MINERAL NUTRIENT RECOVERY FROM PYROLYSIS CO-PRODUCTS

A Dissertation

by

JATARA ROB WISE

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 2012

Major Subject: Soil Science

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Approved by:

Co-Chairs of Committee,	Donald Vietor
	Tony Provin
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	Clyde Munster
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ABSTRACT

Mineral Nutrient Recovery from Pyrolysis Co-Products.

(May 2012)

Jatara Rob Wise, B.S., Lamar University; M.S., Texas A&M University

Co-chairs of Advisory Committee: Dr. Tony L. Provin
Dr. Donald M. Vietor

Pyrolysis is the thermo-chemical degradation of biomass in an oxygen-free environment to product liquid, gaseous, and solid co-products. The liquid co-product, known as bio-oil, can be used as a transportation fuel. The gaseous co-product, known as synthesis gas, can be used to power the pyrolysis reactor or other machinery. The solid co-product, known as bio-char, has been studied as an amendment to enhance soil physical and chemical properties and nutrient status.

Although previous publications have described the beneficial effects of pyrolysis bio-char on soil physical and chemical properties, relatively little has been published on the recovery of mineral nutrients from pyrolysis co-products. This work quantified the recovery of feedstock nutrients (P, K, Ca, and Mg) and micronutrients (Na, Zn, Fe, Cu, and Mn) from pyrolysis co-products from various feedstocks using three distinct pyrolysis reactor designs. The reactors comprised a laboratory-scale fixed-bed reactor and two fluidized-bed reactors located in College Station, TX and Wyndmoor, PA. Nutrient recoveries, on a feedstock basis, were calculated for a comparison of reactor efficiencies. In addition to nutrient recoveries, physical and chemical properties of input biomass and of bio-char generated by each reactor were characterized through ultimate and proximate analyses.

For the fixed-bed reactor, results revealed variation among feedstocks for the recoveries of feedstock sources of macronutrients and Na, Fe, and Cu in pyrolysis co-products. Variation among species was also detected for the recoveries of feedstock sources of P, K, Ca, Mg, and Fe in pyrolysis co-products for samples pyrolyzed using the Wyndmoor reactor. For the College Station reactor, recoveries of feedstock sources of P, K, Ca, and Mg in pyrolysis co-products did not vary among species, but Zn did vary. Ultimate and proximate analyses of biomass and bio-chars generated by the three reactors revealed variation among species. Additionally, the results showed that the recovery of feedstock nutrients varied by reactor design. Statistical analysis revealed high correlations and linear relationships between the recovery of nutrients and reactor mass and energy efficiency and feedstock fiber properties.

DEDICATION

I would like to dedicate this to my mother Viola, my sister Monica, my two nieces Jala and Zaniya, and nephew Jeremiah for all of their love, encouragement and support through this long and difficult journey.

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I would like to thank my committee co-chairs Dr. Donald Vietor and Dr. Tony Provin for taking a chance on me and bringing me into the Department of Soil and Crop Sciences which gave me the opportunity to achieve this lifetime goal. They always encouraged me and, most importantly, critiqued and gave me feedback in a manner that was always encouraging rather than condescending.

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NOMENCLATURE

NCG	Non-condensable gas
NDF	Neutral detergent fiber
ADF	Acid detergent fiber
ADL (DM)	Acid detergent lignin (dry matter)
ADL (OM)	Acid detergent lignin (organic matter)
HES	High-energy sorghum
VCM	Volatile combustible matter
HHV	Higher heating value
UA	Ultimate analysis
PA	Proximate analysis
BET	Brunauer, Emmett, Teller surface area

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1. INTRODUCTION

As the demand for energy within the United States and around the world grows each year, it is imperative that alternative energy sources in addition to traditional petroleum be sought. The majority of the energy in the U.S. originates from fossil fuels. Some sources indicate that U.S. crude oil demand will reach 12.32 quadrillion Btu yr^{-1} by 2035 ("AEO2011 Early Release Overview"). Continued high demand for petroleum, which is nonrenewable, will eventually exhaust existing supplies. In addition, high use of fossil fuels causes atmospheric pollution problems, including global warming and acid rain (Jorgenson, 2006). A shift to non-conventional, renewable energy resources, including wind, solar, hydrothermal, geothermal, and biomass could alleviate fossil fuel demands and associated environmental problems. The need for liquid transportation fuels derived from other sources than fossil fuels has been the focus of most renewable energy research.

One method to method to meet this need is through the conversion of biomass with pyrolysis. Pyrolysis is defined as the thermo-chemical decomposition of organic matter in an oxygen-free environment to produce liquid, gaseous, and solid co-products. These three respective co-products are known as bio-oil, synthesis gas, and bio-char. Pyrolysis has received special attention as it can convert biomass directly into energy products. Bio-oil is currently being investigated as a substitute for crude oil.

This dissertation follows the style of Soil Biology and Biochemistry.

For highly cellulosic biomass feedstocks (i.e. sorghum, switchgrass, ect.), the pyrolyzed liquid fraction usually contains acids, alcohols, aldehydes, ketones, esters, heterocyclic derivatives and phenolic compounds (Yaman, 2004). Bio-oil usually has about half the energy content of crude oil and contains high oxygen and water, acid contaminants, and particulate matter from feedstocks that are corrosive to internal combustion engines (Boyle, 2004). Bio-oil has an acidic pH that averages about 2.5. High water content causes problems with combustion engines during ignition. The average water content of bio-oil ranges from 20 to 30% and the average oxygen content ranges from 40 to 50%.

The non-condensable gaseous (NCG) co-products of pyrolysis comprise ~20% H_2 (molecular hydrogen), ~20% CO (carbon monoxide), ~10 to 15% CO_2 (carbon dioxide), ~2 to 3% CH_4 (methane), ~5% C_2H_6 (ethane), <1% O_2 (oxygen), ~40 to 45% N_2 (nitrogen gas), and ~5% H_2O (condensable water vapors). In addition, small amounts of condensable vapors of liquid hydrocarbons called poly-cyclic aromatic hydrocarbons (PAHs), including pyroligneous acid, acetic acid, turpentine, and some alcohols can be recovered in the NCG fraction. The combination of CO and H_2 makes up what is commonly known as synthesis gas (syngas) or producer gas. For example, the pyrolysis of cellulose ($C_6H_{10}O_5$) produces NCG's and is characterized by the following stochiometric reactions:

$$C_6H_{10}O_5 + heat \rightarrow CH_4 + 3H_2O + 2CO + 3C$$

$$C_6H_{10}O_5 + heat \rightarrow 2.5CH_4 + 1.5CO_2 + 2CO$$

$$C_6H_{10}O_5 + heat \rightarrow 2.5CH_4 + 2.5CO_2 + C$$

$$C_6H_{10}O_5 + heat \rightarrow 5H_2 + 1.5CO_2 + 2CO + 2.5CO.$$

These reactions are endothermic, which means heat is required to complete the reaction. Furthermore, these reactions assume that no oxygen is present as cellulose reaches its ignition point during pyrolysis, which is approximately 232°C. Due to its combustibility, syngas is can be used as an energy source to generate electricity and power the reactor.

The third co-product, bio-char, is similar to charcoal and is the solid devolatilized residue of the biomass (Wang and Yan, 2008). In other words, bio-char is the residue left after the biomass has reached its critical reaction temperature. The bio-char comprises non-combusted organic C and ash. Bio-char can be re-applied back to soil in order to sequester carbon and recycle mineral nutrients. In fact, bio-char sequestration could amount to 5.5 to 9.5 Pg C yr^{-1} if global energy demands were met through pyrolysis (Lehmann et al., 2006). This translates into 37 to 139 million metric tons of feedstock, assuming 50% of bio-char is C and 30% bio-char yield from feedstock.

Recent estimates indicate sustainable global implementation of pyrolysis and recycling of bio-char could potentially off-set a maximum of 12% of current anthropogenic CO_2 emissions (Woolf et al., 2010). In addition to the organic C added through bio-char application to soil, bio-char has been shown to adsorb CO_2 released to the atmosphere from plant decomposition and manmade sources (Van Zwieten et al., 2009). Canadian studies have shown that if 10% of the world net primary production (NPP) of biomass is converted at 50% bio-char and 30% energy from volatiles, 4.8 Gt C yr^{-1} will be sequestered. Additionally, the C in bio-char could be 20% greater than the current annual increase of atmospheric carbon at 4.1 Gt C yr^{-1}(Matovic, 2010). An overview of the pyrolysis process is depicted in Figure 1.

