

Predictions of energy recovery from hydrochar generated from the hydrothermal carbonization of organic wastes

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ABSTRACT

Hydrothermal carbonization (HTC) is a wet, low temperature thermal conversion process that continues to gain significant attention for the sustainable generation of value-added solid, liquid, and gas products from organic waste streams. Although it is well documented that both waste properties (e.g., elemental composition) and carbonization process conditions influence hydrochar properties, their specific influence on the total energy that can be recovered using HTC remains unclear. Non-linear random forest models were developed based on data collected from HTC-related literature to describe hydrochar yield and energy content, both of which are required to determine the total energy recovered in the hydrochar. Results indicate that total recoverable energy from organic wastes using HTC is correlated with feedstock carbon content; overall, the total energy content for feedstocks with carbon contents ranging from approximately 40–48% are similar. In addition, the total energy that can be recovered from the feedstock remains fairly constant when the initial solids concentrations are greater than 20%. Reaction time appears to have little influence on total recoverable energy from each feedstock at reaction times greater than approximately 150 min, while increases in reaction temperature result in a slight decline in total recoverable energy because of decreases in hydrochar yields at higher temperatures.

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1. Introduction

Hydrothermal carbonization (HTC) is a wet, low temperature thermal conversion process that continues to gain significant attention for the sustainable generation of value-added solid, liquid, and gas products from organic waste streams (e.g., Refs. [1–3]). HTC is a unique process in which wet feedstocks are thermally converted without the prerequisite of feedstock drying. HTC occurs at relatively low temperatures (<300 °C) and with relatively low energy inputs. Because this technique requires the presence of moisture, utilization of such a technique is especially well-suited for the recovery of energy from wet organic wastes, such as food and agricultural wastes.

A significant benefit associated with the hydrothermal carbonization of organics is the generation of a variety of value-added products. Process waters resulting from the carbonization process contain several organics that may be recovered (e.g., 5-hydroxymethylfurfural, acetic acid), as well as nutrients. The gas

stream consists primarily of carbon dioxide, but also contains trace levels of valuable substances, including methane, ethane, propane and butane [4]. The solid material generated, referred to as hydrochar, represents the most widely studied product from the HTC process (e.g., Refs. [4–7]). Hydrochar may be used in many potential applications including as a soil amendment, solid fuel, and media for adsorption of contaminants (e.g., Refs. [1,2,8–12]). Because hydrochar is a carbon-rich and energy-dense solid material that has been reported to have a structure similar to that of a lignite coal, significant interest in using this material as a solid fuel source exists. Numerous previous studies have detailed the feasibility and potential environmental advantages associated with using hydrochar as a solid energy source (e.g., Refs. [4,13–15]).

When considering the use of HTC for solid fuel generation, it is important to understand how changes in waste composition (e.g., elemental composition) and carbonization conditions (e.g., reaction time, temperature, and initial solids concentration) influence the energy that can be recovered from the generated hydrochar. Both hydrochar energy content and hydrochar yield (e.g., hydrochar mass) are important when determining the total energy that can be recovered from hydrochar. Results from previously conducted

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studies associated with individual feedstocks detailed in the literature indicate that hydrochar energy content generally increases with increasing reaction temperature and, to some degree, reaction time [4,11,14,16–21]. Conversely, increases in temperature, and to some degree time, generally result in a reduction in hydrochar generation [4,5,16,22–25]. What remains unclear is how the relationship between these hydrochar properties differs based on feedstock type and carbonization conditions. Understanding these relationships using currently available peer-reviewed literature is complicated because each study generally focuses on the carbonization of only a few feedstocks under relatively limited reaction conditions. In addition, changes in reactor size and heating rates complicate comparisons between published studies. Universally applying this published information to describe expected trends associated with hydrochar properties is further complicated by conflicting reports associated with the influence of specific process conditions, such as reaction time (e.g. Refs. [4,11,26,27]) and feedstock type (e.g. Refs. [18,28]). Li et al. [15] developed non-linear statistical models (regression tree and random forest models) predicting hydrochar yield, carbon content, and energy content as a function of feedstock properties and process conditions using data collected from the literature. However, no work was conducted to understand the relationship between hydrochar yield, hydrochar energy content, and the total potentially recoverable energy from the hydrochar.

