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Hydrothermal Carbonization Of Food Waste For Nutrient Recovery And Reuse

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HYDROTHERMAL CARBONIZATION OF FOOD WASTE FOR NUTRIENT RECOVERY
AND REUSE

by

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DEDICATION

I dedicate this work to God to whom I owe all I could ever be in life.

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ABSTRACT

Food waste represents a rather large and currently underutilized source of potentially available and reusable nutrients. Laboratory-scale experiments evaluating the hydrothermal carbonization of food wastes collected from restaurants were conducted to understand how changes in feedstock composition and carbonization process conditions influence primary and secondary nutrient fate. 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. A series of leaching experiments to determine potential solid-phase nutrient availability were also conducted and indicate that, at least in the short term, nitrogen release from the solids is small, while almost all of the phosphorus present in the solids produced from 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, respectively, in the US can be replaced by the nutrients integrated within hydrochar and liquid-phases generated from the carbonization of currently landfilled food wastes.

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CHAPTER 1

INTRODUCTION

1.1 MOTIVATION

During the past twenty years, Hydrothermal carbonization (HTC) has received tremendous interest as a potential waste conversion technique that may promote the recovery of valuable resources (Berge et al., 2011; Funke et al., 2013; Goto et al., 2004; Kim et al., 2014; Li et al., 2013; Liu et al., 2013; Parshetti et al., 2013; Saetea and Tippayawong, 2013). HTC is a thermal process that occurs at relatively low temperatures (180-350 °C) in the presence of self-generated pressures. This process results in the generation of a solid material that has high carbon and energy-densities (typically referred to as hydrochar), a liquid-phase rich in organics, and a small gas-phase that is primarily composed of carbon dioxide (Berge et al., 2011; Cao et al., 2013a; Funke and Ziegler, 2010a; Libra et al., 2011; Lu et al., 2013; Reza et al., 2014). Because of the inherent requirement of moisture during carbonization, investigations aimed at the application of HTC as a waste treatment technique have largely focused on waste streams with high moisture contents. Examples of some of the waste streams investigated as feed for the HTC process include sewage sludge, agricultural residue, anaerobic digestate, and food waste (Li et al., 2013; Mumme et al., 2011; Oliveira et al., 2013).

Food wastes are well suited for conversion using HTC. Food wastes are wet (moisture contents generally > 60%, wet wt. basis), preventing them from being candidates for conversion using traditional dry conversion processes (e.g., incineration, pyrolysis). In addition, food waste represents a large and current underutilized source of nutrients. For example, the US generated 38.4 million tonnes of food waste in 2014(EPA, 2015). In 2011,(Cordell and White, 2011) (Cordell and White) described food waste as one of the renewable sources of phosphorus. One of the most advantageous benefits associated with the HTC of food wastes is the potential for nutrient recovery. Recent concerns associated with the ability of current nutrient supplies to meet future demands (Battistoni et al., 1997; Cai et al., 2013; Mehta et al., 2015) have led to numerous investigations associated with sustainable nutrient use. Currently, most of phosphorus and potassium consumed are from limited and non-renewable reserves. The recovery of nutrients from carbonized food waste presents an alternate route that may potentially reduce the current dependence on virgin nutrient source.

For nutrients to be efficiently recovered from products generated during HTC, it is necessary to identify and understand nutrient fate during carbonization. Adequate knowledge of this may guide in the determination of suitable recovery processes and help identify carbonization conditions that promote the transfer of nutrient to a phase where recovery is most efficient. A limited number of studies have reported the fate of nutrients during carbonization of specific food waste components, such as corn stover, miscanthus, rice hulls, and empty fruit bunches (Nurdiawati et al., 2015; Reza et al., 2013; Smith et al., 2016). The results from these studies shows significant variation in the fate of each nutrient reported with values of phosphorus and potassium retained in the hydrochar ranging from

8-92% and 6-52% respectively. This variation observed suggests that specific characteristics of each feedstock can greatly influence the fate of nutrient during carbonization making it difficult to extend these conclusions to mixed food waste streams. Therefore, investigations specifically aimed at identifying the fate of nutrients during carbonization of food waste are necessary for developing strategies for nutrient reclamation from this waste stream.

1.2 RESEARCH OBJECTIVES

The purpose of this work is to evaluate the fate of nutrients resulting from the carbonization of food waste collected from local restaurants and to ultimately use such information to determine the potential impact on offsetting virgin nutrient acquisition associated with their recovery. The specific objectives of this work include to:

1. Understand how changes in feedstock composition (e.g., food waste with and without packaging materials) and carbonization process conditions (e.g., reaction time and temperature) influence primary (e.g., nitrogen, phosphorus, and potassium) and secondary nutrient fate (e.g., calcium, magnesium, sodium).
2. Determine the total leachable mass of primary nutrients from the solids
3. Investigate the magnitude of possible virgin primary nutrient requirements if food waste were hydrothermally carbonized and nutrient subsequently recovered from the solid and liquid-phases.

1.3 THESIS ORGANIZATION

This thesis contain is made up of four chapters and summarized as follows:

Chapter 1: This chapter describes the motivation and research objectives.

Chapter 2: This chapter provides a critical review on the environmental relevance of nutrient recovery during the hydrothermal carbonization of food waste.

Chapter 3: This chapter describes the fate of nutrient during hydrothermal carbonization of food waste and/or packaging material determined through a series of laboratory-scale experiments. This work has been published in the journal Waste Management (Idowu et al., 2017).

