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Co-pyrolysis of swine manure with agricultural plastic waste: Laboratory-scale study



Kyoung S. Ro^{a,*}, Patrick G. Hunt^a, Michael A. Jackson^b, David L. Compton^b, Scott R. Yates^c, Keri Cantrell^a, SeChin Chang^d

^aUSDA-ARS Coastal Plains Soil, Water & Plant Research Center, Florence, SC, United States

^bUSDA-ARS NCAUR Renewable Products Technology Research, Peoria, IL, United States

^cUSDA-ARS U.S. Salinity Laboratory, Riverside, CA, United States

^dUSDA-ARS SRRC, Cotton Chemistry and Utilization, New Orleans, LA, United States

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ABSTRACT

Manure-derived biochar is the solid product resulting from pyrolysis of animal manures. It has considerable potential both to improve soil quality with high levels of nutrients and to reduce contaminants in water and soil. However, the combustible gas produced from manure pyrolysis generally does not provide enough energy to sustain the pyrolysis process. Supplementing this process may be achieved with spent agricultural plastic films; these feedstocks have large amounts of available energy. Plastic films are often used in soil fumigation. They are usually disposed in landfills, which is wasteful, expensive, and environmentally unsustainable. The objective of this work was to investigate both the energetics of co-pyrolyzing swine solids with spent plastic mulch films (SPM) and the characteristics of its gas, liquid, and solid byproducts. The heating value of the product gas from co-pyrolysis was found to be much higher than that of natural gas; furthermore, the gas had no detectable toxic fumigants. Energetically, sustaining pyrolysis of the swine solids through the energy of the product gas could be achieved by co-pyrolyzing dewatered swine solids (25% m/m) with just 10% SPM. If more than 10% SPM is used, the co-pyrolysis would generate surplus energy which could be used for power generation. Biochars produced from co-pyrolyzing SPM and swine solid were similar to swine solid alone based on the surface area and the ¹H NMR spectra. The results of this study demonstrated the potential of using pyrolysis technology to manage two prominent agricultural waste streams (SPM and swine solids) while producing value-added biochar and a power source that could be used for local farm operations.

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1. Introduction

For the last decade, production agriculture has become more intensive, and the U.S. and the world have seen the number of concentrated animal feeding operations (CAFOs) increase dramatically. Albeit efficient in meat production, CAFOs produce large quantity of manures, which exceeds the capacity of land nearby to assimilate the organic carbon and nutrients in manures. Much of the surplus manures are stored in storage pits and treatment lagoons for a long period of time before use. Also, excess manures are given at no or very low cost to manure dealers/haulers; and these middle men profit from the transport of material/manure to farms and available land located a longer distance from CAFO operations. Recently, biochar made from animal manures has

shown the potential for improving soil fertility, carbon sequestration and water quality (Novak et al., 2009; Ro et al., 2010; Sun et al., 2012; Sun et al., 2011). Biochar refers to the carbonaceous product from pyrolyzing biomass intended for soil application. The current market price of biochar is as high as \$2.20/kg (Batchelor et al., 2012). Manure biochar can be even more valuable with high nutrient contents such as N and P (Cantrell et al., 2012; Hunt et al., 2013; Ro et al., 2010). However, one of major stumbling blocks for producing biochar from animal manures especially from wet manures is its high energy requirement for drying and pyrolysis. Pyrolyzing manure alone is not energetically sustainable due to the manure's high moisture content and low energy density. Ro et al. (2010) reported that it required 232.3 MJ to produce 1 kg of biochar from flushed swine manure with a 3% total solid content. The energy requirement could be substantially reduced by dewatering the flushed swine manure prior to pyrolysis. However, it still requires external energy to make biochar. It is hypothesized that

* Corresponding author. Tel.: +1 8436695203.

E-mail address: kyoung.ro@ars.usda.gov (K.S. Ro).

the process may become energetically sustainable (e.g., no external energy requirement) if the low energy density manures are co-pyrolyzed with high energy density materials, such as plastics. Co-pyrolyzation may also produce additional power to meet the energy demands of farm operations. The energy densities of animal manures range from 14–18 MJ/kg_{db} (db: dry basis) for chicken litter and swine manure, respectively. Plastics have more than twice the energy of animal manures (e.g., 33–46 MJ/kg_{db} for nylon and polyethylene, respectively).

Plastic mulch films have been used for growing vegetables, strawberries, and other row and orchard crops. The benefits of plastic mulch include the ability to modify soil temperature and moisture, to control weeds, to reduce fertilizer leaching, and to decrease soil compaction and root pruning. The use of plastic mulch in the U.S. exceeds 110 million lb annually. (Hemphill, 1993). Unfortunately, most spent plastic mulch films (SPM) are non-biodegradable and are considered a waste product that must be removed from the field. These are major disadvantages of using plastic mulch in addition to its high costs for materials, installation, and removal. Currently, there are very few options for disposal/recycle of SPM. Although plastic mulch can be incinerated to produce heat and power as part of a mixed waste stream of municipal solid waste (MSW), many MSW incinerators are not designed to convert the extra heat generated by plastic combustion. To date, disposal in landfills have been the primary option for spent plastic mulch films. However, availability of landfills in the U.S. are becoming scarce and forcing the development of SPM recycling options and alternative disposal technologies.

Capturing the extractable energy from spent plastic mulch films to produce value-added biochar from animal manures can yield multiple benefits. It provides a viable disposal alternative for both spent plastic mulch films and surplus animal manures, while producing value-added biochar and power. However, there are primary level questions that need to be addressed: (1) Since some plastic mulch wastes were exposed to toxic fumigants such as methyl bromide, could there be the potential emission of these chemicals to the pyrolytic byproducts? (2) What is the optimal mixing ratio for plastic wastes to animal manures to produce biochar in an energetically sustainable manner? (3) Does the biochar produced from co-pyrolyzing animal manures with plastic mulch waste have the same quality as biochar produced from pyrolyzing animal manures alone? In this paper, we report the results of our investigation addressing these issues from co-pyrolyzing selected plastic mulches (SPM) with dewatered swine solids (SS).

