Resource Recovery from Diverted Food Waste via Hydrothermal Carbonization

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EXECUTIVE SUMMARY

The desire for food waste diversion from municipal solid waste (MSW) landfills is steadily increasing. Recently, through current EREF funding, our research group at the University of South Carolina (USC) has demonstrated that hydrothermal carbonization (HTC) may serve as a sustainable and effective approach to manage diverted food waste, resulting in the generation of a high value, energy-rich, coal-like material that has an energy content as high as 33,750 J/g dry solids. Carbonization of food wastes presents a unique opportunity to not only generate a valuable energy source, but to also recover valuable soluble nutrients and produced chemicals from the process water that are otherwise unrecovered or unavailable. The potential revenue expected from the recovery of these resources, coupled with previously documented generation of a high-value coal material, increases the sustainability and economic viability of HTC, providing a compelling argument for continued evaluation of food waste carbonization. The goal of this project is to explore the sustainable and economically beneficial recovery of these resources. The specific objectives of this project include:

- 1. Determine the hydrothermal carbonization operational parameters (e.g., reaction time, reaction temperature) that result in the greatest fraction of extractable nutrients and valuable chemicals (e.g., acetic acid and 5-HMF) in the process water for subsequent sale.
- 2. Evaluate nutrient and chemical (e.g., acetic acid and HMF) recovery techniques.
- Conduct an economic analysis of simultaneous energy, nutrient, and chemical recovery from food wastes converted via hydrothermal carbonization to provide operational guidance.

Laboratory-scale experiments conducted to determine the fate of nutrients during the carbonization of food wastes and mixed food and packaging wastes under different operating conditions are described. At all evaluated reaction times and temperatures, the majority of nitrogen, calcium, and magnesium remain integrated within the solid-phase, while the majority of potassium and sodium reside in the liquid-phase. The fate of phosphorus is dependent on reaction times and temperatures, with solid-phase integration increasing with higher reaction temperature and longer time. Results from the leaching experiments suggest that, at least in the short term, tightly bound nitrogen within the solid matrix is unlikely to be released, while almost all of the phosphorus present in the solids generated when carbonizing at 225 and 250 °C is released. At a reaction temperature of 275 °C, smaller fractions of the solid-phase total phosphorus are released as reaction times increase, likely due to increased solids incorporation. Up to 0.96% and 2.61% of nitrogen and phosphorus-based fertilizers (accounting for recovery in the liquid and solid-phases), respectively, in the US can be replaced by nutrients integrated within hydrohcar and liquid-phases generated from the carbonization of currently landfilled food wastes.

Liquid phase nutrient recovery from the process water using struvite precipitation was evaluated using laboratory-scale experiments and equilibrium modeling. Nutrient recovery via struvite is viable. Adding either $MgCl_2$ or $MgSO_4$ and a base is necessary because of the low pH and Mg^{2+} levels in the HTC process water. Because of the low P:N ratio in the HTC process water,

adding phosphate is needed to maximize nitrogen nutrient recovery. A chemical equilibrium model can reasonably predict the amount of struvite formed and can be used as a basis for the amount of chemicals (i.e., Mg²⁺, base, and/or phosphate) to be added to the system. Fitting experimental titration behavior of the HTC process water is necessary to obtain the required amount of added base. A strategy of pH adjustment with periodic Mg²⁺ and base addition recovered more struvite than a single dose of Mg²⁺ and base in a batch system. Refinement of the operational strategy to include pH control and chemical addition programming in a flow through system during larger scale implementation is recommended.

Laboratory experiments aimed at evaluating the recovery of acetic acid and 5-HMF using liquid-liquid extraction techniques were also conducted. Concentrations of acetic acid and 5-HMF in the process water are significant. When carbonizing to maximize acetic acid concentrations, higher reaction temperatures and longer reaction times are needed. Although liquid-liquid extraction methods to extract acetic acid from deionized water were shown to be feasible, the same methods failed when applied to HTC process water. Investigation of alternative approaches (e.g., membrane separation) is necessary. In contrast, maximizing 5-HMF generation requires lower reaction temperatures and shorter reaction times. A 90% 5-HMF extraction efficiency from the process water was achieved using tetrahydrofuran and sec-butanol with the addition of salt.

Nutrient and 5-HMF recovery from the HTC processing of food waste and mixed food and packaging wastes is technically feasible. A previous project also demonstrated energy recovery from the carbonization of the same materials is technically feasible. An initial assessment of the costs and benefits associated with eight different operational strategies for resource recovery was performed. System costs (e.g., chemical requirements) and benefits (e.g., selling of hydrochar, nutrients, chemicals) were normalized per mass of wet food waste processed and reaction time. Results from this analysis indicate that conducting HTC for resource recovery can be economically viable. Using the hydrochar for energy and recovering nutrients from the HTC process water can be more economically attractive than composting and anaerobic digestion of food wastes. Results also suggest that recovering 5-HMF via liquid-liquid extraction is not currently economically viable. Investigation of alterative liquid-phase resource recovery approaches is needed to improve the economics of this recovery.

A flowchart that provides guidance on carbonizing food wastes for resource recovery is detailed. After specifying the desired resources to recover, the flowchart specifies the HTC processing conditions that maximizes the production of the resource.

Overall, results associated with this EREF funded project indicate that recovering resources from food wastes (and mixed food and packaging wastes) using HTC has promise; significant levels of resources can be recovered that can be economically attractive and, under some conditions, achieve greater profits than composting and anaerobic digestion of food wastes. This work provides the basis for large-scale implementation of this process. As resources become more limited, it will likely become more important to recover resources from food-related waste. HTC is a novel process that can economically and efficiently accomplish this.

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INTRODUCTION

1.0 Project Motivation

The desire for food waste diversion from municipal solid waste (MSW) landfills is steadily increasing. Several States, cities, restaurants, grocery stores/chains, and college campuses encourage food waste diversion. Several States are banning commercial food waste placement in landfills or developing diversion goals/mandates associated with this waste, which includes wastes generated by universities, hotels, restaurants, and other large producers of food waste. College campuses (e.g., University of South Carolina and Texas State University (Sullivan, 2010)) and grocery store chains (e.g., Walmart, Costco) are also promoting the diversion of food waste through either donation to food banks or management via composting or anaerobic digestion. As food waste diversion goals and/or mandates continue to increase, it is important that sustainable and economically beneficial food waste treatment techniques are practiced. Although composting and anaerobic digestion are currently the food waste treatment techniques most often promoted and practiced, each has operational disadvantages. And, although each technique does result in production of a value-added product (e.g., compost and methane gas), the long-term future viability and sustainability of these processes is uncertain.

Recently, through previous EREF funding, our research group at the University of South Carolina (USC) has demonstrated that hydrothermal carbonization (HTC) may serve as a sustainable and effective approach to manage diverted food waste (e.g., Li et al., 2013). Hydrothermal carbonization is a unique process in which wet feedstocks are thermally converted into value-added products without the prerequisite of product drying. Hydrothermal carbonization occurs at relatively low temperatures (< 350° C) and with relatively low input energy requirements (e.g., Funke and Zeigler, 2010; Libra et al., 2011; Lu et al., 2012). Because this technique requires the presence of moisture, utilization of such a technique is best suited for conversion of wet resource-rich wastes, such as foods (~70%, wt. moisture). Results from our work indicate that HTC of food waste is advantageous, resulting in the generation of a high-energy value coal-like solid material that has an energy content as high as 33,750 J/g dry solids. The generation of this solid energy source is advantageous, as there is always a market for energy. In addition, the solid nature of the material permits long-term storage and transportability, allowing material utilization as needed. Results from energy balances indicate HTC of food waste is energetically positive (Li et al., 2013).

It is possible that the sustainability and economic viability of HTC can be improved. Another unexplored advantage associated with HTC is the generation of resource-rich process water. Carbonization of food wastes (and other wet resource-rich feedstocks) presents a unique opportunity to not only generate a valuable energy source, but to also recover valuable soluble nutrients and produced chemicals from the process water that are otherwise unrecovered or unavailable. Food waste contains appreciable fractions of valuable nutrients, including nitrogen, phosphorus, and potassium, correlating to millions of tons of each nutrient that can be recovered each year. Recovery of these nutrients has the potential to result in a large source of yearly income, garnering specific interest from fertilizer manufacturers. Significant fractions of nitrogen and phosphorus have been measured in the process water resulting from the hydrothermal treatment of horse manure, bamboo and restaurant garbage (e.g., Lilliestråle, 2007; Ren et al., 2006; Scheider et al., 2011), suggesting high recovery of these nutrients following carbonization of food wastes is feasible. Hydrothermal carbonization also presents an opportunity to simultaneously produce valuable chemicals from food wastes, including organic acids (e.g., acetic, formic) and 5-hydroxymethylfurfural (5-HMF). These compounds are produced during HTC via the hydrolysis and/or dehydration of components of the feedstock (Funke and Zeigler, 2010; Libra et al., 2011). Several researchers have identified the presence of these compounds in process water from the carbonization of cellulose and other organic feedstocks (e.g., Goto et al., 2004; Lu et al., 2013) and it is expected that these compounds will also be prevalent in the process water resulting from the carbonization of food waste. The global demand and market value associated with each of these compounds is projected to increase significantly (e.g., Plastemart, 2013; Protti-Alvarez, 2013), making their production both environmentally and economically advantageous.

2.0 Project Objectives

As the requirement for food waste diversion continues to become more prevalent, there is a distinct need for exploration of technologies that maximize benefits derived from treatment of the waste. This proposal focuses on exploring the sustainable and economically beneficial recovery of soluble nutrients (e.g., nitrogen, phosphorous, potassium) and production of valuable chemicals (e.g., acetic acid, 5-HMF) from the carbonization of diverted food wastes. There is distinct a need to determine when, and under what conditions, conversion of food wastes via HTC result in optimal generation of these resources. It is also important to determine the efficiency of the recovery processes. Results from this work will be combined with those of our previous EREF grant (Berge and Flora, 2015) to ultimately yield an economically and environmentally beneficial novel approach for the management of food wastes. The specific objectives of this proposed project include:

- 1. Determine the hydrothermal carbonization operational parameters (e.g., reaction time, reaction temperature) that result in the greatest fraction of extractable nutrients and valuable chemicals (e.g., acetic acid and 5-HMF) in the process water for subsequent sale.
- 2. Evaluate nutrient and chemical (e.g., acetic acid and HMF) recovery techniques.
- 3. Conduct an economic analysis of simultaneous energy, nutrient, and chemical recovery from food wastes converted via hydrothermal carbonization to provide operational guidance.

3.0 Nutrient and Chemical Recovery from Food Wastes

Recovery of nutrients and production of valuable chemicals from diverted food wastes would be of great environmental and economic benefit. Concerns associated with declining resources are well documented. One of the National Academy of Engineering's Grand Engineering Challenges relates to the nitrogen cycle, citing the need for engineering innovation to maintain a sustainable food supply, with suggested actions including increasing the efficiency of fertilizer production and food waste recycling (NAE, 2013). Severe issues associated with anticipated worldwide phosphorus shortages are also well documented, and are projected to significantly impact future food supply (e.g., Cordell et al., 2009; Van Vuuren et al., 2010). Estimates suggest phosphorus shortages may occur in 50-100 years, with peak phosphorus production occurring in 2030 (Cordell et al., 2009). Food wastes are an excellent source of nutrients. WERF (2011) report that 2009 market values of nitrogen and phosphorous were \$0.26/kg and \$0.14/kg (values were based on USDA fertilizer use data). It should be noted that the need for nutrients is increasing and will likely drive the economic market, likely increasing their market value over time.

Other chemicals of significant economic value are also generated as a result of the hydrothermal carbonization of food wastes. Acetic acid and 5-HMF are two of the most prominent compounds generated and are also two compounds in which there is significant market. The global demand for acetic acid is increasing significantly and projected to reach 15.5 million tons by 2020 (Plastemart, 2013). Another chemical of increasing demand is 5-hydroxymethylfurfural (HMF). HMF has been labeled as a top value-added chemical and is a platform chemical often used for the production of biofuels and polyesters (e.g., Rosatella et al., 2011). There is growing interest in the production of this product, with construction of HMF manufacturing plants just beginning (Protti-Alvarez, 2013). The demand and market value of these compounds is only expected to increase. Recovery of these from the hydrothermal conversion of food wastes adds tremendous value to the process.

Results and Discussion

1.0 Fate of Nutrients During the HTC of Food Wastes

1.1 Carbon Mass Balances and Hydrochar Yield

Carbon recoveries in all experiments ranged from 90 - 113%. The observed time-dependent carbon distribution trends are similar to that reported by others (e.g., Knezevic et al., 2009, 2010; Li et al., 2013; Lu et al., 2012; Lu et al., 2013; Lu et al., 2014; Lu and Berge, 2014), during which the fraction of carbon found in the solid-phase decreases, while the fractions in gas-phase increase and fractions in the liquid increase and subsequently decrease. After carbonization reactions are complete, the fraction of carbon in the solid, liquid, and gas-phases stabilizes. Results also suggest that the reaction temperatures investigated in this work impart a small influence on carbon distribution following reaction completion; during early times, temperature plays a more significant role on carbon distribution. The fraction of carbon found in the liquid and solid-phases when carbonizing only food waste differs from that found when carbonizing mixed food and packaging wastes. A greater fraction of carbon is integrated within the solids when carbonizing in the presence of packaging materials. Conversely, a slightly lower fraction of carbon is found in the liquid-phase when carbonizing in the presence of packaging materials (Figure 1). Based on these carbon distribution data, carbonization reactions are complete after approximately 4 hours, as evidenced by little changes in carbon distribution following this reaction time.