Chapter 4: This chapter is suggestion for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 HYDROTHERMAL CARBONIZATION

Hydrothermal carbonization (HTC) is a wet thermal conversion process that occurs at relatively low temperatures (180-350) °C and under autogenous pressures (e.g., Berge et al., 2011; Funke and Ziegler, 2010b; Li et al., 2013; Libra et al., 2011). The HTC process mimics the natural coalification of biomass; this process occurs faster because of the higher temperatures and elevated pressures (Ramke et al., 2009; Reza et al., 2014; M.-M. Titirici et al., 2007). During HTC, a series of complex reactions occur, including hydrolysis, dehydration, condensation, polymerization, decarboxylation, decarbonylation, demethoxylation and aromatization (e.g., Cao et al., 2013a; Hoekman et al., 2011; Kruse et al., 2013; Libra et al., 2011; Oliveira et al., 2013; Reza et al., 2016). Unlike other thermochemical conversion processes (e.g., incineration, pyrolysis), one of the most important components of this process is the liquid. The heated liquid acts both as a solvent and as a catalyst. Under HTC conditions, the dielectric constant and density of water are similar to those of organic solvent (Akiya and Savage, 2002; Hoekman et al., 2011). Also, the ionic product of water is known to increase 3 orders of magnitude from a temperature range of 25°C to 300 °C, promoting ionic reactions (Siskin and Katritzky, 2001). As a result of these reactions, value-added solid, liquid and gas products are generated. The

properties of these products largely depend on the starting feedstock and operating conditions (e.g., Falco et al., 2011; Giroto et al., 2015; Hoekman et al., 2013; Li et al., 2015; Lu et al., 2013; Lu, 2014; Mäkelä et al., 2016; Nizamuddin et al., 2016). Several recent reviews have detailed different aspects of carbonization, including reaction mechanisms (Funke and Ziegler, 2010b; Kruse et al., 2013; Libra et al., 2011), effect of process parameters (Hoekman et al., 2011; Nizamuddin et al., 2017), recovery of valuable liquid and solid products (Reza et al., 2014), and material synthesis for various material and/or environmental applications (Libra et al., 2011; M. M. Titirici et al., 2007; Titirici et al., 2012). The products generated from this process, particularly the solids, have the potential to be used in a large variety of applications, including as a soil amendment, energy source, environmental sorbent, and/or a material for energy and/or hydrogen storage (Berge et al., 2011; Falco et al., 2013; Heilmann et al., 2010; Libra et al., 2011; Roman et al., 2013).

The solid product (commonly referred to as hydrochar) is the most evaluated carbonization product. Hydrochar has the potential to be used in a large variety of applications, including as a soil amendment, energy source, environmental sorbent, and/or a material for energy and/or hydrogen storage (Berge et al., 2011; Falco et al., 2013; Heilmann et al., 2010; Libra et al., 2011; Roman et al., 2013). The liquid-phase (also referred to as process water) contains a variety of organics in significant concentrations (e.g., Erdogan et al., 2015; Funke and Ziegler, 2010b; Poerschmann et al., 2013; Stemann et al., 2013; Xiao et al., 2012). Organic acids, particularly acetic acid, are a major component of this phase and are formed as a result of degradation of simple sugars produced during hydrolysis (Berge et al., 2011; Reza et al., 2014). Intermediates such as

5-Hydroxymethylfurfural (5-HMF), furfural, phenol and glucose have also been detected in the process water (e.g., Berge et al., 2011; Broch et al., 2013; Poerschmann et al., 2013; Reza et al., 2014; Stemann et al., 2013; Wang et al., 2012). The least studied carbonization product is the gas phase. The gas-phase generated during HTC is primarily composed of carbon dioxide (Berge et al., 2011; Broch et al., 2013; Funke and Ziegler, 2010b; Li et al., 2013; Mau et al., 2016). Other reported trace components of the gas-phase include methane, ethane, propane, propene, butane, hydrogen, furan, and hydrogen sulfide (e.g., Danso-Boateng et al., 2015; Funke, 2015; Li et al., 2013; Mau et al., 2016).

2.2 ENVIRONMENTAL RELEVANCE OF NUTRIENT RECOVERY

Plant nutrients are essential to ensure the future security of the food supply system. A recent investigation projects that 70-80% of the future food supply depends on the availability of plant nutrients (Rittmann et al., 2011). There are recent projections that suggest that the global population will continue to increase exponentially, potentially reaching 9.3 billion by 2050 (Sakschewski et al., 2014). As a result, the demand for fertilizer required to meet anticipated increases in food production will also increase. For example, (Alexandratos and Bruinsma, 2012) recently estimated that the worldwide fertilizer requirements will reach approximately 263 million tonnes in 2050. There are significant concerns that current nutrient supplies are not sufficient to meet this anticipated demand. Many studies have reported that peak production will be achieved before 2033 (Cordell et al., 2009; Cordell and White, 2011; Mohr and Evans, 2013; Smil, 2000; Vaccari, 2009). Conversely, other studies have suggested that the ultimate recoverable reserve are much larger than previously estimated (Koppelaar and Weikard, 2013; Walan et al., 2014). Variations in these reported estimates are likely due to the difference in models used, and

assumptions made by each study (Walan et al., 2014). Nevertheless, it is clear that phosphate reserves continue to dwindle and the need for research into alternative source or reclaim consumed supply is needed (Adam et al., 2009; Cornel and Schaum, 2009; Le Corre et al., 2009; Tan and Lagerkvist, 2011).

A major concern associated with nitrogen fertilizers is the large amount of energy required to generate synthetic nitrogen fertilizers. It was recently reported that over half of the crops grown globally depend on the availability of synthetic nitrogen fertilizer (Zhang et al., 2015) which is energy intensive (Modak, 2011). (Miranowski, 2005) estimated that the agricultural sector in the US consumes 1.7 quadrillion BTUs of energy, with 26% of the energy consumed utilized for the production of synthetic nitrogen fertilizers. At the global level, it has also been reported that nitrogenous fertilizer production accounts for approximately 1% of the global energy supply (Hitaj and Suttles, 2016).