2. Materials and methods

2.1. Feedstocks

Dewatered swine solids (25% solids) were obtained from a solid–liquid separation system treating flushed manure from a 5600-head finishing swine operation in North Carolina (Vanotti et al., 2009). Once collected, these separated solids underwent solar drying in a greenhouse. For the laboratory batch pyrolysis experiments, the dewatered swine solid (SS) was further dried in an oven at 373 K until the moisture content was less than 7%. Several bundles of very impermeable plastic mulch films (Polygro VIF, Safety Harbor, FL) that had been used for growing water melons and vegetables were collected from the USDA-ARS Vegetable Laboratory, Charleston, SC; heretofore considered spent plastic mulch (SPM). Small portions of the SPM films were separated and dried prior to pyrolysis experiments. Additionally several virgin plastic mulch films were used, including a standard 1-mil high-density polyethylene (HDPE) (Trical, Inc., Hollister, CA), a virtually impermeable film consisting of HDPE co-extruded with a ethyl vinyl

alcohol barrier polymer layer (Hytibarrier, Klerks Plastics, Richburg, SC), a transparent solarization film that included 0.0034% of halosulfuron-methyl (BIG2H39T80, Bayer CropScience, Leverkusen, Germany), and a 1-mil thermic film (XP4692M, Pliant Corp, Washington, GA).

2.2. Bench-pyrolysis system

Fig. 1 shows a schematic of the laboratory batch pyrolysis reaction system employed for this study. It consists of a stainless steel 533 ml batch reactor (63 mm internal diameter and 171 mm height) heated by an external band heater. The reactor temperature and pressure were monitored by a PID controller via an internal thermocouple and pressure transducer. The controller energized the band heater as needed to maintain the target reactor temperature. The temperature and pressure data were stored on a PC. For each run, the reactor was loaded with approximately 30 g of various feedstocks; SS alone, SPM alone, virgin plastic mulch alone, and a 2:1 mixture of SPM + SS. The loaded reactor was sealed and the headspace was flushed with Argon gas at a rate of 1 lpm for a least 10 min. The reactor was then heated to 773 K and maintained for 2 h. After cooling to room temperature, a gas headspace sample was collected in a foil tedlar bag (SKC FlexFoil, Eight Four, PA). In order to recover oil and wax formed on the surface of various parts inside the reactor, the reactor was filled with acetone and stirred for 6 h to dissolve the oil. The reactor contents were then filtered using a vacuum pump and glass microfiber filters. The acetone filtrate was weighed and placed in a refrigerator for storage for later liquid analyses. The filtered solids were weighed and dried in an oven at 378 K overnight. After drying, the dry weight of the solids was recorded. Duplicate pyrolysis runs of each feedstock were conducted.

2.3. Analytical methods

Gas samples were analyzed in triplicate on a HP 6890 GC fitted with a TCD operating at 493 K. Gas separation was accomplished using a Poropak Q column (Restec, Bellafonte, PA, USA) with He as the carrier gas. The column was heated as follows: 313 K for 2 min, ramped to 453 K (40 K/min), held for 5 min, ramped to 473 K (40 K/min), held for 10 min, and returned to 313 K. Gas products were quantified vs calibration of a standard gas mixture consisting of ~3% (wt/vol) each H₂, CH₄, CO, CO₂, C₂H₆, C₂H₄ in He (Linde North America Inc., Murray Hill, NJ, USA) and 5% (wt/vol) each C₃H₈, and C₃H₆ in He (ILMO Specialty Gasses, Jacksonville, IL, USA). Due to the TCD signal damping effect of He on H₂, a standard curve for H₂ was prepared from mixtures ranging from 3% to 50% (vol/vol), resulting in a calibration curve of $y = 24x^{1.5}$ ($R^2 = 0.997$). Liquid samples (the acetone filtrate) were analyzed using a Shimadzu QP2010 SE GC/mass spectrometer/FID. Separations were accomplished using a Supelco Petrocol DH 50.2 (50 m × 0.2 mm × 0.5 μm) column. The oven program was as follows: Initial temperature 323 K for 2 min, ramp at 10 K/min to 373 K, hold 1 min then ramp at 20 K/min to 523 K with a final hold time of 10 min. Methyl octanoate was used as internal standard.

CHN analyses of feedstocks and solid products (i.e., biochar) were performed on a Leco CHN628 (St Joseph, MI, USA). Prior to analysis, samples were dried under vacuum 353 K for 3 h then ground to smallest particle size possible. Samples (120 mg) were combusted in tin foil cups utilizing a burn profile of 20 s high-flow oxygen followed by 150 s medium-flow and then 30 s high-flow to achieve complete combustion and trapping of products; detection of carbon and hydrogen were by IR, while nitrogen was by thermal conductivity.

To compare the difference in chemical structures of labile volatile matter of the biochars made from pyrolyzing SS alone vs.

