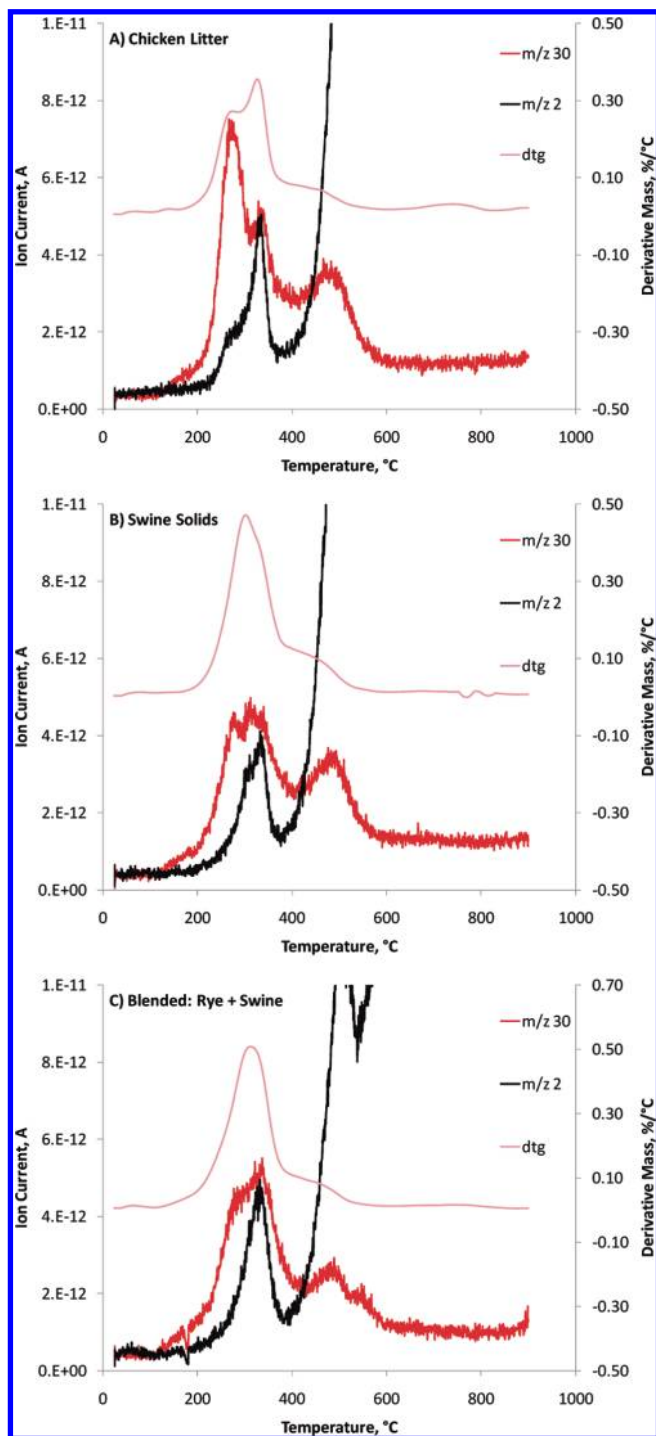


Figure 5. Overlay of DTG during He pyrolysis with selected minor MS current measurements. ( $m/z$  ratio: 30 -  $C_2H_6$ ; 2 -  $H_2$ ).