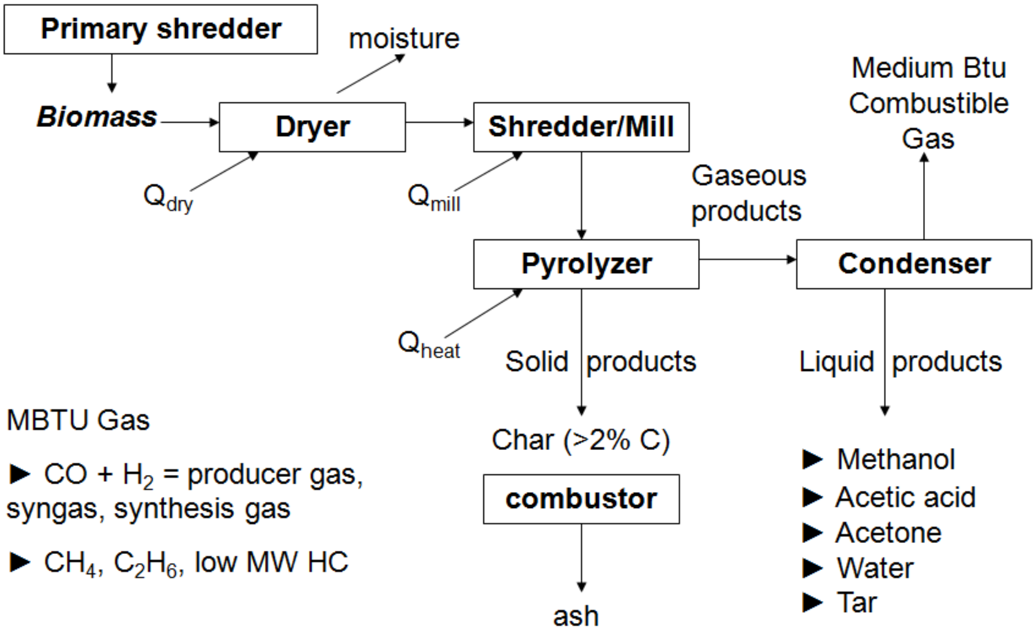

Figure 1. Conceptual framework of the pyrolysis process.

Variation of pyrolysis conditions, including temperature, carrier gas flow rate, and biomass feeding and heating rates affect the yield and properties of bio-oil, bio-char, and synthesis gas. Reactor temperature and biomass feeding and heating rates vary among slow, fast, and flash pyrolysis. Slow pyrolysis is a conventional process in which heating rate is kept slow (5-7 ^{o}C min^{-1}) when compared to fast (300-500°C min^{-1}) or flash pyrolysis (>1000°C min^{-1}). Relatively low heating rate and pyrolysis temperature (< 300 ^{o}C) increases the yield of bio-char in relation to bio-oil and synthesis gas. In contrast, higher temperatures (300 to 500 ^{o}C) and heating rates increase bio-oil yield in fast compared to slow pyrolysis. Flash pyrolysis is an improved version of fast pyrolysis resulting in higher syngas yields. The heating rates are about 1000 ^{o}C min^{-1} and residence times are a few seconds (Capareda, personal communication, September 2010).

Variation of biomass composition, including ligno-cellulosic components, similarly affects yield and composition of pyrolysis co-products. Crops selected as "suitable" biomass crops normally are high in cellulose (>40%), hemicelluloses (>22%), and lignin (>10%). The amount of cellulose, hemicelluloses, and lignin can be estimated using the filter bag system (Pagan et al., 1998). Biomass is processed through wet chemistry to estimate concentrations of neutral detergent fiber (NDF), acid detergent fiber (ADF), acid detergent lignin (ADL), and ash (mostly noncombustible inorganic heavy metals). Alternative chemical methods for quantifying biomass concentrations of soluble fiber and ash have been published by the National Renewable Energy Laboratory (NREL). The standard analytical procedure to estimate structural carbohydrates and lignin (NREL/TP-510-42618) using an high-performance liquid chromatography (HPLC) can be used for extractive-free biomass (Sluiter et al., 2004). Additionally, the NREL standard method for determination of ash in biomass utilizes a common high temperature (550°C) furnace combustion method (Sluiter et al., 2005).

The American Society for Testing and Materials *(*ASTM*)* similarly uses HPLC for a standard test method for the determination of carbohydrates in biomass (ASTM E1758-01(2007).In addition, ash in biomass is quantified through combustion (ASTM E1755-01(2007). In addition to the methods listed above, the Technical Association of the Pulp and Paper Industry (TAPPI) provides methods for estimating carbohydrates (Test Method T 249 cm-85), lignin (Test Method T 222 om-11), and ash (Test Method T 244 cm-99).

Analyses of the chemical and physical properties contribute to evaluations of effects of feedstock properties and pyrolysis conditions on bio-char quality. Physical properties measured for bio-char include BET (Brunauer, Emmett and Teller) surface area, porosity, pore size, and particle density. Chemical properties include proximate analysis (fixed carbon, volatile and ash content of biomass), ultimate analysis (elemental C, H, O, S, N), and heating values (Brewer et al., 2009). A recent publication revealed bio-char surface areas of various treatments of switchgrass, corn stover, and hardwood were low and ranged from 7–50 m^2 g^{-1} as compared to activated carbon, which was an order of magnitude higher. An independent study of switchgrass revealed surface areas of 7.7 and 7.9 m^2 g^{-1}, two orders of magnitude less than surface areas encountered in activated charcoal (Boateng, 2007). Among other physical properties, bulk density of bio-char from pyrolyzed rapeseed cake was 467 kg m^{-3} and the heating value was 25.3 MJ kg^{-1} (Özçimen and Karaosmanoğlu, 2004).

Surface area, porosity, and other bio-char physical properties can affect physical and chemical properties of amended soil, including cation exchange capacity (CEC), surface charge density, and nutrient holding capacity.

Evaluation of bio-char effects on soil requires analyses of the physical and chemical properties of amended soil. Bio-char has been shown to increase SOM (soil organic matter) concentration, decrease nutrient leaching in percolate, increase water retention, improve soil structure, and add essential nutrients back to the soil in long-term human settlements (Steiner et al., 2007). Hundreds of years after application, charred biomass can still be seen in these anthropogenic soils, which exhibit the aforementioned desirable soil traits.

In addition to return of organic C, recovery and conservation of biomass P, K, and other mineral nutrients in recycled bio-char is crucial for sustainable biomass production. Research has revealed that most of these inorganic compounds, especially K, Ca, Na, Si, P, and Cl, are constituents of the ash in biomass feedstocks (Agblevor and Besler, 1996). High recoveries P and K were reported for bio-char derived from fluidized-bed, fast pyrolysis of corn cob and stover feedstocks (Mullen et al., 2010). Using a fluidized-bed fast pyrolysis reactor, it was found that respective corn cob and corn stover bio-chars contained 4.36 and 12.94 g kg^{-1} of P and 43.35 and 23.46 g kg^{-1} of K (Mullen et al., 2010). This translated into74 and 102% recovery of P and a 78 and 89% recovery of K on a feedstock basis, respectively. In addition, studies of fast pyrolysis of stored hybrid poplar, switchgrass, and corn stover feedstocks indicated feedstock concentrations of P and K increased during aging of biomass (Agblevor et al., 1995). Increases in P and K were postulated to be a result of increased inorganic ash content due to losses of structural and nonstructural carbohydrates from environmental exposure of the biomass.

Phosphorus and K are essential to plant growth and development. Recycling of bio-char to soil could reduce the need for K and P fertilizers. This savings in fertilizer and associated labor and equipment costs could enhance the sustainability of biomass production.

Soil applications of bio-char from hardwood added 2.5 x 10^{-4} mg kg^{-1} of P and 17 x 10^{-4} mg kg^{-1} of K to a Midwestern agricultural soil (Laird et al., 2010). Similarly, addition of peanut hull bio-char at rates of 0, 11, and 22 Mg ha^{-1} to a Tifton loamy sand soil increased Mehlich 1 extractable concentrations of N, P, K, Ca, and Mg (Gaskin et al., 2010).

