

Properties of Animal-Manure-Based Hydrochars and Predictions Using Published Models

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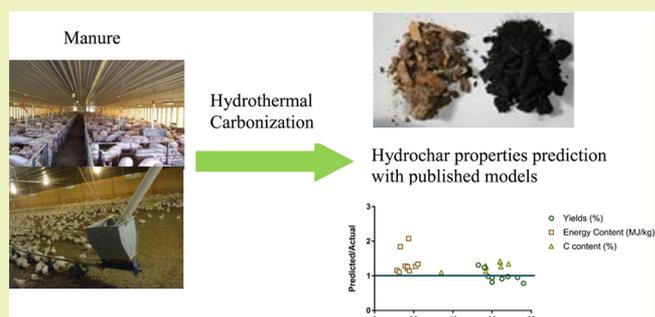
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ABSTRACT: In order to fully utilize hydrothermal carbonization (HTC) to produce value-added hydrochars from animal manures, it is important to understand how process conditions (e.g., temperature, reaction time, solids concentration) influence product characteristics. The effect of process conditions on the extent of carbonization, solid yield, energy density, and combustion characteristics of the hydrochars, as well as the fate of carbon and nitrogen in the three phase process was investigated for swine solids and poultry litter. While hydrothermal treatment increased the percentage of fixed carbon in the solids compared to the original feedstock, increasing the reaction time 5-fold did not increase the percentage of fixed carbon in the hydrochars. Increasing the temperature had an inverse effect on solid yield and, to a lesser extent, energy content. Three different published statistical models in the literature were evaluated for their ability to predict hydrochar properties, based on feedstock properties and process parameters. All three models reasonably predicted the yields and carbon contents; however, prediction of energy contents of animal manure hydrochars was not satisfactory. It is important to develop better predictive models for energy contents of hydrochar for energy application. Furthermore, the current models should be expanded to be able to predict other important properties for developing a sustainable manure-management such as concentration of nutrients and other elements in the hydrochar and process water.

KEYWORDS: Hydrothermal, Carbonization, Livestock waste, Statistical model



INTRODUCTION

Hydrothermal carbonization (HTC) is an emerging technique for the thermochemical conversion of biomass and waste materials and it can play a significant role in strategies for sustainable consumption.¹ HTC occurs in closed systems at relatively low temperatures (180–250 °C) in the presence of water under autogenic pressures. HTC is a low-energy carbon conversion/waste treatment technology with distinct advantages over other thermochemical conversion processes.² By its very nature, HTC is well-suited to manage wet feedstock streams, since predrying prior to processing is not required. HTC in batch reactors differs from combustion, gasification, and pyrolysis, in that it occurs at comparatively lower temperatures, is simpler (e.g., compared to fluidized bed gasification), and the main process product is a carbon-rich char called hydrochar. Gaseous oxidation products, particularly carbon dioxide, are limited during HTC, because, unlike combustion, exposure to oxygen is limited to that initially

present in the reactor headspace, feedstock, and any dissolved oxygen in the water.

Hydrothermal carbonization of wet wastes and residues via a wet thermochemical conversion process can be extremely advantageous, especially for large continuously generated, renewable waste streams that require some degree of management, treatment, and/or processing, such as livestock waste. The current environmental problems arising from inadequate storage and utilization of manure near concentrated animal feeding operation (CAFOs) sites could be avoided through the use of the HTC process in a sustainable manure management system. In comparison to biological treatment, HTC processes are faster and simpler. In addition, HTC process temperatures and pressures can destroy both pathogens

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and antibiotic-resistant genes.³ The overall sustainability of thermochemical conversion processes for these wet waste streams including HTC will ultimately be dependent on combined management concepts for the treatment of the water phase, recovery of nutrients, life cycle analyses, and production of economically viable products.

Various applications exist for the solid char product from HTC (i.e., hydrochar). Hydrochar may be used as a fossil coal alternative to generate power. Results from a life cycle analysis indicate that substituting coal-based energy sources with hydrochar to produce energy will cause a net environmental savings of greenhouse gas emissions.⁴ Hydrochar can also be used as an environmental sorbent. In contrast to the char made from traditional pyrolysis with mostly fused aromatic surface functional groups, the hydrochar has complex surface chemical structures. Hydrochar has diverse surface chemical functional characteristics with alkyl, aromatic, carboxylates, ketone, and other moieties.^{5,6} The surface functional diversity of the hydrochar is advantageous in removing a wide spectrum of both polar and nonpolar organic contaminants from water.^{7–10} The hydrochar can be modified with hydrogen peroxide or activated to enhance the removal of aqueous heavy metals.^{11,12} Hydrochar can also be applied to improve soil quality. The application of hydrochar increased available water capacity of soil, showing the potential to serve as physical soil conditioner.¹³ Hydrochar based on swine manure significantly improved soil fertility while reducing nutrient leaching, preventing potential environmental problems.^{14,15} The versatility of hydrochar in energy production, soil, and environmental applications encourages the use of HTC as a next-generation treatment to valorize wastes and residues.

