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Thermochemical conversion of livestock wastes: Carbonization of swine solids

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ABSTRACT

Slow pyrolysis or carbonization promotes the conversion of animal manures such as swine manure into charcoal. In this paper, the carbonizing kinetics of swine solids taken from different treatment stages were investigated with a thermogravimetric analyzer. Compared to their biologically stabilized counterpart (lagoon sludge) with an activation energy of 160 kJ mol^{-1}, the activation energies for fresh swine solid samples such as homogenized flushed manure and dewatered solids were much lower between 92 and 95 kJ mol^{-1}. Compared to the kinetics of first order decomposition of cellulose, the pyrolytic decomposition of the swine manures were more complex with the reaction orders varying at 3.7 and 5.0. The two different mathematical methods employed in this paper yielded the similar values of activation energy (E) and pre-exponential factor (A), confirming the validity of these methods. The results of this study provide useful information for development of farm-scale swine solid carbonization process.

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1. Introduction

According to the recent study jointly sponsored by the USDA and US DOE, US agricultural lands currently have 35 million dry tons of available, sustainable animal manure (Perlack et al., 2005). The energy content of this sustainable animal manure can be estimated from its higher heat values (HHV), ranging from 7.9 MJ kg TS^{-1} for soil surfaced feedlot manure to 18.2 MJ kg TS^{-1} for flushed dairy manure (Cantrell et al., 2007). Using a simple arithmetic average HHV of different animal manures (13.4 MJ kg TS^{-1}), the annual energy content of the 35 million dry tons of manure is estimated to be approximately 0.43 EJ (i.e., 0.43×10^{18} J). This is about 15% of the total biomass energy consumed in the US annually (Perlack et al., 2005). Assuming an efficiency of 20% for extracting useful energy from the manure (Denmark, 2002) and an energy value of about $50 per barrel of oil equivalent (BOE), this sustainable animal manure can provide energy with an approximate worth of 0.7 billion US dollars per year. This simple calculation clearly demonstrates that effective utilization of this abundant renewable energy source can have significant impact on the US agricultural energy budget and economy.

1.1. Biochemical and thermochemical pathways

There are two pathways of extracting renewable energy from animal manure – biochemical and thermochemical pathways. Biochemical pathways utilize microorganisms or enzymes to convert animal manure into useful energy. Anaerobic digestion of animal manure for methane production is the most common biochemical means of extracting useful energy. Although anaerobic digestion technology is well established and robust, the process is very slow, requiring processing times of days and weeks. In addition, anaerobic digestion still leaves substantial amounts of sludge and supernatant that require further treatment and disposal. In contrast, emerging TCC technologies only require treatment times in the span of minutes to hours. Furthermore, they convert most organic matter into energy-rich and valuable end products such as combustible gases, liquids, and charcoals. These TCC end products can be used as energy intermediates for combined heat and power generation (CHP) or feedstocks for downstream catalytic conversion processes to produce higher value products such as liquid transportation fuels.

There are many TCC technologies that can be integrated with existing animal manure management practices to extract useful energy. Recently Cantrell et al. (in press) reviewed gasification, fast pyrolysis, hydrothermal gasification, and carbonization (slow pyrolysis) technologies for livestock waste-to-bioenergy generation applications. Among these TCC technologies, carbonization of animal manure for producing charcoal (or bio-char) may offer many advantages and usages for farmers. Compared with other sophisticated TCC technologies, such as fluidized bed gasification and fast pyrolysis, carbonization (or slow pyrolysis) requires relatively low technical resources, making the technology suitable for farm-scale process. The bio-char produced from livestock wastes can easily be transported and stored without nuisance odor and deterioration. It can be readily used as a cooking fuel and feedstock for existing coal power plants. Bio-char is superior in quality to

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charcoal made from coal due to its low sulfur content and high reactivity. In addition, bio-char can be activated with steam or chemicals to produce activated carbon. When compared to commercially activated charcoals, activated carbon produced from broiler litter demonstrated higher performance rates in adsorbing heavy metals (Lima and Marshall, 2005). The production cost of activated carbon from broiler litter was \$1.44 kg^{-1}, which was comparable to that of activated carbon from other renewable biomass sources (Lima et al., 2007).