2.3 FOOD WASTE AS A POTENTIAL WASTE STREAM FOR NUTRIENT RECOVERY

Recovery of nutrients from waste streams is a potentially sustainable approach to reducing the demand for virgin nutrients. Over the years, the reclamation of nutrients from waste streams has been limited to the wastewater industry (Cai et al., 2013; El Diwani et al., 2007; Lind et al., 2000; Liu et al., 2011). Common technologies that have been investigated intensively for nutrient recovery from wastewater include struvite precipitation for recovery of ammonia and phosphate (El Diwani et al., 2007; Huang et al., 2015; Le Corre et al., 2009; Song et al., 2011), zeolite ion exchange for recovery of ammonia, potassium and phosphate (Beler-Baykal et al., 2011; Markou et al., 2014), and gas-permeable membranes for ammonia recovery (Semmens et al., 2003; Vanotti and

Szogi, 2010). Struvite precipitation has been reported to achieve 30-99.8% and 72 – 99.7% of ammonia and phosphorus, respectively (Capdevielle et al., 2016; Çelen and Türker, 2001; Foletto et al., 2013; Mehta et al., 2015; Stratful et al., 2001; Zeng and Li, 2006). Zeolite ion exchange has recovered 30-90.4%, 24.7-79.7% and 45.4-91% for ammonia, phosphorus and potassium, respectively (Guo et al., 2008; Kithome et al., 1998; Langwaldt, 2008; Mehta et al., 2015). Gas permable membranes have been reported to recover 84-100% of present ammonia (Semmens et al., 2003; Vanotti and Szogi, 2010).

Another waste stream that has great potential for nutrient reclamation is food waste. Food waste is an abundant waste stream and accounts for a significant fraction of municipal solid waste (MSW) discarded in many parts of the world, particularly in the US. For example, in 2014, the US generated 258.46 million tons of MSW and discarded 135.95 million tons in landfills with food waste accounting for over 21.6% of the total discarded mass (EPA, 2015). Similarly, the National Resource Defense Council (NRDC) reported that approximately 40% of food produced in the US is wasted between the points of production and consumption (NRDC 2012). There are projections that suggest that the mass of generated food waste will continue to increase. For example, Thi et al. (2015) recently reported that the current global food waste generation is expected to increase by 44% by 2025.

Food wastes represent a significant source of nutrients (Opatokun et al., 2015; Pleissner et al., 2013; Zhang et al., 2007). For example, Opatokun et al. (2015) reported that the nitrogen content in food waste from different countries ranges from 1.5-16%. Zhang et al. (2007) reported that the phosphorus, potassium, calcium, and magnesium concentrations were less than 2.2% in the analyzed food waste. Although these reported

concentrations appear relatively small, the availability of underutilized food waste globally would result in a significant mass of each.

Currently, recovery of nutrients and/or resources from food wastes, particularly in the US, is minimal. A large fraction of the food waste generated globally is discarded in landfills (Amini and Reinhart, 2011; Kojima and Ishikawa, 2012; Levis et al., 2010; Lin et al., 2011; Thi et al., 2015). Landfilled food waste undergoes biodegradation and generates a gas stream that is predominantly composed of methane and carbon dioxide (Allen et al., 1997; Levis et al., 2010; Themelis and Ulloa, 2007). Because food waste biodegrades quickly, the gas generated from landfilled food waste is mostly emitted to the atmosphere; thereby increasing environmental degradation with no added value (Cruz and Barlaz, 2010; Jokela and Rintala, 2003). Also, the nutrient content of the food waste is either lost through nitrogenous emissions, solubilizes in landfill leachate or remains buried in landfills, resulting in no recovery (Jokela and Rintala, 2003).

Food wastes diverted from landfills are generally either composted or anaerobically digested (Banks et al., 2011a; Bernstad and la Cour Jansen, 2012; Ike et al., 2010; Jambeck et al., 2006; Levis et al., 2010; Lundie and Peters, 2005; Tognetti et al., 2008). When composting food wastes, the resulting compost is applied as a soil amendment to help improve chemical and biological soil properties, as well as providing a limited source of nutrients to the soil (Sullivan et al., 2002; Tognetti et al., 2008). Factors that may limit the future sustainability of the composting process include the requirement for feedstock purity and the uncertainty of future markets of compost (Levis et al., 2010; Li et al., 2013).

Food wastes are also anaerobically digested. Much like when landfilling food wastes, generation of biogas results. In addition, the digestate can also be used as a soil

amendment (Giroto et al., 2015; Pezzolla et al., 2012). Unlike landfilling, however, gas collection efficiencies associated with anaerobic digestion processes are quite high (> 98%,) (Mata-Alvarez et al., 2000). Potential challenges associated with the anaerobic digestion of food wastes exist, such as high capital costs and long treatment times (Banks et al., 2011b; Li et al., 2013).

2.4 A REVIEW OF THE FATE OF NUTRIENT DURING HTC

The fate nitrogen, phosphorus and potassium during HTC has been evaluated for a variety of feedstock, such as digestates, sewage sludge, agricultural residue (e.g., wheat straw, rice husk) and algae (Funke, 2015; Funke et al., 2013; Li et al., 2013; Mau et al., 2016; Nurdawati et al., 2015; Reza et al., 2013; Smith et al., 2016; Sun et al., 2013; Reza et al., 2016). The results from these studies vary significantly, likely due to changes in feedstock properties and process conditions. This section provides a review of these studies. A summary of the major conclusions associated with studies evaluating the fate of nutrients during HTC is provided in Table 2.1. The information presented in Table 2.1 is limited to the nutrients recovered in the solid-phase because of limited information on nutrients in the liquid-phase.