In order to fully utilize HTC to produce value-added hydrochar from animal manures, it is important to understand how feedstock properties and process conditions (e.g., temperature, reaction time, and solids concentration) influence the extent of carbonization, yield, fate of carbon and nitrogen, and the energy density of hydrochar). However, our understanding of the complex interactions taking place in the HTC process is still very limited and few models exist for predicting hydrochar properties. Recently, progress has been made using two different statistical approaches to describe relationships for the solid yield, carbon, and energy content. Li et al.^{16,17} developed empirical regression models from a meta-analysis of published experimental results for a broad spectrum of feedstocks, while Álvarez et al.¹⁷ described second-order models based on single feedstocks from food processing wastes.^{17,18} The specific objectives of this study were (1) to investigate how various HTC process conditions influence the yield and hydrochar properties, and (2) to evaluate published models to determine if they can be used to predict the properties of the animal manure hydrochars.

MATERIALS AND METHODS

Animal Manure Feedstock. The swine solids were obtained from a solid–liquid separation system that was treating flushed manure from a 5600-head finishing swine operation in North Carolina. Poultry litter was obtained from a 52 000-bird broiler farm in South Carolina. These manures were dried in a greenhouse, milled to pass through a 1 mm screen, and stored in a refrigerator at 4 °C prior to use.

Reactor Systems. Hydrothermal carbonization of the animal manures was conducted in two different types of reactor systems. A nonstirred T316 stainless steel reactor with an external heater (Parr Instruments, Moline, IL) was used to monitor reactor pressure and temperature continuously. The Parr reactor system was heated with a

heating rate of 7 °C/min. In order to efficiently test numerous HTC process conditions in a timely manner, 20 tubular reactors (2.54 cm diameter × 25.4 cm long) were constructed with 304/304L stainless steel pipe with nipples sealed on one end with a pipe cap, and on the other end with a pipe reducer and a gas release valve. All pipe threads were wrapped in Teflon tape prior to sealing. The effective volume of the tubular reactors was 180 mL and system was rated for pressures up to 207 bar. Preliminary experiments were performed with the Parr reactor system to evaluate the pressure buildup under a range of operating conditions, so that the tubular reactors could be safely used. Pressure tests were performed with deionized water alone, as well as with deionized water and swine manure. Based on these pressure tests, we decided not to exceed 100 g of the total mass of water and animal manure in order to safely use the tubular reactors without excessive pressure buildup. After loading animal manure solution, the tubular reactors were sealed, shaken by hand for 1 min, transferred into a Lindberg bench furnace (Lindberg Blue M with retort, Waterton, WI), and allowed to react at preset temperature and time. After the specified time period, the reaction was quenched by immersing the reactors in a tap water bath at room temperature.

HTC Experiments with Tubular Reactors. HTC of swine manure was investigated at two solids contents (20% and 50% total solids (TS)), two reaction time periods (4 and 20 h), and two HTC temperatures (200 and 250 °C). For the chicken litter, HTC experiments were conducted with two solids contents (20 and 50% TS) at 250 °C for 20 h of reaction time. Each of the 10 experimental conditions was evaluated in triplicate, resulting in 30 runs. Reactors with 20% solids content were prepared by transferring 20 g of livestock wastes and 80 g of deionized (DI) water directly into each reactor. Reactors with 50% solids content were prepared by mixing equal amounts of livestock waste and DI water in a beaker and transferring 40 g of the mixture in a reactor.

Feedstock and Product Characterization. The volume of the gas produced in each tubular reactor was measured by collecting the gas in a calibrated bell. The gas composition was analyzed using a gas chromatograph that was equipped with dual thermal conductivity detectors (Gow-Mac Series 580, Bethlehem, PA). The contents of reactors containing 20% solids were filtered through a 1.6 μm glass fiber microfilter and the aqueous filtrate was collected for further analysis. The solids retained on the filter were transferred back into the reactor. For the reactions containing 50% solids, an aqueous phase was not recovered, since water could not be separated from the solids by gravity filtration. In both cases, a tarry residue was also produced, 90 mL of acetone was added to the solids in the reactors, sealed, and mixed in a horizontal shaker for 21–24 h. The contents of the reactors were filtered through the glass fiber microfilter. The hydrochar retained on the filter and the acetone filtrate were dried overnight in an oven at 60 °C and weighed. The solid yield (wt %) was calculated from the ratio of g dried hydrochar/g dried manure and the acetone-soluble residue from the ratio of g acetone filtrate/g dried manure. The total carbon and total combustible nitrogen (TCN) contents of hydrochar were determined using a LECO TruSpec CN analyzer (LECO Corp., St. Joseph, MI). A mass balance on carbon was made for the 20% solid runs by measuring the distribution of carbon between the three phases and relating the mass of carbon in each phase to the initial mass of carbon in the feedstock (carbon recovery, wt %). The carbon content of the acetone-soluble residue was not measured. Proximate analyses of solid samples were performed using the thermogravimetric method.¹⁹ Higher heating values (HHVs) of both feedstock and hydrochar samples were measured using a LECO AC500 Isoperibol calorimeter (LECO Corp., St. Joseph, MI), following ASTM Standard D 5865.²⁰