Bio-char can also be applied to soil as an amendment. Soil application of bio-char not only improves soil fertility and increases crop production, it also offers significant environmental and potential economical benefits (Laird, 2008). Because of its adsorptive capacity, bio-char prevents leaching of pesticides and nutrients from soil. Soil application of bio-char represents a carbon-negative process whereby the environment realizes a reduction in both atmospheric CO_2 and global warming (Lehmann, 2007a,b). Once soil application of bio-char is eligible for carbon credit, farmers can generate significant income from producing and applying bio-char to the soil promoting the "Win-Win-Win" for a "Charcoal Vision" (Laird, 2008; Lehmann, 2007b).

Despite these advantages, relatively little information is available in the technical literature about the kinetics of carbonizing biomass. This information is reported by only handful of researchers (Antal and Gronli, 2003; Caballero and Conesa, 2005; Conesa et al., 1995; Jauhianinen et al., 2004; Mok and Antal, 1983; Narayan and Antal, 1996; Varhegyi et al., 1989, 1993, 1994; Vlaev et al., 2003). However, research on livestock wastes carbonization has not been studied in the same rigor (or enthusiasm) as lignocellulosic biomass. Only a handful of research papers on poultry litter carbonization have been published (Kim and Agblevor, 2007; Whitely et al., 2006). As for carbonizing swine solids, this paper is the first in reporting kinetics of thermal decomposition of swine solids. The swine solids in this study were collected at different stages of a 5600-head feeder-to-finish waste treatment system. The carbonization was studied by thermogravimetric analysis using a one-step global decomposition model. The kinetic information can be used for later design and operation of the carbonization process.

1.2. Thermal decomposition kinetics

Thermogravimetric analysis (TGA) is a widely used technique to study reaction mechanisms and kinetics of solids undergoing thermal decomposition (Caballero et al., 1995; Gauer and Reed, 1998). Pyrolytic decomposition of biomass takes place through a complex network of parallel and competitive reactions. Different kinetic models have been proposed based on different reaction mechanisms (Bradbury et al., 1979; Caballero and Conesa, 2005; Conesa et al., 1995; Jauhianinen et al., 2004; Shafizadeh, 1982; Varhegyi et al., 1993, 1994; Vlaev et al., 2003). Even after 30 years of research, there is still no consensus concerning pyrolysis kinetics of relatively simple cellulose biomass (Gronli and Melaaen, 2000; Varhegyi et al., 1994). Investigating detailed pathways for thermal decomposition of complex biomass such as swine manure is beyond the scope of this study. Instead, we utilized the following one-step global decomposition kinetic model for our swine manure samples.

$$\text{Swine maure} \rightarrow \text{Char} + \text{Volatiles} \times (\text{condensable and non-condensable gases}) \quad (1)$$

The reaction rate is dependent upon both the temperature, and the volatile matter content. The temperature dependence is usually expressed as a reaction coefficient for using an Arrhenius equation. The volatile matter dependence can be expressed as an nth order reaction equation.

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}\exp(-E/RT)dT \quad (2)$$

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

The fractional conversion or the extent of reaction is defined as:

$$\alpha = \frac{m_o - m_T}{m_o - m_f} \quad (3)$$

where, m_o is the initial mass (g), m_T is the mass at temperature T (g), m_f is the final residual mass (g).