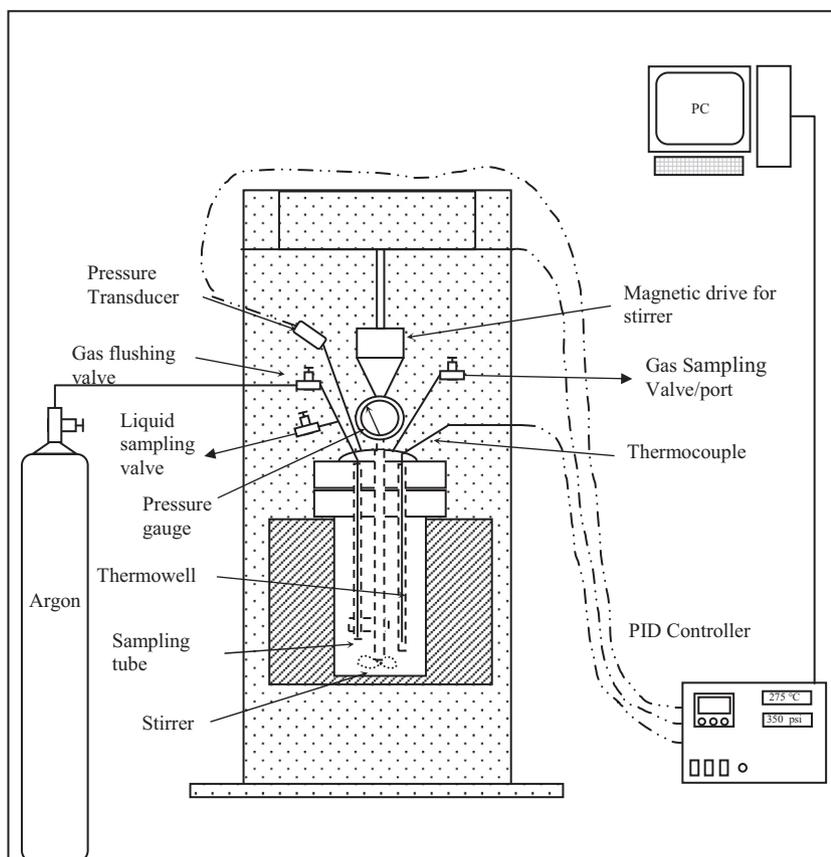


Fig. 1. Schematic diagram of the laboratory batch pyrolysis reaction system.

SS + SPM, proton nuclear magnetic resonance analyses of deuterated dimethyl sulfoxide (DMSO- d_6) extracts of biochar were performed. The DMSO- d_6 extracts were obtained by suspension in chloroform for 1 hour and then filtered through a glass wool packed Pasteur pipette. The resulting extracts were analyzed by proton nuclear magnetic resonance (^1H NMR) spectrometer (Varian Unity plus 400 spectrometer, 400 MHz) at ambient probe temperature. Tetramethylsilane (TMS, 0.0 ppm) in DMSO- d_6 were used as internal reference for NMR measurement.

Four commonly used fumigant samples [methyl bromide (MeBr), 1,3-dichloropropene (1,3-D), chloropicrin (CP), and methyl iodide (MeI)] were analyzed using gas chromatography. MeBr (>99.9% purity) was donated by Trical Inc. (Holister, CA), 1,3-D (98.9% purity, including 50:50 *cis*- and *trans*- 1,3-D isomers) and chloropicrin (99.9%) were donated by Dow Agrosciences (Indianapolis, IN). MeI (>99%) was purchased from Sigma Chemical Co. (St. Louis, MO). A Hewlett–Packard HP 6890 gas chromatograph (GC) equipped with a micro-electron capture detector (μECD) was connected to an Agilent Technologies G1888 Network Headspace Sampler. A DB-VRX fused silica capillary column (30 m \times 0.25 mm i.d. \times 1.4 μm , J&W, Folsom, CA) was used with the following conditions: helium carrier gas flow rate at 1.4 ml min^{-1} ; injector temperature 513 K; detector temperature 553 K; initial oven temperature program of 318 K held for 1 min and then increased to 353 K at 2.5 K min^{-1} . The conditions for the headspace sampler containing a 1000 μL sampling loop were: oven 353 K, loop temperature 363 K, transfer line temperature 373 K, and headspace vial equilibration time in oven for 5.0 min. Retention times of MeBr, MeI, *cis*-, *trans*-1,3-D, and CP were 2.81, 3.88, 10.87, 12.11, and 13.45 min, respectively. Calibration standards for the GC analysis were prepared from their stock solution at seven concentrations in headspace vials and were analyzed at the beginning of each set

of samples. The headspace method and calibration curves employed were able to quantify fumigant concentration at 20 ppb for MeBr and 5 ppb for the other fumigants.

Except for the MeBr's decomposition temperature of 673 K (WHO, 1994), thermal decomposition data for other fumigants are not available in the literature. In this study, the gas-phase concentrations of the fumigants in the produced gas samples were assessed to infer the presence of the fumigants in the pyrolysis products. For soil fumigants, measuring the headspace concentration of an environmental sample is a common practice for determining the total fumigant concentrations of the sample (Jury et al., 1983). This can be accomplished by using Henry's Law and linear equilibrium adsorption relationships that relate the gas phase concentrations to the liquid and solid phases (Wauchope et al., 1992). Since fumigant chemicals have relatively high vapor pressures, measurable head space concentrations would be present if the chemical exists in the liquid and solid phases. Using the Henry's Law and sorption relationships, the liquid-phase and solid phase concentrations can be determined. Therefore, a non-measurable headspace concentration indicates the lack of available fumigant in the liquid and solid phases.

2.4. Thermogravimetric analyses

The feedstock samples were subjected to pyrolytic thermogravimetric analysis runs (TGA) using a TGA–DTA analyzer (TGA/DSC1, Mettler Toledo International Inc., Columbus, OH). Immediately prior to Argon pyrolysis runs, samples underwent a drying step using the TGA to allow for subsequent TGA runs to determine on a dry-basis. All samples were placed in open top Al_2O_3 70 μL crucibles and were pyrolyzed with ultra-high purity Ar as the carrier gas under the following method: 308–1223 K (10 K per min), Ar

flow rate of 80 ml/min; 1223 K hold for 10 min with Ar flow rate of 120 ml/min; controlled cool down to room temperature with Ar flow rate of 80 ml/min.

3. Results and discussion

3.1. Thermo-physical characteristics of raw feedstocks

While other virgin plastic mulch materials contained less than 1.5% ash, soil residues from field use of SPM resulted in a higher ash content of 13.1% (Table 1). As expected, swine solids (SS) contained even higher ash content than SPM. Generally, plastic mulch films had much higher volatile matter (VM) and lower fixed carbon than swine solids. The VM undergoes complex pyrolysis reactions such as dehydration, decarboxylation, depolymerization and carbonation at high temperatures in the absence of oxygen (Basu, 2013; Libra et al., 2011). Plastic decomposition involved combinations of four general mechanisms; chain scission (molecular weight (MW) decrease, volatile formation), cross-linking (chain unsaturation, volatile formation, cross linking), side chain elimination (chair unsaturation, volatile formation, cross linking), and side chain cyclization (SFPE, 2002). As shown in Fig. 2, the thermal decomposition curve of the SS exhibited typical broad decomposition profiles associated with manures (Ro et al., 2010). However, all plastic mulch films had very sharp decomposition curves with narrow degradation temperature ranges. Two to 98% of all VMs of all plastic mulch films were devolatilized within 553–814 K (i.e., T_{onset} to T_{terminal}). The peak decomposition temperatures (T_{peak}) of the plastic mulch films ranged from 718 to 741 K.