Statistical Analysis. A three-factor analysis of variance (ANOVA) was performed using Systat (ver. 9) on the swine solids tubular reactor dataset to evaluate if differences due to temperature, solids percentage, and reaction time were significant. Differences were deemed to be significant when $p < 0.05$. When interaction effects between the factors using the swine solids dataset were significant, a subsequent analysis was performed by fitting the data to a generalized linear model considering only the main effects and the significant interaction effects.

A two-factor ANOVA was performed on the swine solids and poultry litter dataset to evaluate if differences due to feedstock and solids percentage were significant at a temperature of 250 °C and a reaction time of 20 h.

RESULTS AND DISCUSSION

Proximate Characteristics of Feedstocks and Hydrochars. Livestock wastes often contain a large amount of ash, compared to lignocellulosic feedstocks and fossil coal. This can be seen in the proximate analyses of the swine manure solids and raw poultry litter (see Figure 1). The ash contents of

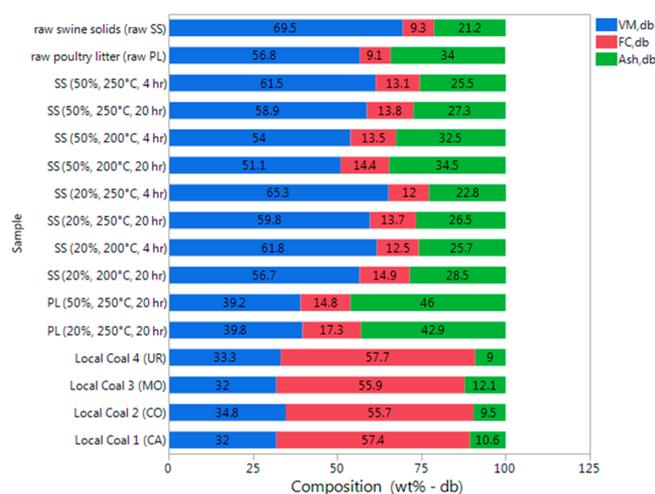


Figure 1. Proximate compositions of raw animal manures and hydrochars, compared to fossil coal samples.

animal manure were much higher than that of wood (typically <5%). Figure 1 also shows that HTC decreased the volatile matter (VM) of raw animal manure feedstock, while fixed carbon and ash contents were increased. However, VM and ash contents of hydrochars were greater than that of fossil coal samples obtained from a local power plant.

Yields, Carbon Content, and Energy Recovery. Table 1 shows the amount of hydrochar recovered as a percentage of the initial feedstock mass added to the reactors for different process conditions. Within the swine solids dataset, higher amounts of hydrochar were recovered at shorter reaction times ($p < 0.001$) (see Table 2). Interaction effects were present between temperature and feedstock solids percentage ($p = 0.012$), and the ANOVA analysis showed that higher amounts of hydrochar were recovered at higher temperatures, with a more pronounced increase in hydrochar recovery at higher feedstock solids percentage. For a temperature of 250 °C and reaction time of 20 h, higher feedstock solids percentage resulted in higher hydrochar recovery ($p < 0.001$), and differences in recovery between the feedstocks were insignificant ($p = 0.929$) (see Table 3).

The carbon and nitrogen content of the hydrochar are also shown in Table 1. The feedstock carbon and nitrogen contents reported for these same feedstocks by Ro et al.³² are 47.3% (0.2%) C and 4.6% (0.1%) N for swine solids, and 34% (0.5%) C and 3.3% (0.0%) N for poultry litter. The values given in parentheses indicate the standard deviation of three replicates. The carbon content of the swine solids hydrochar is higher than that of the feedstock, while the carbon content did not change for the poultry litter. The densification of the swine solids carbon content is consistent with carbonization, which results from the high temperature and resulting high pressure attained in the closed system. The nitrogen content of the hydrochar is lower than the feedstocks, which would indicate that nitrogen leached into the liquid phase and was released into the gas phase. The three-factor ANOVA to evaluate the effects of % solids, temperature, and time on the carbon content for the swine solids hydrochar show significant interaction effects (see Table 2). The hydrochar C content is generally higher with lower % solids, lower temperature, and higher reaction time, but with the magnitude of these changes being dependent on each of the other factors. The hydrochar C content is dependent on the feedstock used ($p < 0.001$; see Table 3), with the hydrochar C from swine solids higher than that of poultry litter. The three-factor ANOVA for the N