Table 3. S-Containing Gases

parameters	ppmv chicken litter	ppmv swine	ppmv blended
hydrogen sulfide	$2.2 \pm 0.1$	$5.7 \pm 3.9$	$2.4 \pm 0.4$
carbonyl sulfide	$256 \pm 6$	$438 \pm 120$	$421 \pm 18$
carbon disulfide	$19.0 \pm 0.7$	$10.5 \pm 2.8$	$13.7 \pm 1.4$
methyl mercaptan	$22.5 \pm 16.3$	$2.5 \pm 0.9$	$1.6 \pm 1.1$
<i>n</i> -propyl mercaptan	$2.5 \pm 0.5$	$4.0 \pm 1.9$	$6.0 \pm 0.0$
dimethyl sulfide	$18.3 \pm 1.4$	$28.4 \pm 7.7$	$36.4 \pm 8.6$
methyl ethyl disulfide	$1.8 \pm 0.4$	$2.3 \pm 0.9$	$4.0 \pm 0.5$
diethyl disulfide	$18.2 \pm 4.9$	$22.4 \pm 3.3$	$58.4 \pm 15.2$
thiophene	$14.5 \pm 1.8$	$14.1 \pm 2.2$	$12.9 \pm 5.3$
C1-benzothiophenes	$4.6 \pm 0.5$	$5.9 \pm 2.4$	$7.9 \pm 0.9$
total sulfur content (molar ppm)	$398 \pm 43$	$577 \pm 156$	$647 \pm 2$

Table 4. Proximate and Ultimate Analyses of Biochar

parameters	chicken litter	swine solid	blended
Proximate Analyses <sup>b</sup>			
moisture (%)	$4.0 \pm 0.6$	$3.4 \pm 0.1$	$3.2 \pm 0.2$
volatile matter (% <sub>db</sub> ) <sup>a</sup>	$16.0 \pm 0.1$	$14.1 \pm 2.5$	$12.7 \pm 3.1$
fixed C (% <sub>db</sub> ) <sup>d</sup>	$30.8 \pm 1.7$	$41.2 \pm 1.3$	$51.6 \pm 2.6$
ash (% <sub>db</sub> ) <sup>b</sup>	$53.2 \pm 1.8$	$44.7 \pm 1.2$	$35.8 \pm 0.5$
HHV (MJ/kg)	$13.5 \pm 0.2$	$18.3 \pm 0.4$	$21.2 \pm 0.2$
Ultimate Analyses <sup>c</sup>			
H (% <sub>db</sub> )	$1.2 \pm 0.1$	$1.9 \pm 0.3$	$1.5 \pm 0.7$
C (% <sub>db</sub> )	$41.5 \pm 0.3$	$50.7 \pm 0.6$	$61.3 \pm 0.4$
O (% <sub>db</sub> )	$0.7 \pm 0.0$	$<0.01$	$<0.01$
N (% <sub>db</sub> )	$2.77 \pm 0.02$	$3.26 \pm 0.08$	$2.85 \pm 0.00$
S (% <sub>db</sub> )	$1.63 \pm 0.15$	$0.66 \pm 0.01$	$0.51 \pm 0.00$

<sup>a</sup> ASTM D3175-07. <sup>b</sup> ASTM D3172. <sup>c</sup> ASTM D3176-02. <sup>d</sup> Calculated as 100-Volatile Matter - Ash.

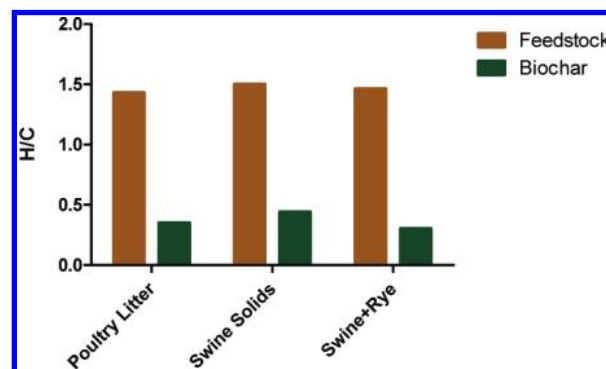


Figure 6. Decrease in H/C ratio after pyrolysis.