The three kinetic parameters or the kinetic triplet (E, A, and n) can be estimated from fitting the thermogravimetric data into differential or integrated forms of Eq. (1) (Gauer and Reed, 1998; Flynn, 1997a,b; Garcia-Nunez et al., 2008; Kim and Agblevor, 2007; Li et al., 2008). The integral method is generally believed to be more reliable then differential methods; however, the temperature integral (the middle exponential integral of Eq. (4)) cannot be solved analytically.

$$G(\alpha) = \frac{A}{\beta}\int_0^T e^{-E/RT}dT = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} \quad (4)$$

Many forms of approximation of the temperature integral have been developed (Gauer and Reed, 1998; Flynn, 1997a,b). When $e^{-E/RT}$ is expressed as an asymptotic series, the temperature integral can be integrated and simplified by ignoring higher-order terms, yielding Eq. (5). Hereafter the approximation will be called the Coats and Refern method (Coats and Redfern, 1964; Gauer and Reed, 1998; Guo and Lua, 2001).

$$G(\alpha) = \frac{ART^2}{\beta E}\left(1 - \frac{2RT}{E}\right)e^{-E/RT} \quad (5)$$

Eq. (5) can be expressed in logarithmic forms for $n = 1$ and $n \neq 1$.

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (\text{for } n = 1) \quad (6)$$

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (\text{for } n \neq 1) \quad (7)$$

Recently, Chen and Liu (2006) developed a new approximation for the temperature integral and the corresponding kinetic equation can be expressed as:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\frac{3(E/RT)^2 + 16(E/RT) + 4}{3(E/RT)^2 + 22(E/RT) + 30}\right) - \frac{E}{RT} \quad \text{for } n = 1 \quad (8)$$

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left(\frac{AR}{\beta E}\frac{3(E/RT)^2 + 16(E/RT) + 4}{3(E/RT)^2 + 22(E/RT) + 30}\right) - \frac{E}{RT} \quad \text{for } n \neq 1 \quad (9)$$

Chen and Liu (2006) claimed that these new equations, when compared to previously developed kinetic equations, provided a better approximation for the evaluation of non-isothermal kinetic parameters with greater accuracy; hereafter, it will be called the Chen and Liu method. Using any of these methods (Eqs. (6)–(9)), the activation energy (E) can be estimated from the slope of a line established from fitting the TG data: $\ln\left(\frac{G(\alpha)}{T^2}\right)$ vs. $1/T$. Since the order of reaction is usually not known beforehand, it is first necessary to fit the TG data with an assumed value of n. If the

assumed reaction order adequately represents the reaction, the line becomes straight. If not, another reaction rate is assumed and the fitted line is examined for straightness. The pre-exponential factor A can be calculated from the intersection of the best fitted line, which is the first term of Eqs. (6)–(9). The mean values of A can be calculated over the temperature range of interest.

$$\bar{A} = \frac{\int_{T_1}^{T_2} A \cdot TdT}{\int_{T_1}^{T_2} TdT} \tag{10}$$

where $\bar{A}$ is the mean pre-exponential factor in the temperature range of T_1 and T_2 (min^{-1}).

2. Methods

2.1. Swine solid samples

A 5600-head finishing swine operation used a waste management system that combined solid–liquid separation with nitrogen and phosphorous removal from the liquid phase (Vanotti et al., 2007). The system was constructed and operated by Super Soils System USA of Clinton, NC. Homogenized flushed manure house effluent was passed through a mobile liquid–solid separation unit with polyacrylamide (PAM) flocculation and rotary press dewatering system. The solid phase was transported off-farm for compost stabilization. The liquid phase continued through biological nitrogen removal and phosphorous extraction treatments (Vanotti and Szogi, 2007). Samples collected from this site were homogenized flushed manure house effluent (HT) and dewatered solids (SS) generated by the liquid–solid separation unit that treated the HT effluent. An anaerobic lagoon sludge sample (LS) was obtained from an anaerobic lagoon in this same operation that provided manure treatment before the new system was installed. The LS was collected using a sludge sampler and it is a composite of eight samples from the lagoon bottom sediments (sludge depth = 0.8 m; lagoon depth = 2.2 m). Characteristics of the original samples are given in Table 1.

