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Kinetics and Energetics of Producing Animal Manure-Based Biochar

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Abstract Pyrolysis of animal manure produces biochar with multiple beneficial use potentials for improving soil quality and the environment. The kinetics and energetics of pyrolysis in producing manure-based biochar were reviewed and analyzed. Kinetic analysis of pyrolysis showed that the higher the temperature, the shorter the reaction time was needed for thermal decomposition and carbonization of animal manure. This kinetic information can assist in producing biochar with a desired proximate composition. Biochar with lower volatile matter (VM) content can be produced with either higher pyrolysis temperature or longer reaction time. Energetically, pyrolysis of wet manures is not sustainable due to high energy needed for drying moisture. However, co-pyrolysis with other high energy density wastes such as agricultural plastic wastes would produce not only energetically sustainable biochar but surplus energy as well. This could be used for local power generation.

Keywords Biochar · Animal manure · Pyrolysis · Kinetics · Energetics

Introduction

Pyrolysis thermochemically decomposes and devolatilizes biomass feedstock to yield a mixture of char, bio-oil, and gases by heating in the absence of oxygen. The composition of the end products is dependent on the operating temperature, pressure, heating rate, reactor medium, feedstock particle size, and residence time [1–6]. In this study, we focus on slow pyrolysis (i.e., reaction time more than 15 min) in producing biochar. Typical pyrolytic carbonization processes require the raw feedstock biomass to be dry before the biomass decomposes thermally from the added heat, resulting in carbonaceous solids called biochar and combustible gases. The gas yield from pyrolysis ranges from 13 to 25 % by weight. The gas contains combustible gases such as H_2, CO, CO_2, hydrocarbons, and condensable tar vapors which form a pyrolytic bio-oil. The bio-oil can be upgraded to transportation fuels by reducing its oxygen content and acidity with a hydrogenation process.

Biochars are made up of a combination of minerals and carbon with a significant portion as fixed carbon. Recently, researchers found that the biochar could improve soil quality and remove environmental pollutants [7–13]. A range of agricultural and organic materials can be used to generate biochar with different characteristics [14]. Both feedstock characteristics and thermal conditions affect the biochar's physical and chemical characteristics [10, 15–18]. Generally, the higher the pyrolysis temperature, the higher the inorganic nutrient contents will be, except for N [19]. Among the variety of potential biomass feedstock candidates for producing good quality biochar, animal manure-based biochar offers many advantages for farmers. It produces more nutrient-rich biochar than plant-based biochar and can be easily transported and stored without nuisance odor and deterioration [3, 8, 16, 20, 21]. Swine manure-based biochar significantly improved soil fertility. The swine hydrochar made from wet pyrolysis had the remarkable ability to retain most of environmentally sensitive nutrients within soil matrix, but not in leachates [11]. Chicken litter biochar can also be used as an adsorbent in removing gaseous ammonia as its sorption capacity is comparable to that of commercial activated carbon and natural zeolite [22]. In addition, the activated carbon produced from pyrolyzing and steam activating broiler litter performed better

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than commercial activated carbon in removing heavy metals [23]. 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 [24].

Despite these advantages of animal manure-based biochar, relatively little information is available in the literature about the kinetics and the magnitude of energy required for carbonizing animal manures. One of the major stumbling blocks for producing nutrient-rich biochar from animal manure may be its high energy requirement for drying [4]. Thorough knowledge on the kinetics and the energetics of biochar production can help us to develop more cost-effective and energetically sustainable ways of making biochar with desired characteristics. The intention of this study is to investigate the kinetics and energetics of making biochar from animal manures under different thermal processing conditions.