A number of studies aimed at evaluating the fate of nutrient during carbonization of different digestates (e.g., cow manure, corn silage digestate, wheat straw digestate and food and agricultural waste digestate) have been reported (Funke et al., 2013; Funke, 2015; Smith et al., 2016; Stutzenstein et al., 2017). Recently, Funke (2015) investigated the fate of nutrients when digestate from two different feedstocks (i.e., wheat straw (WS) and a mixture of 30% cow manure and 70% corn silage (CM-CS) were carbonized under the

same process conditions (220°C ,185 mins). It was observed that 66% and 90% of the initial phosphorus was retained in the hydrochar from the WS and CM-CS digestate, respectively. The author suggested that this difference is likely due to higher precipitation of phosphate with mineral salt in the CM-CS digestate, which had ash concentration that was ~ 370% larger than the ash concentration in WS digestate. On the other hand, a higher percentage of initially present nitrogen was retained in the char from WS than that observed for the CM-CS. The author suggested that a higher percentage of initially present nitrogen in the WS-char is likely due to more ammonia-nitrogen that is either sorbed on the hydrochar, precipitated as salt, or integrated into the char during carbonization of WS. The majority of potassium was found in the process water for both feedstocks investigated.

Funke et al. (2013) also investigated the effect of temperature on the fate of nutrients when carbonizing digestate from wheat straw over a temperature range of 190-250 °C and for a duration of 6 hrs. The results obtained suggest that temperature had a relatively minor impact on the nutrient fate. The percentage of initially present phosphorus and nitrogen retained in the solid phase are similar for all temperatures investigated (e.g., 77-80% and 55-65%, respectively). Stutzenstein et al. (2017) evaluated the effect of temperature, time and initial pH on the fate of nutrients when carbonizing digestate from food and agricultural waste. Results from this study suggest that low temperatures favor retention of both nitrogen and phosphorus in the solid phase. The pH values evaluated had an opposite effect on the fate of nitrogen and phosphorus; high pH promoted the transfer of phosphorus into the solid phase, while a higher percentage of nitrogen remained in the hydrochar at low pH values. The author proposed that higher hydrolysis of organic nitrogen increased with temperature. Consequently, ammonia generated volatilizes thereby

reducing the solid nitrogen at higher pH. Also, increased dissolution of phosphorus at low pH is likely as a result of more charged phosphorus containing compound at lower pH that can easily solubilize in the process water.

Reza et al. (2013) investigated the fate of inorganics when carbonizing four different agricultural residues (Corn stover, Miscanthus, Switch grass, Rice husk). Each feed was carbonized for 5 min over a temperature range of 200-230° C. Results obtained from this study indicate that the percentage of phosphorus and potassium initially in the feedstock that transferred to the solid phase ranged from 8-46% and 6-36%, respectively. For each feedstock investigated, an increase in temperature caused a slight increase in the percentage of initially present phosphorus and potassium retained in the solid phase, which is consistent with results reported by Funke et al. (2013). Similarly, Smith et al. (2016) observed an increase in the initially present phosphorus recovered in the solid-phase when carbonizing willow and oak woods at higher temperatures (see Table 2.1). This effect of temperature on phosphorus may be due to precipitation of phosphorus at higher temperatures. It was recently reported that further dehydration at high temperature enhance the formation of carboxylic acid structure and promotes sorption of metallic cations on char surfaces (Silva et al., 2017). Sorbed cations on hydrochar surfaces may complex with soluble phosphorus and increase the phosphorus transferred to the solid phase. Conversely, the same study (Smith et al., 2016) reported that higher temperatures caused a decrease in the phosphorus transferred into the hydrochar when miscanthus was carbonized at the same process conditions. This observation suggests that feedstock properties influence nutrient fate. The results obtained for all the agricultural residue shows that potassium is primarily transferred to the liquid phase.

Reports from studies aimed at evaluating the nutrient fate during carbonization of sewage sludge suggest that a significant fraction of phosphorus present in the sludge is retained in the hydrochar, particularly at low temperatures. For example, Sun et al. (2013) carbonized sewage sludge at temperatures ranging from 180-240 °C and reaction times ranging from 0.5-1.5 hrs. Results from this study indicate that the majority of initially present phosphorus (> 85%) was retained in the char at all conditions evaluated. The range of initially present nitrogen and potassium recovered in the char are 30-58% and 30-46%, respectively. Similarly, Smith et al. (2016) reported that 92% of initial phosphorus was retained in the hydrochar when sewage sludge was carbonized at 200 °C for 1hr. The percentage of initially present phosphorus recovered in the hydrochar decreased to 53% when the reaction temperature was increased to 250 °C. The percentage of initially present potassium in the char remained relatively stable (around 50-53%) at all conditions evaluated.

Other waste streams that have been carbonized and evaluated for nutrient fate include greenhouse waste, MSW, algae, and cow manure (Smith et al., 2016; Reza et al., 2016). Reza et al. (2016) carbonized cow manure at a temp range of 180-260° C and reaction time (5 and 30mins). Results from this study indicated that reaction temperature had a significant effect on nutrient fate at both reaction times evaluated. The percentage of nitrogen incorporated into the char reduced as temperature increased. A similar trend was observed for phosphorus and potassium. On the other hand, the reaction time had a lower effect on the fate of each nutrient except for phosphorus that increase in the hydrochar at longer reaction time.