Table 1. Experimental Results for the Two Feedstocks at Different Temperatures, Percent Solids, and Reaction Times: Solid Yield as a Percentage of Initial Feedstock Mass, Carbon and Nitrogen Content in the Hydrochar, Energy Content, and the Percentage Recovered in the Hydrochar and Carbon Recovered in the Three Fractions (Hydrochar, Gas, and Liquid)^a

% solids	temp, T (°C)	time (h)	solid yield (wt %)	hydrochar C content (wt %)	hydrochar N content (wt %)	energy content (MJ/kg _{db})	energy recovery (%)	Carbon Recovery (%)				acetone soluble residue (%)
								hydrochar C	gas C	liquid C	overall C	
Swine Solids Feedstock												
20	200	4	65 (3.3)	50 (0.8)	2.8 (0.1)	20.6 (1.3)	69 (4.4)	79 (4.3)	3.2 (0.3)	14 (0.7)	96 (3.9)	9.9 (0.5)
20	200	20	58 (2.4)	51 (0.3)	2.8 (0.1)	22.3 (0.4)	67 (3.0)	72 (3.3)	4.7 (0.2)	13 (2.6)	89 (5.3)	9.8 (0.7)
20	250	4	76 (2.1)	46 (0.5)	3.0 (0.0)	19.7 (0.3)	76 (1.0)	84 (1.5)	1.1 (0.1)	14 (1.9)	99 (3.2)	9.3 (1.0)
20	250	20	60 (2.5)	51 (0.9)	2.7 (0.0)	21.6 (0.7)	66 (0.6)	73 (1.8)	4.1 (0.0)	15 (1.1)	91 (0.7)	7.5 (0.7)
50	200	4	56 (1.9)	44 (0.5)	3.2 (0.0)	18.6 (0.6)	54 (3.1)	61 (2.6)	3.9 (0.4)			23 (2.9)
50	200	20	53 (3.6)	46 (0.2)	3.2 (0.0)	19.5 (0.3)	54 (4.2)	59 (4.2)	4.8 (0.0)			21 (4.7)
50	250	4	73 (9.7)	45 (0.1)	3.4 (0.1)	18.7 (0.2)	70 (9.8)	80 (10)	2.0 (0.3)			15 (2.4)
50	250	20	68 (1.4)	45 (0.7)	3.7 (0.4)	18.4 (0.2)	64 (1.8)	74 (2.2)	3.6 (0.4)			13 (0.9)
Poultry Litter Feedstock												
20	250	20	60 (1.9)	31 (5.3)	2.2 (0.3)	11.6 (0.8)	53 (2.6)	60 (12)	3.5 (0.6)	22 (2.6)	85 (11)	7.9 (0.3)
50	250	20	68 (0.8)	31 (2.6)	2.7 (0.3)	10.3 (1.2)	54 (6.0)	68 (6.3)	4.2 (0.7)			7.8 (2.2)

^aMean and standard deviation of two or three replicates shown in parentheses.

Table 2. Three-Factor ANOVA *p*-Values of the Swine Solids Dataset

factor	<i>p</i> -Value							
	solid yield	hydrochar C fraction	hydrochar N fraction	energy	energy recovered	hydrochar C recovery	gas C recovery	acetone-soluble residue
% solids	0.240	<0.001	<0.001	<0.001	<0.001	<0.001	0.023	<0.001
temperature	<0.001	<0.001	0.004	0.023	<0.001	<0.001	<0.001	<0.001
time	<0.001	<0.001	0.657	<0.001	0.018	0.006	<0.001	0.119
% solids × temperature	0.012	<0.001	0.040	0.512	0.013	0.003	0.415	0.001
% solids × time	0.057	<0.001	0.017	0.007	0.501	0.208	0.002	0.569
temperature × time	0.134	0.041	0.639	0.334	0.084	0.208	0.001	0.599
% solids × temp × time	0.329	<0.001	0.079	0.197	0.722	0.873	0.076	0.677

Table 3. Two-Factor ANOVA *p*-Values of the Swine Solids and Poultry Litter Dataset for a Temperature of 250 °C and a Reaction Time of 20 h

factor	<i>p</i> -Value							
	solid yield	hydrochar C fraction	hydrochar N fraction	energy	energy recovered	hydrochar C recovery	gas C recovery	acetone-soluble residue
% solids	<0.001	0.116	0.002	<0.001	<0.001	0.044	0.956	0.015
feedstock	0.929	<0.001	0.003	0.001	0.791	0.326	0.806	0.009
% solids × feedstock	0.658	0.188	0.230	0.076	0.393	0.413	0.133	0.007

content of the hydrochar also shows interaction effects. A higher N content of the hydrochar is associated with higher % solids in the reactor, with a more pronounced increase in N at higher temperatures and longer reaction times. The increase in the hydrochar N content with increasing % solids can be seen in Table 1 for both swine solids and poultry litter. The value of the N content is dependent on the type of feedstock ($p = 0.003$; see Table 3).