The quantity of bio-char produced and mineral nutrient recovered per unit of feedstock is dependent on pyrolysis conditions. When heating rates are kept slow, bio-char yield per unit of feedstock is greater than liquids or gases. Yet, low recovery of K (~35%) and other nutrients was observed in bio-char derived from slow pyrolysis of sorghum biomass and in soil amended with the bio-char (Schnell et al., 2010). Recovery of less than 10% of biomass K in bio-char derived from slow pyrolysis indicated K and other mineral nutrients could be lost through condensed bio-oil and syngas (Schnell et al., 2011). Elemental analysis revealed that the levels of P and K in bio-oil and bio-char decreased with hot gas filter pore size during pyrolysis of stored switchgrass feedstock (Agblevor et al., 1995). Additional research is needed to evaluate recovery of biomass sources of mineral nutrients in co-products of pyrolysis, including bio-char and bio-oil.

Contrasting nutrient recoveries in bio-char derived from pyrolysis suggest definitive evaluations of mineral nutrient recovery in bio-char and other pyrolysis co-products are needed (Mullen et al., 2010, Schnell et al., 2011). Studies on the fate of minerals during combustion and thermo-chemical conversion processes indicate losses through airborne aerosols need to be evaluated. These aerosols originate from various natural and anthropogenic sources such as the soot from biomass burning, dust storms, and volcanic eruptions. Other studies have reported potassium-salt particles were the most abundant inorganic aerosol constituent in the smoke from biomass burning (Li et al., 2003). The same study indicated that KCl particles from the fires were converted to K_2SO_4 and KNO_3 through reactions with sulfur- and nitrogen-bearing species during aging of smoke from biomass burning (Li et al., 2003).

1.1 Objectives and Hypothesis

The objective of this research is to compare the recovery of feedstock mass, energy, and mineral nutrients in co-products among crop biomass sources using different fast and slow pyrolysis systems. The hypotheses are:

- H_0: The recovery of mineral nutrients, on a feedstock basis, does not depend on biomass species, pyrolysis conditions, or reactor type.
- H_a: There is some dependence.

The H_0 hypothesis, if proven, will validate that bio-char recycling to soil and associated reductions in fertilizer requirements and application costs are similar among biomass feedstocks and pyrolysis-based bioenergy systems. While P and K are essential macronutrients for plant growth and development, other essential nutrients are required in relatively large amounts, including calcium (Ca) and magnesium (Mg). The null hypothesis (H_a) will be investigated for P, K, Ca, Mg and micronutrients (Na, Zn, Fe, Cu, and Mn).

2. MATERIALS AND METHODS

2.1. Feedstock Preparation

High-energy sorghum (*Sorghum bicolor*), switchgrass (*Panicum virgatum*), corn stover (*Zea mays*), and rice stover (*Oryza sativa*) were produced and collected during 2009 from the Texas AgriLife research farms near College Station and Beaumont, Texas. Corn stover was raked and chopped to 6-cm lengths after grain harvest and rice and sorghum were cut just above the soil surface during the grain-filling stage. Winter-dormant switchgrass was cut just above the soil surface during January and chopped to 6-cm lengths. After air-drying under greenhouse conditions, the chopped biomass was ground to pass a 3-cm screen in a Hammer Mill® grinder. In preparation for pyrolysis, biomass was sub-sampled and further ground to pass a 2-mm screen in a Wiley Mill® grinder. The double-ground biomass was further sub-sampled and oven-dried at 65°C over night before pyrolysis.

2.2. Feedstock Fiber Analysis

High energy sorghum (HES), corn stover, rice stover, and switchgrass were harvested, processed and analyzed for soluble and non-soluble fibers and ash contents. Nonstructural and cellulose, hemicellulose, and lignin components of biomass subsamples were analyzed (Van Soest et al., 1991). Concentrations of neutral detergent fiber (NDF), acid detergent fiber (ADF), acid detergent lignin (ADL) were estimated through sequential extraction and gravimetric analysis followed by determination of ash (mostly noncombustible inorganic heavy metals, mineral oxides, and salts). This process consisted of sequential (NDF, ADF, and ADL) filtering of residual biomass after incubation in neutral-detergent and acid-detergent solutions and concentrated sulfuric acid. Figure 2 shows the setup for the NDF and ADF extractions.

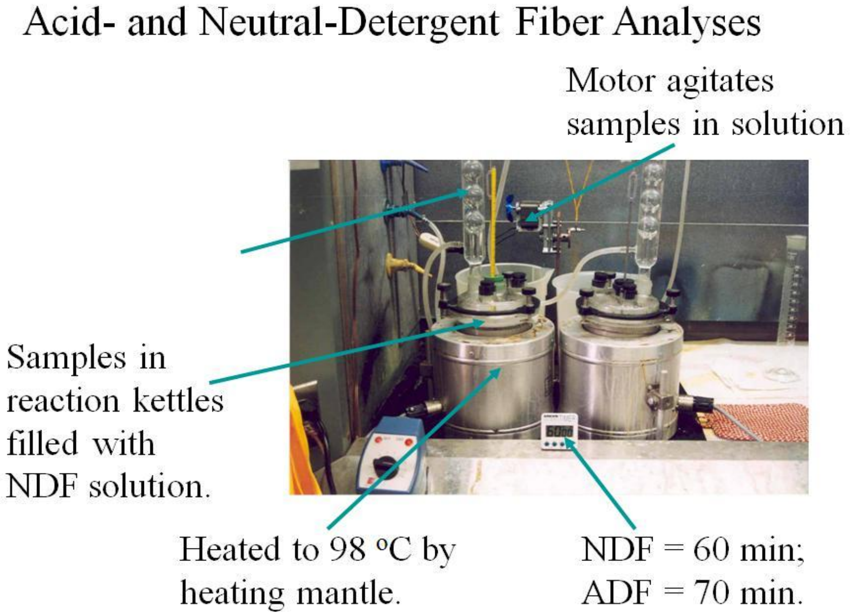

Figure 2. Neutral and acid detergent fiber analysis setup.

Fiber analysis values were used to estimate structural (cellulose and hemicelluloses) and nonstructural (sugars, starches, and pectins) carbohydrates in biomass. Hemicellulose was estimated by subtracting the amount of ADF, ADL, and ash from NDF. The dry weight of cellulose was quantified through subtraction of dry weights of ADL and ash from the dry weight of ADF. Historically, feedstock fiber analysis was used to access fiber digestibility for ruminants. For feedstock evaluations, fiber analyses were used to assess soluble and non-soluble energy within the feedstock, which can potentially be converted to usable energy. If the conversion platform is pyrolysis, the analysis is done to determine feedstock potential to produce bio-oil, bio-char, and synthesis gas.

Filter bags were made by heat-sealing on three sides of a 3” x 5” piece of chemically inert Dacron® fabric with an average pore size of 35.5 microns. The dry weight of the filter bag was recorded before and after filling with approximately 0.5 g of dried and ground biomass. Twenty-four samples along with three empty blank bags were inserted on bottom, middle, and top shelves of a metal rack during each extraction.

Neutral detergent solution comprised a mixture of 30.0 g of Sodium dodecyl sulfate, 18.61g ethylenediaminetetraacetic disodium salt dehydrate (EDTA), 6.81 g Sodium borate, 4.56 g Sodium phosphate dibasic (anhydrous), 10.0 ml Triethylene glycol, and 1 L of distilled water. Reagents were mixed until the solution transparent. Nineteen hundred mL of solution was poured into a glass kettle, which was placed into a heating vat and allowed to reach a temperature of 90°C. Four mL of alpha-amylase was added to the solution while metal shelves containing samples were suspended in the solution and agitated for 75 min. After agitating for 75 min, the solution was poured off and 1900 mL of fresh (70°C-90°C) distilled water containing 4 mL of alpha-amylase was added to the kettle and agitated again for 5 minutes. The rinsing step was repeated once with and once without alpha-amylase. When the rinsing process was complete, the samples were removed and the water was gently pressed from the bags. Rinsed bags were then placed in a 250 mL beaker with enough acetone to cover bags and soaked. After 3 to 5 mins the bags were removed and dried in air and an oven at 102°C for 3 hrs. After removal from the oven, bags were placed into a desiccator to prevent hydration during cooling. After cooling, bags were reweighed. The %NDF was calculated as follows;

$$\%NDF = \frac{(W_{3a} - (W_{1a} x C_{1a}))}{W_{2a}} x100$$

where, W_{1a} is the bag tare weight,
W_{2a} is the sample weight,
W_{3a} is the dried weight of bag with fiber after the NDF extraction process, and
C_{1a} is the blank bag correction (running average of the final oven-dried weight divided by the original bag weight).