Table 1
Characteristics of the manure samples used in the study.[a]

Parameters	Flushed manure (HT) g/L	Lagoon sludge (LS) g/L	Separated manure solids (SS) g/kg
Moisture	942.8	830.5	739.7
Total solids (TS)	57.26	169.47	260.3
Suspended solids (TSS)	22.96	84.00	–
Dissolved solids (DS)	34.20	85.47	–
Volatile solids (VS)	37.98	99.78	–
Volatile suspended solids (VSS)	17.28	50.90	–
COD	44.60	97.65	–
Soluble COD	17.95	1.35	–
BOD	25.47	1.65	–
Soluble BOD	9.40	0.10	–
Total Kjeldahl nitrogen (TKN)	3.001	3.352	60.920[b]
Total phosphorus (TP)	1.135	5.834	34.017[b]
Ash ($\%_{db}$)	37.1	42.7	20.8
Volatile ($\%_{db}$)	55.7	49.0	67.4
Fixed carbon ($\%_{db}$)	8.4	9.1	11.8
Carbon			420.8[b]

[a] Analyses were done using Standard Methods (APHA, 1998). HT is the homogenized flushed manure liquid consisting of raw manure and rinsing water; LS is the sludge obtained from anaerobic lagoon treatment of swine manure; SS is the dewatered solids obtained after passing the HT through a polymer-enhanced solid–liquid separation unit.

[b] TKN, TP and C concentrations of separated solids are given on a dry basis (g/kg dry).

To remove the bulk of initial moisture, the three samples were dried for the thermal analyses. The HT sample was lyophilized for 96 hours using a freeze drier at 223 K and roughly 0.15 Mbar vacuum (Virtis Research Equipment, Gardiner, NY). The SS and LS samples were oven dried at 105 °C. The dried samples were ground to average particle size of 0.25 mm. Guo and Lua (2001) reported that the pyrolysis of small biomass particles with size less than 2 mm was predominantly controlled by reaction kinetics, not heat transfer. Therefore, our TGA experiments would provide for intrinsic kinetic information of swine solids thermal decomposition.

2.2. Thermal analysis

Dried manure samples with an average sample size of 10–30 mg were subjected to pyrolysis using a Mettler-Toledo TGA/SDTA851e apparatus where the mass loss, determined thermogravimetry (TG), and temperature changes (differential thermal analysis, DTA) were recorded simultaneously. This unit operated under a three-point calibration using Indium, Aluminum, and Gold. All samples were placed in an aluminum oxide (Al_2O_3) 70 μl crucible with a lid and pyrolyzed using helium carrier gas at a flow rate of 60 ml min^{-1} within a temperature range from 300 to 1073 K at a constant heating rate of 10 K min^{-1}.

3. Results and discussion

Fig. 1 shows the thermogravimetric diagrams (TGs) of three different swine solids taken from various points in typical swine operation; dry solids extracted from homogenized flushed manure house effluent (HT), dry solids obtained after polymer-enhanced solid–liquid separation (SS) and dry solids from anaerobic lagoon sludge (LS). Thermal decomposition of these dry swine manure solids was achieved in three different temperature regimes; drying, pyrolytic decomposition, and gasification regimes. Up to about 500 K, moisture in the sample was evaporated resulting in weight loss although small amounts of volatile compounds might have also contributed to the weight loss at around 473 K (Whitely et al., 2006). After drying, pyrolytic thermal decomposition reaction took place in the temperature range of about 500–860 K producing condensable and non-condensable volatile gases. For the LS sample, the decomposition rate reached a maximum at 650 K. The decomposition rates for the HT and SS samples achieved a maximum at a cooler temperature, approximately 600 K. At higher temperature (>860 K), gasification reaction took place resulting in further weight reduction. It appears that the pyrolysis reaction of the HT sample consisted of two consecutive reaction steps; the first reaction at 500–700 K and the second one at 700–860 K. These two reaction steps are not very prominent in SS sample although these two samples should have similar chemical compositions. The major difference between these two samples may be the large amount of dissolved solids in HT sample and polyelectrolyte polymeric flocculants added to the SS sample to improve solid dewatering efficiency. Although the dosage of the cationic polyacrylamide flocculant is very low in aqueous phase [polymer application rate was 128 mg L^{-1} (Vanotti and Szogi, 2007)], the fraction of this polymer can be much higher in dried samples. Judging from the fact that the LS sample with higher dissolved solids than HT sample (Table 1) did not produce a prominent second peak, we suspect that presence of the polymeric flocculants added to the SS sample may have had an interactive affect in the thermal degradation of swine manure and masked the appearance of two prominent DTG peaks by broadening the peaks into one prominent peak. Further investigation is needed to verify this speculation. The magnitude of DTG peaks for HT and SS samples were higher than that of LS sample due to stabilization of the readily decomposable volatile matter