Kinetics of Pyrolysis

The kinetics of the pyrolysis (devolatilization) process are often investigated through thermogravimetric analyses (TGA) using He or N_2 as a carrier gas. The weight loss profiles of animal manure solids provide kinetic information about both decomposition temperatures and rates. As an example, the TGA weight loss profile of swine manure is shown in Fig. 1. The weight loss pattern appears to proceed in three consecutive steps. In the first step, the sample is heated to about 523 K and almost no weight loss occurs. In the second stage, which takes place from 523 to 723 K, the samples' volatile matter (VM) is devolatilzed. This results in the rapid loss of weight. In the final stage (723 to 1183 K), a slow decomposition takes place. Here, the remaining sample is carbonized into stable char consisting of mostly ash and fixed carbon contents. This scenario would be the case if one wants to produce biochar with a maximum stability. However, a biochar with a volatile component might be desired for certain applications. In such case, the carbonization process would be conducted at a lower temperature. A shorter carbonization time will also retain volatile components. Since animal manures are a complex mixture of cellulose, hemicellulose, lignin, protein, etc., the overall outcome of animal manure pyrolysis is the summation of each individual pyrolysis reactions. Each component has different thermal decomposition characteristics. For example, cellulose has a unique thermal decomposition pattern with a sharp peak decomposition temperature below which not much cellulose decomposes, regardless of reaction time. In contrast, the thermal decomposition of animal manures is dependent upon reaction times at ranges of temperatures due to the complex makeup of animal manures. Therefore, it is assumed that both reaction time and pyrolysis temperatures influence thermal decomposition beyond temperatures above 423 K.

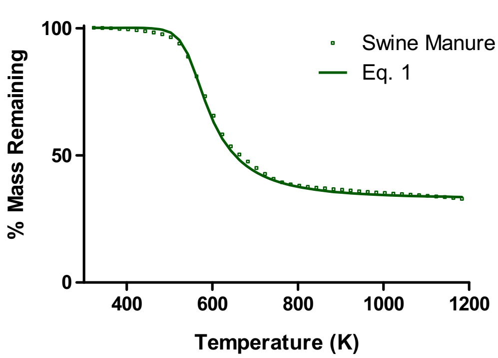

Fig. 1 TGA weight loss profile for swine manure sample (Eq. 1 with E = 92.7 kJ/mol, Log A = 8.0, β = 10 K min^{-1}, and n = 3.7 [25])

The optimal termination time or temperature for desired biochar quality can be estimated by utilizing pyrolysis kinetics and the feedstock proximate composition. Assuming the one-step global pyrolytic decomposition kinetic model, swine manure thermogravimetric data can be fitted using the well-known Arrhenius equation (Eq. 1).

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}\exp\left(-E\Big/RT\right)\mathrm{dT} \tag{1}$$

where

A pre-exponential factor (min^{-1})
E activation energy (kJ mol^{-1})
R gas constant (8.314 J mol^{-1} k^{-1})
T temperature (K)
t time (min)
n order of reaction

$$\alpha = \frac{m_o - m_T}{m_o - m_f} = \text{fraction of conversion}$$

m_o initial dry mass (g)
m_T mass at temperature T (g)
m_f final residual mass, consisting of mostly fixed carbon and ash (g)
β constant heating rate = dT/dt (K min^{-1}).

The fraction of VM conversion α can be calculated as a function of pyrolysis reaction time at a desired pyrolysis temperature by substituting β = dT/dt into Eq. 1 and integrating it with a constant T.

$$\propto\; = 1-\exp\left\{-A\,\exp\left(\frac{-E}{RT}\right)t\right\} \text{ for } n = 1 \tag{2a}$$

$$\propto\; = 1-\left\{1-(1-n)A\,\exp\left(-\frac{E}{RT}\right)t\right\}^{1/_{1-n}} \text{ for } n \neq 1 \tag{2b}$$

The swine manure weight loss data in Fig. 1 was fitted with Eq. 1 using literature kinetic parameter values for swine manure [25]. Values of various animal manure pyrolysis kinetic parameters from the literature are shown in Table 1. The kinetic information is useful in estimating the extent of reaction (or the fraction of VM conversion) and eventually designing pyrolysis system such as size, reaction time, and processing flow rate to produce biochar with desired characteristics.