Table 5. N-P-K-S Contents of Biochar and Feedstocks

	parameters	chicken litter	swine solid	blended
N	feedstock (mg/g dm)	32.7 ± 0.3	45.8 ± 1.3	34.2 ± 4.0
	biochar (mg/g dm)	27.7 ± 0.2	32.6 ± 0.8	28.5 ± 0.0
	%N remaining in biochar	39 ± 8	32 ± 7	34 ± 15
P	feedstock (mg/g dm)	6.2 ± 3.7	23.7 ± 0.8	17.4 ± 0.8
	biochar (mg/g dm)	17.2 ± 2.0	71.5 ± 1.3	50.5 ± 3.3
	%P remaining in biochar	129 ± 115	137 ± 29	119 ± 49
K	feedstock (mg/g dm)	27.9 ± 0.6	8.5 ± 0.0	9.4 ± 0.4
	biochar (mg/g dm)	67.7 ± 2.0	25.6 ± 1.1	28.8 ± 0.6
	%K remaining in biochar	113 ± 24	137 ± 30	127 ± 51
S	feedstock (mg/g dm)	8.1 ± 1.0	9.3 ± 0.4	6.8 ± 2.6
	biochar (mg/g dm)	16.3 ± 1.5	6.6 ± 0.1	5.1 ± 0.0
	%S remaining in biochar	94 ± 28	32 ± 7	31 ± 21

**Energetics of Pyrolyzing Animal Manures.** The amount of energy needed to pyrolyze the blended manures can be divided into drying and sensible heat to raise dried feedstock to pyrolysis temperature (i.e., 620 °C in this case). The drying energy requirement was estimated by adding the heat to raise the wet feedstock to 100 °C and the latent heat of vaporization to evaporate water in the feedstock. Thermal efficiency of 80% was used in calculating drying energy requirements. Heat capacity of wood (1.7 kJ/kg/K) was used to estimate the sensible heat requirement for dry matter. Because the pyrolysis reactor was sufficiently well insulated, the sensible heat requirement lost during pyrolysis was assumed to be 5%. The heat of pyrolysis reaction of manure was assumed to be similar to that of cellulosic pyrolysis. Using Figure 19 of Mok and Antal,<sup>42</sup> the heat of pyrolysis reaction was estimated by a rough linear regression with respect to char yield. The reaction was exothermic at an average char yield of 31% (daf) - 576 kJ/kg. Chicken manure with typical moisture content of 50% needs an additional 3.1 MJ per kg of biochar produced as shown in

**Table 6. Energetics of Animal Manure Pyrolysis (MJ/kg Biochar)**

parameters	chicken litter	swine solid (flushed)	swine solid (dewatered)	blended
heat for drying	6.9	242.6	22.9	10.0
sensible heat (100 to 620 °C)	1.8	2.1	2.1	2.1
heat loss by carbonizer	0.1	0.1	0.1	0.1
heat of reaction	-0.8	-1.1	-1.1	-1.2
energy in produced gas	-4.9	-11.4	-11.4	-10.6
balance	+3.1	+232.3	+12.5	+0.5

Table 6. For wet manure such as flushed swine manure from animal house with a moisture content of 97%,<sup>43</sup> a huge amount of energy is needed to dry the manure before pyrolysis: 232.3 MJ per 1 kg biochar. This energy requirement can be substantially reduced by dewatering the flushed manure. For dewatered swine solids with 75% MC, the additional heating requirement was reduced to 12.5 MJ per kg biochar. When the dewatered swine solid is mixed with 10% MC rye grass, the resulting mixture had 56% MC. The overall energy balance for the mixed swine solids became almost neutral with additional heating requirement of only 0.5 MJ. Heating requirements for producing the same amount of biochar can be substantially reduced by mixing wet biomass with dry plant biomass such as hays and woods.