Understanding the total energy that can be recovered from hydrochar generated from a range of organic wastes over a range of reaction conditions remains unclear and is the objective of this study. To evaluate this, non-linear random forest models were developed based on data collected from HTC-related literature to describe hydrochar yield and energy content, both of which are required to determine the total energy recoverable in the hydrochar. Subsequently, these random forest models were used to determine how different properties of organic wastes and carbonization process conditions influence the total energy that can be recovered from hydrochar generated using HTC.

2. Materials and methods

2.1. Data collection

A survey of existing HTC-related literature in scientific databases (including Science Direct, Web of Knowledge, and Google Scholar) available through August 2017 was conducted, following procedures outlined by Ref. [15]. Feedstock properties, process conditions and carbonization product information from each study were tabulated (see Table 1). Feedstock properties collected from the

literature include proximate analysis parameters (ash content, volatile matter, and fixed carbon), ultimate analysis parameters (carbon, hydrogen, and oxygen content), and chemical composition (cellulose, hemicellulose, and lignin content). Feedstock lignin, cellulose, and hemicellulose contents are not routinely reported in HTC-related studies. Therefore, if these properties were not reported, literature searches were conducted to obtain these properties for the specific feedstock, following that reported in Ref. [15]. Process conditions collected for this study include initial solids concentration, reaction temperature, and reaction time. The hydrochar properties modeled in this work include hydrochar yield (mass of dry recovered solids per mass of initial dry feedstock, % dry basis) and hydrochar energy content (MJ/kg, dry basis). Hydrochar yield is indicative of the amount of hydrochar obtained and the energy content represents the calorific value of the hydrochar. For hydrochar yield and energy content, 649 and 475 data points were collected, respectively, from the literature. The total recoverable energy from the hydrochar (MJ/kg dry feedstock) is calculated by multiplying the energy content of the hydrochar (MJ/kg dry hydrochar) by the hydrochar yield (% dry wt.).

A total of 138 papers associated with hydrothermal carbonization processes conducted between 180 and 350 °C that reported solid yields, energy contents, and/or elemental composition of the solid, liquid, and/or gas products were collected, resulting in a total of 1429 data points. These collected data represent the carbonization of a variety of feedstocks over a large range of process conditions. The most commonly evaluated reaction temperature and initial solids concentrations were 250 °C and 20%, respectively. Reaction times ranging from 0.03 to 120 h were investigated, with the majority of studies conducted at reaction times less than 200 min. Reactor size was also variable among the collected studies, with the majority of the studies conducted in reactors that were less than 1000-mL. Twenty-seven different feedstocks were carbonized, with food and food wastes and wood representing the feedstocks with the greatest number of data points.

2.2. Model development

Non-linear random forest models were developed to describe the relationship between all independent and dependent parameters. A series of models representing all possible combinations of non-correlated parameters were developed. Correlated parameters were defined as those with a correlation coefficient greater than 0.8 [29,30]. Distance correlation tests, which measure the dependence between two random variables, were used to evaluate correlations associated with nonlinear relationships. Random forests are tree-based models and often described as a robust black box approach [31,32]. Random forest models were developed using the “randomForest” function of the “randomForest” package in R.

2.3. Model simulations

To evaluate how changes in feedstock properties influence the total energy that can be recovered from the hydrochar, average feedstock properties associated with several organic wastes were modeled. The organic wastes modeled and their properties are included in Table 2. When investigating the influence of these feedstocks on the total energy that can be recovered from the hydrochar, the simulations were conducted over the following range of process conditions:

- Reaction time = 6–6680 min (44 points)
- Reaction temperature = 185–345 °C (17 points)
- Initial solids content = 3–47.5% (dry wt.) (10 points)

Table 1
Feedstock properties and process conditions investigated in this study.

Parameter	Unit
Ash	%, dry basis
Volatile matter	%, dry basis
Fixed carbon	%, dry basis
Carbon	%, dry basis
Hydrogen	%, dry basis
Oxygen	%, dry basis
Polarity	— ¹
Cellulose	%, dry basis
Hemicellulose	%, dry basis
Lignin	%, dry basis
Initial solids concentration	%, dry basis
Temperature	°C
time	min

¹ This parameter is unitless.