Trends associated with hydrochar yield are also consistent with that previously reported for a variety of feedstocks (e.g., Li et al., 2013; Lu et al., 2012; Lu and Berge, 2014). The solids recovered decrease with both reaction time and temperature (Figure 2), resulting from the increased transfer of components of the feedstock to the liquid and gas-phases that occurs at higher reaction temperatures and/or longer reaction times. Hydrochar yields associated with experiments conducted with mixed food and packaging wastes are similar to those achieved when carbonizing at 225 °C. These data also suggest that transfer of inorganic compounds from the solid-phase to the liquid or gas-phases continue after organic carbon-based transformations are complete; at 275 °C, the solid yields do not appear to have stabilized until after 8 or 16 hours.

The solids recovered from the carbonization of food waste and packaging materials separately were used to predict the mass of solids recovered when carbonizing food waste in the presence of packaging materials following procedures outlined by Li et al (2013) and Lu and Berge (2014). Results from this analysis indicate that solid recoveries are relatively uninfluenced by the presence of packaging materials, with the ratio of the predicted to experimental values ranging from 0.90 to 0.98 (Figure 3a).





(C)

Figure 1. Distribution of carbon following the carbonization of food waste and mixed food and packaging wastes in the: (a) solid-phase, (b) liquid-phase, and (c) gas-phase. Error bars represent the standard deviation of the conducted experiments. Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which only packaging was carbonized are represented by the abbreviation of P. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation of P. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.



Figure 2. Solids recoveries resulting from the carbonization of food waste and mixed food and packaging wastes at all reaction times evaluated. Error bars represent the standard deviation of the conducted experiments. Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which only packaging was carbonized are represented by the abbreviation of P. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.



Figure 3. Ratio of predicted and actual parameters when carbonizing mixed food and packaging materials at 250 °C: (a) solid-phase and (b) liquid-phase.

1.2 Nutrient Fate

1.2.1 Separated Food Waste

The influence of reaction time and temperature on nutrient fate resulting from food waste carbonization differs for each nutrient evaluated. Total recovered nitrogen (from the solid and liquid-phases) ranged from 89 – 130%, with the average total recovery reducing with reaction time. This result suggests that the presence of gas-phase nitrogen species is possible, with their concentrations slightly increasing with reaction time. Gas-phase nitrogen species were not measured in these experiments. Funke (2015) measured small concentrations of N2O (volume fractions of up to 0.001) when carbonizing different digestates. Gas-phase ammonia-nitrogen presence is not expected in these studies because conditions are not conducive to ammonia-nitrogen partitioning to the gas-phase; gas samples are taken in cooled systems following carbonization and in which the pH of the process water is always < 7. It should be noted, however, that at the high temperatures experienced during carbonization, gas-phase ammonia may be present. If collecting such gas for heat recovery, measurement of real-time ammonia concentrations at the elevated temperatures is necessary.



Figure 4. Fraction of total nitrogen in the solid-phase. Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.







Figure 5. Fraction of nutrients in the liquid-phase: (a) total nitrogen, (b) phosphorus, (c) potassium, (d) sodium, (e) calcium, and (f) magnesium. Error bars represent the standard deviation of the conducted experiments. Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.

Reaction temperature and time appear to impart only a small influence on nitrogen fate (Figure 4 and 5). Changes due to reaction temperature and time are most significant at early reaction times. The majority of initially present nitrogen (> 50%) remains integrated within the solid-phase at all reaction temperatures and times. Total nitrogen concentrations in the liquid-phase are also uninfluenced by reaction temperature and time. However, liquid-phase ammonia-nitrogen concentrations are impacted by reaction temperatures and longer times (Figure 6), similar to those reported by Kruse et al. (2016). These results suggest that once the organic fraction of nitrogen is released to the liquid-phase, conversion to ammonia-nitrogen occurs. Conversion of organic-nitrogen to ammonia under high temperature and pressure environments has been previously reported (Sato et al., 2014).

The majority of initially present potassium (> 75%) and sodium (> 75%) reside in the liquidphase following carbonization of food waste, with specific reaction conditions imparting little influence on this distribution (Figure 5) after 4 hours. Potassium and sodium have large water solubilities, so this result is expected. This is also consistent with many previously published reports (e.g., Funke 2015; Funke et al., 2013).

Phosphorus fate does depend on reaction time and temperature. Phosphorus integration within the liquid-phase decreases with reaction temperature and time (Figure 5b). This decreasing trend of phosphorus in the liquid-phase corresponds to increases in the fraction of initially present phosphorus integrated within the solid-phase as the reaction time and temperature increase (note that the trend associated with the solid-phase is a result of a calculation). These trends may result from precipitation with cations present in the process water (e.g., calcium, magnesium, aluminum, iron) and/or integration within the solids via sorption. The pH of the process water following carbonization increases with reaction time, but is always less than 6.6, with higher pH values resulting when carbonizing at higher reaction temperatures. This increase in pH correlates with the increasing trend of phosphorus integration within the solids, suggesting this integration may result from precipitation-induced phenomena. Phosphate sorption to any deposited and active iron and/or aluminum sites is also possible, which has been observed in soils and clays (e.g., Giesler et al., 2005; Takaya et al., 2016; Violante and Pigna, 2002).



Figure 6. Ammonia-nitrogen concentrations in the liquid-phase for all reaction temperatures, times, and feedstocks evaluated. Error bars represent the standard deviation of the conducted experiments. Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.

Based on results from solid-phase ³¹P-NMR (Figure 7a contains some representative spectra), fractions of initially present phosphoesters (e.g., lipids) in the food waste are hydrolyzed to phosphates as food wastes are carbonized. Following 24-hours of carbonization, some phosphoesters remain integrated within the solids at all evaluated reaction temperatures, suggesting either sequestration and/or incomplete conversion of the initially present phosphorus-containing material. Based on comparisons between the normalized aggregate areas (area/number of scans) of the phosphoester regions present in the ³¹P-NMR spectra, reaction time, temperature, and presence of packaging materials play a role in phosphoester hydrolysis (Figure 7b). The phosphoester content of the solids generated at the different reaction temperatures when carbonizing only food wastes is smallest after carbonizing for 24 hours and decreases with increasing reaction temperature. The presence of phosphate in the solids is observed at all reactions times when carbonizing at 225 and 275°C, respectively, consistent with the relative degree of hydrolysis occurring at each temperature. The presence or absence of phosphoester with the relative degree of hydrolysis occurring at each temperature.

hydrolysis, phosphate dissolution in the liquid-phase, interaction with metal complexes, and/or instrument detection limits. Phosphate-metal precipitates may be formed, which are difficult to distinguish using standard ³¹P-NMR. These results differ from those reported for the carbonization of sewage sludges. Huang and Tang (2015) report that all initially present phosphoesters are hydrolyzed when carbonizing sewage sludges. However, initially present phosphoesters in the sludges are significantly lower than those found in food waste. Liquid-phase ³¹P-NMR results from select process waters indicate that > 99% the phosphorus present in the process water is in the form of phosphate (data not shown).

The majority of initially present calcium (> 50%) also remains integrated within the solidphase at the majority of the reaction times and temperatures (Figure 5). After 4 hours, reaction temperatures and time appear to impart a slight influence on calcium fate. Integration of calcium within the solid-phase increases with reaction temperature. After a reaction period of 4 hours, calcium integration within the solid-phase stabilizes. Similarly, with the exception of carbonizing for 1 hour, the majority of magnesium remains integrated within the solid-phase (Figure 5). The degree of this integration increases with reaction temperature and time, with trends stabilizing after 16 hours for all reaction temperatures.





Figure 7. ³¹P-NMR results from hydrochar generated during the carbonization of food and mixed food and packaging wastes: (a) representative ³¹P-NMR spectra for food waste and hydrochars generated when carbonizing at 250°C and (b) normalized phosphoester areas detected in the hydrochars generated at select reactions times and temperatures (note that the lines are provided for visual guidance). Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.

1.2.2 Influence of Packaging Material Presence

The nutrient masses resulting from the carbonization of food waste and packaging materials separately in both the solid and liquid-phases can be used to predict the distribution of each nutrient in the mixed food waste and packaging experiments. Results from this analysis, coupled with experimental results (Figure 5), indicate that the presence of packaging materials does influence the fate of most of the nutrients evaluated.

All solid-phase nutrients, with the exception of magnesium, are under-predicted (Figure 3a), suggesting the presence of packaging materials promotes either nutrient precipitation, nutrient chemical incorporation within the solid matrix during carbonization, and/or nutrient sorption to the solids, leading to their greater retention in the solid-phase. It is not possible to determine which (or if all) of these processes cause greater nutrient retention in the solid-phase. Although the total nitrogen content of the solid-phase is under-predicted, the ratios of predicted to experimental values (1.0 to 0.83) suggest such predictions are reasonable.

The composition of packaging materials (e.g., paper, plastics, and cardboard) may promote enhanced nutrient precipitation. The cardboard and paper components of the packaging materials used in this work contain approximately 8 and 3 times more calcium than that found in the food waste. In addition, packaging materials typically contain significantly greater levels of iron, aluminum, and chromium (Li et al., 2015) than food wastes, all potentially contributing to possible enhanced precipitation and/or sorption. The pH of the process water following carbonization of mixed food and packaging materials is always less than 4.7, suggesting precipitation in these experiments may be limited. Enhanced sorption of phosphate to active aluminum or iron sites on the hydrochar may also occur (e.g., Giesler et al., 2005; Takaya et al., 2016; Violante and Pigna, 2002).

Based on comparisons between the normalized aggregate areas of the phosphoester regions present in the ³¹P-NMR spectra, the presence of packaging materials decreases (or slows down) phosphoester hydrolysis (Figure 7b). In addition, when carbonizing food and packaging materials, no phosphates are observed in the solids, only phosphoesters. The presence or absence of phosphate in solids may be indicative of either kinetic effects associated with phosphoester hydrolysis, phosphate dissolution in the liquid-phase, interaction with metal complexes, and/or instrument detection limits.

Greater integration of potassium and sodium in the solids is not likely due to precipitation because of their high water solubilities. Instead, it is more likely greater retention of these nutrients is due to either sorption and/or incorporation within the solid matrix during carbonization. Incorporation of greater calcium in the solid-phase may result from either sorption or precipitation.

1.3 Nutrient Availability

Because the majority of the nitrogen and phosphorus found in the food waste remains integrated within the solids following carbonization, a series of leaching experiments were conducted to determine availability of nutrients in the hydrochar when applied to soil as an amendment. Nitrogen and phosphorus present in the dried solids result from either: (1) processes occurring during hydrothermal carbonization (e.g., chemically integrated with the solids and/or sorbed on the solid matrix) or (2) are a result of deposition of nutrients present in the bound process water during solids drying. It is assumed that nutrients deposited during solids drying and those sorbed on the solids matrix are more loosely bound than those integrated within the solids matrix via chemical reactions.

Results from experiments associated with the leaching of total nitrogen from hydrochars generated from food waste with and without packaging material suggest that the majority of leached nitrogen is from the nitrogen deposited on/within the hydrochar matrix during the evaporation of bound process water (Figure 8). At each reaction condition, the mass of nitrogen deposited on the hydrochar from liquid evaporation (based on the mass of nitrogen in the liquid that is evaporated during oven drying) is always greater than the mass of released total nitrogen (Figure 8), except for the mildest carbonization condition (e.g., 225 °C and 1 hr). These results suggest that, at least in the short term, most nitrogen is either tightly bound within the solid matrix or is present in an insoluble form and is unlikely to be released in the liquid-phase. It should also be noted that carbonization at more mild conditions (e.g., lower reaction times and shorter reaction temperatures) may reduce the fraction of tightly bound nitrogen or formation of high molecular weight insoluble nitrogen, as suggested by the result at 225 °C and 1 hour; more experiments at such conditions are needed to substantiate this hypothesis. It is possible

that additional nitrogen will be released from the solids if hydrochar degradation occurs. These results also suggest that is may be more beneficial to recover nitrogen from the process water.

Results associated with the release of solid-phase phosphorus are different. Almost all of the phosphorus present in the solids at reaction temperatures of 225 and 250 °C is released (Figure 9). At a reaction temperature of 275 °C, smaller fractions of the total phosphorus present in the solids are released as reaction times increase, likely due to increased solids recalcitrance (e.g., Enders and Lehman, 2012). These results suggest that recovery of phosphorus from the solids is feasible, and when considering strategies for using hydrochar as a fertilizer, reaction temperatures should remain below 275 °C.



Figure 8. Comparison between the total nitrogen deposited in the hydrochar from process water evaporation and the total nitrogen released from the sequential extraction experiments. Error bars represent the standard deviation of the conducted experiments.



Figure 9. Percentages of phosphorus released during the sequential extraction experiments. Error bars represent the standard deviation of the conducted experiments.

1.4 Potential Environmental Implications

A potential environmental benefit associated with using HTC to treat/manage food wastes is the ability to recover and use the nutrients embedded within these wastes. Accomplishing this nutrient recycling has the potential to reduce the need for acquiring virgin nutrients required to produce chemical fertilizers, ultimately reducing the stresses on current nutrient supplies and reducing the energy required with this acquisition. Recycling of nutrients from products resulting from HTC may occur separately or simultaneously from the liquid and solid-phases.

1.4.1 Nutrient Recovery from the Solid-Phase

Using the experimental data obtained from this work (e.g., solid yields and leaching of solidbound nutrients), estimates of potential nutrient recovery from currently landfilled food wastes were performed. Table 1 contains the information used to estimate the amount of fertilizer that can be replaced by recycling nutrients following the carbonization of food wastes. These calculations were performed for a range of food waste masses diverted from landfills (10 to 100% diversion). Figure 10 shows the average percentages of nitrogen and phosphorus fertilizers that can be replaced with nutrients available from the hydrochar. Table 2 presents the HTC conditions yielding the maximum hydrochar nutrient recovery, as well as the percentage of fertilizer used in the US in 2011 that can be replaced with the hydrochar generated from food waste carbonization. These results indicate that the generated hydrochar can replace only a small fraction of the currently used nitrogen and phosphorus-based fertilizers (0.61% and 2.06%, respectively). Although these fractions are not large, substitution of these fertilizes with the recovered nutrients from food wastes would alleviate the dwindling phosphorus supply. In addition, mostly non-renewable energy used for synthesizing chemical fertilizers will be reduced. Table 3 presents the energy savings resulting from replacing chemical fertilizers with recycled nutrients from the hydrochar (note that this value does not include any energy-related needs/savings associated with the HTC process). It should also be noted that the hydrochar contains appreciable levels of secondary nutrients, particularly calcium and magnesium. Leaching experiments were not conducted to evaluate the availability of these nutrients, but it is likely that some of them may be slowly released in soils, providing an extra benefit.