## Conclusions

Three different animal manure feedstocks (chicken litter, swine solids, swine/rye grass) were pyrolyzed at 620 °C using a proprietary skid-mounted system. Swine solid produced gas with the highest HHV, that was slightly below than that of methane, followed by the mixture of swine solids with rye grass and chicken litter. Biochar yield from pyrolysis ranged from 43 to 49% based on dry weight. Approximately 53 and 20% of carbon of the feedstock were recovered in biochar and product gas, respectively. Whereas the heating values of the biochar made from swine solids and mixture were between high and low rank coals, the heating value of the poultry litter biochar was slightly below that of low rank lignite. This was likely because of its high ash content. Approximately 50 and 25% of the feedstock energy were retained in biochar and produced gases, respectively. The biochars contained higher P and K and slightly lower N and S than that of original feedstock. The nutrient contents of biochar would suggest that it can be used as a low-grade fertilizer to improve soil fertility. Whereas 3.1 MJ of additional energy is needed to produce 1 kg of biochar from 50% MC chicken litter, 232.3 MJ of external energy is needed for flushed swine manure with 97% MC. However, dewatering of the flushed swine manure substantially reduced the energy requirement by 19 fold. Furthermore, biochar almost without any external energy could be produced by mixing of rye grass with the dewatered swine solids. This suggests the possibility of producing value-added biochar and even extra power from wet animal wastes if these wet feedstocks can be copyrolyzed with other waste feedstocks such as waste plastic pellets that are drier and more energy dense than rye grass.

## Acknowledgment

This research was conducted under the USDA-ARS NFCA 58-6657-9-235. The authors thank Dr. Joel Keller of R&A Energy Solutions, LLC and Mr. Brian Rayles of US Innovation

Group for their cooperation. The authors are grateful to Mr. Mel Johnson and Jerry Martin II for aid in sample collection and analyses. The author is also grateful to personnel from Super Soil Systems USA, Clinton, NC, and Mitch Tyner chicken farm in SC for providing samples. Mention of trade name, proprietary product, or vendor is for information only and does not guarantee or warrant the product by the USDA and does not imply its approval to the exclusion of other products or vendors that may also be suitable.

**Note Added after ASAP Publication:** After this paper was published ASAP September 14, 2010, corrections were made to Table 6 and to the paragraph below it. The revised version was published September 20, 2010.