Table 2
Organic waste properties.

Feedstock	Pol.	Cel.*	Hem.*	Lig.*	Ash*	VM*	FC*	C*	H*	O*
Algae	0.9	6.5	18.6	1.4	19.7	63.3	11.8	41.5	6.3	34.8
Food waste	0.9	38.4	10.7	13.9	8.5	74.6	15.7	47.9	6.7	40.2
Grass	1.0	39.7	35.3	11.6	2.8	84.4	12.7	45.4	6.1	44.3
Agricultural wastes and residues	0.8	31.1	13.4	12.8	10.1	74.5	13.6	45.3	5.9	36.7
Paper waste	1.3	87.4	8.4	2.3	10.5	80.3	9.3	36.3	5.1	48.3
Wastewater digestate	0.9	37.2	18.8	17.8	22.8	58.1	11.9	40.6	5.5	33.3
Mixed MSW	1.2	41.0	9.8	17.3	16.9	72.5	9.0	36.5	4.8	41.4
Animal waste	0.7	19.3	18.0	6.7	17.7	68.1	11.5	46.2	5.8	26.9
Wood	0.9	49.7	17.0	23.4	2.2	86.2	12.1	48.4	6.2	44.8
Straw	1.0	50.0	33.5	9.1	6.5	78.1	15.1	43.9	5.5	43.8

*all units are %, dry weight.

Pol. = polarity; Cel. = cellulose; Hem. = hemicellulose; Lig. = lignin; C = carbon; H = hydrogen; O = oxygen.

To investigate how each process parameter influences the total energy that can be recovered from the hydrochar of each feedstock, predictions were averaged over the other process conditions in the ranges reported above. For example, to examine the effect of temperature, the mean and standard deviation of the total energy predicted at each temperature is taken by averaging over 44 values of time and 10 values of initial solids content.

3. Results and discussion

3.1. Model development

3.1.1. Hydrochar yield

Results from the random forest models indicate that (1) feedstock ash content and volatile matter, and (2) feedstock carbon content and polarity are highly correlated (correlation coefficient > 0.8). Therefore, four random forest models representing all possible combinations of non-correlated model parameters were developed to describe hydrochar yield. The R^2 values associated with all random forest models are the same, and are greater than 0.9, suggesting all these models fit the char yield data quite well. More information associated with these models can be found in Ref. [15].

3.1.2. Hydrochar energy content

Results from non-linear correlation tests indicate that feedstock ash content is highly correlated (correlation coefficient > 0.8) with volatile matter. Two random forest models representing all possible combinations of non-correlated model parameters were developed to describe hydrochar energy content. All random forest models investigated similarly predict hydrochar energy content and suggest good predictive capability. More information associated with these models can be found in Ref. [15].

3.1.3. Total energy recoverable from the hydrochar

The total energy that can be recovered from the hydrochar (MJ/kg dry feedstock) was determined by multiplying the results from the hydrochar yield and hydrochar energy content models associated with each combination of random forest models (a total of 8 values for each condition). These models fit the data well, as illustrated in Fig. 1.

3.2. Influence of feedstock type on total energy

Fig. 2 presents the results associated with the total energy that can be recovered from different organic wastes (at a constant reaction temperature, time, and initial solids concentration). In this plot, the feedstocks are listed in order of lowest carbon content to greatest carbon content (see Table 1 for the exact carbon contents

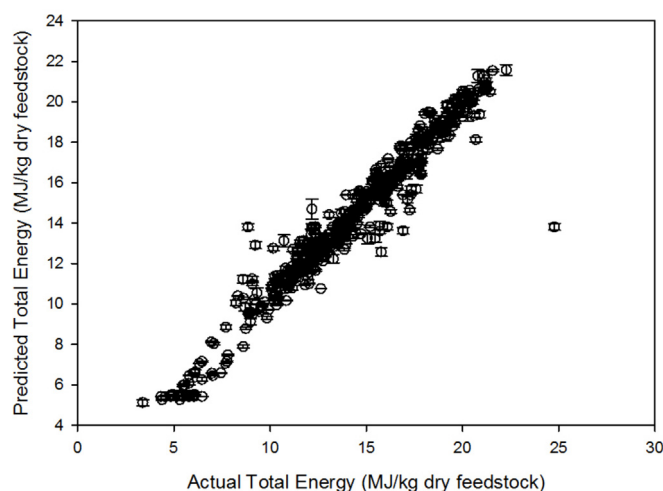


Fig. 1. Model predictions compared to the experimental results.