To determine ADF, a procedure similar to NDF was performed although different chemicals were used to make the acid detergent. The formula for calculating the % ADF is;

$$\%ADF = \frac{(W_{3b} - (W_{1a} x C_{1a}))}{W_{2b}} x100$$

where, W_{1a} is the bag tare weight,
W_{2b} is the sample dry weight after NDF extraction,
W_{3b} is the dry weight of bag with fiber after the ADF extraction process, and
C_{1a} is the blank bag correction (running average of the final oven-dried weight divided by the original bag weight).

To determine ADL, the dried samples from the ADF process were placed into a 3L beaker and covered with approximately 250 mL of 72% $H_2 SO_4$. To keep bags submerged, a 2L beaker was placed inside the 3L beaker. The bags were initially agitated and the 2L beaker was oscillated up and down approximately 30 times at 30-min intervals. After 3 hr, the $H_2 SO_4$ solution was poured off and the bags were rinsed four times with tap water. After rinsing with water, bags were submerged in 250 ml of acetone for 3 minutes to remove water. After air drying, bags were oven-dried at 105° C for 2-4 hours. Bags were removed from the oven, flattened to remove air, cooled to ambient temperature, and weighed. Ash content was determined by placing the bag in pre-weighed crucible at 550°C for 3 hr before cooling and weighing. The formulas for calculating the %ADL and %Ash are;

$$\%ADL\ (DM) = \frac{(W_{3c} - (W_{1a} x C_{1a}))}{W_2} x100$$

$$\%ADL\ (OM) = \frac{(W_{4a} - (W_{1a} x C_{2a}))}{W_2} x100$$

where, W_{1a} is the bag tare weight,
W_{2a} is the sample weight,
W_{3c} is the dried weight of bag with fiber after the ADL extraction process,
W_{4a} is the weight of organic Matter (OM) (Loss of weight on ignition of bag and fiber residue), and
C_{1a} is the blank bag correction (running average of the final oven-dried weight divided by the original bag weight).
C_{2a} is the ash corrected blank bag (Loss of weight on ignition of bag/original blank bag).

Ash was calculated using the following formula;

$$\%ADL(ash) = \frac{\mathrm{W_{5a}} - \mathrm{W_{1a}}}{\mathrm{W_{2a}}} \times 100$$

where, W_{3c} is the dried weight of bag with fiber after the ADL extraction process, and
W_{5a} is the ash weight of the bag with fiber after combustion.

Percent cellulose, hemicellulose, and soluble sugars were estimated from the following formulas;

$$\%Cellulose \approx \%ADF - \%ADL$$

$$\%Hemicellulose \approx \%NDF - \%ADF$$

$$\%Sugars \approx 100 - \%NDF.$$

2.3. Pyrolysis Using Fixed-bed Reactor (College Station, TX)

A fixed-bed reactor system was used for slow pyrolysis of feedstock samples under controlled conditions. The pyrolyzer was assembled using stainless steel tubing and Thermolyne® tube furnace (Fig. 3). The pyrolyzer system consisted of a 1-inch diameter Thermolyne® tube furnace with a 2.5-cm o.d. type 316 stainless steel tube, 75 cm in length. Type 316 is austenitic, non-magnetic, and thermally non-hardenable stainless steel that is resistant to corrosion. The dorsal side of the input end of the tube was tap-drilled with a ¼-inch bit and fitted with copper tubing to allow for injection of nitrogen (N_2) gas. The output end of the tube was fitted with a 1-inch threaded reducer fitting, followed by a 1-inch 90° elbow, a 1-inch stainless steel nipple, a 1-inch to ½-inch stainless steel reducer fitting, a ½-inch nipple, a ½-inch to ¼-inch reducer fitting, and ¼-inch food grade polyethylene tubing leading to the oil collection vessel and gas traps. Compressed N_2 was chosen as the inert gas medium to displace O_2 within the pyrolyzer reactor.

Sixteen treatment combinations (4 feedstocks by 2 flow rates by 2 temperatures0 were chosen for the pyrolysis of high-energy sorghum (HES), switchgrass, corn stover, and rice biomass. Inert gas flow rates of 1 L min^{-1} and 2 L min^{-1} were measured using a rotometer. Reactor temperatures were 500°C and 600°C. The treatment array consisted of the four biomass sources, each pyrolyzed for 20 min. at 600°C and 1 L min^{-1}, 600°C and 2 L min^{-1}, 500°C and 1 L min^{-1}, and 500°C and 2 L min^{-1}. (Pütün et al., 2001). Each biomass source was subsampled and weighed (approximately 2.5 g) for each of 6 pyrolysis runs. Subsamples were loaded into a stainless steel boat and inserted within the stainless steel reactor tube (Fig. 3). Bio-char, bio-oil, or HCl trap solutions were each pooled over the six runs to make up a replication for each combination of biomass species, reactor temperature, and N_2 flow rate.

The design comprised a complete, randomized, split-split-factorial design. In this design, the biomass species was the "whole factorial," temperature was the "sub-factorial," and flow rate was the "sub-sub-factorial." Three replications of each combination of treatments provided a blocking variable.

Figure 3. Tube furnace used for fixed-bed, slow pyrolysis experiments.

2.4. Pyrolysis Using Bench-scale Fluidized-bed Reactors (Wyndmoor, PA and College Station, TX)

Three replications of each corn stover, sorghum and switchgrass biomass were pyrolyzed using a bench-scale fluidized-bed fast pyrolysis reactor. The reactor, located at the USDA Eastern Regional Research Center in Wyndmoor, PA, comprised a state of the art reactor vessel system and associated auxiliary systems for biomass feeding and injection, char collection, vapor condensation for bio-oil recovery, and instrumentation for data acquisition and control (Boateng et al., 2007). For all runs, the pyrolysis conditions were: temperature (~500°C), inert gas flow rate (~70 L min.$^{-1}$). The layout for the fast pyrolysis reactor in Wyndmoor, PA is shown in Figure 4. The same biomass species were also pyrolyzed using a fluidized-bed fast pyrolysis system designed by Sergio Capareda of the Department of Biological and Agricultural Engineering, College Station, TX. The reactor consists of an auger-fed biomass feeder, vertical tube furnace reactor, two in-series char collection bins, vapor condensation setup for bio-oil recovery, and a NCG flow meter. Reactor temperatures (~500°C) and nitrogen flow rate (40 L min.$^{-1}$) were monitored through a data acquisition and control center adjacent to the reactor system. For both fluidized-bed, fast pyrolysis systems, three feedstocks were pyrolyzed at one temperature and one inert gas flow rate.

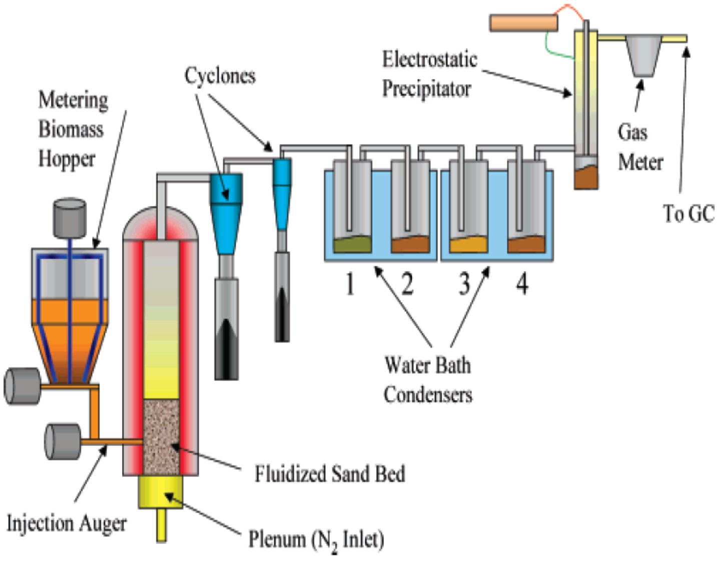

Figure 4. Layout for Wyndmoor, PA fluidized-bed pyrolysis reactor (Boateng et al., 2007).