## Literature Cited

- (1) Perlack, R. D.; Wright, L. L.; Turhollow, A. F.; Graham, R. L.; Stokes, B. J.; Erback, D. C. *Biomass as a feedstock for a bioenergy and bioproducts industry: The technical feasibility of a billion-ton annual supply*; U.S. Department of Energy, 2005; DOE/GO-102005-2135.
- (2) Ro, K. S.; Cantrell, K. B.; Hunt, P. G.; Ducey, T. F.; Vanotti, M. B.; Szogi, A. A. Thermochemical conversion of livestock wastes: Carbonization of swine solids. *Bioresour. Technol.* **2009**, *100*, 5466.
- (3) Ro, K. S.; Cantrell, K.; Elliott, D.; Hunt, P. G. Catalytic wet gasification of municipal and animal wastes. *Ind. Eng. Chem. Res.* **2007**, *46* (26), 8839.
- (4) Stone, K. C.; Hunt, P. G.; Coeffey, S. W.; Matheny, T. A. Water quality status of a usda water quality demonstration project in the eastern coastal plain. *J. Soil Water Conserv.* **1995**, *50* (5), 567.
- (5) Cantrell, K.; Ro, K.; Mahajan, D.; Anjom, M.; Hunt, P. G. Role of thermochemical conversion in livestock waste-to-energy treatments: Obstacles and opportunities. *Ind. Eng. Chem. Res.* **2007**, *46* (26), 8918.
- (6) He, B. J.; Zhang, Y.; Funk, T. L.; Riskowski, G. L.; Yin, Y. Thermochemical conversion of swine manure: An alternative process for waste treatment and renewable energy production. *Trans. ASAE* **2000**, *43* (6), 1827.
- (7) Priyadarsan, S.; Annamalai, K.; Sweeten, J. M.; Mukhtar, S.; Holtzaple, M. T. Fixed-bed gasification of feedlot manure and poultry litter biomass. *Trans. ASAE* **2004**, *47* (5), 1689.
- (8) Cantrell, K. B.; Ro, K. S.; Mahajan, D.; Anjom, M.; Hunt, P. G. Role of thermochemical conversion in livestock waste-to-energy treatments: Obstacles and opportunities. *Ind. Eng. Chem. Res.* **2007**, *46*, 8918.
- (9) Cantrell, K. B.; Ducey, T. F.; Ro, K. S.; Hunt, P. G. Livestock waste-to-bioenergy generation opportunities. *Bioresour. Technol.* **2008**, *99*, 7941.
- (10) Bridgwater, A. V.; Peacocke, G. V. C. Fast pyrolysis processes for biomass. *Renew. Sust. Energ. Rev.* **2000**, *4* (1), 1.
- (11) Beck, S. R.; Huffman, W. J.; Landeene, B. L.; Halligan, J. E. Pilot plant results for partial oxidation of cattle feedlot manure. *Ind. Eng. Chem. Process Des. Dev.* **1979**, *18* (2), 328.
- (12) Cantrell, K. B.; Ro, K. S.; Hunt, P. G., *Multi-utilization of swine manure as a bioenergy feedstock: Carbonization and combustion*. ASABE Paper 09-6810, 2009.
- (13) Gaskin, J. W.; Steiner, C.; Harris, K.; Das, K. C.; Bibens, B. Effect of low-temperature pyrolysis conditions on biochar for agricultural use. *Trans. ASABE* **2008**, *51* (6), 2061.
- (14) Godbout, S.; Larouche, J. P.; Belzile, M.; Verma, M.; Lemay, S. P.; Pelletier, F.; Solomatnikova, O.; Hamelin, L. *Biofuel production from swine manure solids using vacuum pyrolysis: A preliminary study*. ASABE Paper 096859, 2009.
- (15) Gordillo, G.; Annamalai, K. Adiabatic fixed bed gasification of dairy biomass with air and steam. *Fuel* **2010**, *89*, 348.
- (16) Lima, I. M.; Boateng, A. A.; Klasson, K. T. Pyrolysis of broiler manure: Char and product gas characterization. *Ind. Eng. Chem. Res.* **2009**, *48*, 1292.
- (17) Ngo, T.-A.; Kim, J.; Kim, S.-S. Characteristics and kinetics of cattle litter pyrolysis in a tubing reactor. *Bioresour. Technol.* **2010**, *101*, S104.
- (18) Priyadarsan, S.; Annamalai, K.; Sweeten, J. M.; Mukhtar, S.; Holtzaple, M. T. Fixed-bed gasification of feedlot manure and poultry litter biomass. *Trans. ASABE* **2004**, *47*, 1689.
- (19) Sa'nchez, M. E.; Martí'nez, O.; Go'mez, X.; Mora'n, A. Pyrolysis of mixtures of sewage sludge and manure: A comparison of the results obtained in the laboratory (semi-pilot) and in a pilot plant. *Waste Management* **2007**, *27*, 1328.