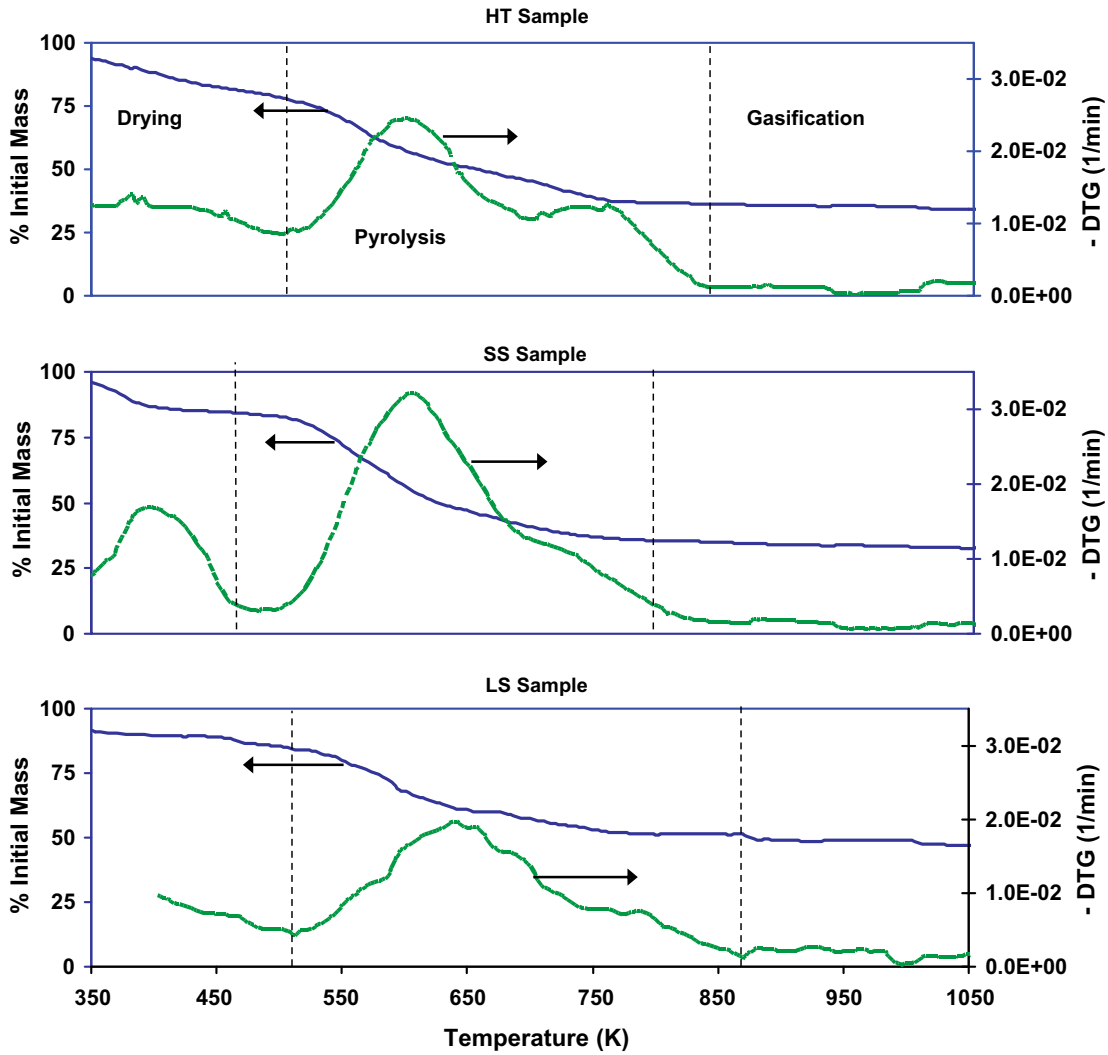

Fig. 1. TG and DTG diagrams of swine samples undergoing drying, pyrolysis, and gasification (—TG and ---DTG).

in treatment lagoons. This same phenomenon was noted by Smidt and Lechner (2005) after analyzing the stability of composting organic matter with DTG peaks becoming less pronounced as the sample aged.

Because we were primarily interested in carbonizing livestock wastes into bio-char, only the kinetic parameters for the temperature range promoting the carbonization process (i.e., 500–800 K) were estimated. We evaluated the TG data using Eqs. (6)–(9) with assumed values of n from 1 to 10. Shown in Fig. 2 are the coefficients of determination of straight lines fitting $\ln\left(\frac{G(\alpha)}{T^2}\right)$ vs. $1/T$ for the assumed reaction orders. As evidenced by the fact that $R^2 > 0.9$, the data fit