Parameter	Value	Source
Landfilled Food Waste	26.7 million tonnes	USEPA, 2016
Food Waste Moisture Content	70 % (wet wt.)	Tchobanoglous, 1993
Amount of phosphorus (as P ₂ O ₅)-based fertilizer		
used in 2011 in the US	3.92 million tonnes	USDA, 2013
Amount of nitrogen (as N)-based fertilizer used in		
2011 in the US	11.65 million tonnes	USDA, 2013
Amount of potassium (as K ₂ O)-based fertilizer used		
in 2011 in the US	4.16 million tonnes	USDA, 2013
Energy required to manufacture phosphorus-based		
(as PO ₄ ³⁻) fertilizer	7,700 kJ/kg	Gellings and Parmenter, 2004
Energy required to manufacture nitrogen-based		
fertilizer	69.530 kJ/kg	Gellings and Parmenter, 2004

Table 1. Data used to estimate the amount of fertilizer that can be replaced by recyclin	g
nutrients following the carbonization of food wastes.	



Figure 10. Percentage of nitrogen and phosphate fertilizers that can be replaced by nutrients released from the hydrochar: (a) nitrogen and (b) phosphate. Each bar represents the average value associated with all reaction times evaluated. Error bars represent the range (max and min) of the data at each condition. Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.

Nutrient	Reaction Temperature (°C)	Reaction Time (hr)	Recoverable Nutrient Mass (mg/g dry hydrochar)	% Replacement of fertilizer used in 2011
Total Nitrogen	225	1	11.1	0.61
Phosphorus (as P ₂ O ₅)	250	1	13.8	2.06

Table 2. Maximum nutrient recovery from the solid-phase*.

*Assuming 100% diversion of food wastes from landfills in the US

Table 3. Energy savings associated with replacing virgin fertilizer with hydrochar-based fertilizer (kl).

Carboniza	tion Conditions	Nitrogen Fertilizer		r Phosphate Fertilizer	
Feedstock	Temperature	min	max	min	max
FW	225	1.66E+12	4.91E+12	5.74E+11	7.68E+11
FW	250	1.40E+12	4.18E+12	6.64E+11	8.33E+11
FW	275	5.54E+11	4.11E+12	1.49E+11	7.04E+11
FW + P	250	5.65E+11	3.16E+12	4.24E+11	5.88E+11

1.4.2 Nutrient Recovery from the Liquid-Phase

Recovery of nutrients from the process water may also be possible. Table 4 presents the HTC process conditions in which the maximum nutrient recovery in the liquid is achieved, as well as the percentage of fertilizer used in the US in 2011 that can be replaced by recycling these nutrients from food waste. The information in this table is based on the data in Table 1 and assuming 100% of food wastes landfilled are carbonized. It is important to note that these calculations assume that only nutrients found in the process water drained via gravity will be applied as a fertilizer. Additional nutrient recovery from the liquid will be possible if liquid recovery via mechanical processes occurs. Du et al. (2012) report that diluted process water can serve as an effective fertilizer for cultivating microalga Chlorella vulgaris, suggesting that this assumption may be valid. Conversely, Bargmann et al. (2013) report components present in HTC process water adversely influence plant growth/germination. However, no studies specifically evaluating the ability of the process water from food wastes and mixed food and packaging wastes to serve as an effective fertilizer have been reported in the literature. Additional studies are necessary to confirm that the other organic compounds present in the liquid do not cause any inhibitory effect on plant growth or present any environmental concerns. If using the process water as a fertilizer, secondary nutrients will also be added to the soil. The nutrient mass per mass of wet food waste of each of these nutrients is provided in Figure 11.

1.4.3 Combined Nutrient Recovery from the Liquid and Solid-Phases

The carbonization process conditions associated with optimal nitrogen and phosphorus recovery from the solid and liquid-phases are different (Tables 2 and 4). The optimal HTC process conditions for the maximum possible recovery of the nutrients from both hydrochar and its process water are shown in Table 5. Using these data, it is estimated that up to 0.96% and 2.30% of nitrogen and phosphorus-based fertilizers in the US (accounting for recovery from both hydrochar and the process water), respectively, can be replaced by the nutrients integrated

within hydrochar and process water generated from the carbonization of currently landfilled food wastes.

Tuble 4. Maximum nathent recovery nom the inquiti phase .						
Nutrient	Reaction Temperature (°C)	Reaction Time (hr)	Recoverable Nutrient Mass (mg/g wet food waste)	% Replacement of fertilizer used in 2011		
Total Nitrogen	275	16	2.9	0.66		
Phosphorus (as P ₂ O ₅)	275	8	1.05	0.71		
Potassium (as K ₂ O)	275	24	2.06	1.32		

Table 4. Maximum nutrient recovery from the liquid-phase*.

*Assuming 100% diversion of food wastes from landfills in the US

Table 5. Optimal operating conditions for maximum average combined nutrient recovery from the solid and liquid-phases*.

Nutrient	Reaction Temperature (°C)	Reaction Time (hr)	% Replacement of fertilizer used in 2011
Total Nitrogen (as N)	225	1	0.96
Phosphorus (as P ₂ O ₅)	250	24	2.30

*Assuming 100% diversion of food wastes from landfills in the US





Figure 11. Time and temperature dependent availability of secondary nutrients in the liquid: (a) sodium, (b) calcium, and (c) magnesium. Experiments in which only food waste was carbonized are represented by the abbreviation of FW. Experiments in which mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.

2.0 Nutrient Extraction from the HTC Process Water Via Struvite Precipitation

Figure 12 shows the pH, phosphate, and ammonia levels over 36 hours in a simulated nutrient solution with a 1:1 P:N and 1.3:1 Mg:N ratio with different levels of NaOH addition. Upon addition of MgCl₂ and NaOH, the solution pH increased from an initial value of 4.2 to greater than 8.0 (Figure 12c), a range that has been reported to be favorable to struvite precipitation (Booker et al., 1999, Miles and Ellis, 2001, Wang et al., 2005). Higher amounts of NaOH addition resulted in higher pH levels during the experiments, with the highest pH recorded immediately after NaOH was added to solution. The pH slightly drifted downward with time, with a corresponding slight increase in phosphate (Figure 12a) and decrease in ammonia concentrations (Figure 12b). This continuous change in solution composition indicates that precipitation is not complete and struvite precipitation kinetic limitations exist. The pH (Figure 12f) and phosphate (Figure 12d) in the control experiments remained relatively constant. Slight decreases in the ammonia concentrations were observed (Figure 12e) with ammonia removal of 37% over 36 hours recorded with 19.3 mL of added NaOH. The pH in this specific control experiment was > 9.7, and ammonia removal is due to stripping. Figure 12b shows that the decrease in ammonia occurred primarily in the first hour, during which decreases in ammonia in the control experiments (Figure 12e) were less than 12%. Because precipitation kinetics is generally faster than the rate of mass transfer of ammonia from the liquid phase to the gas phase, most of the disappearance of ammonia in solution can be attributed to struvite precipitation, especially when the pH during active precipitation is lower than the pKa value for ammonia (=9.3).

Visual MINTEQ was used to explain the complex inter-relationship between pH and precipitate formation. Although Visual MINTEQ is an equilibrium modeling software and does not inherently capture the kinetic limitations observed in the experiments, equilibrium models can be used to simulated ultimate endpoints in the process. The equilibrium model can also be used to evaluate the effects of specific parameters (e.g., type of precipitate formed), which cannot be naturally separated or controlled in precipitation experiments. Figure 13 shows the simulated pH when the initial solution is titrated with a 5 N NaOH solution. Also shown are the pH values immediately following NaOH addition and at 36 hours in the experiments in Figure 12c. If precipitate formation were artificially excluded from the model, the pH is predicted to reach values greater than 9.5 based on the volume of NaOH added in the experiments. Precipitate formations. The model indicates that the precipitation reactions are still incomplete; changes in solution composition can still be expected after 36 hours.

Figure 14 shows the predominant precipitates predicted at equilibrium with different amounts of NaOH added are MgHPO₄·3H₂O and struvite. MgHPO₄·3H₂O precipitate forms immediately with small amounts of NaOH added to solution. This is coupled with a decrease in Mg²⁺ and phosphate in the system. A slight decrease in NH₄⁺ occurs because of dilution during the titration simulation. Struvite forms when 9.7 mL of NaOH is added, which corresponds to a solution pH of 5.9. Struvite ultimately dominates beyond 14.6 mL of added NaOH, where the pH is greater than 6.5. Small amounts of Mg₃(PO₄)₂ are predicted beyond 19.5 mL of added NaOH (pH>7.5). Mg(OH)₂ and MgO are not predicted to form within the experimental/simulation conditions.



Figure 12. (a) Phosphate, (b) ammonia, and (c) pH for different volumes of added 5N NaOH for a simulated nutrient solution with a 1:1 P:N ratio and a 1.3:1 Mg:N ratio. (d) Phosphate, (e) ammonia, and (f) pH for different volumes of added 5N NaOH for a simulated nutrient solution without the addition of MgCl₂.



Figure 13. Equilibrium pH predicted for the simulated nutrient solution in the presence and absence of precipitates. Also plotted are the experimental pH values at time = 0 hours and 36 hours from Figure 1c.



Figure 14. Predicted total dissolved and precipitate species in the simulated nutrient solution with different amounts of NaOH added.

The type of precipitate formed affects the nature of pH changes in solution. Figure 15 shows the pH predicted if only MgHPO₄· $3H_2O$ or struvite is formed. The solution pH decreases with

MgHPO₄ formation at a pH < 9 because of the combination of reactions,

$$Mg^{2+} + HPO_4^{2-} \rightarrow MgHPO_4 \cdot 3H_2O_{(s)}$$

$$H_2PO_4^{-} \rightarrow HPO_4^{2-} + H^+$$
(2)

Although $H_2PO_4^{2-}$ predominates at pH values between the pK_{a,2} and pK_{a,3} values of phosphate (i.e., between 7.2 and 12.3), phosphate speciation shifts due to reaction (2) when reaction (1) proceeds. This shift causes a release in H⁺ equivalents and a decrease in pH. In contrast, at a pH > 10, the shift in phosphate equilibrium occurs due to reaction (3), resulting in an uptake of H⁺ equivalents and an increase in pH,

$$PO_4^{3-} + H^+ \rightarrow HPO_4^{2-} \tag{3}$$

In ideal solutions containing only phosphate, the exact pH where the shift in pH increase/decrease occurs is at the midpoint of the $pK_{a,2}$ and $pK_{a,3}$ values (i.e., a pH of (7.2 + 12.3)/2 = 9.75). This exact value will shift when other species present in solution interact with phosphate species. These species are cation-phosphate complexes (e.g., $KH_2PO_{4(aq)}$, $K_2HPO_{4(aq)}$, $KHPO_{4^-}$) that are accounted for in the equilibrium model. The pH value for the shift in the solution simulated is this case is 8.6.

Figure 15 also shows that except at extremely high pH values, struvite formation always results in a decrease in pH due to the release of H⁺ equivalents in the reaction,

$$Mg^{2+} + NH_4^{+} + H_n PO_4^{3-n} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O_{(s)} + nH^+$$
(4)

where n=0,1,2 (Li et al., 2012). The continuous decrease in pH observed in Figure 15 and Figure 1c coupled with the decrease in ammonia concentrations in Figure 1b indicate that struvite precipitation is incomplete. Because of the complex structure and composition of the amorphous precipitate in reaction (4), ammonia diffusion into an MgHPO₄ solid limits the formation of struvite.



Figure 15. Predicted pH changes in the simulated nutrient solution if either MgHPO₄·3H₂O_(s) or struvite precipitates in solution with different amounts of NaOH added. Also plotted are the experimental pH values at time=0 hours and time =36 hours from Figure 1c.

Figure 16 shows the complex relationship between pH, predominant precipitates, and total dissolved species at equilibrium for our experimental conditions. A decrease in pH results in an increase in total dissolved phosphate at equilibrium. This is consistent with the observations in Figure 1a where phosphate levels slightly increase with time as the pH decreases. Although the total dissolved ammonia is also shown to increase with a decrease in pH at equilibrium, the experimental ammonia levels are still far away from equilibrium such that diffusion of ammonia into the precipitate to form struvite dictates the overall observed changes in ammonia. Table 6 shows the predicted equilibrium concentrations of ammonia and phosphate as well as the experimental observations after 36 hours. The observed values indicate that the system with 18 mL of added NaOH is closest to equilibrium while the other systems are not. In the other systems, ammonia is expected to decrease beyond 36 hours as it is incorporated into MgHPO₄ and precipitated as struvite, resulting in a decrease in pH and an increase in phosphate concentrations. Ammonia stripping is also possible when the pH of the system at high pH values. Further experiments were designed with shorter reaction times to limit ammonia stripping,



Figure 16. Predicted total dissolved and precipitate species in the simulated nutrient solution at different pH values.

Table 6. Predicted equilibrium and observed pH, phosphate, and ammonia levels after 36 hours
for various volumes of NaOH added to a 500 mL solution.