The fate of carbon in the system is also shown in Table 1. Most of the carbon in the original two feedstocks remained in the solid phase, with recoveries ranging from 59% to 84%. A small amount of carbon was transferred to the gas phase (1.1%–4.8%). Carbon in the gas phase was composed primarily of carbon dioxide (ranging from 98.3% to 99.9%) with the remainder being methane. Carbon monoxide was not detected. Carbon in the liquid phase was measured only in reactors with 20% feedstock solids, because the liquid was completely associated with the solids in the reactors with 50% solids. Carbon recoveries in the liquid ranged from 13% to 22%. Overall carbon recoveries ranged from 85% to 99% in reactors with 20% solids.

Further analysis of the results combined with the three-factor ANOVA (Table 2) show that a longer reaction time resulted in less carbon recovery in the hydrochar ($p = 0.006$). In contrast, higher temperatures result in more hydrochar carbon recovery, with a more pronounced increase at higher feedstock % solids. The converse is observed for carbon recovery in the gas phase, where more carbon dioxide is produced at a longer reaction time but with more pronounced increases at lower solids concentration and higher temperature. For a temperature of 250 °C and reaction time of 20 h, higher feedstock % solids resulted in higher hydrochar carbon recovery ($p < 0.001$) (see Table 2) but no significant differences were observed for gas-phase carbon production. Differences in hydrochar carbon recovery and gas-phase carbon production between the feedstocks were insignificant (see Table 3). The amount of acetone-soluble residue was higher for reactors with 50% solids (7.8%–23% by mass), compared to reactors with 20% solids (7.5%–9.9% by mass). The acetone-soluble residue increased

with higher % feedstock solids and decreased with temperature, but with a more pronounced decrease observed at higher % feedstock solids. Differences in the acetone-soluble residue were observed between feedstocks where higher residues were measured at higher % solids for the swine solids but no changes were observed for poultry litter, as a function of % solids.

Comparison of Experimental Results with Published Models. Promising inroads to understanding the interactions between process conditions and hydrochar properties have been made through work on modeling the effects of the HTC process using linear and nonlinear regression methods. In the following, the experimental results for the animal manure hydrochars are compared to values predicted by three statistical models. Two are based on an analysis of experimental results for a wide variety of feedstocks (e.g., food wastes, agricultural residues, algae, cellulose, glucose, lignin; see the work of Li et al.¹⁶) while one is based on single feedstocks from food processing wastes.^{17,18}

Multiple Linear and Regression Tree Models. Linear and nonlinear models developed by Li et al.¹⁶ were used to predict the char properties measured in this study. Li et al.¹⁶ developed multiple linear regression (MLR) and regression tree (RT) models to predict hydrochar yield (%), energy content (MJ/kg), and carbon content (%). These models are based on published HTC-related data (a total of 313 papers were analyzed and 985 data points were collected) for a wide variety of feedstocks and reaction conditions for unwashed hydrochars. MLR is a linear regression approach that is frequently used for developing predictive relationships between dependent and independent variables. However, because this regression technique assumes a linear relationship between variables, the ability to interpret important relationships in complex systems may be limited. RT analyses are nonlinear, representing a nonparametric technique in which no a priori relationships between variables are assumed. RTs are binary trees generated through the splitting of dependent variables into nodes following recursive partitioning rules.²¹ RT models provide several advantages, including the generation of a graphical representation that provides insight into the interaction

Table 4. MLR Models and Input for the RT Models

dependent parameter	equation ^a	adjusted R ²
MLR Models		
solids yield (% db)	$\text{yield} = -1.12\text{Ash}_{\text{feed}} - 1.22\text{VM}_{\text{feed}} - 1.58\text{FC}_{\text{feed}} + 1.63\text{C}_{\text{feed}} - 4.89\text{H}_{\text{feed}} - 0.73\text{O}_{\text{feed}} + 0.43\text{Solids}_{\text{initial}} - 0.21\text{T}_{\text{final}} + 9.70\frac{\text{HT}}{t} + 1.36\text{HR} - 22.19\text{VR} + 212.76$	0.63
hydrochar carbon content (%C, db)	$\%C \text{ in char} = -0.94\text{Ash}_{\text{feed}} - 0.75\text{VM}_{\text{feed}} + 0.55\text{FC}_{\text{feed}} + 0.40\text{C}_{\text{feed}} + 4.18\text{H}_{\text{feed}} + 0.30\text{O}_{\text{feed}} + 0.0005t - 5.65\frac{\text{HT}}{t} - 0.36\text{HR} - 0.00009V - 12.68$	0.79
energy content (kJ/g, db)	$\text{energy} = -0.45\text{Ash}_{\text{feed}} - 0.43\text{VM}_{\text{feed}} + 0.41\text{FC}_{\text{feed}} + 2.35\text{H}_{\text{feed}} - 0.16\text{T}_{\text{final}} + 0.0005t + 0.52\text{HT} - 2.11\frac{\text{HT}}{t} + 25.25\text{HR} - 12.73\text{VR} - 22.74$	0.79
RT Models		
solids yield (% db)	Ash _{feed} , VM _{feed} , FC _{feed} , C _{feed} , O _{feed} , Solids _{initial} , T _{final} , t, HT/t	0.76
hydrochar carbon content (%C, db)	Ash _{feed} , VM _{feed} , C _{feed} , H _{feed} , O _{feed} , Solids _{initial} , t, HR, HT/t	0.84
energy content (kJ/g, db)	VM _{feed} , FC _{feed} , C _{feed} , H _{feed} , O _{feed} , t, HT/t	0.80