The fate of nutrients during carbonization of specific food wastes, such as empty

fruit bunch, orange pomace and mixed food waste, have also been reported (Erdogan et al., 2015; Nurdiawati et al., 2015; Smith et al., 2016). The results obtained from these studies vary significantly, particularly with the fate of phosphorus and potassium. The percentage of initially present phosphorus and potassium retained in the solid-phase ranged from 27-100% and 3-52%, respectively. Erdogan et al. (2015) reported that temperature and time had a minimal effect on the fate of nitrogen and potassium during carbonization of orange pomace.

Table 2.1: Fate of Nutrient during HTC of Different Feedstocks.

Information on Feedstock		Process Conditions				Percentage of Initially Present Nutrient Recovered in the Hydrochar						Ref
Category	Carbonized Feed	Solid Conc. %	pH	Temp (°C)	Time (hrs.)	Nitrogen		Phosphorus		Potassium		
						N (%)	Summary	P (%)	Summary	K (%)	Summary	
Digestate	Wheat straw digestate	15-20	NR	220	3.1	88.0	• Results suggest that feedstock properties influence the fate of N.	66.0	• Results suggest that feedstock properties influence the fate of P	28.0	• Results indicate the majority of K resides in the liquid-phase. • Result suggest feedstock properties do not influence the fate of K.	Funke et al 2015
	30% cow manure and 70% corn silage digestate	20				62.0		90.0		18.0		
	Wheat straw digestate	5	NR	190-250	6	55-65	• Majority of initially present N was retained in the char at all temperatures; Retention increases with reaction temperature	77-80	• Majority of initially present P was retained in the char; Retention was not influenced by reaction temperature.	NR	NR	Funke et al 2013
	Food and agric. Digestate and citric acid	5	3.3	180	1, 6.5	47.5, 60.4	• Low pH and low temperature promoted N retention in the char. • Result suggest that PC influences the fate of N.	9.5-21.5	• Results suggest that high pH and low temperatures promote P retention in the char. • Result suggest that PC influences the fate of P.	NR	NR	Stutzenstein et al 2017
				200	3.75	40.7		34.5				
				220	1, 6.5	29.9, 20.8		19.4, 26.3				
				245	5	9.8		12.0				
			5.5	165-230	3.8	26.5-54.3		30.2-58				
				200	8.3	28.2		40.7				
			8.0	180	1, 6.5	26.1-26.5		42.9-49.2				
				220	1, 6.6	16.8, 15.3		42.7, 22.9				

N= Nitrogen, P = Phosphorus, K =Potassium, PC= Process condition , NR=Not reported

Continuation of Table 2.1

Sludge	Sewage sludge	14.1	6.3	180	0.5-1.5	49-58	<ul style="list-style-type: none"> • Results suggest that temperature decreases the % of initially present N retained in the char • Reaction time does not appear to influence N fate, except at low temperatures. 	90-92	<ul style="list-style-type: none"> • Majority of initially present P was retained in the char and remained stable over all process conditions investigated. 	42-46		Xiao Han Sun et al 2013
				200		43-46		91-95		42		
				220		37-38		90-93		41-42		
				240		30-31		85-90		30		
	Sewage sludge	NR	NR	200,250	1	NR	NR	92,53	<ul style="list-style-type: none"> • Increases in reaction temperature reduced the % of initially present P retained in the char 	50, 53	<ul style="list-style-type: none"> • About half of the initially present K was retained in the char 	Smith et al 2016
Agricultural Residue and Forest Waste	Corn stover	16.7	NR	200-230	0.08	NR	NR	8-22	<ul style="list-style-type: none"> • % of initially present P retained in the char increased with temperature for all each feedstock investigated 	8-36	<ul style="list-style-type: none"> • Reaction temperature increased the % of initially present K retained in the char. 	Reza et al 2013
	Miscanthus							10-42		11-20		
	Switch grass							18-25		6-21		
	Rice husk							21-46		15-24		
	Willow	NR	NR	200,250	1	NR	NR	28,59	<ul style="list-style-type: none"> • % of initially present P retained in the char increased with reaction temperature for willow and oak wood. An opposite trend was observed for miscanthus. 	16	<ul style="list-style-type: none"> • Increases in reaction temperature decreased the % of initially present K retained in the char. • Temperature had no effect on the fate of K in willow wood 	Smith et al 2016
	Oak wood			200,250	1	NR		57,82		31,16		
	Miscanthus	NR	NR	200,250	1	NR		50,30		29,12		
	Wheat straw	6	7.9	190-250	6	47-64	<ul style="list-style-type: none"> • Result suggest that reaction temperature increased the % of initially present N retained in the char. 	36-78	<ul style="list-style-type: none"> • % of initially present P retained in the char increased with reaction temperature 	NR	NR	Funke et al 2013

N= Nitrogen, P = Phosphorus, K =Potassium, PC= Process condition , NR=Not reported