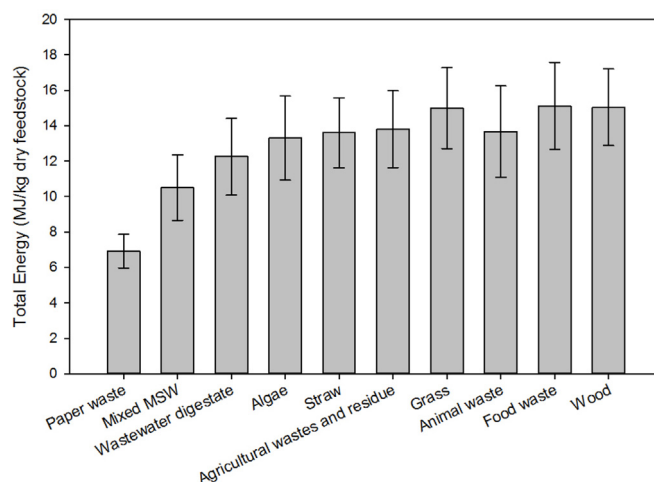


Fig. 2. Total energy recoverable from different organic wastes. Note the wastes are listed in order of their carbon content, ranging from the lowest value (left) to the greatest value (right). Each value represents the average value obtained from all random forest models over all time, temperature, and initial solids concentrations. The error bars represent the standard deviations associated with these predictions.

associated with each feedstock). The total energy values are average values associated with the total energy recovery associated with each combination of random forest models (total of 8) over all time, temperature and initial solids concentrations (see section 3.1). The

error bars represent the standard deviations associated with the predictions. These results suggest that the average total recoverable energy is linearly correlated with feedstock carbon content, as an increase in total energy is observed from the left to right. These results also suggest that over all reaction temperatures, times, and initial solids concentrations, the total energy content for feedstocks with carbon contents ranging from approximately 40–48% are similar. Correlations between the average total energy and the feedstock properties were investigated, but no significant correlations were observed. These results suggest that when considering the carbonization of feedstocks for generation of an energy source, feedstock carbon content should be considered and that feedstocks with higher carbon contents are preferred.

3.3. Influence of process conditions on total energy

Figs. 3–5 indicate how changes in individual process conditions influence the total energy recovered from hydrochar generated from each of the 10 organic wastes (see Table 1) investigated in this study.

3.3.1. Initial solids concentration

As shown in Fig. 3, with the exception of paper waste, the total energy that can be recovered from the feedstock increases as the initial solids concentration increases to approximately 20%. This observation is consistent with that reported in the literature and likely related to the total mass of hydrochar generated. Generally, studies report that as the initial solids concentration increases, solid yields increase [4,23,33], possibly due to solubility saturation effects. Interestingly, at initial solids concentrations greater than

20%, the total energy that can be recovered from each feedstock remains relatively constant over a range of temperatures and times. Because carbonizing at greater initial solids concentrations does not influence the total energy recovered, carbonizing at these conditions may allow more efficient processing of the feedstocks. The absolute value of the total energy that can be recovered from the hydrochar from each feedstock follows the trends described in Fig. 2.

The decreasing trend in total energy recovered from paper waste at initial solids concentrations greater than 8% is likely due to changes in hydrochar generation with this waste material. Paper waste has a different chemical composition than the other wastes investigated in this study; the cellulose content is significantly larger than all of the other wastes. Low hydrochar yields have been reported for paper waste (e.g. Refs. [1,25]).

Overall, these results suggest that carbonizing at solids concentrations of at least 20%, with the exception of paper waste, will maximize the potential for energy recovery from the feedstock. It is important to note that carbonizing at larger initial solids concentrations does not appear to have a significant impact on the total recoverable energy. In addition, Li et al. [15] report that hydrochar yields are most sensitive to initial solids concentration, while hydrochar energy contents are not sensitive to initial solids concentration. Therefore, these results suggest that larger hydrochar yields are more important than hydrochar energy content when considering the total energy that can be recovered from the hydrochar. It is important to note, however, that other properties of the hydrochar that may influence its combustion characteristics were not included in this analysis [34].