^aC_{feed} = carbon content of the feedstock (% db); H_{feed} = hydrogen content of the feedstock (% db); O_{feed} = oxygen content of the feedstock (% db); Ash_{feed} = ash content of the feedstock (% db); VM_{feed} = volatile matter content of the feedstock (% db); FC_{feed} = fixed carbon content of the feedstock (% db); Solids_{initial} = initial feedstock concentration (% solid); T_{final} = final reaction temperature (°C); t = reaction time (min); HT = heating time (min); HT/t = heating time to reaction time ratio; HR = heating rate (°C/min); V = volume (mL); VR = volume ratio.

between parameters. A disadvantage of RTs, however, is that they often result in heavily parametrized, discontinuous models that may be more complicated to use.¹⁶

The three equations from the MLR are listed in Table 4. The input data required for the models include a series of both feedstock properties and process conditions. Required input data differ for each model and are listed as variables in each regression equation, as outlined in Table 4. Table 4 also contains a list of the input data for the regression tree models (see Li et al.¹⁶ for the model structures). The feedstock data used in these models includes the proximate data reported in Figure 1 (e.g., ash, fixed carbon, and volatile matter) and the ultimate analysis data (e.g., carbon, nitrogen, and nitrogen) reported for these same feedstocks by Ro et al.²² Heating rates associated with this study were not measured. Therefore, if needed, reactor temperatures reported by Lu et al.²³ were used to determine the heating rate. The tubular reactors used in that study are the same as those used in this work. The heating rates were calculated assuming a constant and linear rate, as described by Li et al.¹⁶ Reactor heating times are defined as the time it takes to heat the reactor from room temperature (assumed to be 25 °C) to the final desired temperature and reaction times equal to zero represent the time when reactor heating commences.

Both model types were used to calculate the hydrochar solid yield, energy content, and carbon content from all experimental HTC conditions in this work. A comparison of the predicted values to experimental results is shown in Figure 2. The RT and MLR models both appear to predict hydrochar solid yields and carbon contents relatively well. While the MLR model appears to better predict hydrochar carbon content (100% of the experimental data are predicted within 13% of the experimental value), the RT model comes closer to the values for the hydrochar yields. The variability between the predicted and experimental values for both hydrochar energy content and yield are expected. It is important to note that these models are based on literature-collected data in which the hydrochar was not washed or altered prior to analysis.¹⁶ In the experiments