Continuation of Table 2.1

Others Wastes	Green house waste	NR	NR	200,250	1	NR	NR	41,67	• % of initially present P retained in the char increased with reaction temperature for each feedstock investigated except for micro algae	40,4	• Increases in reaction temperature decreased the % of initially present K retained in the char	Smith et al 2016
	MSW							71,77		36.12		
	Macro algae							76,88		24,13		
	Micro algae							40,24		14,4		
	Cow manure	16.7	7.2	180-260	0.08	77.3-42	• Results suggest that increases in reaction temperature decreased the % of initially present N retained in the char; Retention is not influenced by reaction time	68.6-54.7	• Majority of initially present P was retained in the char; retention decreased with increases in reaction temperature and increased with reaction time	37.4-9.7	• Increases in reaction temperature decreased the % of initially present K retained in the char	Reza 2016
					0.5	73-55.2		100.8-81.3		33.6-5.1		
Food Waste Component	Orange pomace	11.1	NR	175	0.5-2	37-42	• Results suggest that % of PC does not influence the fate of N	27-46	• Results suggest that both temperature and time increases the transfer of initially present P into the char	28-37	• % of initially present K in the liquid phase increases as reaction temperature increases.	Erodgan 2015
				190	0.5-2	35-36		42-88		27-33		
				225	0.5-2	31-36		86-91		19-25		
				260	0.5-2	33-35		83-100		12-22		
	Empty fruit bunch	9.1	NR	180, 220	0.5	71, 63	• % of initially present N retained in the char decreases with increases in reaction temperature	90.3, 91.5	• Results suggest that temperature has no influence on the fate of P at short reaction tome	47,35	• % of initially present K retained in the char decreases with increases in reaction temperature	Anissa Nurdiaawat 2015
	Food waste	NR	NR	200,250	1	NR	NR	53,85	• % of initially present P retained in the char increased with reaction temperature	7,3	• Majority of initially present K is found in the liquid-phase	Smith 2016

N= Nitrogen, P = Phosphorus, K =Potassium, PC= Process condition , NR=Not reported

CHAPTER 3

HYDROTHERMAL CARBONIZATION OF FOOD WASTE FOR NUTRIENT RECOVERY AND REUSE¹

¹ Hydrothermal carbonization of food waste for nutrient recovery and reuse, Idowu, I., Li, L., Flora, J.R., Pellechia, P.J., Darko, S.A., Ro, K.S., Berge, N.D., 2017. Waste Management, 69, 480-491. Reprinted here with permission of publisher

ABSTRACT

Food waste represents a rather large and currently underutilized source of potentially available and reusable nutrients. Laboratory-scale experiments evaluating the hydrothermal carbonization of food wastes collected from restaurants were conducted to understand how changes in feedstock composition and carbonization process conditions influence primary and secondary nutrient fate. 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. A series of leaching experiments to determine potential solid-phase nutrient availability were also conducted and indicate that, at least in the short term, nitrogen release from the solids is small, while almost all of the phosphorus present in the solids produced from 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, respectively, in the US can be replaced by the nutrients integrated within hydrochar and liquid-phases generated from the carbonization of currently landfilled food wastes.

3.1 INTRODUCTION

Concerns associated with anticipated future nutrient demands required to satisfy projected increases in food production due to the growing population are well documented (e.g., Cordell et al., 2009; Dawson and Hilton., 2011). Alexandratos and Bruinsma (2012) estimate worldwide fertilizer requirements will reach approximately 263 million tonnes in 2050. Challenges associated with achieving this level of fertilizer production stem from dwindling nutrient (particularly phosphorus) availability, inefficient nutrient use and/or recovery from residual materials, and/or high energy demands associated with fertilizer production (e.g., Cordell et al., 2009; Dawson and Hilton., 2011). Developing effective strategies to overcome these challenges is critical for meeting future food demands.

One promising and potentially sustainable approach to alleviating some of these challenges is to recover nutrients from food waste using hydrothermal carbonization (HTC). Food waste represents a rather large and currently underutilized source of potentially available and reusable nutrients. In 2014, 38.4 million tonnes food waste were generated in the United States (US) (USEPA, 2016), which contain significant amounts of available nitrogen, phosphorus, and potassium. HTC is a thermal conversion process in which wet feedstocks are converted into value-added liquid, solid (also referred to as hydrochar), and gaseous products (Berge et al., 2011; Funke and Ziegler, 2010b; Libra et al., 2011; Sevilla and Fuertes, 2009; Titirici and Antonietti, 2010) without the need for feedstock drying prior to conversion, at relatively low temperatures ($<350\text{ }^{\circ}\text{C}$), and with relatively low input energy requirements (Berge et al., 2011; Funke and Ziegler, 2010a; Li et al., 2013; Libra et al., 2011). Managing food wastes using HTC has the potential to reclaim nutrients from these food wastes in a form that may be directly used as a

fertilizer/soil amendment, potentially reducing the need for acquisition of virgin nutrients and thus reducing energy demands associated with fertilizer manufacturing.

The feasibility and environmental benefits associated with the HTC of different food wastes (e.g., corn, artichoke waste, onion, fish, mixed urban food waste) and food-related residues (e.g., corncob, grape seeds, rice hull, tomato peels) have been previously reported (e.g., Benavente et al., 2015; Cao et al., 2013b; Li et al., 2013; Lu and Berge, 2014; Oliveira et al., 2013; Reza et al., 2013; Sabio et al., 2016). Understanding the fate of nutrients as a result of food waste carbonization is necessary to develop a nutrient recovery and recycling strategy. The fate of nitrogen, phosphorus, and/or potassium has been evaluated for a variety of feedstocks, including animal manures (e.g., cow, horse), bamboo, various digestates, straws, algae, and sewage sludge (Ekpo et al., 2016; Erdogan et al., 2015; Funke et al., 2013; Funke, 2015; Heilmann et al., 2014; Smith et al., 2016; Reza et al., 2016; Zhang et al., 2014). Nutrient fate reported in these studies varies significantly because of changes in feedstock composition/properties and process conditions, complicating the extension of such information to that of different feedstocks.