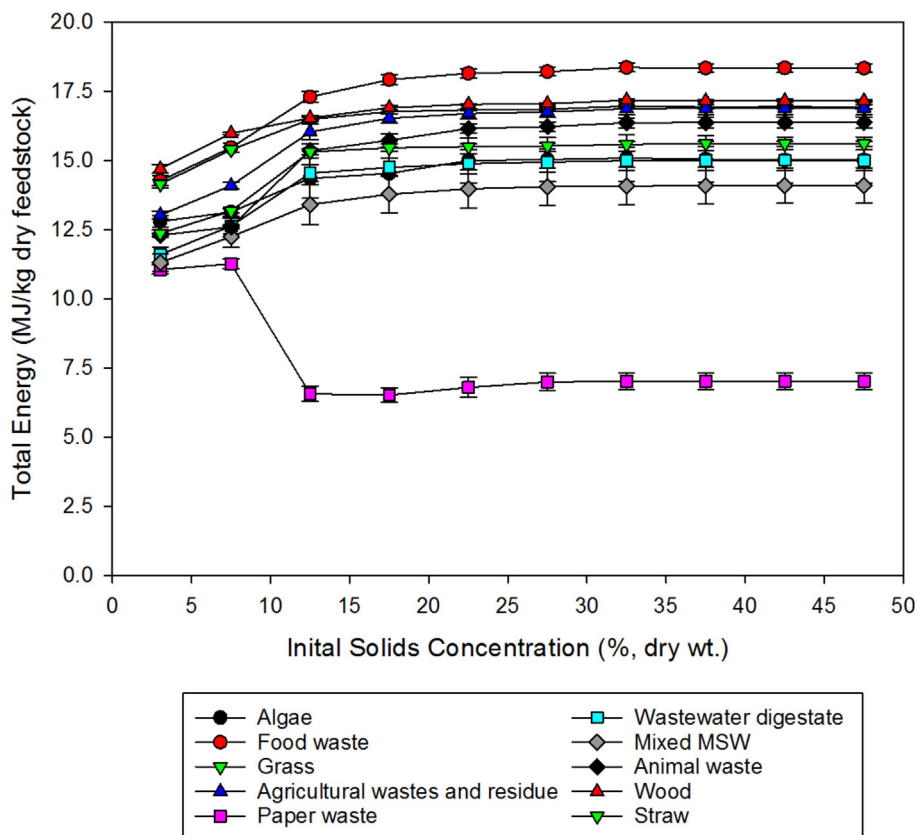


Fig. 3. Total energy recoverable from different organic wastes as a function of initial solids concentration. Each value represents the average value obtained from all random forest models over all reaction temperatures and times. The error bars represent the standard deviations associated with these predictions.