Using Eqs. 2a and 2b along with these kinetic parameters, the pyrolysis reaction time required for desired conversion and temperature can be estimated theoretically (Fig. 2). The higher the pyrolysis temperature, the more conversion was achieved for all three animal manures. For chicken litter, it took less than 9 min to achieve 99 % conversion at 873 K. At 774 K, 25 min was required for the same conversion. At 713 K, the poultry litter only achieved 93 % conversion even after 30 min of pyrolysis. In contrast, because of their higher reaction orders, the conversions of either swine or dairy manures quickly increased to more than 60 % in the first few minutes. After the initial rapid conversions, the conversions of both manures increased very slowly. At 15 min of reaction time, the conversions at 773 K for chicken litter, swine manure, and dairy manure were 94, 94, and 92 %, respectively. The extent of VM conversion during carbonization process influences the proximate composition of the biochar produced.

The proximate composition of biochar consists of the fractions of moisture, volatile matter (VM), fixed carbon (FC), and ash contents. Because VM plays an important role on its stability, soil nitrogen transfer formation, and plant growth when applied to soil [32, 33], it is desirable if we can produce biochar with a certain VM content. The kinetic information can assist in producing biochar with desired biochar yields and proximate compositions. The biochar yield (Y) along with its proximate component distribution as a function of pyrolysis reaction time can be estimated by Eq. 3.

$$Y = \frac{M_{bc}}{M_o} = \left(1 - f_{FC(db)} - f_{ash(db)}\right)(1-\alpha) + \left(f_{FC(db)} + f_{ash(db)}\right) \quad (3)$$

where

M_{bc} biochar dry mass (kg)
M_o initial feedstock dry mass (kg)
$f_{FC(db)}$ fixed carbon fraction of feedstock, dry wt. basis (−)
$f_{ash(db)}$ ash content of feedstock, dry wt. basis (−).

Table 1 Pyrolysis kinetic parameters for animal manures

Feedstock	n	E (kJ/mol)	Log A (min^{-1})	References
Swine manure	3.7–5.0	92.7–160.6	8.0–14.2	[4, 25]
Chicken litter	1	52.1–464	3.1–19.5	[26–29]
Feedlot manure	–	173.5	–	[30]
Dairy manure	2.3–6.4	84.5–93.6	5.9–8.6	[31]

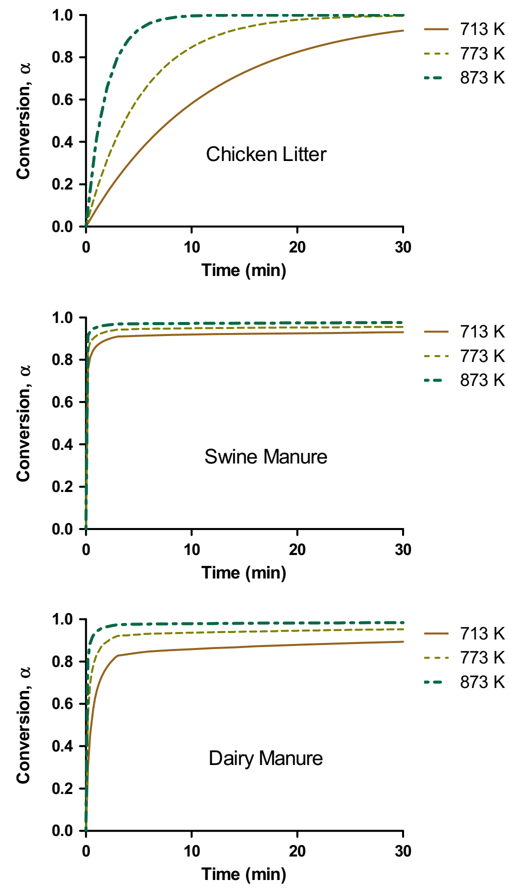

Fig. 2 Fraction of conversion at three different pyrolysis temperatures [Kinetic parameters used for chicken litter [26], $A = 1.76 \times 10^3$ min^{-1}, $E = 58.76$ kJ mol^{-1}, and $n = 1$; swine manure [4], $A = 1.02 \times 10^8$ min^{-1}, $E = 92.7$ kJ mol^{-1}, and $n = 3.7$; dairy manure [31], $A = 7.33 \times 10^5$ min^{-1}, $E = 84.53$ kJ mol^{-1}, and $n = 2.33$]