Relatively little information associated with the fate of primary (e.g., nitrogen, potassium, and phosphorus) and secondary (e.g. calcium, sodium, and magnesium) nutrients as a result of the carbonization of mixed restaurant-generated food wastes exists. Benavente et al. (2015) and Reza et al. (2013) evaluated the fate of nutrients of specific food wastes, reporting that between approximately non-detectable levels to 50% and 5–55% of initially present phosphorus and potassium, respectively, ultimately reside in the hydrochar following the carbonization of olive mill, canned artichoke, and orange juice wastes and rice hull. The reported variability associated with nutrient fate in these studies

suggests that information specific to the carbonization of restaurant-generated food waste is needed before an appropriate strategy for reclaiming nutrients from this waste stream can be developed.

The purpose of this work is to evaluate the fate of nutrients resulting from the carbonization of food waste collected from local restaurants and to ultimately use such information to determine the potential impact associated with offsetting the need for virgin nutrient acquisition and fertilizer production if using the generated solids as a fertilizer. The specific objectives of this work include to: (1) understand how changes in feedstock composition (e.g., food waste with and without packaging materials) and carbonization process conditions (e.g., reaction time and temperature) influence primary (e.g., nitrogen, phosphorus, and potassium) and secondary nutrient fate (e.g., calcium, magnesium, sodium), (2) determine the total leachable mass of primary nutrients from the solids, and (3) investigate the reduction of virgin primary nutrient requirements if food wastes were hydrothermally carbonized and nutrients subsequently recovered from the solid and liquid-phases.

3.2 MATERIALS AND METHODS

3.2.1 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). Briefly, 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 constraints. 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 3.1).

Table 3.1. Collected food waste and packaging material properties*.

Waste Component	Moisture Content (wet wt.%)	C (% dry wt.)	N (% dry wt.)	P (% dry wt.)	K (% dry wt.)	Ca (% dry wt.)	Mg (% dry wt.)	Na (% dry wt.)
Food Waste	63.79 (0.71)	50.90 (0.57)	3.18 (0.15)	0.42 (0.01)	0.52 (0.01)	0.21 (0.01)	0.05 (0.001)	1.11 (0.04)
Paper	24.52 (6.42)	46.80 (1.12)	0.21 (0.15)	0.02 (0.003)	0.05 (0.006)	0.55 (0.43)	0.03 (0.01)	0.18 (0.06)
Cardboard	12.79 (4.59)	41.43 (1.75)	0.09 (0.02)	0.01 (0.005)	0.05 (0.04)	1.68 (0.31)	0.04 (0.02)	0.11 (0.01)
Plastic	4.10 (2.03)	80.54 (5.42)	0.22 (0.29)	0.01 (0.004)	0.03 (0.01)	0.12 (0.08)	0.01 (0.004)	0.05 (0.03)

*All values represent average values of at least 5 samples. Values in parenthesis represents standard deviation

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 h, or until the dried sample mass remained 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. This acid digestion process involved first ashing the samples in a muffle furnace and subsequently dissolving the ash in 6N HCl.

3.2.2 Batch HTC experiment

All batch carbonization experiments were conducted following procedures previously described (Berge et al., 2011; Li et al., 2013; Lu et al., 2012). Briefly, 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 h. 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 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 at 250 °C. The first set of experiments was conducted to determine how reaction temperature and time influence nutrient fate. In these experiments, the food was carbonized at the as received solids content (36.2% dry solids). 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 these 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 either in a 1 or 3-L foil gas sampling bag. Gas composition of these samples was analyzed using GC-MS (Agilent 7890) with 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 were 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 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.

3.2.3 Sequential nutrient extraction experiments

Experiments evaluating total leachable 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 phosphorus leachability was Mehlich 3 (0.2 N CH_3COOH , 0.25 N NH_4NO_3 , 0.013 N HNO_3 , 0.015 N NH_4F , 0.001 M EDTA,

Aqua Solutions), which has been commonly used to evaluate plant available phosphorus in different soil matrices (e.g., Wuenscher, Unterfrauner et al. 2015). When evaluating the leaching of the nitrogen species, 0.01M CaCl₂ was used as an extractant (e.g., Li et al., 2012; Mengel et al., 2000).

After the hydrochar mass and extract volume were added to each centrifuge tube, the tubes were capped and mixed in a rotary mixer for 24 h. 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-h. This process continued until three sequential extractions occurred, which, based on results from preliminary experiments, was 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).

3.2.4 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 H_3PO_4 , and referenced externally with $\text{NH}_4 \cdot \text{H}_2\text{PO}_4$ which was assigned a value of 0.72 ppm.

Solution-state ^{31}P 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 25 °C. A 200 ppm window centered at 0 ppm (with respect to H_3PO_3) was collected using 30degree pulses and a 5s relaxation delay. Inverse-gated ^1H broadband decoupling was used to minimized nuclear over hauser enhancements. The neat liquids were spiked with 5% D_2O for field-frequency lock and required 256-1024 added transients.

3.3 RESULTS AND DISCUSSIONS

3.3.1 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 (Knezevic et al., 2009, 2010; Li et al., 2013; Lu et al., 2012, 2013; 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 the 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 3.1). Based on these carbon distribution data, carbonization reactions are complete after approximately 4 h, 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 3.2), 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 h.

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 3.3a).

Figure 3.1. 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 mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P.

Figure 3.2. 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 mixed food waste and packaging materials were carbonized are represented by the abbreviation FW + P

(a)

(b)

Figure 3.3. Ratio of predicted (following procedures outlined by Li et al., (2013) and Lu and Berge (2014) and actual parameters when carbonizing mixed food and packaging materials at 250 °C: (a) solid-phase and (b) liquid-phase.

3.3.2 Nutrient fate

3.3.2.1 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.