3.2. Thermal decomposition kinetics

Assuming a one-step global decomposition kinetic model, the thermal degradation rate can be expressed as an n -th order reaction kinetic equation (Ro et al., 2009).

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \exp(E/RT) dT \quad (1)$$

where A is the pre-exponential factor (s^{-1}), E is the activation energy (kJ mol^{-1}), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature (K), n is the order of reaction, α is the fractional conversion, β is the constant heating rate or dT/dt (K s^{-1}), and t is the time (s). The fractional conversion of the reaction is defined as:

$$\alpha = \frac{m_0 - m_T}{m_0 - m_f} \quad (2)$$

where m_0 is the initial mass (g), m_T is the mass at temperature T (g), and m_f is the final residual mass (g). Integration of Eq. 1 using the temperature integral approximation developed by Coats and Redfern (1964), the conversion can be expressed as:

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (\text{for } n = 1) \quad (3)$$

$$\ln \left[\frac{1 - (1-\alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (\text{for } n \neq 1) \quad (4)$$

Table 1

Properties of spent plastic mulch (SPM), swine solid (SS), and other raw plastic film feedstocks and their pyrolytic degradation temperatures.

	Volatile matter (%) _{db}	Fixed carbon (%) _{db}	Ash (%) _{db}	T_{onset} ($\alpha = 0.02$) (K)	T_{peak} (K)	T_{terminal} ($\alpha = 0.98$) (K)
SPM	80.0 ± 2.7	0.7 ± 0.5	13.1 ± 1.6	593	741	782
SS	64.8 ± 1.2	13.1 ± 0.7	22.3 ± 0.6	434	567	1164
Hytibarrier	99.7 ± 0.1	0.3 ± 0.1	0.0 ± 0.03	555	718	814
Thermic	99.9 ± 0.04	0.1 ± 0.05	0.0 ± 0.04	589	738	791
Bayer CS	98.8 ± 0.1	0.0 ± 0.1	1.2 ± 0.02	553	723	761
1 mil HDPE	99.9 ± 0.02	0.1 ± 0.02	0.0 ± 0.01	576	729	771

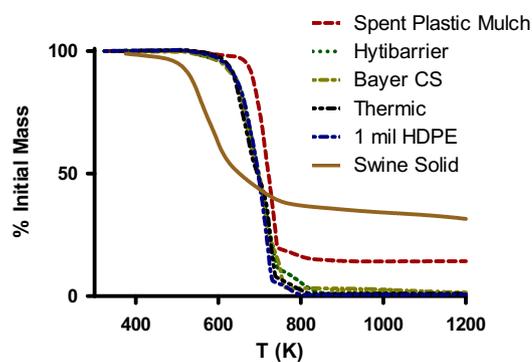


Fig. 2. TGA pyrolytic curves of spent plastic mulch, other virgin plastic mulch, and swine solids (308–1223 K; 10 K min^{-1} ; Ar 80 ml min^{-1}).

Kinetic parameters that fit the TGA data of the SPM were similar to that for polyethylene pyrolysis kinetic parameters ($E = 241 \text{ kJ/mol}$, $A = 10^{15} \text{ s}^{-1}$, and $n = 1$ in Westerhout et al., 1997) as shown in Fig. 3 and Table 2. The kinetic parameters for SS ($E = 92.7 \text{ kJ/mol}$, $A = 1.7 \times 10^6 \text{ s}^{-1}$, and $n = 3.7$) reported by Ro et al. (2009) fit well for the swine solid in this study. While the order of reaction rate for SPM, HDPE and Hytibarrier (Hy) was unity, the other plastic mulch films such as Bayer CS and Thermic underwent higher orders of reaction rate of 2.44 and 2.03, respectively.

Using the kinetic information, one can estimate the reaction time required to achieve desired degree of decomposition at a designed pyrolysis temperature. Substituting $\beta = dT/dt$ and integrating the Eq. 1 from ($t = 0$, $\alpha = 0$) to ($t = t$, $\alpha = \alpha$) with $n = 1$ for the SPM and $n = 3.7$ for SS, the combined conversion of the mixture can be expressed as:

$$\alpha = (1-f) \left[1 - \exp(-A_{pm} \exp\{-E_{pm}/RT\}t) \right] + f \left[1 - (1 + 2.7A_{ss} \exp\{-E_{ss}/RT\}t)^{-1/2.7} \right] \quad (5)$$

where f is the fraction of SS in the mixture, A_{pm} , A_{ss} , E_{pm} , E_{ss} are pre-exponential factors and activation energies for SPM and SS, respectively. Eq. 5 was used to estimate the reaction time required for desired conversion at selected pyrolysis temperatures with our 2:1 mixed feedstock of SPM and SS (Fig. 4). It takes less than 1 min to achieve 94% conversion at 773 K while it takes 18 min at 700 K, and only achieves 44% even after 30 min at 650 K. Therefore, our pyrolysis temperature of 773 K and a reaction time of 2 h should complete the devolatilization reaction.

3.3. Produced gas characteristics

One of the potential concerns for the spent plastic mulch films was the emission of toxic fumigant chemicals such as methyl bromide. From analyzing the produced gases from pyrolysis of SPM alone and SPM + SS, there was no detection of any of the four commonly used fumigants (MeBr, 1,3-D, MeI, and CP). This was not surprising since soil fumigants have low sorption coefficients (Papiernik et al., 1999; Wauchope et al., 1992). Moreover, the plastic mulch films were usually exposed to sun and soil for a long

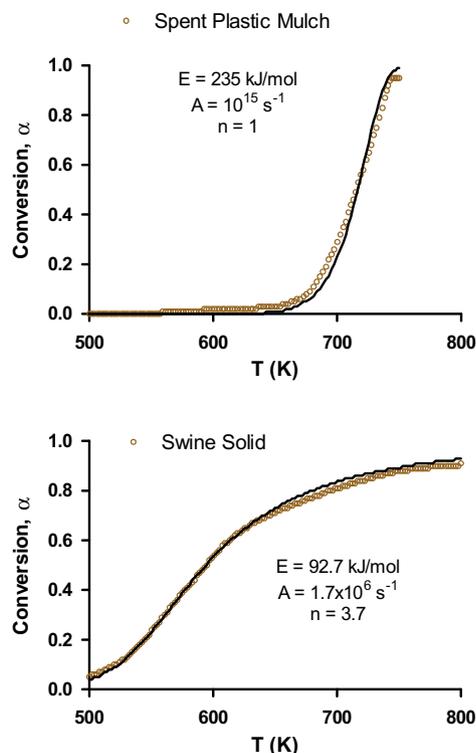


Fig. 3. Comparison of simulated conversions of spent plastic mulch and swine solids with experimental data at 10 K/min heating rate.