The fraction of conversion (α) in Eq. 3 is determined from Eqs. 2a and 2b at a defined pyrolysis temperature and a reaction time. The first term in Eq. 3 represents the volatile matter (VM) of dry matter (i.e., $1 - f_{FC(db)} - f_{ash(db)})(1-\alpha)$ at various pyrolysis reaction time. At time = 0 ($\alpha = 0$), the first term becomes VM of feedstock. The second term represents the inert material, i.e., fixed carbon and ash.

Using Eqs. 2a. 2b, and 3 along with proximate analysis results of animal manure feedstock, the yield and various fractions of biochar can be estimated. For example, Fig. 3a shows the yield, volatile matter, fixed carbon, and ash contents of chicken litter biochar pyrolyzed at 773 K at different reaction times. The same kinetic parameter values used for Fig. 2 were used to generate Fig. 3. The chicken litter biochar yield at the end of 30 min of pyrolysis was 43 %. The volatile matter fraction decreased to negligible while the fix carbon and ash fractions increased to 21 and 79 % of dry biochar, respectively. Figure 3c shows the yield also decreased with increase in pyrolysis temperature until all VM had been devolatilized at 773 K, then stayed at 43 %. The FC and ash contents increased

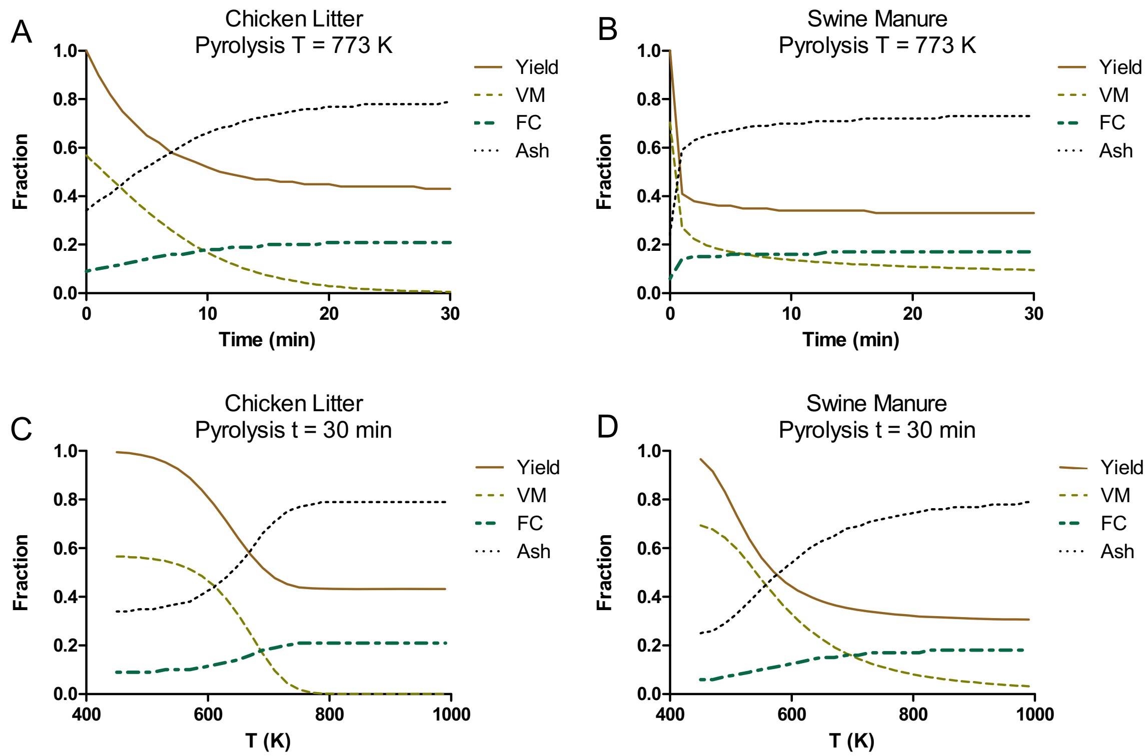

Fig. 3 Yields and various fractions of chicken litter and swine manure biochar samples **a**, **b** Pyrolyzed at 773 K for different reaction time. **c**, **d** Pyrolyzed for 30 min at different pyrolysis temperature

with pyrolysis temperature up to 773 K, then stayed at 21 and 79 %, respectively. Similar trends were observed for swine manure pyrolysis (Fig. 3b and d). These analyses demonstrated that the biochar's volatile fraction decreases with the increase in pyrolysis temperature and reaction time as observed by other researchers [16].

Energetics of Producing Biochar from Pyrolysis