2.5. Bio-char Solvent Washes

Particle surface area was compared between acetone washed and unwashed bio-char. This washing procedure was performed in three steps, which included extraction, decanting and evaporation of acetone, and bio-char drying. For the extraction, approximately 20 g of bio-char was added to a tarred 250 mL Erlenmeyer flask and placed into a 70^0 C oven for a minimum of 12 hours. After drying, the flask and bio-char combination was placed into a desiccator for 30 min to cool before reweighing. One hundred mL of acetone was added to completely immerse the bio-char within the flask. If bio-char was not completely immersed, acetone was added in 25 mL increments until submerged. The total amount of acetone added was recorded. Bio-char immersed within acetone was incubated in a 50°C water bath (approximately 10°C cooler than the boiling point of the acetone) for 2 hr. After removal from the water bath, flasks were allowed to cool to room temperature. Acetone was decanted from each flask through a funnel lined with a number 1 grade Whatman filter into a 2000-mL Erlenmeyer flask. Acetone-soaked bio-char was returned to 250-mL Erlenmeyer flask. The acetone extraction was repeated until the acetone decanted from bio-char was clear.

After the final acetone wash, the total volume of acetone used was recorded. Acetone-washed bio-char was air-dried in the fume hood until no visible solvent was left in the 250-mL flask. Air-dried bio-char was placed in an oven for drying at 70^0 C for a minimum of 12 hrs, placed in a desiccator for 30 min., and weighed.

The volume of decanted acetone was reduced through evaporation. The original 2000-mL Erlenmeyer flask with acetone was placed into a water bath and bath temperature was raised to the boiling point of the acetone. When acetone was evaporated to a volume near 100 mL, the remaining volume was transferred into a tarred 250-mL beaker. To remove additional oils, the 2000-mL flask was rinsed several times with 10 mL of acetone. Acetone was evaporated from the 250-mL beaker in a water bath until the acetone volume was reduced to approximately 10 mL. The beaker was then removed from the water bath and allowed to dry in fume hood. After acetone was evaporated, the 250-mL beaker was placed in a 70^0 C oven for 12 hrs, cooled in a desiccator for 30 minutes and reweighed (B. Allen, personal communication, May 2011).

2.6. Bio-char, Bio-oil, and Gas-trap Processing

The interior surfaces of the reactor and bio-oil condensers were washed with acetone and pooled with bio-oil that was condensed and collected during pyrolysis of the six biomass subsamples of each replication. The acetone in the acetone-bio-oil mixture was evaporated at room temperature prior to bio-oil analysis.

The bio-oil was ashed in a muffle furnace using porcelain crucibles at 800°C for 4 hrs prior to dissolution in 4 mL of concentrated HCl, which was brought to volume with dionized water in a 100-mL volumetric flask. Inductively coupled plasma optical emission (ICP) spectroscopy was used to analyze subsamples of each volume of diluted HCl solution. A SPECTRO ARCOS® axial ICP instrument was used for quantifying Ca, Mg, K, and P.

A 200-mg sample of bio-char was ashed and similarly analyzed. In addition to the ashing method, modified Kjeldahl sulfuric acid digest (Parkinson and Allen, 1975) was used in preparation for ICP analysis of mineral nutrients in all biomass and fluidized-bed reactor bio-chars. Modified Kjedhal with K_2SO_4 and $CuSO_4$ substituted for Li_2 SO_4 is used routinely for analysis of total N and other minerals, except boron and sulfur. The contents of the acid trap for NCG were collected and diluted with deionized water prior to ICP analysis. Similar to the NCG solution, the ICP was used to analyze water-extractable nutrients in bio-char, bio-oil, and biomass.

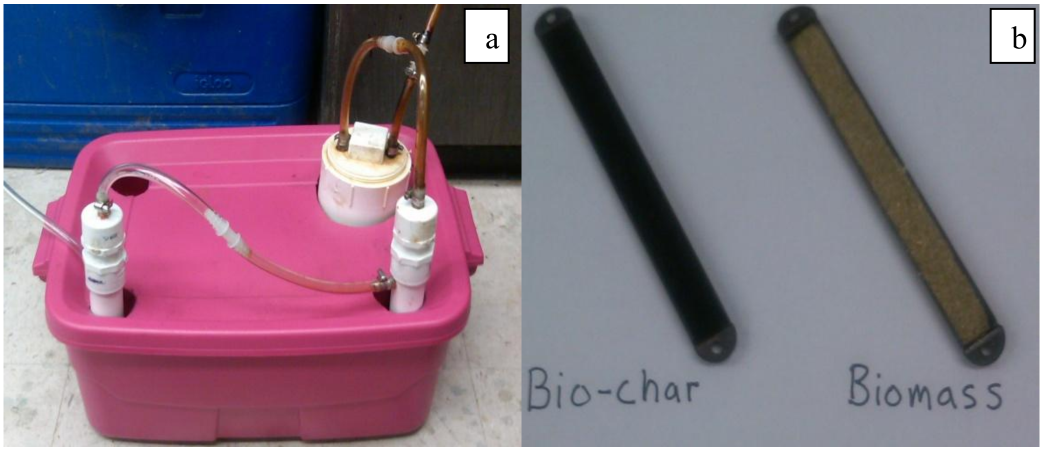

Figure 5. NCG trap setup (a) and boats loaded with pre-pyrolysis biomass and post-pyrolysis bio-char (b).

2.7. Bio-char Physical and Chemical Properties

Bio-char physical and chemical properties, including BET surface area, heating value, and proximate and ultimate analysis of biomass or bio-char samples were performed at the Texas AgriLIFE Bio-energy Testing and Analysis (BETA) Laboratory. BET surface area was determined using the Quantachrome NOVA® surface area analyzer according to ASTM D6556-Standard Test Method for Carbon Black-Total and External Surface Area by Nitrogen Adsorption. This standard test method measures total and external surface area of carbon blacks based on multi-point nitrogen adsorption. The nitrogen surface area (NSA) measurement is based on the Brunauer, Emmett, Teller *(*BET*)* theory and includes the total surface area, inclusive of micropores, pore diameters less than 2 nm according to ASTM D6556. Higher heating value (HHV) was determined using a bomb calorimeter (Parr® 6200 Isoperibol calorimeter) according to ASTM D240-Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels. This standard test method determines heat of combustion (the energy available from a fuel).

Proximate analysis (PA) was determined using ASTM D7582-Standard Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis.
This standard test method determines moisture, ash yield, volatile matter, and fixed C left in the material after volatile materials are driven off) by difference. Ultimate analysis (UA) was determined using ASTM D5291-Standard Test Methods for Instrumental Determination of C, H, and N in Petroleum Products and Lubricants. This standard test method is for instrumental determination of total C, total H, total N, and total O (by difference). Data collected for this research is presented in Table 1.

2.8. Statistical Analysis

Statistical analysis was completed for the laboratory scale fixed-bed, slow pyrolysis system and both fluidized-bed, fast pyrolysis systems. Analysis of variance (ANOVA) and the "Student's t" test were used for comparisons among feedstock sources and pyrolysis conditions (JMP, Version 8. SAS Institute Inc., Cary, NC, 1989-2007). For analyses of fixed-bed pyrolysis, inert gas flow-rate, temperature, and crop species were independent variables. Dependent variables comprised feedstock composition, bio-char properties and feedstock mass and nutrient recovery in pyrolysis co-products. For the fixed-bed reactor, means were computed for three replications, which each comprised 6 runs. For the fluidized-bed reactors, all means represented three replications. An ANOVA was used to compare feedstock and bio-char properties and nutrient recovery among the three crop species for each fluidized-bed system.

Correlation and simple linear and multiple linear regression analyses were used to evaluate relationships among mass, energy, and nutrient recoveries.

Table 1. Pyrolysis conditions and data collected from each reactor design.