Solution Component		mL of 5N NaOH added			
		18	18.5	19	19.3
рН	Observed	7.45	8.07	9.27	9.665
	Predicted	6.69	6.83	7.05	7.25
PO₄, mg/L	Observed	190	17	3	2
	Predicted	188	175	161	153
NH4-N, mg/L	Observed	218	215	314	263
	Predicted	235	169	104	65

Equilibrium calculations show that high levels of pH are desirable for struvite formation, but experimental results show a slow decrease in ammonia concentration over extended time periods. A strategy of initial pH adjustment followed by the periodic addition of MgCl₂ and NaOH was tested to allow fresh MgHPO₄·3H₂O_(s) surfaces to be formed that can be transformed to struvite. Figure 17 shows that the equilibrium predictions follow the experimental data reasonably well. There is a slight overprediction in the phosphate levels, and an underprediction in NH₄-N at times > 60 min, indicating that equilibrium is still not achieved. The overall trend in pH is captured by the model, with the initial drop in pH indicative of struvite formation and the rise in pH after 48 minutes caused by the final addition of NaOH. The control experiment with no MgCl₂ addition showed an initial pH of 9.74 that increased with the periodic NaOH addition, with a pH of 10.8 registered at 60 minutes. The ammonia removed through mixing/stripping at such high pH was 7.9%. The same amount of ammonia stripping is not expected during the precipitation experiments because the pH was less than the ammonia pKa 12 minutes after the experiment started.



Figure 17. (a) Phosphate, (b) ammonia, and (c) pH when an initial pH adjustment was followed by periodic MgCl₂ and NaOH addition for a simulated nutrient solution with a 1:1 P:N ratio and a 1.3:1 Mg:N ratio.

Assuming that all observed ammonia removal from solution was incorporated into struvite, Table 7 shows struvite formation as a percentage of initial ammonia present during periodic vs single dosage addition of MgCl₂ and NaOH. Maximum struvite formation is observed with initial pH adjustment and periodic MgCl₂ and NaOH addition. This approach is adopted for the remainder of the study.

Experimental Protocol	Struvite formed
Periodic MgCl ₂ and NaOH addition (total 19.5 mL)	90%
Single dose MgCl ₂ + 18 mL 5 N NaOH	86%
Single dose MgCl ₂ + 18.5 mL 5 N NaOH	85%
Single dose MgCl ₂ + 19 mL 5 N NaOH	85%
Single dose MgCl ₂ + 19.3 mL 5 N NaOH	84%

Table 7. Struvite formed after 1 hour with different experimental protocols.

Because the equilibrium model reasonably described the fate of ammonia and phosphate during periodic addition of MgCl₂ and NaOH, the model was used to calculate the amount of NaOH added to maximize struvite formation for different P:N and Mg:N ratios in the 1/10 scale simulated nutrient solution experiments. The same approach was used for the HTC process water except that NaOH titration was initially performed to evaluate the buffer capacity of the system and provide a basis for the amount of NaOH that had to be added to the system. Using the concentrations of the measured compounds, the titration curve was simulated using Visual

MINTEQ. Figure 18 shows that the titration behavior predicted from the measured concentrations was poor. Although the acetate concentration for the system was known, it is possible that other volatile fatty acids with a similar pKa to acetic acid were present in the system. It is also reasonable to assume that other organic buffers are present because of the high COD of the process water. Additional acetate was arbitrarily selected to represent these other buffering species. The additional acetate concentration was varied in 0.01M intervals and the total concentration with the smallest sum of the squares of the differences between the data and the model calculations was selected. Figure 17 shows the best fit where the acetate concentration was 0.25 M. The reasonable model fit justifies the selection of acetate to represent the additional buffer species.



Figure 18. Titration of HTC process water and equilibrium model calculations.

Figure 19 shows the that the amount of struvite formed as a percent of the maximum possible struvite formation is proportional to the P:N ratio when an excess of MgCl₂ is added to solution (Mg:N > 1.0) up to a P:N ratio of 0.8. Struvite formation levels off beyond a P:N of 0.8 due to kinetic limitations. The P:N ratio in the HTC process water was only 0.3, with an observed struvite formation of 22%. In addition to MgCl₂ addition, phosphate would have to be amended to the HTC process water to recover ammonia and maximize struvite formation.


Figure 19. Struvite formation for different P:N ratios for pH adjustment with periodic MgCl₂ and NaOH addition after a 1 hour reaction period.

Figure 20 shows a tendency of the equilibrium model to overpredict the experimentally observed amount of struvite formed as a percent of the maximum possible struvite formation. Despite the complexities of the HTC process water chemistry and the kinetic limitations in the system, the equilibrium model can still be used to serve as a rational chemical basis for guiding experiments and to predict struvite precipitation. With this confidence in the equilibrium model calculations, the effects of different sources of magnesium for struvite precipitation were evaluated. Figure 21 shows that the amount of struvite formed when using MgSO₄ is practically the same as when using MgCl₂ for conditions identical to Figure 14. Adding MgO is also possible, but its solubility is extremely low. It is anticipated that if struvite precipitation is implemented on a larger scale to recover nutrients, concentrated MgCl₂ and MgSO₄ solutions will be added to HTC process water. On the other hand, MgO will require the addition of an acid to create a concentrated solution and will incur additional unnecessary costs. If added directly as a solid, slow MgO dissolution kinetics have been reported to limit struvite precipitation (Li et al., 2012). Thus, the form of magnesium added to the HTC process water will ultimately be determined by the relative cost of MgCl₂ or MgSO₄.



Figure 20. Equilibirum model predictions and experimentally observed struvite formation for periodic MgCl₂ and NaOH adjustment after a 1 hour reaction period.



Figure 21. Equilibrium model predictions for different forms of Mg²⁺ addition for a simulated nutrient solution.

3.0 Feasibility of Acetic Acid and 5-Hydroxymethylfurfural Recovery from HTC Process Water

- 3.1 Acetic Acid Concentrations and Recovery
- 3.1.1 Process Water Concentrations

Acetic acid concentrations in the process water at each reaction time and temperature are presented in Figure 22. The largest average concentrations of acetic acid (~16 g/L and 18 g/L) were observed when hydrothermally carbonizing food waste at 275°C for 16 hours and carbonizing mixed food and packaging wastes at 250°C for 16 hours. Reaction times appear to impart a negligible impact on acetic acid trends. Reaction temperature, however, does appear to influence acetic acid concentrations. Concentrations in the process water when carbonizing at 275°C are larger than those obtained when carbonizing mixed food and packaging materials are larger than can be explained by those in the process water when separately carbonizing food and packaging materials (Figure 22b). It is possible that this occurs because of the presence of a catalyst that promotes food waste decarboxylation. However, the mechanisms associated with these increased acetic acid concentrations are currently unknown.





Figure 22. Acetic acid concentrations in process water following the carbonization of: (a) food waste only and (b) mixed food and packaging wastes.

Table 8 presents a comparison between acetic acid concentrations and/or masses measured in this study with those reported in the literature for a variety of feedstocks that have been carbonized over a variety of reaction times and temperatures. As shown, the range of concentrations measured in the process water in this study are significantly greater than those associated with the carbonization of other studies. Acetic acid is generated during feedstock hydrolysis and, based on literature-reported data, is not converted or incorporated within the char over time (e.g., Basso et al., 2013; Lu et al., 2013). It should be noted, however, that comparing the acetic acid masses generated when carbonizing food and/or mixed food and packaging wastes in this study to other literature-reported studies is complicated and should be done with caution. It is likely that reaction kinetics, which vary with reactor volume, initial solids concentration, and reaction temperature, influence acetic acid formation.

Using the experimental data obtained from this work (e.g., acetic acid concentrations and liquid recovery), estimates of acetic acid masses that have the potential to be recovered from currently landfilled food wastes were performed. Table 9 contains the data used to estimate these masses. These calculations were performed for two conditions: (1) all liquid containing acetic acid is recovered (even liquid remaining bound in the generated hydrochar following gravity drainage), representing a true maximum value and (2) the potentially recoverable acetic acid mass if only recovering this compound in process water that drains from the system via gravity. For each of these conditions, the maximum and minimum acetic acid values were used to generate the potential range of recoverable acetic acid. These calculations were performed for a range of food waste masses diverted from landfills (10 to 100% diversion). Figure 23 presents the results from this analysis for food waste alone (Figure 23a) and mixed food and

packaging wastes (Figure 23b). The potential recoverable mass of acetic acid is quite large, representing a viable source of this compound.

Feedstock	Reaction	Reaction	Solids	Concentration in	% of dry	Source
	Temp (°C)	Time (hr)	Concentratio	the liquid (g/L)	feedstock	
			n			
Food waste	225	1 - 24	36%	9.8 - 12.7	21 - 24	This study
Food waste	250	1 - 24	36%	9.4 - 12	20 - 22	This study
Food waste	275	1 - 24	36%	4 - 19	18 - 36	This study
Mixed food and	250	1 - 24	46%	9.8 - 19	18 - 24	This study
packaging wastes						
Packaging wastes	250	1 - 24	17%	6.5 – 7.5	36 - 40	This study
Tahoe mix	155 - 295	0.5	11.3%		0.14 - 4.56	Hoekman et al., 2013
Loblolly pine	175 - 295	0.5	11.3%		0.40 - 5.20	Hoekman et al., 2013
Pinyon/Juniper	175 - 295	0.5	11.3%		0.66 - 5.83	Hoekman et al., 2013
Sugarcane Bagasse	175 - 295	0.5	11.3%		1.15 - 8.11	Hoekman et al., 2013
Corn stover	175 - 295	0.5	11.3%		0.79 - 8.43	Hoekman et al., 2013
Rice hulls	175 - 295	0.5	11.3%		0.76 - 6.51	Hoekman et al., 2013
Dry poplar wood	220	4	5%	8.5		Stegman et al. 2013
chips						
Wheat straw	190 - 270	6	4 – 7%	1 – 2.3		Becker et al., 2014
Wheat straw	190 - 270	6	4 – 7%	0.8 - 1.6		Becker et al., 2014
digestate						
Poplar wood	190 - 270	6	4 – 7%	1.6 - 2.6		Becker et al., 2014
Pine wood	190 - 270	6	4 – 7%	0.6 - 1.3		Becker et al., 2014
Massaranduba	190 - 270	6	4 – 7%	0.8 - 2.1		Becker et al., 2014
Garapa	190 - 270	6	4 – 7%	0.2 - 1.9		Becker et al., 2014
Xylose	190 - 270	6	4 – 7%	0.35 - 9.0		Becker et al., 2014
Cellulose	190 - 270	6	4 – 7%	0.02 - 0.3		Becker et al., 2014
Orange pomace	175 - 260	0.5 - 2	11%	1.4 - 3.7		Erdogan et al., 2015

Table 8. Acetic Acid concentrations and/or masses measured in this study compared with literature-reported values.

Table 9. Data used to estimate potential recoverable acetic acid mass.

Parameter	Value	Source
Landfilled Food Waste (in 2014)	29.4 million tons	USEPA, 2016
		Tchobanoglous,
Food Waste Moisture Content	70 % (wet wt.)	1993
Food waste only:		
Max. recoverable acetic acid:		
Complete liquid recovery (275°C, 8 hour):	557.7 mg AA/g dry waste	This study
Recovery from drained liquid only (275°C, 16 hour):	225.2 mg AA/g dry waste	This study
Min. recoverable AA:		
Complete liquid recovery (275°C, 1 hour):	179.4 mg AA/g dry waste	This study
Recovery from drained liquid only (250°C, 1 hour):	35.0 mg AA/g dry waste	This study
Mixed food and packaging waste:		
Max. recoverable AA:		
Complete liquid recovery (250°C, 16 hour):	235.9 mg AA/g dry waste	This study
Recovery from drained liquid only (250°C, 16 hours):	75.4 mg AA/g dry waste	This study
Min. recoverable AA:		
Complete liquid recovery (250°C, 4 hours):	177 mg AA/g dry waste	This study
Recovery from drained liquid only (250°C, 4 hour):	40.7 mg AA/g dry waste	This study



Figure 23. Range of acetic acid masses that have the potential to be recovered from HTC process water following the carbonization of: (a) food waste only and (b) mixed food and packaging wastes.

3.1.2 Extraction Method Development

Carboxylic acids, particularly acetic acid, have been routinely recovered from various liquid streams via reactive extraction (e.g., Hong and Hong, 2000; Hong et al., 2001; Mahfud et al., 2010; Rasrendra et al., 2011). Reactive extraction involves the use of an extracting solvent that contains a dilutent that reacts with acetic acid in the aqueous-phase, enhancing its partitioning to the solvent-phase (e.g., Hong et al., 2001). When an amine-based dilutent is used, the following reactions occur: (1) dissociation of the acid, (2) proton transfer to the amine, and (3) recombination to an ammonium salt (Hong et al., 2001). Based on previously established procedures for acetic acid extraction from different liquids (e.g., Mahfud et al., 2010), a mixture of dichloromethane (DCM) and 0.5 M tri-n-octylamine (TOA) was used. For comparative purposes, acetic acid extraction was also evaluated in DCM and THF/B. To determine the ability of each solvent to extract acetic acid from water, experiments were conducted over a range of acetic acid concentrations (5 - 15 g/L) and a range of salt concentrations (0-100 g/L). Acetic acid concentrations were measured in the aqueous and solvent-phases. Distribution coefficients (k_d , acetic concentration in the solvent-phase/acetic acid concentration in the water phase) were calculated for each extraction. The larger the k_d, the greater fraction of acetic acid in the solventphase, which is desired in this study.

Results from this analysis are presented in Figure 24 and indicate that DCM alone is ineffective at extracting acetic acid. The most effective extractant is the DCM+TOA. However, the extraction efficiency decreases with increasing salt concentrations, consistent with that reported by others (Jun et al., 2007). The conductivity associated with the process what is near the experiments conducted at 10 g/L salt. At a salt concentration of 100 g/L, the THF/B is at least equally effective at extracting acetic acid as the DCM+TOA at 10 g/L and more effective than extracting with DCM. The acetic acid concentration also influences its extraction. As acetic acid concentration increases, so does the k_d . At salt concentrations (10 g/L) and acetic acid concentrations (15 g/L) representative of what is typically found in process water, it is expected that only 50-60% of acetic acid will be extracted, irrespective of whether DCM+TOA or THF/B (with the addition of salt) is used.