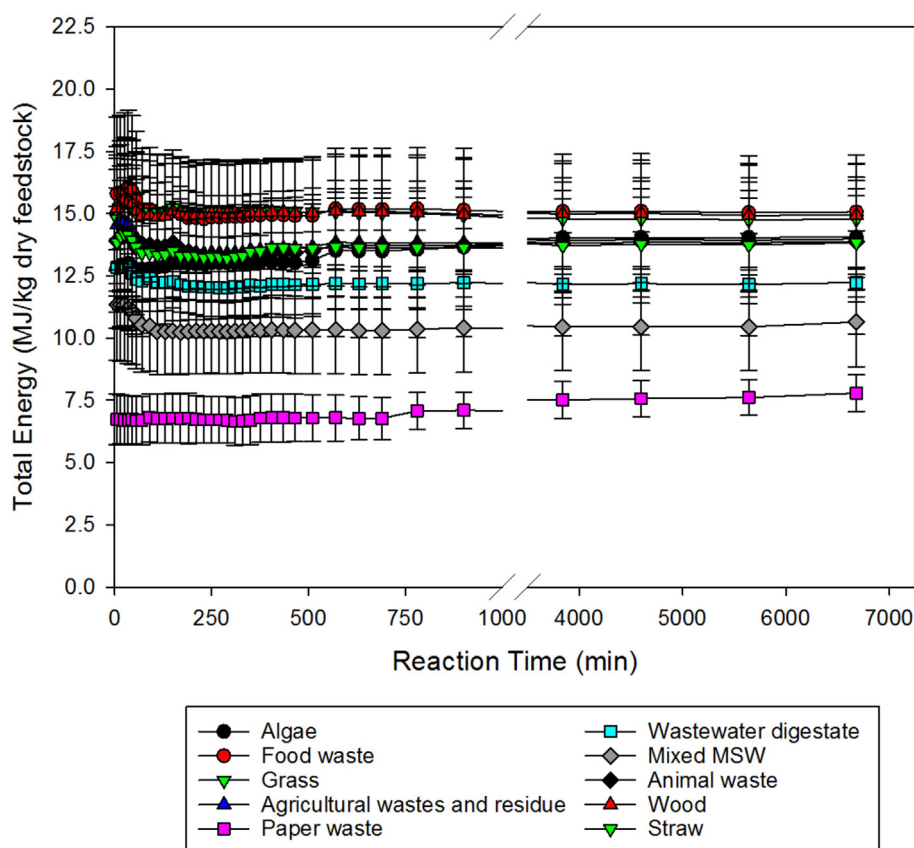


Fig. 4. Total energy recoverable from different organic wastes as a function of reaction time. Each value represents the average value obtained from all random forest models over all reaction temperatures and initial solids concentrations. The error bars represent the standard deviations associated with these predictions.

3.3.2. Reaction time

The influence of reaction time on total energy is illustrated in Fig. 4. As shown, reaction time appears to have little effect on total recoverable energy from each feedstock. There is a slight decrease in total recoverable energy during the first 150 min of carbonization. Following that, the total recoverable energy remains fairly constant. It should be noted that although a decline during early times is observed, the standard deviations associated with these results suggest this decline may not be statistically significant.

These results are consistent with some of the trends reported in the literature. At short reaction times, process conditions have been reported to impart a greater influence on hydrochar yield and hydrochar energy content [15]. It has been reported that at short reaction times, significant fractions of the feedstock are solubilized, with hydrochar formation decreasing and then subsequently increasing over time and leveling off to a maximum level [26]. Similar trends with hydrochar energy contents have been reported [4,17,20,25,26,33]. When investigating the feedstock properties and carbonization conditions most sensitive to hydrochar yields and energy contents, Li et al. [15] report that hydrochar energy content is sensitive to reaction time; hydrochar yield is not sensitive to reaction time.

These results are significant, as they indicate that short reaction times that are often described in the currently-available literature can be used when carbonizing to optimize energy recovery from the hydrochar. Utilizing shorter reaction times has the potential to decrease HTC process energy needs and may allow for more efficient processing of large masses of waste. In addition, these results appear to suggest, much like those associated with initial solids concentrations, that maximizing the recoverable energy from the

hydrochar requires maximizing hydrochar yields. This conclusion is often overlooked, with studies focusing on carbonizing at higher temperatures to maximize hydrochar energy density. It is important to note, however, that other properties of the hydrochar that may influence its combustion characteristics were not included in this analysis. Although the total recoverable energy may be maximized at short reaction times, it is possible that the chemical properties of the hydrochar are not suitable for combustion processes [34]. Investigating the solids structure over time is important to consider.

3.3.3. Reaction temperature

The influence of reaction temperature on total recoverable energy from hydrochar generated from each was material is illustrated in Fig. 5. These results indicate that there is a slight decline in the total recoverable energy as the reaction temperature increases, which is often overlooked in studies that focus on generating hydrochar for solid fuel purposes. Although hydrochar energy content has been reported to increase with increasing reaction temperature (e.g. Refs. [11,18,19]), this trend is likely a result of decreasing hydrochar yields with increasing temperature [5,24]. Previously published reports indicate that as reaction temperature increases, hydrochar yield decreases (e.g., Ref. [13]). Reductions in hydrochar yield likely result because increases in temperature increase the potential for compound volatilization and dissolution and because the extent of feedstock hydrolysis and dehydration increase with reaction temperature. As a result, there is less char that can be used to generate energy. Li et al. [15] report that reaction temperature plays an influential role on both hydrochar energy content and hydrochar yields.