Feedstock	Bio-char	Bio-oil	NCG	BET	HHV[1]	Temperature (°C)	Flow rate (L min^{-1})	UA[2]	PA[3]	Nutrients[4]
Fixed-bed, slow pyrolysis (College Station, TX)										
HES	*	*	*	N/A[5]	**	500, 600	1, 2	**	**	***
Switchgrass	*	*	*	N/A	**	500, 600	1, 2	**	**	***
Corn stover	*	*	*	N/A	**	500, 600	1, 2	**	**	***
Rice Biomass	*	*	*	N/A	**	500, 600	1, 2	**	**	***
Fluidized-bed, fast pyrolysis (College Station, TX)										
HES	*	*	N/A	**	**	500	40	**	**	***
Switchgrass	*	*	N/A	**	**	500	40	**	**	***
Corn stover	*	*	N/A	**	**	500	40	**	**	***
Fluidized-bed, fast pyrolysis (Wyndmoor, PA)										
HES	*	*	N/A	**	**	500	70	**	**	***
Switchgrass	*	*	N/A	**	**	500	70	**	**	***
Corn stover	*	*	N/A	**	**	500	70	**	**	***

"*" indicates co-product was obtained,
"**" indicated type of analyses performed on feedstock, bio-char, bio-oil and NCG (if obtained),
"***" indicates indicated nutrient analysis performed on feedstock, bio-char, bio-oil and NCG (if obtained),
[1] HHV=Higher heating value of bio-char,
[2] UA=Ultimate analysis of bio-char,
[3] PA=Proximate analysis of bio-char,
[4] Nutrients=Nutrients (P, K, Ca, Mg) and micronutrients (Na, Fe, Zn, Cu, Mn), and
[5] N/A=Data not obtained.

3. RESULTS AND DISCUSSION

3.1 Feedstock Analysis

This study began with analysis of the feedstock fiber properties of corn stover, HES, switchgrass, and rice stover. Fiber analyses comprise NDF, ADF, ADL (DM), ADL (OM), ash, cellulose, hemicellulose, and soluble sugars. Results of the analysis are presented in Tables 2 and 3. In addition to fiber properties, ultimate and proximate analyses of feedstocks (Tables 4 and 5) were done along with feedstock macro and micronutrients concentrations (Tables 6 and 7).

Neutral detergent fiber kg^{-1} of feedstock varied among species. The highest NDF kg^{-1} of feedstock was found in switchgrass followed by statistically similar amounts in both corn stover and HES. Among all feedstocks, rice biomass had the least NDF kg^{-1} of feedstock. Acid detergent fiber kg^{-1} of feedstock varied amongst species. Similar to NDF, switchgrass had the highest ADF kg^{-1} of feedstock. After switchgrass, statistical ranking of ADF kg^{-1} of feedstock was HES, corn stover and then rice stover. Acid detergent lignin (dry matter) and ADL (organic matter) kg^{-1} of feedstock varied among species. Both ADL (DM) and ADL (OM) had the same statistical ranking; switchgrass and HES were similar and higher than both corn and rice stover. Ash kg^{-1} of feedstock also varied among species. Switchgrass had the highest amount of ash kg^{-1} of feedstock followed in ranking by similar amounts for both HES and rice stover and then corn stover.

Table 2. Feedstock fiber properties of biomass species used in pyrolysis experiments.

Species	NDF	Std Dev	ADF	Std Dev	ADL(DM)	Std Dev	ADL(OM)	Std Dev	ADL(ash)	Std Dev
g kg^{-1}										
Feedstock comparison										
Corn stover	767.8b†	10.2	461.7c	7.0	70.3b	6.4	56.9b	6.4	64.5b	14.6
Switchgrass	829.5a	9.3	553.8a	9.0	117.6a	6.8	101.4a	8.2	91.2a	4.0
HES	758.2b	12.2	506.6b	31.8	122.3a	10.3	100.0a	6.7	28.5c	18.1
Rice Biomass	662.0c	34.8	340.2d	15.4	75.9b	13.0	53.9b	13.1	22.2c	10.2

†Means within a column followed by the same letter do not significantly differ (0.05 level).

Table 3. Feedstock structural and nonstructural carbohydrates of biomass species used in pyrolysis experiments.

Species	Cellulose	Std Dev	Hemicellulose	Std Dev	Sugars	Std Dev
g kg^{-1}						
Feedstock comparison						
Corn stover	326.3b†	19.0	241.7a	18.5	167.8c	15.6
Switchgrass	325.0b	14.4	204.6b	8.9	79.2d	10.1
HES	355.9a	13.8	223.5ab	27.6	213.2b	15.3
Rice Biomass	303.7b	39.4	238.3a	18.9	315.9a	34.1

†Means within a column followed by the same letter do not significantly differ (0.05 level).

Neutral detergent fiber kg^{-1} of feedstock for this study was high when compared to 719 g kg^{-1} for switchgrass grown on conservation lands (Mulkey and VN Lee, 2006). Similarly, ADF kg^{-1} of feedstock for the current study was high when compared to an ADF kg^{-1} of feedstock of 421 for switchgrass in the aforementioned published study. Published data on smooth bromegrass revealed 580g NDF kg^{-1} of feedstock., which was also low compared to feedstocks in the current study (Casler, 2001). In a study of corn stover feedstock, investigators found values of 680g NDF kg^{-1} of feedstock; 364g ADF kg^{-1} of feedstock; and 21g ADL(DM) kg^{-1} of feedstock (Wolfrum et al., 2009). These values are well below related values for corn stover feedstock in the current study.

Reasons for variation in feedstock fiber properties depend on many factors. Variables such as growing conditions and harvest date could potentially affect feedstock properties. For example, the switchgrass used in the current study had reached maturity and was harvested in January after being exposed to freezing conditions. This could have been the reason for higher values of NDF, ADF, and ADL.

Cellulose, hemicellulose, and soluble sugars kg^{-1} of feedstock varied among species (Table 3). High-energy sorghum had the highest amount of cellulose kg^{-1} of feedstock followed by statistically similar amounts in corn stover, switchgrass, and rice biomass. Rice biomass and corn stover contained the highest hemicellulose kg^{-1} of feedstock followed in ranking by HES and switchgrass. The highest soluble sugars kg^{-1} of feedstock was found in rice biomass. Rice biomass was followed in ranking by HES, corn stover, and switchgrass.

In an investigation of corn stover, researchers found 335g cellulose kg^{-1} of feedstock, which is similar to corn stover cellulose kg^{-1} of feedstock of the current study

(Isci et al., 2008). Researchers studying corn stover in China found 277g cellulose kg^{-1} of feedstock, which is below related values in the present study (Chen et al., 2011a). In contrast, published data revealed 550g cellulose and 280g hemicellulose kg^{-1} of feedstock in bamboo biomass (Chen et al., 2011c).

Variation in feedstock structural and nonstructural carbohydrates was dependent on species. As with feedstock fiber properties (Table 2), differences can be primarily attributed to harvest date.

The results of proximate and ultimate analyses of the feedstocks used in this dissertation are given in Tables 4 and 5. The amount of water kg^{-1} feedstock varied among species (Table 4). The highest amount of water kg^{-1} feedstock was found in HES and corn stover. Switchgrass had the least amount of water kg^{-1} feedstock. The amount of water kg^{-1} feedstock in rice biomass was statistically in between switchgrass and HES and corn stover. Volatile combustible matter (VCM) kg^{-1} feedstock varied among species. The most VCM kg^{-1} feedstock was found in corn stover, HES, and rice stover, both of which were statistically similar. Switchgrass contained the least VCM kg^{-1} feedstock. Fixed C, ash, and HHV (MJ) kg^{-1} feedstock did not vary among species.

In a recent publication, ultimate analysis of sugar cane begasse revealed 88g water kg^{-1} feedstock; 716g VCM kg^{-1} feedstock; and 87g ash kg^{-1} feedstock (Gami et al., 2011). When compared to the current study, water and ash kg^{-1} feedstock was high whereas VCM was comparable.

Table 4. Proximate analysis of feedstocks used in pyrolysis experiments.

Species	Moisture	Std Dev	VCM	Std Dev	Fixed C	Std Dev	Ash	Std Dev	HHV	Std Dev
	g kg^{-1}								MJ kg^{-1}	
Corn stover	60.6a[†]	3.2	759.6a	34.3	132.3a	2.2	47.5a	44.4	18.1a	0.5
HES	70.3a	5.3	710.1a	11.1	124.3a	9.2	50.6a	51.4	19.7a	2.0
Switchgrass	49.1b	10.1	642.3b	53.5	156.4a	22.2	42.1a	31.5	16.8a	6.7
Rice Biomass	59.3ab	9.3	724.5a	61.2	135.5a	3.7	39.8a	25.0	21.0a	0.8

†Means within a column followed by the same letter do not significantly differ (0.05 level).

Table 5. Ultimate analysis of feedstocks used in pyrolysis experiments.