Table 2
Kinetic parameters for the pyrolysis of various plastic mulches.

	T (K)	wt%	n	A (s ⁻¹)	E (kJ/mol)	R ²
SPM	663–744	5–95	1	1.7×10^{10}	172	0.994
Hy	607–793	5–95	1	1.2×10^5	101	0.992
Bayer CS	606–758	5–95	2.44	1.4×10^{10}	162	0.990
Thermic	619–758	5–95	2.03	1.1×10^9	149	0.978
1 mil HDPE	613–733	5–95	1	1.3×10^7	126	0.995

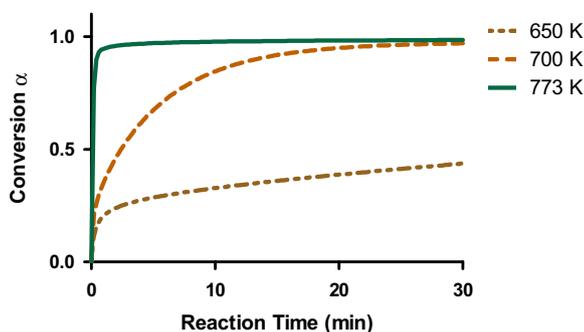


Fig. 4. Conversion of 2:1 mixture of spent plastic mulch with swine solids at different reaction temperatures.

period of time allowing the fumigants to degrade or photolysis in soil (Gan and Yates, 1996; Ma et al., 2001) or volatilized (Papiernik et al., 2011; Yates et al., 2003) even before the start of the pyrolysis process.

Table 3 shows the compositions of major energy gases from pyrolyzing various mixtures of SS and SPM. Pyrolysis of SS alone produced combustible gas with a higher heating value (HHV) of 24.5 MJ/S m³, which was slightly lower than that reported by Ro et al. (2010) from pyrolyzing SS at 893 K. Pyrolyzing SPM alone

produced combustible gas with a much higher HHV of 45.7 MJ/S m³. The mixed feedstock (2:1 mixture of SPM and SS) produced combustible gas with slightly less HHV (41.6 MJ/S m³). As shown in Table 3, similar trends of pyrolyzing either virgin Hy plastic mulch film or the mixture of Hy and SS were evident as shown in Table 3. The produced gas from pyrolyzing SPM + SS mixture had much higher HHV than that of natural gas (36.5 MJ/S m³). Because of higher oxygen content of SS (24.9% estimated from assuming the remainder of chemical element of the raw SS in Table 5 were ash and oxygen), significantly more CO₂ was produced from pyrolyzing SS than from the plastic mulch films or the mixtures (Paradela et al., 2009). However, more H₂ was formed from pyrolysis of the SS although its H content was lower than the plastic mulch films. The high C content of the plastic mulch films used H to produce gaseous hydrocarbons, which is thermodynamically more favorable than forming H₂ at lower temperatures (He, 2012). Although Kim et al. (1997) reported higher C₂H₄ and C₃H₆ contents from pyrolyzing plastic wastes at 911 to 1008 K, significantly more CH₄, C₂H₆, and C₃H₈ were produced in our experiments. Lower pyrolysis temperature and longer residence time might have been the reasons for the differences.

3.4. Liquid product characteristics

The GC mass spectral data of the liquid phases resulting from the pyrolysis of SS and SPM + SS are shown in Fig. 5a and b, respectively. While quantification of the compounds identified in the spectra was beyond the scope of this study, it was readily evident that the pyrolysis of SPM + SS produced dramatically more hydrocarbons than SS alone. Relative to chemical composition, the liquid originating from pyrolyzing SS contained benzene, toluene, ethylbenzene, and xylenes (BTEX) along with nitrogen-containing compounds like methylpyridine, 4-Methyl-3-penten-2-one, 4-Amino-4-methyl-2-pentanone, and 2,2,6,6-tetramethyl-4-piperidinone. The liquid originating from pyrolyzing SPM + SS was dominated by hydrocarbons resulting from pyrolysis of plastic mulch film. The SPM + SS pyrolysis liquid also contained BTEX, along with a homologous series of α -olefins and *n*-alkanes ranging from six-carbon 1-hexene to the 20-carbon analogue. Other notable peaks included the fatty acids palmitic acid and oleic acid and the long chain alcohols 1-docosanol and 1-tetracosanol. These compounds have potential uses in either the petrochemical industry or liquid fuels after distillation and upgrading.

3.5. Biochar characteristics

Pyrolysis of SS alone produced 38.9% solid products (i.e., biochar), while the SPM + SS produced 27.9% biochar (Table 4). This reduction in biochar yield of the mixed feedstock was due to the fact that SPM contributed a small char yield (18.4%) with high ash content (44.6%). In contrast, pyrolysis of Hy produced the char yield of 9.1% with very small ash content (0.7%). All biochars produced from pyrolysis of SS, SPM + SS, or HY + SS contained small volatile matter (VM) ranging from 6.8% to 10.9%. Yet, they all contained high fixed carbon contents ranging from 44.6% to 64.7%.