rather well regardless of the reaction orders assumed. The optimal orders of reaction were 3.7 for SS and 5.0 for HT and LS. These values of n were higher than cellulosic pyrolysis reactions that are predominantly first order (Antal and Gronli, 2003; Mok and Antal, 1983). However, the swine solids decomposition reaction orders were still lower than that of the wasted activated sludge undergoing decomposition in the temperature range of 473–676 K with n ranging from 4.1 to 7.95 (Chu et al., 2001). There was good agreement between the observed TGA data and simulated fraction conversions (Fig. 3) using the optimal values of kinetic parameters, reaction orders, and coefficients of determination (Table 2).

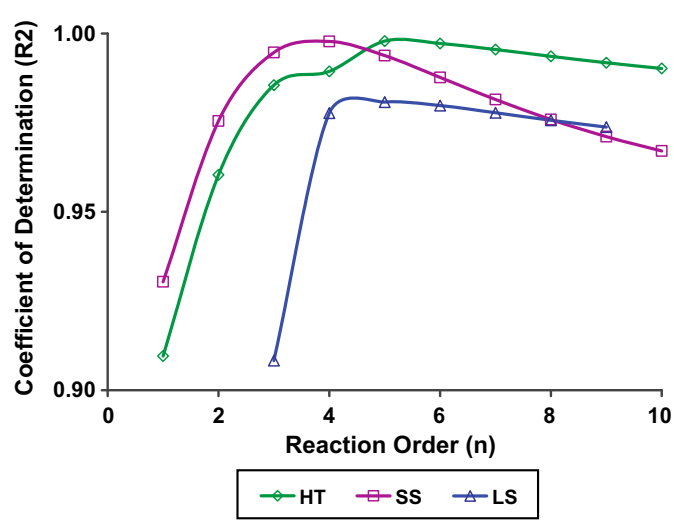

Fig. 2. Coefficients of determination of assumed pyrolytic decomposition reaction orders of swine samples.