Reaction temperature and time appear to impart only a small influence on nitrogen fate (Figs 3.4 and 3.5). Changes due to reaction temperature and time are most significant at early reaction time. 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 temperature and time, with ammonia concentrations increasing with higher reaction temperatures and

longer times (Figure 3.6), 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 liquid-phase following carbonization of food waste, with specific reaction conditions imparting little influence on this distribution (Figures 3.5) after 4 h. Potassium and sodium have large water solubilities, so this result is expected. This is also consistent with many previously published reports (Funke et al., 2013; Funke, 2015).

Phosphorus fate does depend on reaction time and temperature. Phosphorus integration within the liquid-phase decreases with reaction temperature and time (Figure 3.5b). 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; Chen, Lin et al. 2017).

Based on results from solid-phase ^{31}P -NMR (Figure 3.7a 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-h 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 ^{31}P -NMR spectra, reaction time, temperature, and presence of packaging materials play a role in phosphoester hydrolysis (Figure 3.7b). The phosphoester content of the solids generated at the different reaction temperatures when carbonizing only food wastes is smallest after carbonizing for 24 h and decreases with increasing reaction temperature. The presence of phosphate in the solids is observed at all reactions times when carbonizing food wastes at 250 °C, but only at late (24 h) and early times (1 h) when carbonizing at 225 and 275 °C, respectively, consistent with the relative degree of hydrolysis occurring at each temperature. 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. Phosphate-metal precipitates may be formed, which are difficult to distinguish using standard ^{31}P -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 ^{31}P -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 solid-phase at the majority of reaction times and temperatures (Figures 3.5). After 4 h, 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 h, calcium integration within the solid-phase stabilizes. Similarly, with the exception of carbonizing for 1 h, the majority of magnesium remains integrated within the solid-phase (Figures 3.5). The degree of this integration increases with reaction temperature and time, with trends stabilizing after 16 h for all reaction temperatures.

3.3.2.2 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 (Figures 3.5), 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 3.3a), 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 (Table 3.1). In addition, packaging materials typically contain significantly greater levels of iron, aluminum, and chromium 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 ^{31}P -NMR spectra, the presence of packaging materials decreases (or slows down) phosphoester hydrolysis (Figure 3.7b). 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.

Figure 3.4. 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 3.5. 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

Figure 3.6. 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

(a)

(b)

Figure 3.7. ^{31}P -NMR results from hydrochar generated during the carbonization of food and mixed food and packaging wastes: (a) representative ^{31}P -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.

3.3.3 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 3.8). 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 3.8), except for the mildest carbonization condition (e.g., 225 °C and 1 h.). 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 h. 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 it 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 3.9). 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 Lehmann 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 3.8. 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 3.9. Percentages of phosphorus released during the sequential extraction experiments. Error bars represent the standard deviation of the conducted experiments.

3.3.4 Potential environmental implication

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.

3.3.4.1 Nutrient recovery from the solid-phase

Using the experimental data obtained from this work (e.g., solid yields and leaching of solid-bound nutrients), estimates of potential nutrient recovery from currently landfilled food wastes were performed. Table 3.2 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 3.10 shows the average percentages of nitrogen and phosphorus fertilizers that can be replaced with nutrients available from the hydrochar. Table 3.3 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 fertilizer with the recovered nutrients from food wastes would alleviate the dwindling phosphorus supply. In addition, mostly nonrenewable energy used for synthesizing chemical fertilizers will be reduced. Table 3.4 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.

Figure 3.10. 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.

Table 3.2. Data used to estimate the amount of fertilizer that can be replaced by recycling nutrients following the carbonization of food wastes

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 3.3. Reaction conditions resulting in the maximum average nutrient recovery from the solid-phase*.

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

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

Table 3.4. Average energy savings associated with replacing virgin fertilizer with hydrochar-based fertilizer (kJ)*

Carbonization Conditions		Nitrogen Fertilizer		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

3.3.4.2 Nutrient recovery from the liquid-phase

Recovery of nutrients from the process water may also be possible. Table 3.5 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 3.2 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 plants 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 3.11.

Table 3.5. Maximum average nutrient recovery from the liquid-phase*.

Nutrient	Reaction Temperature (°C)	Reaction Time (hr)	Recoverable Nutrient Mass (mg/g wet food waste)	% Replacement of fertilizer used in 2011
Total Nitrogen (as N)	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

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

(a)

(b)

(c)

Figure 3.11. 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.

3.3.4.3 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 3.3 and 3.5). The optimal HTC process conditions for the maximum possible recovery of the nutrients from both hydrochar and its process water are shown in Table 3.6. 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.

Table 3.6. 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

3.4 Conclusion

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.

CHAPTER 4

FUTURE WORK

The results from this project reveal the percentage of primary and secondary nutrients that may potentially be recovered from the liquid and solid phase when food waste is hydrothermally carbonized. Maximizing the percentage of nutrients recovered from each phase with minimal environmental impact is desirable. Additional work investigating the potential for recovering the nutrients from each phase and the corresponding environmental implications of both recovery and use are important aspects of work that is still needed. Some important components of future work are as follows:

- *Optimization of nutrient extraction from HTC process water.* The HTC process water is a complex matrix with properties that differ significantly at different process conditions. The feasibility of nutrient recovery from HTC process water using processes commonly applied to wastewater (i.e. struvite precipitation, ion exchange) should be explored.
- *Evaluation of the potential of using hydrochar as fertilizer.* The availability of nutrients and environmental impacts of land application of the hydrochar needs to be investigated.

- *Comparison to other approaches:* A comparison of the economic benefits and environmental impacts associated with hydrothermal carbonization of food wastes for nutrient reclamation with other current approaches used to manage food wastes is needed

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