Species	N	Std Dev	C	Std Dev	H	Std Dev	S	Std Dev	O	Std Dev
	g kg^{-1}									
Corn stover	6.2a[†]	2.3	439.8b	23.4	53.9b	42.9	1.1a	19.2	499.0a	43.5
HES	3.5c	34.1	462.9ab	10.9	65.6a	27.7	1.5a	5.4	466.5a	53.1
Switchgrass	4.8b	29.9	472.3a	1.8	50.3b	9.9	1.7a	93.2	470.9a	2.11
Rice Biomass	4.6b	3.1	477.2a	79.3	59.3b	60.1	1.0a	39.9	487.9a	9.1

†Means within a column followed by the same letter do not significantly differ (0.05 level).

Researchers studying switchgrass and corn stover feedstocks found ultimate analyses results of 50 and 54g water kg^{-1} feedstock; 40 and 46g ash kg^{-1} feedstock; and HHV's of 19.53 and 18.66 MJ kg^{-1} feedstock (Neves et al., 2011). All of the aforementioned values were comparable with the present study.

Nitrogen, C, and H kg^{-1} feedstock varied among species (Table 5). Corn stover had the most N kg^{-1} feedstock. The next highest amount of N kg^{-1} feedstock was in HES and rice stover. High-energy sorghum contained the least amount of N kg^{-1} feedstock. The highest amounts of C kg^{-1} feedstock were found in switchgrass and rice stover. Corn stover contained the least amount of C kg^{-1} feedstock. High-energy sorghum contained the most H kg^{-1} feedstock, followed by similar amounts of corn stover, switchgrass, and rice stover. No differences in S or O kg^{-1} feedstock were detected.

Ultimate analysis of switchgrass and corn stover feedstocks revealed 5.8 and 8.8g N kg^{-1} feedstock; 469 and 460g C kg^{-1} feedstock; 58 and 59g H kg^{-1} feedstock; 420 and 414g O kg^{-1} feedstock; and 1.1 and 1.2g S kg^{-1} feedstock (Neves et al., 2011). All elements were similar to the values in Table 5 with the exception of H kg^{-1} feedstock, which was lower. Research investigating sweet sorghum, switchgrass, corn straw, and rice straw found ultimate analysis results of 4, 7, 6, and 8g N kg^{-1} feedstock; 474, 472, 450, and 400g C kg^{-1} feedstock; 58.1, 57.9, 59.1 and 45.6g H kg^{-1} feedstock; and 0.9, 1, 0.7, and 1.3g S kg^{-1} feedstock (Song et al., 2011). These values are consistent with the values of the present study in Table 5.

Water and ash kg^{-1} feedstock was high for the tested species. Research has determined that feedstocks with low moisture and ash contents are the most suitable for combustion (McKendry, 2002). Biomass species such as switchgrass, sorghum, and rice are known to contain considerable amounts of ash (Monti et al., 2008). Switchgrass feedstock was harvested after freezing and desiccation, which could be the reason for the high amount of C kg^{-1} feedstock. The rice biomass used in the current study contained high amounts of C and fixed C kg^{-1} feedstock and had the highest HHV (MJ) kg^{-1} feedstock. This could have been a result of grains still present in the feedstock. Variation in results of feedstock proximate and ultimate analyses can be predominately attributed to harvest dates, growing conditions, and harvesting practices. This was true, in particular for switchgrass, for the reasons mentioned earlier.

Phosphorus concentrations varied among feedstocks. Corn stover had the highest mg of P kg^{-1} feedstock. Switchgrass and HES had the next highest amounts with rice stover containing the least (Table 6). Potassium concentrations varied among feedstocks as well. The most mg of K kg^{-1} feedstock was found in HES, followed by corn stover, switchgrass, and rice biomass. Differences among species were detected for Ca. Switchgrass contained the most mg of Ca kg^{-1} feedstock. Corn stover had the next highest, followed by HES and rice stover. Variation among feedstocks was detected for Mg concentrations. The highest concentration of Mg was found in corn stover. High-energy sorghum had the next highest amount of mg of Mg kg^{-1} feedstock, followed by switchgrass and rice stover.

Sodium concentrations did not vary among species (Table 7). However, concentrations in Zn did vary among feedstocks. The most mg of Zn kg^{-1} feedstock was in both corn stover and switchgrass.

Table 6. Initial feedstock nutrient concentrations.

Species	P	Std Dev	K	Std Dev	Ca	Std Dev	Mg	Std Dev
mg kg^{-1}								
Corn stover	4952a[†]	81.6	549.5E+02b	2389	168.8E+02ab	4894	5430a	60.6
Switchgrass	3607ab	423.6	209.8E+02c	2249	191.4E+02a	890.6	3012c	45.4
HES	3367ab	171.4	626.8E+02a	1072	142.5E+02b	108.6	3730b	82.5
Rice Biomass	1651b	46.4	170.9E+02d	692.9	2528c	186.6	1571d	4.5

†Means within a column followed by the same letter do not significantly differ (0.05 level).

Table 7. Initial feedstock micronutrient concentrations.

Species	Na	Std Dev	Zn	Std Dev	Fe	Std Dev	Cu	Std Dev	Mn	Std Dev
mg kg^{-1}										
Corn stover	449.7a[†]	2.7	106.3a	7.8	252.1a	32.7	23.3a	4.7	156.6b	8.7
Switchgrass	289.7a	4.7	100.6a	7.6	187.4b	43.4	13.6b	1.0	112.3c	8.9
HES	291.3a	8.1	62.8b	2.6	78.0c	2.5	11.9bc	0.7	61.8d	5.3
Rice Biomass	315.3a	3.21	29.5c	0.5	34.9c	1.7	8.3c	0.2	217.1a	4.1

†Means within a column followed by the same letter do not significantly differ (0.05 level).

The next highest Zn concentration was found in HES and the least in rice stover. Differences among species were detected in Fe concentrations. The most mg of Fe kg^{-1} feedstock was contained in corn stover. Switchgrass had the next highest concentration, followed by similar amounts in HES and rice biomass. Milligrams of Cu kg^{-1} feedstock varied among species. In descending order, corn stover had the highest concentration, followed by switchgrass, HES, and rice biomass. Variation in Mn concentrations was detected among species. The most mg of Mn kg^{-1} feedstock was found in rice biomass. Corn stover had the next highest concentration of Mn, followed by lesser amounts in switchgrass and HES.

A recent study on corn stover revealed a 2.15g P kg^{-1} feedstock (Mullen et al., 2010). This value is less than half the equivalent corn stover P concentration in the current study. The same publication unveiled macronutrient concentrations in corn stover of 4.44g K, 3.25g Ca, and 2.34g Mg kg^{-1} feedstock and micronutrient concentrations of 0.23g Na, 2.35g Fe, and 0.98g Mn kg^{-1} feedstock. All concentrations of the previous study were low compared to the present study, with except for Fe and Mn. Researchers investigating various biomass crops found nutrient concentrations of 3.1g P, 10.8g K, 2.4g Ca, and 0.08g Na kg^{-1} feedstock in fresh switchgrass (Agblevor et al., 1995). These concentrations are lower than switchgrass nutrients concentrations in Tables 6 and 7. The same study also found 0.8g P, 3.3g K, 4.1g Ca, and 0.01g Na kg^{-1} feedstock in fresh hybrid poplar *(Populus deltoides* **x** *nigra var. Caudina).* When compared to the nutrient concentrations various species of the current study, these concentrations are low as well.

When compared to published data, nutrient concentrations for current study were high. A reason for high nutrient concentrations in switchgrass could be attributed to being harvested from relatively nutrient-rich soils. High-energy sorghum's and corn stover's high nutrient concentrations could have been due to soil contamination.

3.2. Fixed-bed, Slow Pyrolysis

Slow or conventional pyrolysis is characterized by slow biomass heating rates (~10°C min^{-1}), a temperature range between 300 to 650°C and, lengthy vapor residence times (5-30 min) (Overend et al., 1985). During slow pyrolysis, the biomass is slowly decomposed (devolatilized). Tar and bio-char are solid co-products along with bio-oil and NCG's. After the primary reactions have occurred during pyrolysis, re-polymerization or recombination reactions can contribute to co-product composition and quality during condensation of gases.