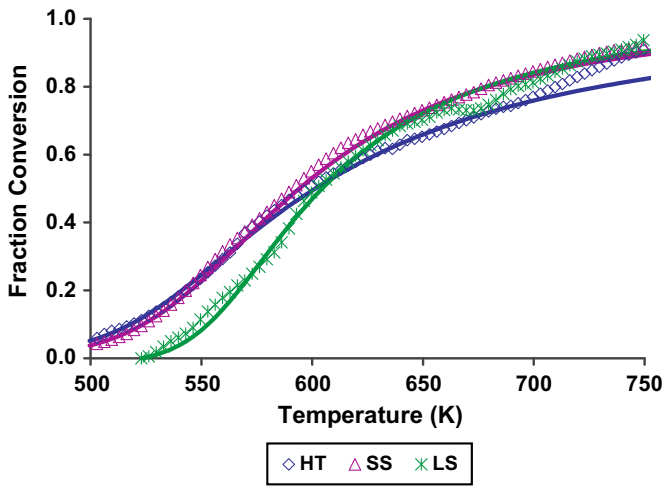

Fig. 3. Comparison between experimental data and model simulation.

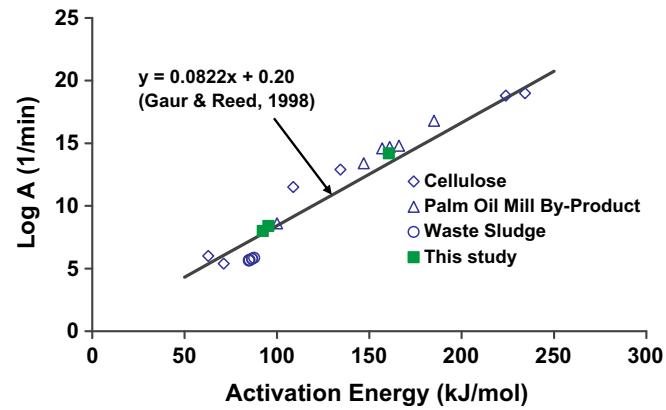

Fig. 4. Linear relationship between log A and E. Data sources: cellulose (Gauer and Reed, 1998); palm oil mill by-product (Garcia-Nunez et al., 2008); waste activated sludge (reaction (1) at 8 °C/min of Chu et al., 2001).

Table 2
Kinetic parameters for pyrolysis reactions of swine samples.

Sample	n	E (kJ mol^{-1})	log$A$ (min^{-1})		T (K)	R^2
			Eq. (7)	Eq. (9)		
HT	5.0	95.4	8.4	8.4	500–696	0.998
SS	3.7	92.7	8.0	8.0	480–693	0.998
LS	5.0	160.6	14.2	14.2	506–746	0.981

Since the second right terms in both Eqs. (7) and (9) are the same and we fit the data $\ln\left(\frac{G(\alpha)}{T^2}\right)$ vs. $1/T$, the two equations would have yielded the same slope (i.e., E/R). Therefore, the two equations would yield the same activation energy (E). However, the pre-exponential factor was determined from the first right terms of Eqs. (7) and (9). Although these terms are mathematically quite different, they both yielded the same values of pre-exponential factor, confirming the validity of the two different methods of kinetic parameter estimation.

The activation energies for HT and SS samples were similar, representing the lower end of reported biomass activation energies in the literature, 51–275 kJ mol^{-1} (Garcia-Nunez et al., 2008; Grioui et al., 2007; Li et al., 2008; Shen et al., 2007; Varhegyi et al., 1989, 1993). The activation energy for lagoon sludge was higher. Therefore, it requires higher temperature to initiate decomposition reaction (Fig. 3). The portions of volatile matter of the lagoon sludge that could be readily decomposed by low heating had likely been stabilized by microbial activities as indicated by the fact that BOD and soluble COD of LS sample were significantly lower than that of HT sample (Table 1). This may explain the higher activation energy and relatively higher thermal decomposition onset temperature.