Table 5 shows the C, N, H contents of raw SS, plastic mulch films, and the biochars for these feedstock materials. The C contents of the raw plastic mulch films were similar to that of waste post-consumer plastic compositions prepared by a dry preparation method provided by the Duales System Deutschland (Kim et al., 1997; Shah et al., 1999). The carbon content of SS only slightly increased from raw SS to SS biochar. In contrast, the C contents decreased for the SS mixed with plastic mulch films biochars. On the basis of biochar yield and C contents of feedstocks and biochars, about 42%, 24.5%, and 20.9% of feedstock carbon were

Table 3

Gas composition and higher heating value (HHV) from the pyrolysis at 773 K of swine solids (SS), spent plastic mulch (SPM), Hytibarrier (Hy) plastic film and their mixtures.

Gases (% v/v)	SS	SPM	SPM + SS (2:1)	Hy	Hy + SS (2:1)
H ₂	12.6 ± 6.0	4.7 ± 0.5	6.7 ± 1.8	3.8 ± 0.5	7.7 ± 2.1
CO	2.8 ± 1.2	0.7 ± 0.2	1.2 ± 0.1	4.0 ± 0.04	2.3 ± 0.04
CH ₄	27.3 ± 5.5	43.6 ± 4.5	39.3 ± 2.3	38.8 ± 10.3	42.8 ± 2.6
CO ₂	30.9 ± 6.5	0.3 ± 0.1	6.0 ± 0.6	0.2 ± 0.02	5.9 ± 1.7
C ₂ H ₄	1.2 ± 0.4	1.5 ± 0.1	1.4 ± 0.01	1.4 ± 0.3	1.6 ± 0.4
C ₂ H ₆	10.8 ± 1.0	23.5 ± 4.0	21.2 ± 2.4	22.2 ± 3.0	21.3 ± 0.4
C ₃ H ₆	2.0 ± 0.7	2.4 ± 0.1	2.2 ± 0.2	2.8 ± 0.7	2.7 ± 0.6
C ₃ H ₈	3.8 ± 1.1	12.4 ± 2.0	11.2 ± 1.4	12.6 ± 1.9	9.2 ± 2.1
HHV (MJ/m ³)	24.5	45.7	41.6	43.8	41.9

Table 4

Proximate analyses and yields of biochar/char from swine solids (SS), spent plastic mulch (SPM), Hytibarrier (Hy) plastic film and their 2:1 blends.

	Volatile matter ^a (% _{db})	Fixed carbon (% _{db})	Ash (% _{db})	Biochar yields (% _{db})
Biochar from SS	10.9 ± 0.9	44.6 ± 2.1	44.4 ± 1.9	38.9 ± 8.6
Biochar from SPM + SS	6.8 ± 0.7	52.4 ± 4.8	40.8 ± 4.8	27.9 ± 2.9
Biochar from Hy + SS	7.7 ± 0.2	64.7 ± 2.8	27.6 ± 2.8	21.8 ± 1.2
Char from SPM	4.2 ± 0.9	51.2 ± 5.6	44.6 ± 5.5	18.4 ± 1.4
Char from Hy	10.4 ± 0.4	88.9 ± 0.4	0.7 ± 0.1	9.1 ± 2.2

^a %_{db} = Percentage based on dry weight basis.**Table 5**

Elemental analyses of raw feedstocks and biochar/chars; swine solids (SS), spent plastic mulch (SPM), Hytibarrier (Hy) plastic film and their 2:1 blends.

	C% _{db}	H% _{db}	N% _{db}	C/N recovery in biochar	
Raw SS	43.1 ± 0.3	6.6 ± 0.2	3.1 ± 0.02		
Raw SPM	72.3 ± 0.2	11.2 ± 0.3	1.2 ± 0.04		
Raw Hy	80.0 ± 0.1	12.7 ± 0.2	3.3 ± 0.04		
Biochar from SS	46.5 ± 0.4	1.8 ± 0.1	3.3 ± 0.1	C (%)	N (%)
Biochar from SPM + SS	55.2 ± 0.4	1.7 ± 0.02	2.0 ± 0.03	42.0 ± 0.5	41.2 ± 1.2
Biochar from Hy + SS	65.0 ± 1.4	2.2 ± 0.2	2.6 ± 0.1	24.5 ± 2.6	29.5 ± 3.1
				20.9 ± 1.2	17.8 ± 1.0

recovered in biochar for SS, SPM + SS, and Hy + SS, respectively (Table 5). Similar recoveries of N were observed for these mixed feedstocks. The stability of volatile matter C and plant availability of N of these biochars in soil environment will be important in soil applications for carbon sequestration and plant growth. The chemical structures of the biochar volatile matter along with its surface area will play critical roles in interactions with soil microbes and plants (Insam and Seewald, 2010; Spokas et al., 2011).

In order to assess if there was any significant structural difference among mixtures the biochars made from SS and SPM, their surface area and labile volatile matter chemical structures were compared. The Brunauer–Emmett–Teller (BET) surface area for SS biochar and SS + SPM biochar were 7.0 ± 1.5 and 5.7 ± 0.3 m²/g, which were not significantly different ($P = 0.142$, unpaired t-test with Welch's correction). Fig. 6 presents the proton nuclear magnetic resonance (¹H NMR) spectra for the DMSO-d₆ extracts of raw SS, SS biochar, and SS + SPM biochar. These chemical structures in the labile volatile matter of these biochars and raw SS, as depicted in the NMR spectra, would interact with various components of the soil matrix. For the raw SS (Fig. 6, spectrum 1), diverse chemical functionalities of the labile volatile matter were evident: the chemical shifts between 0.5 and 2.3 ppm belong to the organic aliphatic proton groups such as M-CH₂R, M-Ph, M-C(=O)R, M-C(=O)OR, M-C(=O)NR₂, M-NR₂, and M-CN (M = methyl, methylene, or methane; R = alkyl group; Ph-phenyl) (Silverstein et al., 1991). Similar diversity of the raw SS was reported from ¹³C NMR analyses (Cao et al., 2011). After pyrolysis, most of these aliphatic groups of the raw SS were volatilized as shown in the spectrum of the SS biochar in Fig. 6 (spectrum 2). Compared to that of the SS biochar, spectrum 3 (SPM + SS biochar) shows almost identical chemical structures of volatile matter. Similar surface

area and the chemical structures of labile volatile matter of these two biochars made from pyrolysis of SS alone and SPM + SS suggest similar functional characteristics of these biochars when applied to soil. However, more in-depth study on C sequestration via soil incubation and/or a plant growth study using these biochars is needed to confirm the functional similarity.