Another important factor for developing, evaluating, designing carbonization processes is the amount of the total energy required to convert the raw animal manure feedstock into biochar (Q_{input}). This greatly depends on its proximate composition, especially moisture contents, which can vary greatly from farm and animal. The proximate composition, consisting of moisture (MC), ash, VM, and FC, of the various animal wastes is listed in Table 2. Although the moisture contents of animal manures as excreted have relatively narrow range of 74 to 92 % [34], that of animal manures from different manure management practices greatly vary from 6 to 98 % as shown in Table 2. The higher the moisture contents, the more energy is required to carbonize the animal manure into biochar because of high drying energy requirement.

Q_{input} includes the energy to dry raw animal manure (Q_{dry}), sensible heat to raise the temperature of dried manure to a

Table 2 Proximate compositions of various animal wastes

Manures	VM (Wt_{db})[c]	FC (Wt_{db})	Ash (Wt_{db})	MC_{wet}[d]	References
Dairy[a]	80.7–83.8	4.5	14.8–16.2	54–98	[16, 34, 35]
Paved feedlot[b]	64.6–76.7	7.9–15.2	15.4–20.2	49–86	[16, 35, 36]
Unpaved feedlot[b]	33.8	7.5	58.7	33	[34, 35]
Poultry litter	40.3–74.3	8.8–15.8	16.9–43.9	30–65	[16, 34, 35]
Swine	68.7–73.6	5.6	20.9–31.3	90–99.6	[16, 34, 35]
Turkey litter	74.0	5.7	20.3	6–47	[16, 36]

[a] manure from dairy operations for milk

[b] manure from cattle feeding operations for meat

[c] Wt_{db} = % oven-dry (100 °C) weight basis

[d] MC_{wet} = % moisture as received

desired pyrolysis temperature (Q_{sen}), heat of pyrolysis reaction (Q_{rxn}), and the energy lost to due to imperfect insulation and heat transfer (Q_{loss}).

$$Q_{input} = Q_{dry} + Q_{sen} + Q_{rxn} + Q_{loss} \quad (4)$$

where

Q_{input} total energy required for carbonization (kJ hr^{-1})
Q_{dry} drying energy (kJ hr^{-1})
Q_{sen} sensible heat required (kJ hr^{-1})
Q_{rxn} heat of reaction (kJ hr^{-1})
Q_{loss} heat lost (kJ hr^{-1}).