3.1.3 Extraction Efficiency in Process Water

Results from extracting acetic acid from process water resulting from the carbonization of food wastes at 275°C at a reaction time of 16 hours are shown in Table 10. Because salt concentrations have a negative impact on acetic acid recovery using DCM+TOA, process water diluted in half was also extracted using DCM+TOA (conductivity of 23.1 mS/cm). Salt was added to the process water that was exposed to the THF/B extractant. Surprisingly, results from these extractions indicate that recovery of acetic acid via liquid-liquid extractions is not feasible. It is hypothesized that constituents present in the process water (other than salts) interfere with this extraction, likely reacting with the TOA and rendering it ineffective at reacting with acetic acid. Explanations for the ineffectiveness of acetic acid partitioning to the THF/B phase are currently unknown. If the desire is to recover acetic acid from the process water, alternative approaches must be investigated.



Figure 24. Distribution coefficients associated with the extraction of acetic acid (AA) using different solvent mixtures (DCM = dichloromethane, TOA = tri-n-octylamine, THF/B = tetrahydrofuran and butanol).

Solvent	Process Water Conductivity	Average k _d	% acetic acid in the solvent-
	(mS/cm)		phase
DCM+TOA	40.6	an	0
DCM+TOA	23.1	na	0
THF/B	134.1	na	0

Table 10. Results from the Extraction of Acetic Acid.*

*experiments were conducted in triplicate. Values represent averages. Acetic acid recoveries ranged from 92% to 126%, validating these results.

3.2 5-HMF Concentrations and Recovery

3.2.1 Process Water Concentrations

5-HMF concentrations in the process water at each reaction time and temperature are presented in Figure 25. The largest average concentration of 5-HMF (> 5,000 mg/L) was observed when hydrothermally carbonizing food waste at 225°C for 1 hour. 5-HMF concentrations in the process water decrease with increasing reaction temperatures and increasing reaction times. These observed time and temperature dependent trends are consistent with literature-reported information associated with 5-HMF formation and its subsequent incorporation within the hydrochar and/or conversion to other compounds (e.g., Aydincak et al., 2012; Lu et al., 2013). The high concentrations of 5-HMF measured at early reaction times are representative of 5-HMF formation via saccharide dehydration. As reactions proceed, the 5-HMF is ultimately converted into different byproducts (e.g., formic and levulinic acids) and/or incorporated within the hydrochar via polymerization and aromatization (e.g., Aydincak et al., 2012; Lu et al., 2013),

resulting in a decrease in the concentrations found in the process water. Generally, as carbonization reaction temperatures increase, the degree of solids polymerization and aromatization increases, potentially explaining the decrease in liquid-phase 5-HMF at higher reaction temperatures.

Similarly to that reported for acetic acid, the concentrations of 5-HMF found in the process water when carbonizing mixed food and packaging materials are larger than can be explained by the 5-HMF found in the process water when separately carbonizing food and packaging materials (Figure 25b), suggesting there is some synergistic relationship between the food and packaging materials that promotes larger concentrations of 5-HMF in the process water. The mechanisms associated with this synergy are currently unknown. It is hypothesized that less 5-HMF is ultimately incorporated within the solids under these conditions, suggesting that the solids generated when carbonizing in the presence of packaging materials are not as aromatic. It is also possible that this increase in observed liquid-phase 5-HMF concentrations results because the kinetics of carbonizing in the presence of packaging materials is slower than carbonizing each separately. If this is true, carbonizing this mixed feedstock for longer reaction times would reduce the 5-HMF concentrations found in the process water. Additional work is required to evaluate these hypotheses and determine the mechanisms associated with this synergy.

Comparing the 5-HMF masses generated when carbonizing food and/or mixed food and packaging wastes in this study to other literature-reported studies is complicated and should be done with caution. It is likely that reaction kinetics, which vary with reactor volume, initial solids concentration, and reaction temperature, influence 5-HMF formation and subsequent incorporation in the hydrochar. Table 11 presents 5-HMF concentrations and/or masses in this study as well as those reported in the literature for a variety of feedstocks that have been carbonized over a variety of reaction times and temperatures. As shown, for the most part, the 5-HMF masses and/or concentrations measured in this study are within the range of those reported by others. One exception to this observation is the information reported by Hoekman et al. (2012). Their 5-HMF masses are consistently an order of magnitude greater than those reported in this work. It is possible these differences result from changes in carbonization operation and/or feedstock.

Using the experimental data obtained from this work (e.g., 5-HMF concentrations and liquid recovery), estimates of 5-HMF masses that have the potential to be recovered from currently landfilled food wastes were performed. Table 12 contains the data used to estimate these masses. These calculations were performed for two conditions: (1) all liquid containing 5-HMF will be recovered (even liquid remaining bound in the generated hydrochar following gravity drainage), representing a true maximum value and (2) the potentially recoverable 5-HMF mass if only recovering this compound in process water that drains from the system via gravity. For each of these conditions, the maximum and minimum 5-HMF values were used to generate the potential range of recoverable 5-HMF. These calculations were also performed for a range of food waste masses diverted from landfills (10 to 100% diversion). Figure 26 presents the results from this analysis for food waste alone and mixed food and packaging wastes. Each figure presents the two ranges of potentially recoverable 5-HMF, taking into account both the minimum and maximum values. As shown, if carbonizing to achieve maximum 5-HMF production, the mass of 5-HMF that can be recovered is quite significant. The optimal operating conditions associated with 5-HMF generation are shown in Table 12.



Figure 25. 5-HMF concentrations in process water following the carbonization of: (a) food waste only and (b) mixed food and packaging wastes.

Feedstock	Reaction	Reaction	Solids	Concentration in	% of drv	Source
	Temp (°C)	Time (hr)	Concentratio	the liquid (mg/L)	feedstock	
			n			
Food waste	225	1 - 24	36%	53 – 5,200	0.01 - 0.83	This study
Food waste	250	1 - 24	36%	22.5 - 48.5	0.004 - 0.010	This study
Food waste	275	1 - 24	36%	6 - 165	0.001 - 0.006	This study
Mixed food	250	1 - 24	46%	73 - 189	0.017 – 0.026	This study
and packaging						
wastes						
Packaging	250	1 - 24	17%	12 - 337	0.006 - 0.17	This study
wastes						
Tahoe mix	155 - 295	0.5	11.3%		0.01 - 2.0	Hoekman et al., 2013
Loblolly pine	175 - 295	0.5	11.3%		0.06 - 4.41	Hoekman et al., 2013
Pinyon/Juniper	175 - 295	0.5	11.3%		0.06 – 1.75	Hoekman et al., 2013
Sugarcane	175 - 295	0.5	11.3%		0.02 – 1.98	Hoekman et al., 2013
Bagasse						
Corn stover	175 - 295	0.5	11.3%		0.04 – 0.68	Hoekman et al., 2013
Rice hulls	175 - 295	0.5	11.3%		0.03 - 1.79	Hoekman et al., 2013
Dry poplar	220	4	5%	1,230		Stegman et al. 2013
wood chips						
Glucose	180	4	5%		0.0304	Aydincak et al., 2012
Lactose	180	4	5%		0.3814	Aydincak et al., 2012
Olive oil waste	180	4	5%		0.0081	Aydincak et al., 2012
Hazelnut shell	180	4	5%		0.0257	Aydincak et al., 2012
Wheat straw	190 - 270	6	4 – 7%	5 - 400		Becker et al., 2014
Wheat straw	190 - 270	6	4 – 7%	20 - 50		Becker et al., 2014
digestate						
Poplar wood	190 - 270	6	4 – 7%	20 - 1,000		Becker et al., 2014
Pine wood	190 - 270	6	4 – 7%	5 – 2,350		Becker et al., 2014
Massaranduba	190 - 270	6	4 – 7%	5 – 1,200		Becker et al., 2014
Garapa	190 - 270	6	4 – 7%	5 – 1,000		Becker et al., 2014
Xylose	190 - 270	6	4 – 7%	0 - 5		Becker et al., 2014
Cellulose	190 - 270	6	4 – 7%	3 – 3,400		Becker et al., 2014
Orange	175 - 260	0.5 - 2	11%	0 - 680		Erdogan et al., 2015
pomace						

Table 11. 5-HMF concentrations and/or masses measured in this study compared with literature-reported values.

Parameter	Value	Source
Landfilled Food Waste (in 2014)	29.4 million tons	USEPA, 2016
		Tchobanoglous,
Food Waste Moisture Content	70 % (wet wt.)	1993
Food waste only:		
Max. recoverable 5-HMF:		
Complete liquid recovery (225°C, 1 hour):	8.28 mg 5-HMF/g dry waste	This study
Recovery from drained liquid only (225°C, 1 hour):	3.23 mg 5-HMF/g dry waste	This study
Min. recoverable 5-HMF:		
Complete liquid recovery (275°C, 16 hours):	0.01 mg 5-HMF/g dry waste	This study
Recovery from drained liquid only (275°C, 16 hours):	0.01 mg 5-HMF/g dry waste	This study
Mixed food and packaging waste:		
Max. recoverable 5-HMF:		
Complete liquid recovery (250°C, 16 hours):	0.26 mg 5-HMF/g dry waste	This study
Recovery from drained liquid only (250°C, 16 hours):	0.08 mg 5-HMF/g dry waste	This study
Min. recoverable 5-HMF:		
Complete liquid recovery (250°C, 8 hours):	0.17 mg 5-HMF/g dry waste	This study
Recovery from drained liquid only (250°C, 4 hours):	0.04 mg 5-HMF/g dry waste	This study

Table 12. Data used to estimate potential recoverable 5-HMF mass.



(a)



Figure 26. Range of 5-HMF masses that have the potential to be recovered from HTC process water following the carbonization of: (a) food waste only and (b) mixed food and packaging wastes.

3.2.2 Extraction Method Development

Based on previously established procedures for 5-HMF extraction from different liquids (e.g., Liu et al., 2014), two solvents were evaluated for their potential to extract 5-HMF: (1) dichloromethane (DCM) and (2) a 4:1 volumetric mixture of THF and butanol (THF/B). To determine the ability of each solvent to extract 5-HMF from water, experiments were conducted over a range of 5-HMF concentrations (10 - 5,000 mg/L) and a range of salt concentrations (0-100 g/L). When extracting with THF/B, only a salt concentration of 100 g/L was evaluated because at lower salt concentrations, a separate THF/B-phase does not exist. When extracting with DCM, the 5-HMF concentration was only measured in the aqueous-phase (measured in non-aqueous-phases was not possible), thus the fraction of 5-HMF in the solvent-phase was determined using mass balances. When extracting with THF/B, the 5-HMF concentrations in both phases were measured. The 5-HMF mass recoveries when extracting with THF/B ranged from 100-130% for all experiments. Distribution coefficients (k_d, 5-HMF concentration in the solvent-phase/5-HMF concentration in the water phase) were calculated for each extraction. The larger the k_d, the greater fraction of 5-HMF in this study.

Results from this analysis are presented in Figures 27 and 28. These results indicate that 5-HMF concentrations less than 100 mg/L in the process water will have a significant impact on 5-HMF recovery. This range reflects the majority of the 5-HMF concentrations found in the process water (see Figure 25). The impact of this concentration, however, differs when using DCM or THF/B as the extracting phase; greater 5-HMF recovery occurs at higher 5-HMF concentrations when extracting with THF/B, while the opposite is true when extracting with DCM. Initial salt concentration does appear to have some influence on recoverable 5-HMF (Figure 27). Based on these results, extracting with THF/B is far superior to that that can be achieved with DCM (see Figure 28). For this extraction to occur, however, 100 g/L of salt must be added to the process water prior to extracting.



Figure 27. 5-HMF distribution coefficients when extracting with DCM at different initial 5-HMF concentrations and salt concentrations.



Figure 28. 5-HMF distribution coefficients when extracting with DCM and THF/B at different initial 5-HMF concentrations (all at 100 g/L salt).

3.2.3 Extraction Efficiency in Process Water

Results from extracting 5-HMF from process water resulting from the carbonization of food wastes at 225°C at a reaction time of 1 hour are shown in Table 13. The conductivity of the process water was 19.12 mS/cm. Salt was added to the process water that was exposed to the THF/B extractant, resulting in a conductivity of 90 mS/cm. For comparative purposes, extractions with both DCM and THF/B were conducted. The distribution coefficients achieved from this experiment are quite similar for the THF/B extraction, but half of that expected for the extraction with DCM. According to Mohammad et al. (2016), extraction efficiencies may be influenced by the type of salt and other constituents present in the sample. Therefore, this difference is not surprising. These results do confirm that the preferred extractant is THF/B and that, on average, approximately 90% of 5-HMF found in the process water can be extracted into this phase. The implications of the data presented in Figure 26; lines are drawn to illustrate how the ranges of 5-HMF recovery change.

101	Table 15. Results from the Extraction of 5 fight.				
Solvent	Average k _d	% 5-HMF in the solvent-phase			
DCM	0.43	30			
THF/B	4.18	90			

Table 13.	Results fro	om the Extr	action of 5	-HMF.*
10010 10.	nesures ne	And the Extra		

*all experiments were conducted in triplicate. Values represent averages. 5-HMF mass balance recoveries ranged from 100 – 114%



(a)



Figure 29. Range of 5-HMF masses that have the potential to be recovered from HTC process water following the carbonization of: (a) food waste only and (b) mixed food and packaging wastes. The areas between the red dashed lines represent the recoverable 5-HMF when extracting with THF/B.