3.6. Energetics

When the raw feedstock was pyrolyzed, the stored energy was re-distributed to the gas, liquid, and solid products. For SS, 43.4% of the feedstock energy (15.9 MJ_{HHV}/kg) was retained in the biochar, while 32.2% and 24.4% of the feedstock energy were retained in produced gas and liquid, respectively (Table 6). However, for the plastic mulch films, the majority of the feedstock energy was retained in the liquid, 53% and 54% for SPM and Hytibarrier film (Hy), respectively. Less than 10% of the raw plastic mulch film energy was retained in its char. When the plastic mulch films were mixed with SS, about equal distributions of the feedstock energy were retained in produced gas and the liquid.

In order to estimate the amount of energy needed to produce 1 kg of biochar, the energy requirement was divided into drying energy for water evaporation and the sensible heat to raise the dried feedstock to the pyrolysis reaction temperature of 773 K. The energy needed to reduce the raw feedstock's moisture content was estimated by adding the heat to raise the raw feedstock to 373 K and the latent heat of vaporization for moisture evaporation. The thermal efficiency of the drying process was assumed to be 80%, while the insulation heat loss through the pyrolysis reactor system surface was assumed to be 5% (Ro et al., 2010). Due to limited availability of related swine thermal characteristics, the heat

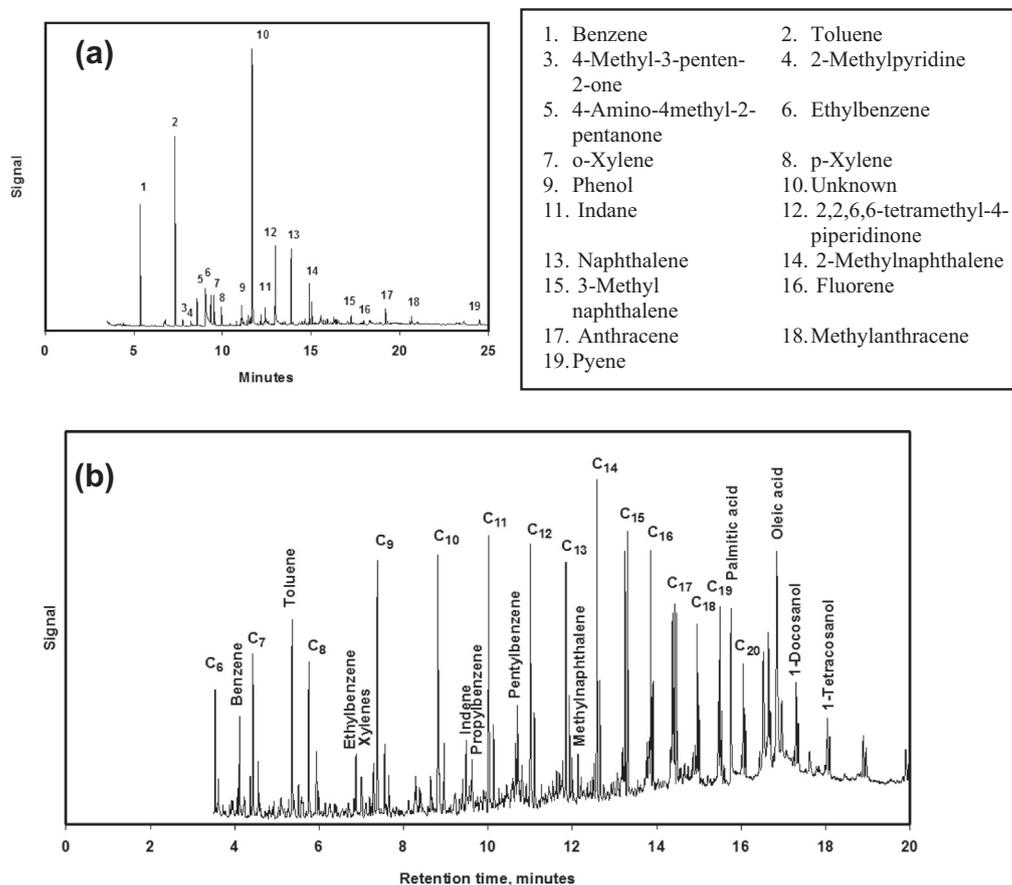


Fig. 5. (a) GC chromatogram of the SS pyrolysis liquid (b) GC chromatogram of the SPM + SS pyrolysis liquid. The peaks labeled by carbon number represent α -olefins and n -alkanes of this carbon number with the olefins being the larger peak of the pair with the exception of the C₁₅ pair.

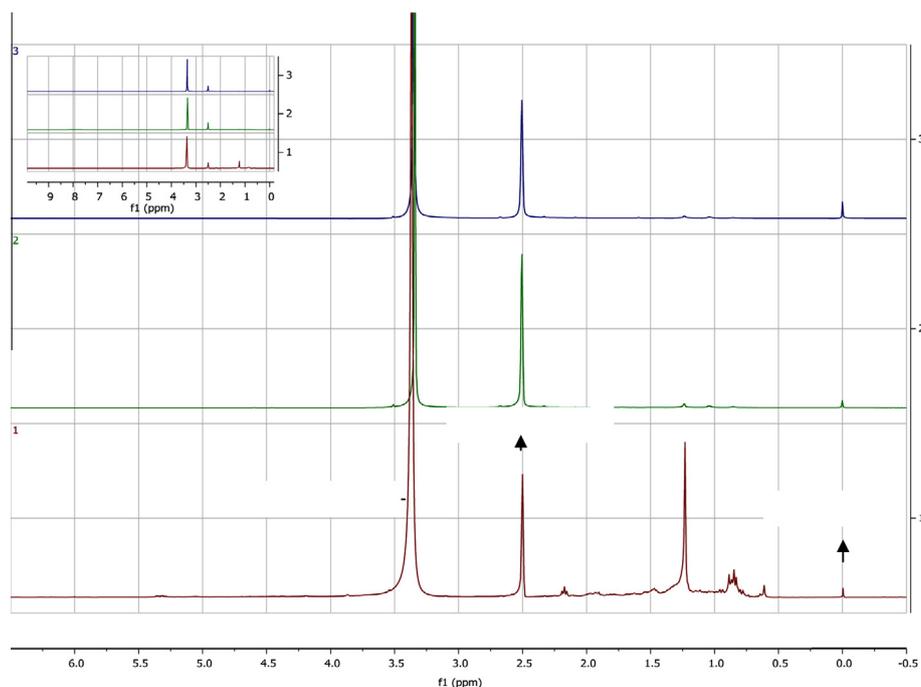


Fig. 6. Proton nuclear magnetic resonance (NMR) spectrum chemical shifts (F1, ppm) for the DMSO-d₆ extracts from raw SS (1, bottom), SS biochar (2, middle), and SPM + SS biochar (3, top).