The drying energy requirement Q_{dry} consists of the energy to raise both moisture and dry matter mass fractions of the raw biomass feedstock to 100 °C and the latent heat of vaporization to evaporate moisture. We assumed complete drying of feedstock when it reaches 100 °C. The drying energy requirement can be calculated as follows:

$$Q_{dry} = \int_{T_\infty}^{373} C_{p,feed} \dot{m}\, dT + \gamma_w f_w \dot{m} \quad (5)$$

where

$C_{p,feed}$ specific heat capacity of feedstock (kJ kg^{-1} K^{-1})
$\dot{m}$ mass flow rate of as received feedstock (kg hr^{-1})
f_w initial mass fraction of water, wet basis (−)
γ_w latent heat of vaporization of water (2257 kJ kg^{-1})
T_∞ ambient temperature (K)

Assuming the heat capacity of initial wet animal manure (or as received) is the sum of individual heat capacities of moisture (MC), dry-ash-free matter (daf) and ash, the following equation was used to estimate the heat necessary to dry the manure feedstock at 100 °C.

$$C_{p,feed} = f_w C_w + f_{daf} C_{daf} + f_{ash} C_{ash} \quad (6)$$

where

f_{daf}, f_{ash} initial mass fractions of daf and ash, respectively, wet basis (−)
C_w, C_{daf}, C_{ash} heat capacity of water, daf, and ash, respectively, (kJ kg^{-1} K^{-1}).

The heat capacity of daf was assumed to be the average heat capacity of cellulose avicel between 40 and 80 °C, 1.39 kJ kg^{-1} K^{-1} [37]. An average heat capacity of coal ash (0.79 kJ kg^{-1} K^{-1}) from 298 to 373 K [38] was used for C_{ash} in Eq. 6.

The heat capacity of dried feedstock beyond 373 K was assumed to be made up of each component according to its mass fractions, volatile matter (VM), fixed carbon (FC), and ash contents. The heat capacities of graphite (0.717 kJ kg^{-1} K^{-1}) was used for that of FC. An average heat capacity (2.77 kJ kg^{-1} K^{-1}) of primary volatile matter (VM released at relatively lower temperatures) of coal [39] from 450 to 750 K was used for that of VM. An average heat capacity of coal ash (0.93 kJ kg^{-1} K^{-1}) from 373 to 773 K was used for that of ash. Using these values, the sensible heat requirement to raise the dried biomass to the desired pyrolysis temperature can then be estimated using Eq. 7.

$$Q_{sen} = \int_{373}^{T} \dot{m}_d \left(2.77 f_{VM} + 0.717 f_{FC} + 0.93 f_{ash} \right) dT \quad (7)$$

where

$\dot{m}_d$ mass flow rate of dried feedstock (kg hr^{-1})
f_{FC}, f_{VM} mass fractions of FC and VM in dried feedstock, respectively, (−).

The heat of reaction Q_{rxn} is determined by the sum of heat of formation of reactants and products. For exothermic reactions, Q_{rxn} is negative. If the heating values of the feedstock and the pyrolysis products are known along with their elemental compositions, the values of heat of formation can be estimated using heats of combustion of C, H, N, and S to CO_2, H_2O, NO_2, and SO_2. However, complete elemental compositions of all end products of pyrolyzing animal manures especially tar vapors and the corresponding heating values are not available in the literature. Therefore, the heat of reaction of animal manure pyrolysis was assumed to be similar to that of cellulosic pyrolysis. The following linear relationship was established using the heat of cellulosic pyrolysis reaction data reported in Fig. 19 of [40].

$$Q_{rxn} = -41.23\, Y_{char} + 702.13 \quad (8)$$

where

Q_{rxn} heat of pyrolysis reaction (kJ kg_{daf}^{-1})
Y_{char} char yield based on dry-ash-free, daf (%)

The dry-ash-free (daf) matter consists of VM and FC. Based on this equation, the heat of the pyrolysis reaction becomes exothermic for Y_{char} >17 %. For the swine manure biochar in Fig. 3, Y is 33 %, but the yield based on daf (Y_{char}) is 12 %. The heat of pyrolysis reaction for swine manure is then 207.4 kJ kg_{daf}^{-1} according to Eq. 8.