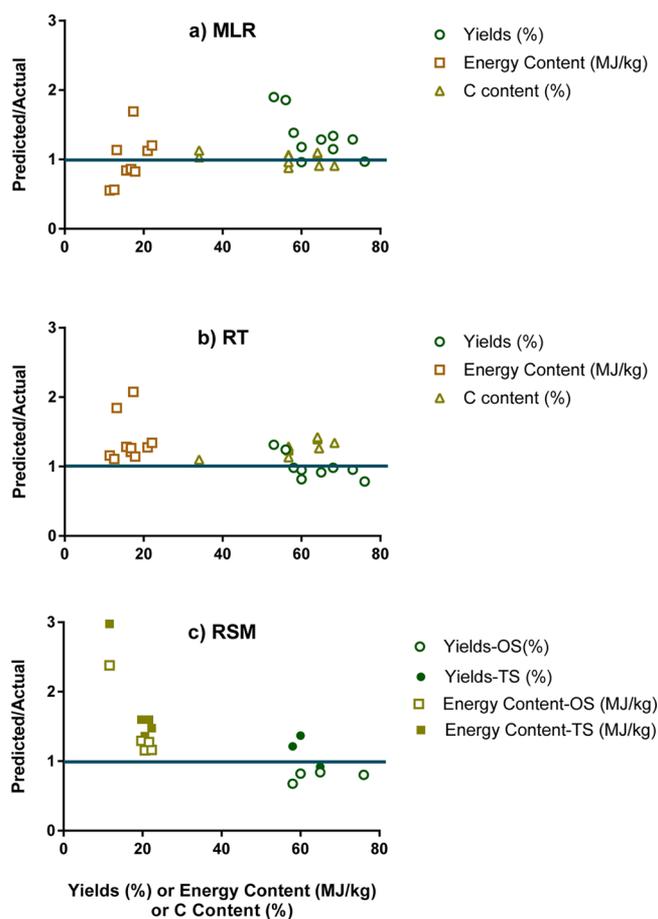


Figure 2. Comparison of the predicted results from the published models to the observed experimental values for swine solids and poultry litter hydrochar for solid yield, energy and carbon contents: (a) multiple linear regression (MLR) model, (b) regression tree (RT) model; and (c) response surface methodology (RSM) models for olive stone and tomato seed.

associated with this work, the hydrochar was washed with acetone prior to analysis. Thus, deviation from the predicted values is expected. Acetone washing likely influences yields and solids energy contents by solubilizing/removing components from the solid phase. The majority of the hydrochar energy content, carbon content, and yields are overpredicted, providing evidence that this claim is valid. It is also possible that the high ash content of the poultry litter, and also possibly the swine solids, likely influences these results. The ash content of these animal wastes exceeds the greatest feedstock ash content (ash content = 28.3%, dry basis) used to develop these regression models. Overall, despite these differences, this comparison shows good agreement between experimental and predicted values. For all parameters and all models, the majority of the experimental data can be predicted within 30% of the experimental values. These results suggest that the models developed by Li et al.¹⁶ can be used as a screening tool to reasonably predict carbonization product characteristics. As more HTC-related data are published, these models can be expanded.

Second-Order Models Based on Response Surface Methodology (RSM). Álvarez-Murillo et al.¹⁷ found that the effects of HTC process conditions (i.e., temperature T , reaction time t , % solids expressed as the liquid/solid mass ratio R) on the solids yield and energy content (higher heating value HHV) of hydrochar made from olive stones were nonlinear. They designed sets of experiments with different biomasses based on response surface methodology (RSM) to develop second-order statistical models that can describe the nonlinear effects.^{17,18} RSM is a group of statistical techniques to model and optimize the nonlinear response of interest to several variables.²⁴ The second-order statistical models for the various biomasses follow the general form

$$Y = A_0 + A_1R + A_2T + A_3t + A_4RT + A_5Rt + A_6tT + A_7R^2 + A_8T^2 + A_9t^2 \quad (4)$$

where Y is the product parameter of interest, e.g. solid yield, and the coefficients A_i are determined for each feedstock. Values for the coefficients were determined using normalized and nonnormalized data and are shown in Table 5 for the olive stone (OS) feedstock.²⁵ The interactions between the factors can be interpreted by looking at the normalized coefficients (using a coded unit analysis). These are compared below to the results of the ANOVA analysis. The nonnormalized coefficients

Table 5. Quadratic Normalized and Nonnormalized Model Coefficients in eq 4 for Olive Stone HTC

coefficient	factor	Normalized		Non-normalized	
		solid yield	HHV	solid yield	HHV
A_0		43.634	26.223	191.6668	-17.1036
A_1	R	3.442	0.333	-2.0290	0.1361
A_2	T	-5.562	2.790	-0.9826	0.3318
A_3	t	-3.241	1.093	-2.1147	0.1104
A_4	$R \times T$	3.269	-0.003	0.0218	0.0000
A_5	$R \times t$	-0.814	0.055	-0.0163	0.0011
A_6	$T \times t$	1.426	0.005	0.0048	0.0000
A_7	R^2	-1.616	-0.442	-0.0658	-0.0044
A_8	T^2	1.110	0.235	0.0012	-0.0007
A_9	t^2	2.535	-0.371	0.0251	-0.0004

(using the original units) are used to predict values for the solid yield and energy content of the animal manures.

The normalized coefficients in Table 5 show trends similar to those observed in the three-factor ANOVA in Table 2: e.g., temperature has a large effect on both solids yield and energy content, and the interactions between the factors % solids and temperature has a greater effect on solids yield, while % solids and time has a greater effect on the energy content. However, the ANOVA analysis does not consider the nonlinearity of the relationship. The quadratic terms are relatively high in the case of solids yield for olive stone (OS) char. The advantage of the second-order statistical model is the ability to measure the relative intensity of the effects due to the different factors and describe a continuous relationship between them for use in further analysis and kinetic modeling.

The non-normalized coefficients in Table 5 for OS hydrochars and those found for tomato seed (TS) hydrochars were used to predict values for the animal manure hydrochars at 20% solids (Figure 2c). The 50% solids experiments exceed the range of operating conditions used to develop the models for OS and TS chars. Figure 2c shows that the solids yield values of the SS hydrochar are similar to those predicted by both models for the shorter reaction time of 4 h. However, only the OS model seems to describe the effect of the longer reaction time on solids yield for both swine solids and poultry litter. The energy content of the animal manure hydrochars are better predicted by the OS-char model. However, again, a large deviation for the poultry litter hydrochars can be observed, because of their high ash content (~50%), compared to the much lower ash content in the olive stone and tomato seeds (~5%–9%, respectively).^{25,26} This comparison highlights the fact that, although these models were calculated for different HTC materials, some common trends can nevertheless be found.