4.0 Economic Analysis

Figures 30-37 present results associated with the economic analyses for each scenario (see Table 14). Results indicate that selling the hydrochar for energy purposes (Scenario E, Figure 36), with no resource recovery from the process water, represents the most economically viable approach. Carbonizing for energy recovery at 225°C or 250°C for reaction times equal to or less than 8 hours are economically favorable, with the greatest potential profit occurring at a reaction time of 1 hour. The second most potentially economically viable approach is selling the hydrochar as an energy source and recovering nutrients in the liquid-phase via struvite precipitation (scenario B-1). Economically favorable results associated with this scenario occur at the following reaction times and temperatures: (1) all reaction times when carbonizing at 225°C, (2) reaction times of less than 4 and 8 hours when carbonizing food wastes and mixed food and packaging wastes, respectively, at 250°C, and (3) 1 hour when carbonizing at 275°C. The greatest benefit in this scenario occurs at a reaction temperature of 225°C and a reaction time of 1 hour. Other economically viable scenarios include: A-1, B-2, and F (Figures 30, 32, and 37). In scenario B-2, carbonizing for 1 hour at all reaction temperatures is economically favorable, while in scenario A-1, only carbonizing for 4 hours at 225°C is economically viable. In scenario F, carbonizing at 225°C for all reaction times is economically viable.

Cooperio ID	Resources Recovered				
Scenario ID	Solids	Liquid			
A-1	Nutrients	Nutrients (via struvite precipitation); no additional phosphorus added			
A-2	Nutrients	Nutrients (via struvite precipitation); additional phosphorus added to maximize N recovery			
B-1	Energy	Nutrients (via struvite precipitation); no additional phosphorus added			
B-2	Energy	Nutrients (via struvite precipitation); additional phosphorus added to maximize N recovery			
С	Energy	5-HMF			
D	Nutrients	5-HMF			
E	Energy	none			
F	Nutrients	none			

Table 14. Scenarios Modeled.

Results associated with scenarios C and D (Figures 34 and 35) suggest that recovering 5-HMF from the process water is not economically viable; the costs associated with the chemicals required for recovery of 5-HMF are greater than the benefits associated with their recovery (based on current market prices). Tetrahydrofuran is the most expensive chemical used; identifying other, less expensive solvents would be advantageous and may result in economically favorable recovery of 5-HMF. These losses may also be used to set tipping fees associated with operating these scenarios.













Figure 33. Potential profit associated with scenario B-2.







Figure 35. Potential profit associated with scenario D.



Figure 36. Potential profit associated with scenario E.



Figure 37. Potential profit associated with scenario F.

These results suggest that, on average, recovering nutrients from the process water (scenarios A-1 and B-1) is more economically advantageous than recovering 5-HMF (scenarios C and D) and that adding additional phosphorus (scenarios A-2 and B-2) to maximize nitrogen recovery is more expensive than recovering nutrients based on available phosphorus and nitrogen in the process water. To increase the economic profitability of scenarios involving liquidphase nutrient and/or chemical acquisition, the following must occur: (1) the selling price of nutrients or the chemicals needs to increase, (2) the costs associated with the chemical requirements needs to decrease, and/or (3) an alternative, less expensive approach for nutrient/chemical recovery needs to be identified. It should be noted that in the case of nutrients, it is anticipated that the market value of nitrogen and phosphorus will increase. Significant amount of work has been devoted to recovering and preserving these nutrients because of concerns with future availability. As supply of these nutrients decreases, it is likely their market value increase significantly. It is unknown, of course, how significant of an increase in nutrient market value can be expected. Another option for liquid-phase nutrient acquisition is the recovery using zeolites (e.g., Batstone et al., 2015). Recovery via zeolite only requires the addition of purchased zeolites. Costs associated with zeolites vary significantly, depending significantly on the type of zeolite desired (which cannot be determined at this point).

For the recovery of 5-HMF from the liquid-phase to be economically viable across the majority of reaction times ad temperatures, the selling price of 5-HMF should increase by 3 orders of magnitude or reductions in chemical requirements is needed. The market value of this compound is also expected to increase, but it is difficult to predict the extent of this increase. Alternative

approaches for 5-HMF removal may involve adsorption or membrane processes, both of which have the potential to reduce the chemical processing requirements.

It should also be noted that the recovery of process water resources using the methods evaluated in this work is environmentally advantageous. Recovering nutrients and ultimately offsetting emissions associated with the acquisition of virgin materials is advantageous. Assessing the magnitude of such impacts is outside the scope of this work and requires a life cycle assessment.

4.1 Comparison to Anaerobic Digestion and Composting Processes

Using procedures described previously and literature reported values associated with recoverable resources, the profits associated with composting and anaerobic digestion were estimated. For each process, a residence time of 30 days was assumed. Data from the literature associated with nutrient fate and energy content in the solid and gas-phases were used (Tables 15 and 16). Several assumptions were made to convert these data to the appropriate units required in this study (Table 17). Prices used in previous analyses associated with recoverable nutrients and energy were also used in this analysis (see methods section). The data used in this analysis and the results from this analysis are presented in Tables 15 - 17.

Feedstock	C/N	%N	%P
Food Waste ¹	12.02	3.78	NR
Kitchen Biowaste ²	13	2.6	0.37
Food, yard trimmings, wood waste ³	NR	1.0 - 1.8	0.25 - 0.28
Unspecified MSW ⁴	10-20	1-1.4	0.8-1.2
Human and animal food wastes⁵	31-51	0.9-1.6	NR
Food Waste ⁶	20	1.6	0.6

Table 15. Nutrient Content of Compost.

¹Lee et al., 2004; ²Himane and Hanninen, 2011; ³Sullivan et al., 1998; ⁴Rasapoor et al., 2009; ⁵Chang and Chang, 2010; ⁶Lin, 2008

NR = not reported

Table 16. Nutrient Content of the Digestate from the Anaerobic Digestion of Food Waste.

Feedstock	C/N	%N	%P
Food Waste ¹	NR	15	0.7
¹ WRAP, 2011			

NR = not reported

waste.						
		Feedstock	Solid-Phase		Gas-Phase	
	Residence	Moisture	N (mg N/g wet	P (mg N/g wet	kJ/g wet	Profit (\$/g wet
Process	Time	Content (%)	food waste)	food waste)	waste	food – hr)
Composting ¹						
,2	30 days	70	4.5	1.35	n/a	8.19 x10 ⁻⁷
Anaerobic						
Digestion ^{1,3}	30 days	70	6.99	0.63	4.2	1.37 x 10⁻ ⁶

Table 17. Data and Results Associated with Composting and Anaerobic Digestion of Food Waste.

¹data associated with the feedstocks most closely representing food waste were averaged

²assumptions associated with the nutrient values: solids yield = 48% (Levis and Barlaz, 2011); compost moisture content = 50% (Levis and Barlaz, 2011)

³assumptions associated with the nutrient values: solids yield = 34% (Levis and Barlaz, 2011); digestate moisture content = 75% (WRAP, 2011)

Figures 38 – 42 compare the potential profit when carbonizing for resource recovery (for scenarios with economic viability) with that of composting and anaerobic digestion. Table 18 contains the scenarios (reaction times and temperatures) that are at least as economically attractive as composting and anaerobic digestion of food waste (this list is in no particular order).



Figure 38. Comparison between scenario A-1 and composting and anaerobic digestion.



Figure 39. Comparison between scenario B-1 and composting and anaerobic digestion.



Figure 40. Comparison between scenario B-2 and composting and anaerobic digestion.



Figure 41. Comparison between scenario E and composting and anaerobic digestion.



Figure 42. Comparison between scenario F and composting and anaerobic digestion.

Table 18. Scenarios at Least As Economically Attractive as Composting and AnaerobicDigestion of Food Wastes.

Scenario	Conditions
B-1	225°C: 1 – 8 hours 250°C: 1-4 hours (food and mixed food and packaging) 275°C: 1 hour
B-2	225, 250, and 275°C: 1 hour
E	225°C: 1 – 8 hours 250°C: 1-4 hours (food and mixed food and packaging)

CONCLUSIONS

1.0 Fate of Nutrients During the HTC of Food Wastes

Results from this work indicate that at all evaluated reaction times and temperatures, the majority of nitrogen, calcium, and magnesium remain integrated within the solid-phase, while the majority of potassium and sodium reside in the liquid-phase. The fate of phosphorus is dependent on reaction times and temperatures, with solid-phase integration increasing with higher reaction temperature and longer time. Results from the leaching experiments suggest that, at least in the short term, nitrogen within the solid matrix is unlikely to be released because it is either tightly bound within the solids matrix or in an insoluble form, while almost all of the phosphorus present in the solids generated when carbonizing at 225 and 250 °C is released. At a reaction temperature of 275 °C, smaller fractions of the solid-phase total phosphorus are released as reaction times increase, likely due to increased solids incorporation. Using these data, it is estimated that up to 0.96% and 2.30% of nitrogen and phosphorus-based fertilizers (accounting for recovery in the liquid and solid-phases), respectively, in the US can be replaced by nutrients integrated within hydrochar and liquid-phases generated from the carbonization of currently landfilled food wastes.

2.0 Nutrient Extraction from the HTC Process Water Via Struvite Precipitation

Struvite precipitation can be used to recover nutrients (nitrogen and phosphorus) from HTC process water obtained from carbonizing food waste. Adding either MgCl₂ or MgSO₄ and a base is necessary because of the low pH and Mg²⁺ levels in the HTC process water. Addition of MgO is not recommended because of its low solubility. Because of the low P:N ratio in the HTC process water, adding phosphate is needed to maximize nitrogen nutrient recovery. Despite experimental kinetic limitations in struvite precipitation, a chemical equilibrium model can reasonably predict the amount of struvite formed and should be used as a basis for the amount of chemicals (i.e., Mg²⁺, base, and/or phosphate) to be added to the system. Fitting experimental titration behavior of the HTC process water is necessary to obtaining the required amount of base addition. A strategy of pH adjustment with periodic Mg²⁺ and base addition was found to overcome some kinetic limitations and recover more struvite than a single dose of Mg²⁺ and base in a batch system. Refinement of the operational strategy to include pH control and chemical addition programming in a flow through system during larger scale implementation is needed to further overcome kinetic limitations.

3.0 Feasibility of Acetic Acid and 5-Hydroxymethylfurfural Recovery from HTC Process Water

Concentrations of both acetic acid and 5-HMF in the process water from the carbonization of food wastes and/or mixed food and packaging wastes are significant, suggesting that recovery of these compounds has the potential to generate revenue. When carbonizing to maximize acetic acid concentrations, larger reaction temperatures and times should be used. However, recovery of acetic acid using liquid-liquid extraction techniques does not appear feasible. Alternative approaches may be considered, such as membrane separation. When carbonizing to maximize 5-HMF generation, lower reaction temperatures and times should be used. When extracting with THF/B, the addition of salt is required and an extraction efficiency of approximately 90% can be

achieved.

4.0 Economic Analysis

An economic analysis was performed to evaluate the potential from recovering solid and liquid-phase resources following the carbonization of food wastes. Results from this analysis indicate that conducting HTC for resource recovery can be economically attractive and can, under some conditions, achieve greater profits than composting and anaerobic digestion of food wastes. Results also suggest that recovering 5-HMF via liquid-liquid extraction is not currently economically viable. Investigation of alterative liquid-phase resource recovery approaches is needed to improve the economics of this recovery.

5.0 Overall Implications

Results from this work have been compiled to develop a flowchart that provides guidance on carbonizing food wastes for resource (e.g., nutrients, energy, and 5-HMF) recovery. This flowchart is presented in Figure 43. Before using this flowchart, one must determine the resources desired to recover: nutrients (liquid and/or solid), energy (solid), and/or 5-HMF. Because the recovery of acetic acid from the process water using liquid-liquid extraction was not deemed feasible, acetic acid is not included in this flowchart. Once the resources are chosen, the flowchart should be followed to determine the preferred operational strategy.

It is important to note that this flowchart only describes technical guidance. No economic considerations have been included in this figure. Results from the economic analysis conducted indicate that resource recovery from food wastes following HTC is economically feasible. Before following the guidance provided in Figure 43, a more specific economic analysis should be conducted to determine overall system economic viability.

Results from this work support the use of HTC as a means to recover resources from food wastes. An economic analysis was performed to evaluate the potential of recovering solid and liquid-phase resources following the carbonization of food wastes. Results from this analysis indicate that conducting HTC for resource recovery can be economically attractive and can, under some conditions, achieve greater profits than composting and anaerobic digestion of food wastes. It should be noted that capital, operating, and maintenance costs were not included in this analysis. Results also suggest that recovering 5-HMF via liquid-liquid extraction is not currently economically viable. Investigation of alterative liquid-phase resource recovery approaches is needed to improve the economics of this recovery.

Overall, results associated with this EREF funded project indicate that recovering resources from food wastes (and mixed food and packaging wastes) using HTC has promise: significant levels of resources can be recovered that can be economically attractive and, under some conditions, achieve greater profits than composting and anaerobic digestion of food wastes. This work provides the basis for large-scale implementation of this process. As resources become more limited, it will likely become more important to recover resources from food-related waste. HTC is a novel process that can economically and efficiently accomplish this.



Figure 43. Flowchart providing guidance on carbonizing food wastes for resource (e.g., nutrients, energy, and 5-HMF) recovery.

MATERIALS AND METHODS

1.0 Fate of Nutrients During the HTC of Food Wastes

1.1 Food and Packaging Material Acquisition and Properties

Food waste was periodically collected from restaurants located near the University of South Carolina (Columbia, SC), following procedures outlined by Li et al. (2013). This food waste consisted of a variety of different components, including seafood, meats, bread, pasta, potatoes, vegetables, and condiments. Immediately following collection, the waste was weighed and non-food materials (e.g., packaging) and food containing bones were removed. Packaging materials were subsequently separated into three categories: (1) paper, (2) cardboard, and (3) plastics. Food containing bones was not used in this study because of experimental constrains (e.g., reactor size). The food waste was subsequently mixed and homogenized with a food-grade blender (Ninja Master Prep, Euro-Pro Operating LLC). All packaging materials (e.g. paper, plastic, cardboard) were shredded using a titanium paper shredder (25 by 4 mm strips). All food and packaging wastes were frozen until use.