- (20) Serio, M. A.; Bassilakis, R.; Kroo, E.; Wojtowicz, M. A. Pyrolysis processing of animal manure to produce fuel gases. *Fuel Chemistry Division Preprints* **2002**, 47 (2), 588.
- (21) Sheth, A. C.; Bagchi, B. Investigation of nitrogen-bearing species in catalytic steam gasification of poultry litter. *J. Air & Wastes Management Assoc.* **2005**, 55, 619.
- (22) Sheth, A. C.; Turner, A. D. Kinetics and economics of catalytic steam gasification of broiler litter. *Trans. ASABE* **2002**, 45 (4), 1111.
- (23) Singh, K.; Risse, M.; Worley, J.; Das, K. C.; Thompson, S. *Adding value to poultry litter using fractionation, pyrolysis, and pelleting*. ASABE Paper 074064 2007.
- (24) Tu, D.; Dong, H.; Shang, B. *Pyrolysis behavior of selected manures using tg-ftir techniques*. ASABE Publication Number 701P0408 2008.
- (25) Young, L.; Pian, C. C. P. High-temperature, air-blown gasification of dairy-farm wastes for energy production. *Energy* **2003**, 28, 655.
- (26) Ro, K. S.; Cantrell, K. B.; Hunt, P. G. Efficiency of a skid-mounted pyrolysis system for power production from animal manures. *Prep. Pa.-Am. Chem. Soc. Div. Fuel Chem.* **2009**, 54 (2), 1065.
- (27) ALEC Arizona laboratory for emerging contaminants. <http://www.alec.arizona.edu/services.html>.
- (28) USEPA Microwave assisted acid digestion of siliceous and organically based matrices. In: *Test methods for evaluating solid wastes, physical/chemical methods*; SW-846; Washington, DC, 2008.
- (29) Cantrell, K. B.; Martin II, J. H.; Ro, K. S., Application of thermogravimetric analysis for the proximate analysis of livestock wastes. *Journal of ASTM International* **2010**, Accepted January 13, 2010. DOI-10.1520/JAI102583.
- (30) Varhegyi, G.; Antal, M. J., Jr.; Szekeley, T.; Till, F.; Jakab, E. Simultaneous thermogravimetric-mass spectrometric studies of the thermal decomposition of biopolymers. 1. Avicel cellulose in the presence and absence of catalysts. *Energy Fuels* **1988**, 2 (3), 267.
- (31) Biagini, E.; Fantei, A.; Tognotti, L. Effect of the heating rate on the devolatilization of biomass residues. *Thermochim. Acta* **2008**, 472 (1–2), 55.
- (32) Whitely, N.; Ozao, R.; Cao, Y.; Pan, W. P. Multi-utilization of chicken litter as a biomass source. Part ii. Pyrolysis. *Energy Fuels* **2006**, 20 (6), 2666.
- (33) Biagini, E.; Tognotti, L. Comparison of devolatilization/char oxidation and direct oxidation of solid fuels at low heating rate. *Energy Fuels* **2006**, 20 (3), 986.
- (34) Bernhart, M. E.; Fasina, O. Physical properties and pyrolysis behavior of fractionated poultry litter. *Trans. ASABE* **2009**, 52 (2), 531.
- (35) Shao, J.; Yan, R.; Chen, H.; Wang, B.; Lee, D. H.; Liang, D. T. Pyrolysis characteristics and kinetics of sewage sludge by thermogravimetry fourier transform infrared analysis. *Energy Fuels* **2008**, 22 (1), 38.
- (36) Lee, D. H.; Yang, H.; Yan, R.; Liang, D. T. Prediction of gaseous products from biomass pyrolysis through combined kinetic and thermodynamic simulations. *Fuel* **2007**, 86, 410.
- (37) Novak, J. M.; Busscher, W. J.; Laird, D. A.; Ahmedna, M.; Watts, D. W.; Niandou, M. A. S. Impact of biochar amendment on fertility of a southeastern coastal plain soil. *Soil Science* **2009**, 174 (2), 105.
- (38) Rutherford, D. W.; Wershaw, R. L.; Cox, L. G. *Changes in composition and porosity occurring during the thermal degradation of wood and wood components*; Reston, VA, 2005.
- (39) Rezaian, J.; Cheremisinoff, N. P. *Gasification technologies: A primer for engineers and scientists*. 2005.
- (40) Laird, D. A. The charcoal vision: A win-win-win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. *Agronomy Journal* **2008**, 100 (1), 178.
- (41) Lehmann, J.; Kern, D. C.; Glaser, B.; Woods, W. I. *Amazonian dark earths: Origin, properties, management*. Kluwer: The Netherlands, 2003.
- (42) Mok, W. S.-L.; Antal, M. J., Jr. Effects of pressure on biomass pyrolysis. II. Heats of reactions of cellulose pyrolysis. *Thermochim. Acta* **1983**, 68, 165.
- (43) Vanotti, M. B.; Szogi, A. A.; Millner, P. D.; Loughrin, J. H. Development of a second-generation environmentally superior technology for treatment of swine manure in the USA. *Bioresour. Technol.* **2009**, 100, 5406.

Received for review May 25, 2010

Revised manuscript received August 25, 2010

Accepted August 27, 2010

IE101155M