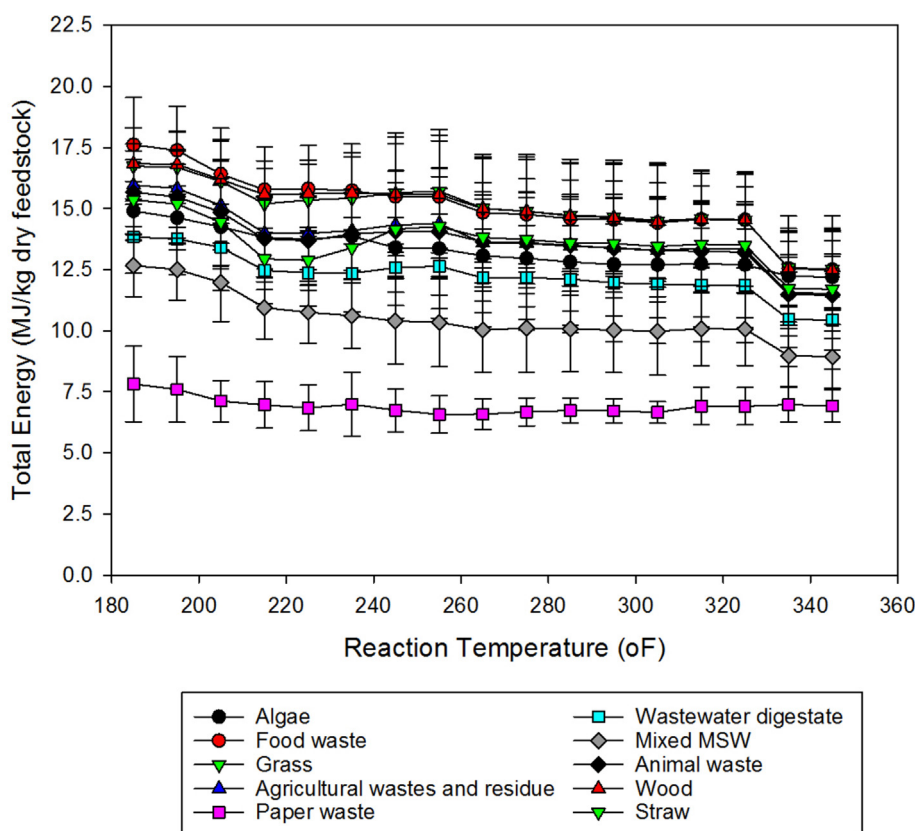


Fig. 5. Total energy recoverable from different organic wastes as a function of reaction temperature. Each value represents the average value obtained from all random forest models over all reaction times and initial solids concentrations. The error bars represent the standard deviations associated with these predictions.

These results suggest that carbonizing at lower temperatures will maximize the potential recoverable energy from the hydrochar, likely because hydrochar yields are greater under these conditions. However, it is also important to investigate other properties of the hydrochar that may influence its combustion prior to determining the most appropriate temperature. Previous studies report that hydrochar combustion also depends on hydrochar structure, which has been reported to change significantly with reaction temperature [5,34,35].

4. Conclusions

Results from this study indicate that the total energy that can be recovered from the 10 organic wastes investigated in this study is appreciable. When investigating how feedstock composition influences changes in the total recoverable energy, total recoverable energy is correlated with feedstock carbon content; over a range of reaction temperatures, times, and initial solids concentrations, the total energy content for feedstocks with carbon contents ranging from approximately 40–48% are similar. In addition, it was determined that the total energy that can be recovered from the feedstock remains fairly constant at initial solids concentrations greater than 20%. Reaction time appears to have little influence on total recoverable energy from each feedstock at reaction times greater than approximately 150 min, and increases in reaction temperature result in a slight decline in total recoverable energy because of decreases in hydrochar yields at higher temperatures. These results also appear to indicate that to maximize the total energy that can be recovered from hydrochar, significant attention should be paid to hydrochar yields; the mass of hydrochar appears to be more significant than its energy content. It is important to note, however,

that properties of the hydrochar that may influence its combustion suitability and/or efficiency were not included in this analysis. Understanding the relationship between feedstock properties, carbonization conditions, and hydrochar properties that influence its combustion is needed and is a logical next step to this work.

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