The moisture, carbon, nitrogen, phosphorus, potassium, calcium, and magnesium contents of the collected food waste and packaging materials were measured (Table 19). The moisture content of the separated components was measured using a gravimetric technique. A mass of each component was dried in a laboratory oven at 80°C for at least 48 hours, or until the dried sample mass remains constant. Following drying, the carbon and nitrogen contents of the samples were measured using an elemental analyzer (Perkin Elmer 2400). Phosphorus, potassium, calcium, and magnesium contents of these materials were measured on aqueous filtrates of acid digested materials by inductively coupled plasma (ICP) by the Agricultural Service Laboratory at Clemson University. The dry digestion process involved first ashing the samples in a muffle furnace and subsequently dissolving the ash in 6N HCl.

					5 0			
	Moisture							
Waste	Content (%,	C (%,	N (%,	P (%,	K (%,	Ca (%,	Mg (%,	Na (%,
Component	wet wt.)	dry wt.)	dry wt.)	dry wt.)	dry wt.)	dry wt.)	dry wt.)	dry wt
Food								
Waste	63.79	50.90	3.18	0.42	0.52	0.21	0.05	1.11
Paper	24.52	46.80	0.21	0.02	0.05	0.55	0.03	0.18
Cardboard	12.79	41.43	0.09	0.01	0.05	1.68	0.04	0.11
Plastic	4.10	80.54	0.22	0.01	0.03	0.12	0.01	0.05

Table 19. Collected food waste and packaging material properties*.

*All values represent average values of at least 5 samples.

1.2 Batch HTC Experiments

All batch carbonization experiments were conducted following procedures previously described (Berge et al., 2011; Li et al., 2013; Lu et al., 2012). Briefly, approximately 40 g of room temperature food waste and/or packaging materials were placed in 160-mL stainless steel tubular reactors (2.54 cm i.d., 25.4 cm long, MSC, Inc.) fitted with gas-sampling valves (Swagelock, Inc.). All reactors were subsequently sealed and heated in a laboratory oven to the desired

temperature. Reactors were sacrificially sampled over a period of 24 hr. All experiments were conducted in triplicate. Based on results from Li et al. (2013), the sample masses of food and/or packaging materials used in this study are sufficient for obtaining reproducible results.

Three sets of carbonization experiments were conducted: (1) experiments in which separated food waste (solids concentration representing as-received waste, 36.2%, dry wt.) was carbonized at three different temperatures (225, 250, and 275 °C), (2) experiments containing food and packaging materials to evaluate the influence of packaging on food waste carbonization at 250 °C, and (3) experiments carbonizing packaging materials only. The first set of experiments was conducted to determine how reaction temperature and time influence nutrient fate. The second set of experiments was conducted to evaluate the influence of packaging materials on nutrient fate. In these experiments, a packaging concentration of ~20% (dry wt.) was evaluated. The third set of experiments, containing only packaging materials, was conducted to understand the nutrient fate when carbonizing packaging materials. These experiments were conducted at a packaging concentration of 20% (dry wt.); deionized water was added to achieve this solids concentration.

At each sampling time, reactors were removed from the oven and immediately submerged in a cold-water bath. Following cooling, the produced gas was collected in either a 1 or 3-L foil gas sampling bag. Gas composition of these samples was analyzed using GC-MS (Agilent 7890) using the method previously described by Li et al (2013). Gas volumes were measured with a large volume syringe (S-1000, Hamilton Co.).

The process liquid and solid were separated via vacuum filtration through a 0.45 µm cellulose nitrate membrane filter (Whatman International Ltd.). The process water was analyzed for typical water quality parameters. Liquid conductivity and pH were measured using electrodes (Thermo Scientific Orion). Liquid chemical oxygen demand (COD) was measured using HACH reagents (HR + test kit, Loveland, CO). Liquid total organic carbon (TOC) was measured using a TOC analyzer (TOC-Vcsn, Shimadzu). Liquid-phase ammonia-nitrogen and total nitrogen was measured using HACH reagents for the salicylate and persulfate digestion methods, respectively (HACH test kits, Loveland, CO). Total phosphorus, potassium, calcium, sodium and magnesium were analyzed using ICP by the Agricultural Service Laboratory at Clemson University.

All collected solids were dried at 80°C and moisture contents measured, following procedures previously described. The carbon and nitrogen content of the solids were analyzed using an elemental analyzer (Perkin Elmer 2400). Previously published literature (e.g., Enders and Lehmann, 2012) report that solid-phase measurements of potassium, calcium, and magnesium can be complicated by the chemical recalcitrance and varied composition of the solid matrix in which they are integrated (Enders and Lehmann, 2012), with greater variability between measurement approaches (e.g., wet digestion, dry digestion) as carbonization conditions become more severe (e.g., higher temperatures and longer times). Results from solid-phase analyses using a dry digestion process in which aqueous filtrates of acid digested materials by ICP from this work confirm this phenomenon (data not shown). Therefore, solid-phase phosphorus, potassium, calcium, sodium, and magnesium were calculated as the difference between the mass of each found in the initial food waste samples and that measured in the liquid-phase, assuming 100% recovery of these elements.

1.3 Sequential Nutrient Extraction

Experiments evaluating leachable total nitrogen and phosphorus mass from the hydrochar were conducted to determine potential nutrient release if using the hydrochar as a fertilizer or if extraction of nutrients from the hydrochar is desired. For each experiment, approximately 35-mL of an extractant was added to either 0.1 g or 0.2 g of dried hydrochar in plastic 35 mL centrifuge tubes. These solid to liquid ratios were chosen based on results from preliminary experiments conducted to determine ratios that maximized nitrogen and phosphorus removal in each extraction, while remaining above method detection limits, with the larger mass of solid used in the experiments evaluating the release of total nitrogen. The extractant used in the experiments to evaluate the leachability phosphorus, was Mehlich 3 (0.2 N CH₃COOH, 0.25 N NH₄NO₃, 0.013 N HNO₃, 0.015 N NH₄F, 0.001 M EDTA, Aqua Solutions), which has been commonly used to evaluate available phosphorus in different soil matrices (e.g., Wuenscher et al., 2015). When evaluating the leaching of the nitrogen species, 0.01M CaCl₂ was used as the extractant, following that reported by others (e.g., Mengel et al., 2000; Li et al., 2012).

Once the hydrochar mass and extract volume were added to each centrifuge tube, the tubes were capped and the mixture was mixed in a rotary mixer for 24 hours. Subsequently, all tubes were then centrifuged at 3,000 rpm for 30 minutes. Approximately 32 mL of supernatant was then removed from each vial and subsequently replaced with same volume of extractant. These vials were then placed in the rotary shaker for an additional 24-hours. This process continued until three sequential extractions occurred, which, based on results from preliminary experiments, is sufficient to remove leachable nutrient mass to levels below detection limits. All collected supernatant was filtered through a 0.2-um hydrophobic polytetrafluoroethylene (PTFE) filter prior to analysis. The phosphorus concentrations in the liquid samples were analyzed at the Agricultural Service Laboratory at Clemson University by ICP. The total nitrogen concentrations in the liquid-phase were measured using a Total Nitrogen Analyzer (Shimadzu, model TNM-L).

1.4 Solid and Solution-State ³¹P-NMR

Solid-state ³¹P spectra were collected on a Bruker Avance III-HD 500 MHz spectrometer (202.49 MHz) using a 1.9mm MAS probe. The spectra were collected at ambient temperature with sample rotation rate of 20 kHz. ¹H dipolar decoupling was performed with SPINAL64 modulation and 145kHz field strength. Bloch decays were collected with a 25 ms acquisition time over a 590 ppm spectra width with a relaxation delay of 5s. Chemical shifts are reported with respect to H₃PO₄, and referenced externally with NH₄ • H₂PO₄ which was assigned a value of 0.72 ppm.

Solution-state ³¹P spectra were collected on a Bruker Avance III-HD 400 MHz spectrometer (162.03 MHz) using a 5mm Bruker Prodigy cryo-probe. Sample temperature was regulated at 25C. A 200 ppm window centered at 0 ppm (with respect to H₃PO₃) was collected using 30 degree pulses and a 5s relaxation delay. Inverse-gated ¹H broadband decoupling was used to minimized nuclear Overhauser enhancements. The neat liquids were spiked with 5% D₂O for field-frequency lock and required 256-1024 added transients.

2.0 Nutrient Extraction from the HTC Process Water Via Struvite Precipitation

HTC process water analysis showed low P:N ratios as well as limited amounts of Mg²⁺ that can participate in phosphate and struvite precipitation after pH adjustment. Because of the

limited process water that can be harvested within the laboratory scale reactors, preliminary experiments were performed using simulated nutrient solutions to evaluate strategies for chemical addition and pH adjustment and to optimize struvite precipitation. Equilibrium modeling was also used to design the experiments and analyze results. Final experiments were performed using HTC process water obtained after hydrothermally carbonizing food waste at 250 °C for 4 hours.

2.1 Experiments

A simulated HTC nutrient solution composed of 0.11 M KH₂PO₄ and 0.11 M NH₄Cl was prepared in deionized (DI) water. The NH₄-N concentration selected for the experiments was representative of the values observed in the HTC process water obtained under different temperatures and reaction times. A 1:1 P:N was selected with the intent of maximizing struvite precipitation in the simulated solutions; later experiments evaluate the effect of different P:N ratios on struvite precipitation. 50 mL of a 1.29 M MgCl₂ solution prepared in DI water was added to 450 mL of the simulated HTC nutrient solution. This resulted in a Mg:N ratio of 1.3 where struvite precipitation is not Mg²⁺ limited. Different amounts of 5.0 N NaOH were added to raise the pH and to evaluate the effect of different pH levels on struvite precipitation. MgCl₂ was not added to the control experiments. All experiments were performed in duplicate. Samples were withdrawn periodically over 36 hours for phosphate and ammonia analysis. The solution pH was also measured periodically over the same period.

A similar experiment was performed where the pH of 450 mL of the simulated nutrient solution was increased with the addition of 14.5 mL of 5 N NaOH, followed by the periodic addition of 10 mL of a 1.29 M MgCl₂ solution and 1 mL of 5N NaOH over 1 hour to achieve the same final dose of Mg²⁺. The total amount of NaOH corresponded to a dose that maximized struvite precipitation based on equilibrium modeling predictions. This strategy was designed to form new MgHPO₄ surfaces that NH₄⁺ can diffuse into, thereby enhancing struvite precipitation. Samples were withdrawn for phosphate and ammonia analysis prior to each periodic addition. The solution pH was also measured periodically over the same period. Final experiments with the simulated HTC nutrient solution were performed on a 1/10 scale (i.e., 45 mL nutrient solution) with different P:N and Mg:N ratios using the strategy of pH adjustment followed by periodic MgCl₂ and NaOH addition over 1 hour. The target P:N ratios were obtained by mixing different solutions with different P levels but with the same N concentration. The total NaOH added also corresponded to an overall dose that maximized predicted struvite precipitation. These smallscale experiments simulated procedural testing prior to experiments with the HTC process water. Final ammonia, phosphate, and pH were measured in these small-scale experiments. All experiments were performed in duplicate.

Initial titration of 50 mL HTC process water with 5.0 N NaOH was performed to characterize the buffer capacity of the process water and allow calculation of the amount of NaOH required for maximum struvite precipitation with different P:N and Mg:N ratios. Different P:N ratios were obtained by the adding phosphate to the HTC process water and subsequently using different mixing ratios of the original and phosphate amended process water. Final ammonia, phosphate, and pH were measured in these small-scale experiments. All experiments were performed in duplicate.

2.2 Analytical Methods

Samples for phosphate and ammonia analysis were filtered through a 0.2 µm polytetrafluoroethylene (PTFE) filter, acidified using HCl, and stored in a refrigerator prior to analysis. Both the phosphate and ammonia concentrations were analyzed using HACH reagents. Phosphate was analyzed using PhosVer[®] 3 ascorbic acid method with acid persulfate digestion, ammonia was analyzed using the AmVer[™] salicylate method. pH was measured using a Thermo Scientific Orion electrode calibrated with certified standard solutions

2.3 Precipitation Modeling

Equilibrium modeling was performed using Visual MINTEQ 3.1 (Gustafsson, 2017). The builtin thermodynamic database was used in all calculations. The concentrations used as input to the model reflect values obtained from actual measurements. Majority of the simulations were titrations that evaluate the effect of changes in speciation due to pH adjustment and periodic MgCl₂ and NaOH addition. Precipitate species specified corresponded to the predominant simple precipitates expected in solution (e.g., Mg(OH)₂, MgHPO₄·3H₂O_(s), struvite). The effect of different magnesium sources (MgCl₂, MgSO₄, and MgO) were also investigated.

3.0 Feasibility of Acetic Acid and 5-Hydroxymethylfurfural Recovery from HTC Process Water

3.1 Acetic Acid Measurement

Acetic acid concentrations in the process water and aqueous and non-aqueous phases of liquid-liquid extraction experiments were analyzed using GC-MS (Agilent 7890). Liquid samples (0.5 uL) were routed through a DB-Wax ultra inert column (30m long, 0.25 mm id, 0.5 um thickness, J&W Scientific). Helium was introduced at a flowrate of approximately 1.5 mL/min. Initial oven temperature was 100°C. After 1 min, the temperature was increased at a rate of 10°C/min until a final temperature of 230°C was achieved. The inlet temperature was set at 250°C and a solvent delay time of 3-min was observed. Acetic acid standards were made by diluting glacial acetic acid (Fisher Scientific, Inc.) with DI water and used when analyzing HTC process water and the aqueous-phases from the extraction experiments. When analyzing the acetic acid concentrations in a solvent phase, all standards were prepared in the same solvent/solvent mixture. All process water samples were filtered with a 0.20 um syringe filter (PTFE Fluoropore, Millex) prior to analysis.