The plots of the statistical models shown in Figures 3a and 3b, however, highlight that the models are highly nonlinear, especially for solids yield. The experimental values of the four SS chars at the appropriate operating conditions are shown in blue in the figures. As already seen in Figure 2, the values do not agree with the model values, although the trends in Figure 2c were similar. However, this comparison highlights that assuming linear relationships between char characteristics and operating conditions can be deceptive. In addition, additional factors could play a role. The interactions revealed by the second-order analysis shows that we must design our experiments to uncover this complexity. Alvarez et al.¹⁷ have shown that using a RSM design, a central composite design, the effect of three operating parameters on HTC solids and liquids characteristics from one biomass can be analyzed with a small number of runs ($N = 18$) in order to develop a second-order model. The comparison of experimental results to predicted values from the few models available shows that much work is still necessary to produce better data and models that allow us to see the complex interactions between feedstock properties, process conditions, and product properties.

CONCLUSIONS

The following conclusions can be drawn from this work:

(1) Although hydrothermal treatment increased the percentage of fixed carbon in the solids, compared to the original feedstock, increasing the reaction severity did not increase the fixed carbon in the hydrochars. Increasing the

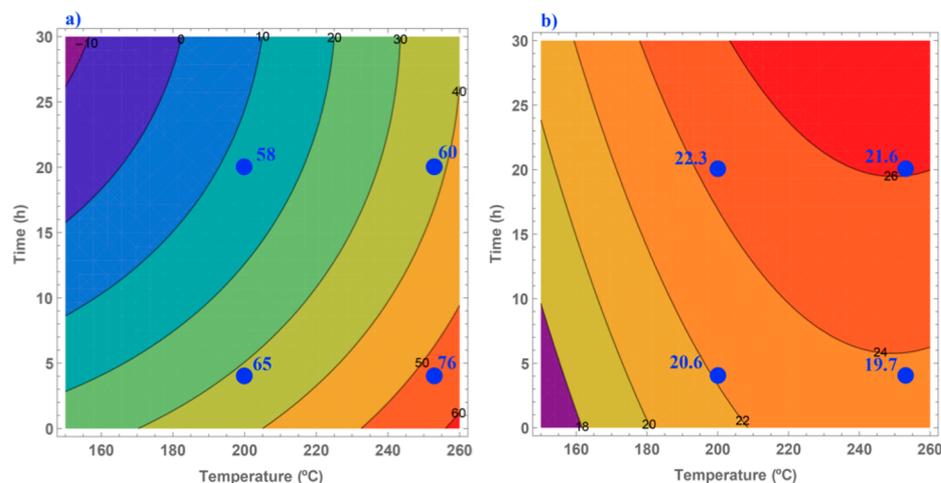


Figure 3. Statistical models for OS char, revealing the influence of time and temperature on (a) solids yield and (b) HHV for a constant solid-to-liquid ratio ($R = 25$, 20% solids). Blue points and numbers are experimental values for SS char ($R = 25$, 20% solids).

temperature had an inverse effect on solids yield and, to a lesser extent, energy content.

(2) The three-factor ANOVA of the swine solids hydrochar showed that the interactions between the factors % solids and temperature have a greater effect on solids yield, while % solids and time have a greater effect on the energy content. Both interactions affect the hydrochar C content—with higher C content at lower % solids and temperature. In contrast, the N content of the hydrochar increased at higher % solids and temperature.

(3) Comparison of the experimental and predicted solids yield and carbon content of the two animal manure hydrochars from the two modeling approaches indicate good agreement, suggesting such approaches may be used to predict these hydrochar properties generated from animal wastes. However, the prediction of energy contents was not satisfactory, and it is recommended to develop better predictive models for energy contents of hydrochar for energy application.

(4) Furthermore, the current models should be expanded to be able to predict other important properties for developing sustainable manure management (e.g., concentration of nutrients and other elements in the hydrochar and process liquid). A better understanding of how feedstock properties and process conditions influence the characteristics of the hydrochar is needed to improve hydrochar property predictions over applicable carbonization conditions. Additional statistical and/or multiphysics models that include more feedstock and hydrochar properties, as well as a wider range of process conditions that impart the greatest influence on the HTC process, should be developed. In addition, the development of multiphysics models that combine both heat and mass transfer, and thermochemical kinetics should also be developed. All developed models be validated and calibrated over the large range of possible feedstock properties and process conditions used during HTC.

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Notes

The authors declare no competing financial interest.

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