Using the above equations, the total and the individual components of energy requirements for producing 1 kg of biochar from pyrolyzing swine manure were calculated. Various energy requirements for pyrolyzing a swine manure with 70 % of the dry matter as VM to achieve Y_{char} = 12$\%_{daf}$ are shown in Fig. 4. Since swine manure gathered by flushing the stalls contains only about 5 % solids and 95 % water, but the moisture content can be reduced by subsequent dewatering process, the energy requirement is shown as a function of moisture fraction from 70 to 95 % moisture contents. The heat

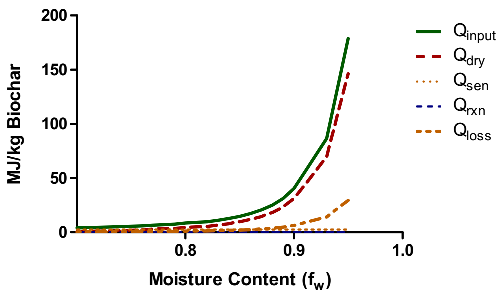

Fig. 4 Total and individual components of the energy requirements for producing 1 kg biochar from swine manure with various moisture contents

loss was estimated assuming 80 % thermal efficiency in drying and 5 % of sensible heat loss due to imperfect insulation [3]. Based on these assumptions, the total energy required to produce 1 kg of biochar from the flushed swine manure was 179 MJ, of which 82 % was used to dry the flushed swine manure (146 MJ). Both the sensible heat requirement and the heat of reaction were negligible, 2.6 and 0.5 MJ, respectively. The heat loss was about 16 % of the total heat requirement (29 MJ). The total energy requirement would be substantially reduced if the wet flushed swine manure were to be dewatered to a solid cake with 25 % solids (31 MJ). Energy requirements of other animal manures such as dairy manures were omitted due to space limitation but could easily be calculated with the same procedure.

In contrast to pyrolysis oil, which needs to be further upgraded to be useful, pyrolysis gas products are combustible and can be readily used to sustain pyrolytic carbonization process. Assuming about 25 % of energy content of raw swine manure (i.e., 19.5 MJ kg^{-1} dry matter) converts to combustible gas after pyrolysis [3], the useable energy from the combustible gas would be 9.6 MJ kg^{-1} biochar. Even with dewatered swine manure with 75 % MC, the energy from the pyrolysis gas would not be enough to sustain pyrolytic carbonization process and would need additional energy of 21 MJ to produce 1 kg biochar. One can utilize produced biochar to provide additional energy needed for pyrolysis. However, utilizing biochar as an energy source will not be profitable as the biochar price is very high compared to energy costs. For example, the price of coal is only about $50/t while that of biochar ranging from $82 to 4590/t [41]. The gaseous energy production can be increased by mixing with high-energy density feedstocks such as agricultural waste plastics. Ro et al. (2014) reported that only about 20 % (*w*/*w*) plastic mulch waste (HHV = 39.7 MJ kg^{-1} dry matter) mixed with the flushed swine manure with 97 % MC produced enough energy from its pyrolysis gas to offset the energy requirement in producing 1 kg of biochar [4]. By adding more plastic wastes to the swine manure in the pyrolysis process, surplus energy would be generated, which could be used for local power generation. Although the biochars produced from pyrolyzing swine manure with and without plastic wastes showed similar surface functionalities, more detailed analyses of the biochar qualities and interactions with soil are needed to evaluate the impacts of soil application of these biochars.

Conclusions

The kinetics and energetics of producing animal manure-based biochar were reviewed and analyzed. Kinetic analysis of animal manure pyrolysis showed that most of the raw manures were devolatilized after 15 min of pyrolysis reaction at 873 K. Increase in pyrolysis temperature or reaction decreases the yield and VM content of biochar. Pyrolysis kinetic information can be used to produce biochar with desired proximate composition. Pyrolysis of wet swine manure even after dewatering was not energetically sustainable due to very high drying energy required. However, co-pyrolyzing with high-energy content feedstocks such as plastic mulch waste produced enough energy in the form of combustible gas that it would not only produce energetically sustainable biochar but surplus energy as well. That surplus energy could be used for local power generation.

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