Table 6

Distribution of feedstock energy in gas, liquid, and solid products when pyrolyzing swine solids (SS), spent plastic mulch (SPM), Hytbarrier (Hy) plastic film and their 2:1 blends.

% Feedstock energy	SS	SPM	Hy	SPM + SS	Hy + SS
In produced gas	32.2	37.9	38.4	40.3	39.0
In biochar or char	43.4	9.1	7.6	17.9	15.7
In Liquid ^a	24.4	53.0	54.0	41.8	45.3

^a Determined by the difference.

Table 7

Pyrolysis energetics of plastic mulch films^a (SPM and Hy) and mixed with swine solids^a (SS).

Parameters	SS	SPM + SS	Hy + SS
Heat for drying (MJ/kg)	-25.2	-5.8	-7.4
Sensible heat from 100 to 500 °C (MJ/kg)	-1.5	-2.1	-2.6
Heat loss by reactor systems (MJ/kg)	-0.1	-0.1	-0.1
Energy produced in gas (MJ _{HHV} /kg)	+13.2	+46.0	+61.0
Balance (MJ/kg)	-13.6	+38.1	+50.9

^a 25% solids for dewatered swine solids, 10% moisture for plastic mulch films.

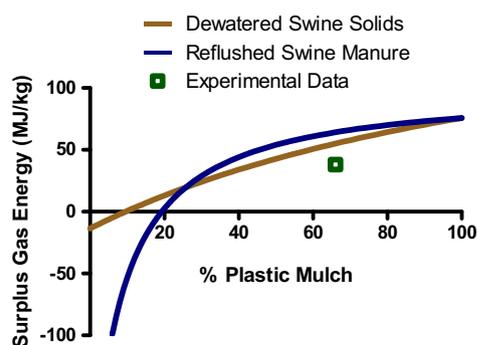


Fig. 7. Surplus gas energy (MJ per kg biochar produced) produced from pyrolyzing swine solids mixed with various amount of plastic mulch film.

capacity of dried cattle manure (i.e., 1.44 kJ/kg/K) was used to estimate the heat need to raise the dried feedstock to the pyrolysis temperature (Bohnhoff and Converse, 1987). The heat of reaction for SS + SPM mixture was assumed to be thermally neutral. When co-pyrolyzing SS and SPM, the energy in the produced gas alone was more than enough to carry out the pyrolysis operation. The dewatered SS mixed with 67% of SPM and HY produced surplus gas energies of 38.1 and 50.9 MJ/kg biochar, respectively, as shown in Table 7. Fig. 7 shows the surplus gas energy per kg of biochar produced from pyrolyzing dewatered or reflushed SS mixed with various amounts of SPM. The moisture contents of dewatered and reflushed SS were assumed to be 75% and 97%, respectively. The amount of SPM needed to achieve energetically sustainable pyrolysis of dewatered SS using the energy of its product gas was only 10%. Even for the wet reflushed SS, only 20% SPM was needed to balance the energy requirement with its product gas energy. These analyses clearly demonstrated that the energy stored in SPM could easily be utilized in pyrolyzing wet manures to produce both value-added biochar and surplus energy. Assuming 0.24 Mg/yr of SPM is available in the U.S., the energy for the SPM is enough to potentially produce 0.67 Mg of biochar from dewatered SS (i.e., about \$307 million based on \$2.20/kg market price). Furthermore, reduction of landfill tipping fees associated with both the manure and SPM disposal would make this co-pyrolysis process even more attractive for farmers.

4. Conclusions

Gas, liquid, and solid products from co-pyrolysis of swine solids (SS) with spent plastic mulch films (SPM) were analyzed along with their thermal decomposition kinetics and energetics. All plastic mulch films had very narrow decomposition temperature ranges with peak temperatures at around 718 to 741 K. The SS had more broad decomposition temperature range with a peak temperature at 567 K. Subsequent kinetic analysis showed that, for the 2:1 SPM + SS copyrolysis, less than 1 min at 773 K (or 18 min at 700 K) was required to achieve 94% conversion. None of the four fumigants popularly used in the U.S. was detected in the gas produced from pyrolysis of SPM or its mixture with SS. While the HHV of produced gas from SS pyrolysis was slightly below that of natural gas, co-pyrolysis of SS with SPM produced combustible gas surpassing natural gas HHV. Compared to pyrolyzing SS alone, co-pyrolysis of SPM + SS produced considerably more hydrocarbon-rich liquid. This hydrocarbon-rich liquid could be used as either liquid fuels after upgrading or chemical feedstock for petrochemical industry. Biochar yield from the mixed feedstock (2:1 SPM + SS) was about 28%; this was a decrease in SS alone exhibiting a 39% biochar yield. Both biochars had similar surface areas and volatile matter chemical structures judging by the ¹H NMR spectra, suggesting similar functionalities when applied to soil. Even though the energy produced in the liquid was not even considered in this analysis, balancing the energy requirement for pyrolyzing dewatered SS (25% total solids) with only gas energy could be achieved with only about 10% SPM. Increasing the SPM contribution would generate surplus gas energy available for other facility power needs; it can also allow for more direct use of flushed manures (i.e., no dewatering pretreatment necessary). The results of this study showed good potential of using pyrolysis technology to manage two agricultural waste streams (spent plastic mulch films and swine solids) while producing value-added biochar and power.

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