3.2 5-HMF Measurement

5-HMF concentrations in the process water and in the aqueous-phases of all 5-HMF extraction experiments were measured using HPLC with diode array detection (Agilent, 1200) at a wavelength of 280 nm and a C18 column (LiChrospher RP-18, 150mm x 4.6 mm, 5um, Grace Division of Discovery Sciences). The mobile-phase was introduced at a flowrate of 1.0 mL/min and consisted of a mixture of methanol and 0.1 mM sulfuric acid at a ratio of 1:9. The column temperature remained constant throughout the measurement at 30 °C. Sample volumes of 20 uL were injected. Standards were made using purchased 5-HMF (98%, Acros Organics, Inc.).

Measuring 5-HMF concentrations in the HTC process water using this method was complicated by the presence of large concentrations of other organics present in the samples. This complex matrix required 5-HMF concentrations be determined using a standard addition method. A spike of concentrated 5-HMF was added to each process water sample prior to

analysis. 5-HMF concentrations were determined based on spike recovery; 5-HMF mass recovered in excess of the spiked mass was identified as the 5-HMF concentration in the process water. Integration of these spiked peaks required the use of valley-to-valley peak integration. This approach required perpendicular lines be drawn from the valley immediately before and after the 5-HMF spike to an extended normal baseline. This integration process was conducted, at a minimum, of two times for each sample. To reduce the uncertainty associated with determining 5-HMF concentrations using this integration approach, each sample was spiked with two different 5-HMF concentrations and, as described previously, integrated at least twice. All reported concentrations are representative of the two different spikes and the associated series of integrations. All process water samples were filtered with a 0.20 um syringe filter (PTFE Fluoropore, Millex) prior to analysis.

3.3 Extraction Experiments

Several series of liquid-liquid extraction experiments were conducted to evaluate potential approaches to recover acetic acid and 5-HMF from the process water. Initial experiments were aimed at determining the conditions that result in greatest partitioning of acetic acid and 5-HMF in the solvent-phase. In these experiments, different concentrations of 5-HMF and acetic acid, spanning the concentrations found in the process water, were prepared in DI water and subsequently mixed with different solvents/solvent mixtures (including: dichloromethane (DCM, 99.6%, Fisher Scientific), tetrahydrofuran (THF, Fisher Scientific), sec-butanol (B, EMD Chemicals), and tri-n-octylamine (TOA, Fisher Scientific)). Solvents or solvent mixtures were chosen based on literature reporting successful extraction/recovery of these compounds. Because the process water contains high ionic strength and ionic strength has been shown to influence compound extraction, all experiments were also conducted over a range of salt concentrations (sodium chloride, Fisher Scientific). Salt concentrations were chosen to evaluate a large range of potential ionic strengths. The conductivity of the process water and salt solutions was measured using a conductivity probe (Mettler Toledo) and the results are presented in Figure 44. Table 20 lists the different combinations of acetic acid, 5-HMF, salt concentrations, and solvents evaluated.



Figure 44. Relationship between salt concentration and solution conductivity. The shaded region represents the conductivity range of the process waters generated in this study when carbonizing food and mixed food and packaging wastes.

Compound	Solvents	Compound Concentrations	Salt Concentrations
Extracted		(mg/L)	(g/L)
Acetic Acid	DCM	5,000, 10,000, 15,000	0, 1, 10, 100
	DCM/TOA	5,000, 10,000, 15,000	0, 1, 10, 100
	THF/B	5,000, 10,000, 15,000	100*
5-HMF	DCM	5, 10, 25, 100, 1,000, 5,000	0, 1, 10, 100
	THF/B	5, 10, 25, 100, 1,000, 5,000	100

Table 20. Acetic Acid and 5-HMF Extraction Conditions Evaluated.

DCM = dichloromethane (99.6%, Fisher Scientific)

DCM/TOA = dichloromethane 0.5 M tri-n-octylamine (TOA)

THF/B = tetrahydrofuran (Fisher Scientific, Inc.) and sec-butanol (EMD Chemicals), mixed at a 4:1 volume ratio *separate phases do not exist at the lower salt concentrations evaluated

Extraction experiments were performed by mixing either 5 mL of water at specific acetic acid, 5-HMF concentrations in different salt concentrations (Table 20), or process water with 5 mL of a solvent or solvent mixture in 22-mL glass vials. All vials were sealed and subsequently mixed end-over-end for a period of at least 20 hours. Following mixing, the contents of all vials were emptied into 10-mL graduated cylinders and the volume of each phase was measured. These experiments were conducted in duplicate. Samples of the water and/or solvent phase were taken and analyzed for 5-HMF or acetic acid.

The solvents resulting in the greatest recovery of each compound were then applied to the process water containing the largest acetic acid and 5-HMF concentrations. If an emulsion was present that did not separate via gravity, the samples were centrifuged at 3,000 rpm for 10 min prior to analysis. Samples from each phase were taken and the acetic acid or 5-HMF concentrations were subsequently measured following previously described procedures.
4.0 Economic Analysis

Results from all experiments detailed in this report provide information associated with potentially recoverable nutrients and chemicals. Energy recovery from the carbonization of food wastes and mixed food and packaging wastes was detailed in a previous EREF final report (Berge and Flora, 2015). The purpose of this work is to investigate the economic viability of recovering nutrients, chemicals (e.g., 5-HMF), and/or energy from products generated during the HTC of food wastes. Based on the results presented in this report, several operational strategies for recovering resources from wastes using HTC are possible and are presented in Figure 45. Although not explicitly illustrated in Figure 45, strategies in which resources are only recovered from the solid or only from the liquid are also possible. An economic analysis accounting for the chemical costs and resulting economic benefits associated with each system will be conducted and used to develop economically viable HTC operational strategies.



(b)



Figure 45. Operational strategies for the recovery of resources from food wastes using HTC: (a) nutrient recovery from hydrochar and process water, (b) nutrient recovery from process water and energy generation from hydrochar, (c) 5-HMF recovery from the process water and electricity generation from the hydrochar, and (d) 5-HMF recovery from the process water and using the hydrochar as a source of nutrients.

4.1 Economic Analysis Approach

An economic analysis associated with eight different operational strategies was conducted. Figure 45 illustrates each operational strategy. In addition to the four strategies presented in Figure 45, strategies in which only the hydrochar was processed for nutrients or energy were also evaluated. A list of all evaluated scenarios is provided in Table 21. The economics associated with a system in which residential food waste is separately collected and carbonized in a centralized carbonization facility was described in a previous EREF project report (Berge and Flora, 2015). Because carbonization facility capital costs and separate food waste collection costs are assumed to be the same in each scenario, these were neglected from this analysis. In this analysis, all system costs (e.g., chemical requirements) and benefits (e.g., selling of hydrochar, nutrients, chemicals) were tabulated and normalized per mass of wet food waste processed and reaction time to illustrate potential profits. The difference in electricity needs because of changes in reaction temperature were also accounted for using the following expression:

$$q = mC_{p}dT$$
 (5)

where, q=heat required (J), m is the mass of wet waste (g), C_p is the heat capacity of the waste (J/g-°C), and dT is the change in temperature (225°C was used as the point of comparison). The heat capacity of the waste is unknown; therefore the heat capacity of water was used to represent the waste in these calculations (4.184 J/g-°C). It is assumed that the carbonization process is perfectly insulated.

Seenaria ID	Resources Recovered		
Scenario ID	Solids	Liquid	
A-1	Nutrients	Nutrients (via struvite precipitation); no additional	
		phosphorus added	
A-2	Nutrients	Nutrients (via struvite precipitation); additional	
		phosphorus added to maximize N recovery	
B-1	Energy	Nutrients (via struvite precipitation); no additional	
		phosphorus added	
ЪЭ	Energy	Nutrients (via struvite precipitation); additional	
B-2		phosphorus added to maximize N recovery	
С	Energy	5-HMF	
D	Nutrients	5-HMF	
E	Energy	none	
F	Nutrients	none	

Table 21. Scenarios Modeled.

It should also be noted that additional income may come from tipping fees/collection rates, which were not included in this analysis.

4.1.1 Nutrient Recovery from the Hydrochar

Monetary gains associated with selling the hydrochar as a potential fertilizer are based on the solids nitrogen and phosphorus content. Nutrients from the hydrochar are those that were recovered during the sequential extraction experiments described previously. These values represent a conservative estimate of available nitrogen and phosphorus. Selling prices associated with the nitrogen and phosphorus were taken from projections provided in WERF (2011), and are included in Table 22.

4.1.2 Nutrient Recovery from Process Water via Struvite Precipitation

Two operational scenarios involving the recovery of nitrogen (in the form of ammonia) and phosphorus in the gravity-drained liquid via struvite precipitation were included in this analysis. The first involves processing of the process water as received. The second involves supplementing the system with additional phosphorus to maximize nitrogen recovery. Nutrient recovery using struvite precipitation requires the addition of a magnesium source and sodium hydroxide for pH adjustment. Specific needs of each of these chemicals is based on experimental findings previously described. Magnesium chloride was chosen as the magnesium source because it is less expensive than magnesium sulfate. The costs associated with these chemicals are provided in Table 23. The benefits associated with this process are the recovery of the nitrogen and phosphorus. Based on experimental results, it was assumed that all phosphorus was recovered, with the appropriate corresponding fraction of nitrogen also recovered (1:1 ratio). In the scenarios involving the addition of phosphorus, costs associated with the needed phosphorus were subtracted from the benefits of that recovered. Selling prices associated with the nitrogen and phosphorus were taken from projections provided in WERF (2011), and are included in Table 22.

4.1.3 5-HMF Recovery from Process Water

5-HMF recovery requires the addition of THF/B and sodium chloride. Specific needs of each of these chemicals is based on experimental findings described previously. The costs associated with these chemicals are provided in Table 23. Based on experimental results, it was assumed that 90% of all liquid-phase 5-HMF is in the gravity drained liquid is recovered. Selling prices associated with the 5-HMF are included in Table 22.

4.1.4 Energy Recovery from Hydrochar

The economics associated with selling of the generated hydrochar for energy generation follows the procedure used in a previous EREF project report (Berge and Flora, 2015). Because hydrochar has not been previously sold for energy generation purposes, it is assumed that the char will be sold at prices equivalent to coal. Coal prices were taken from the US Energy Information Administration (EIA, 2017). The energy values of the hydrochar were taken from similar experiments that are described in Berge and Flora (2015). No transportation costs associated with this material are included; it is assumed those costs will ultimately be included in the selling price.

Product		Price (\$/ton)	Source			
	Nitrogen (solid and liquid)	165	WERF, 2011			
Phosphorus (solid and liquid)		84	WERF, 2011			
	5-HMF (liquid)	453,600	Alibaba.com, 2017			
	Energy (solid)	46.25	EIA, 2017			

Table 22. Selling Prices of Resources Generated during the HTC of Food and/or Mixed Food and Packaging Wastes.

Table 23. Chemical Costs Associated with Resource Recovery from HTC Process Wate	r
Generated from the HTC of Food and/or Mixed Food and Packaging Wastes.	

Chemical	Price (\$/lb)	Source
Struvite Precipitation:		
MgCl ₂	0.13875	ICIS Industries, 2016
NaOH	0.16	Alibaba.com, 2017
5-HMF Recovery:		
Tetrahydrofuran	1.55	ICIS Industries, 2016
Butanol	0.675	ICIS Industries, 2016
Salt	0.034	Fisher Scientific, 2017

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APPENDIX A: LIST OF PROJECT PUBLICATIONS AND KEY DELIVERABLES

Specific products developed from this study

- 1. Operational guidance associated with recovering resources from food wastes using hydrothermal carbonization.
- 2. An economic model describing profits from resource recovery.
- 3. The following publications/presentations are a result of this work:

Peer Reviewed Publications

1. Idowu, I., Li, L., Flora, J.R.V., Pellechia, P., Darko, S.A., Ro, K.S., Berge, N.D. (2017). Hydrothermal carbonization of mixed food waste for nutrient recovery and reuse, *Waste Management* 69, 480-491.

Conference Proceedings

1. Berge, N.D., Flora, J.R.V., Idowu, I., Li, L., Ro. K.S. (2017). Sustainable Conversion of Food Wastes to Value-Added Products. To be included in the proceedings of the Sixteenth International Waste Management and Landfill Symposium in Sardinia, Italy, October 2017.

Conference Presentations

- Idowu, I., Li, L., Flora, J.R.V., Darko, S.A., Berge, N.D. (2017). Hydrothermal Carbonization Of Mixed Food Waste For Nutrient Recovery and Reuse. To be presented at the 1st International Symposium on Hydrothermal Carbonisation, Queen Mary, University of London, April 3-4 2017.
- 2. Berge, N.D. (2017). Developing Waste Management Approaches to More Sustainably Manage Discarded/Lost Food Waste. To be presented at the 2017 Institute of Food Technologies, Las Vegas, NV, June 25-28, 2017.
- 3. Berge, N.D., Flora, J.R.V., Idowu, I., Li, L., Ro. K.S. (2017). Sustainable Conversion of Food Wastes to Value-Added Products. To be presented at the Sixteenth International Waste Management and Landfill Symposium in Sardinia, Italy, October 2017.
- 4. Berge, N.D., Flora, J.R.V., Idowu, I., Li, L. Ro. K.S. (2017). Using HTC to Beneficially Recover Resources from Food Wastes. To be presented at the 2017 Fall American Chemical Society National Meeting, Washington, DC, August 2017.

Seminar Presentation

1. Berge, N.D. (2016). Resource Recovery from Food Wastes: Hydrothermal Carbonization and Comparisons to Other Diversion Strategies. Webinar Presented for EREF, September 8, 2016.