We compared the kinetic parameters of other materials such as cellulose, palm oil mill by-products, and waste activated sludge. As shown in Fig. 4, there was a clear linear relationship between E and log$A$ for these different materials. This linear "compensation effect" relationship between E and log$A$ is well known for the cellulose pyrolytic decomposition in the temperature range of about 553–673 K (Gauer and Reed, 1998). The compensation effect has been used to explain the wide range of reported activation energy for cellulose pyrolysis. Narayan and Antal (1996) concluded that different thermal lag characteristics of experiments might be the cause of the compensation effect. Others attributed sample size, heating rate, variation of the mathematical analyses, and instrumental errors to the compensation effects (Gauer and Reed, 1998). However, it is particularly important to appreciate the excellent conformation of the kinetic parameters of these different feedstock materials (i.e., lignocellulosic, activated sludge, and swine solids) obtained from different instruments and mathematical methods to the linear relationship. Moreover, it was determined solely from cellulose pyrolysis data. Accordingly, this is a strong suggestion of yet-another unknown factor explaining the linearity of E vs. log$A$. Further investigation of this "compensation effect" is needed, but it was beyond the scope of this paper.

We also investigated if our TGA data could be fitted to diffusion-controlled reaction models suggested by Brown et al. (1980). Heat is first transmitted to the particle surface by means of radiation and natural convection inside the crucibles of the TGA oven and then to the interior particles. The increase in the inside particle temperature first causes the vaporization of moisture. Secondly, pyrolytic decomposition reactions are initiated producing condensable (tar) and non-condensable gases. These gases migrate through the solid pores to the outside of particles. If particles are large and diffusion rates of these gases are slow, tar vapors inside the particles may have enough time to react with already formed char located near the surface of the particles. This is critical in the formation of secondary chars affecting surface area of char (Mok and Antal, 1983; Mok et al., 1992; Koufopanos et al., 1991). Garcia-Nunez et al. (2008) reported that the pyrolysis reaction of palm oil mill by-products occurring at higher temperature range (ca. 473–873 K, estimated from their Fig. 6) obeyed the diffusion-controlled two-dimensional reaction model. The two diffusion-controlled reaction models that we evaluated are:

$$G(\alpha) = \alpha^2 \quad \text{for one-dimensional diffusion} \tag{11}$$

$$G(\alpha) = (1-\alpha)\ln(1-\alpha) + \alpha \quad \text{for two-dimensional diffusion} \tag{12}$$

None of these models produced good linear fit of our TGA data with R^2 values mostly less than 0.3. This is not surprising considering the fact that our solid samples were finely ground to an average particle size of 0.25 mm. Neither mass nor heat transfer did not play a significant role due to the small dimensions of particles. For our tested particle size, the effectiveness factor (i.e., the ratio of the apparent overall reaction rate to the intrinsic reaction rate) suggested by Koufopanos et al. (1991) is practically unity.

4. Conclusions

Carbonizing kinetics of swine solids taken from different stages of waste treatment were investigated with a thermogravimetric

analyzer. Activation energy for fresh swine solid samples such as homogenized flushed manure (HT) and the dewatered solids (SS) were much lower than that of biologically stabilized lagoon sludge (LS). The onset pyrolysis temperature of LS with higher activation energy was slightly higher than that of other solids with lower *E*. The reaction orders of 3.7 and 5.0 were higher than the predominantly first order for cellulose pyrolysis, but lower than that of activated sludge pyrolysis. Our TGA data did not follow the diffusion-controlled reaction models. The values of *E* and log*A* of these swine solids along with other lignocellulosic biomass and activated sludge closely followed the linear relationship (compensation effect) determined from cellulose pyrolysis kinetic studies. The two methods, Coats and Redfern and Chen and Liu methods, employed in this paper yielded the identical values of *E* and *A*, confirming the validity of these methods. These carbonization kinetic parameters provide useful information for development of farm-scale swine solid carbonization process.

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Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture.

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