For this study, a 4 by 2 by 2 (4 species, 2 temperatures, and 2 flow rates) split-split-factorial design was used. This design fostered the evaluation and analysis of dependent variables' response to independent variables. Statistical analyses revealed the majority of interactions among main effects on nutrient recoveries was inconsistent for bio-oil and HCl trap solutions (at the $p=0.05$ level) (Appendix Tables A-1 and A-2). In the absence of interactions, differences among main effects were the focus of evaluations.

3.2.1. Fixed-bed Pyrolysis Bio-char and Bio-oil Characterization

Corn stover, HES, switchgrass, and rice stover were pyrolyzed using a fixed-bed, slow pyrolysis system. For fluidized-bed, fast pyrolysis only the HES, switchgrass, and corn stover feedstocks were pyrolyzed. For both systems, bio-char and bio-oil co-products were collected and weighed after pyrolysis. Bio-char and bio-oil weights and the original biomass input weights were used to calculate yields of bio-char and bio-oil per kg of feedstock (Table 8).

Table 8. Mean yields of bio-char and bio-oil kg^{-1} feedstock for fixed-bed, slow pyrolysis.

Species	Bio-char	Std Dev	Bio-oil	Std Dev
g kg^{-1}				
Corn stover	223.4bc†	8.9	66.7c	21.9
Switchgrass	217.8c	21.7	179.3a	44.0
HES	238.1b	33.6	121.0b	50.1
Rice Biomass	322.7a	16.1	46.7c	16.6

†Means within a column followed by the same letter do not significantly differ (0.05 level).

Bio-char yield varied among feedstocks. Bio-char generated from slow pyrolysis of rice biomass had the highest yield followed by HES and similar amounts of corn stover and switchgrass. The bio-char yield kg^{-1} corn stover was substantially higher than previously reported (~150 g kg^{-1}) for slow pyrolysis of corn stover at 676.85°C (Demirbas, 2004). Lower pyrolysis temperatures of 500 and 600°C used in this study could have increased bio-char yields kg^{-1} compared to the previous study. Bio-char yield typically decreases with increasing reactor temperature (Brown, 2009). However, bio-char yield kg^{-1} feedstock for slow pyrolysis of birch wood (~288 g kg^{-1}) and spruce wood (330 g kg^{-1}) were in better agreement with the slow pyrolysis bio-char's in Table 2 (Roberts et al., 2009). Bio-char yield from slow pyrolysis of sunflower oil cake at 500°C was even greater (363.6 g kg^{-1}) than rice biomass in the present study Table 2 (Karagöz, 2009).

In contrast to variation of bio-char yields among species, bio-oil yield kg^{-1} feedstock was greatest for switchgrass. In addition, bio-oil yield was greater for HES than for corn and rice biomass. In the present study, bio-oil yields kg^{-1} corn stover were low compared to a yield of ~250 g kg^{-1} from corn cobs slowly pyrolyzed at 500°C (Demiral et al., 2011). Corn stover used in the present study comprised primarily leaves, husks and stems, which could have reduced yields of condensable gases compared to corn cobs alone. In addition, bio-oil yields in the present study were relatively low compared to yields (464 g kg^{-1}) reported for the slow pyrolysis of linseed at 550°C and laurel (219.1 g kg^{-1}) at 500°C (Acikgoz and Kockar, 2009; Ertas and Hakki Alma, 2010).

In addition to variation among species, variation of pyrolysis temperature and inert gas flow rate can affect yield of bio-oil kg^{-1} feedstock. However, interactions between pyrolysis temperatures and inert gas flow rates used in this study were inconsistent. This lack of significance is most likely due to the continual development of bio-oil collection methods and apparatuses. Continuous adjustments, upgrading, and inefficiency of the bio-oil collection system often resulted in escape of thick, dark smoke to the exhaust hood which likely contained condensable bio-oil, some of which was condensed inside the polyethylene tubing at the end of the condensing system.

Proximate and ultimate analyses of the bio-chars generated from slow pyrolysis are given in Tables 9 and 10.

Table 9. Proximate analysis of fixed-bed, slow pyrolysis bio-chars.

Species	Moisture	Std Dev	VCM	Std Dev	Fixed C	Std Dev	Ash	Std Dev	HHV	Std Dev
	g kg^{-1}								MJ kg^{-1}	
Corn stover	59.5a†	29.2	321.9a	38.8	302.6b	25.3	375.5c	36.0	15.7c	1.2
Sorghum	67.5a	37.0	235.5b	41.8	318.3b	48.1	446.2b	34.8	18.8b	0.7
Switchgrass	73.5a	8.0	291.5ab	43.5	473.6a	70.6	234.9d	36.9	14.1d	0.3
Rice Biomass	65.1a	11.1	227.4b	23.7	282.5b	52.4	490.0a	36.7	22.0a	1.0

†Means within a column followed by the same letter do not significantly differ (0.05 level).

Table 10. Ultimate analysis of fixed-bed, slow pyrolysis bio-chars.

Species	N	Std Dev	C	Std Dev	H	Std Dev	S	Std Dev	O	Std Dev
	g kg^{-1}									
Corn stover	12.3a†	.0.9	548.7b	21.5	22.1a	3.2	2.4a	0.4	414.6c	19.9
Sorghum	7.9a	1.5	417.8c	37.6	17.8b	2.1	1.7b	0.2	554.9b	37.8
Switchgrass	9.5a	2.5	590.6a	36.3	22.2a	2.2	1.4b	0.3	376.3d	33.6
Rice Biomass	10.4a	1.1	380.4d	22.9	17.7b	2.1	1.6b	0.3	589.9a	22.3

†Means within a column followed by the same letter do not significantly differ (0.05 level).

Water concentrations in bio-char were not statistically different amongst species, but VCM, fixed C, ash, and HHV did vary (Table 9). For ultimate analysis, concentrations of C, H, S, and O varied among species, but N did not. Results of proximate and ultimate analyses of bio-chars compared in the present study were comparable to bio-char derived from slow pyrolysis of laurel at 500°C : C (562.9 g kg^{-1}), H (35.7 g kg^{-1}), O (370.1 g kg^{-1}) , and an HHV of 20.75 MJ kg^{-1} feedstock (Ertas and Hakki Alma, 2010). In contrast, N concentrations were greater for laurel. For ultimate analyses, lower N concentrations in initial laurel feedstock (30.2 g kg^{-1}) as compared to feedstocks used in this study (see Material and Methods) may have been the reason for the lower concentration of laurel N in bio-char. Conversely, slow pyrolysis of nitrogen-rich (134 g kg^{-1}) casein feedstock revealed high N concentration in bio-char (90.2 g kg^{-1}). Yet, other components of ultimate analysis of casein were comparable to the present study: C - 606.9 g kg^{-1}, H - 7 g kg^{-1}, O - 290.0 g kg^{-1}, ash - 145.0 g kg^{-1}, water - 45.6 g kg^{-1}. In contrast, VCM (112.4 g kg^{-1}) of casein was low compared to the proximate analysis of feedstocks in this study (Purevsuren et al., 2003). This implies that the chemical makeup of bio-chars derived from biomass feedstocks could be fundamentally different from animal-derived bio-chars.

Variation in ash kg^{-1} bio-char can be attributed to high amount of ash kg^{-1} feedstock. In particular, rice stover feedstock is known to contain high amounts of silica ash (Schultz et al., 1984). In addition, proximate analysis of switchgrass feedstock revealed the highest amount of fixed C kg^{-1} of feedstock for all tested feedstocks, which explained why switchgrass bio-char contained the highest amount of fixed C kg^{-1} bio-char. A similar relationship for C kg^{-1} feedstock was found between ultimate analysis of switchgrass feedstock and switchgrass bio-char.

3.2.2. Mineral Nutrient Recovery from Fixed-bed, Slow Pyrolysis Co-products

Corn stover, switchgrass, HES, and rice biomass were subjected to slow pyrolysis conditions and resulting co-products were captured and analyzed for macro and micronutrient concentrations. After the analysis was complete, the mass of nutrient from the bio-char, bio-oil, and NCG co-products were individually calculated and compared to the mass of nutrient in the original feedstock. From these values, percent of nutrient recovered, on a mass basis, was calculated for all pyrolysis experiments according to the following formula;

$$\%\text{Recovery} = \frac{m_{\text{Co-product nutrient}}}{m_{\text{feedstock nutrient}}} x100\%$$

where, $m_{\text{Co-product nutrient}}$ is the mass of nutrient in the co-product in mg, and
$m_{\text{feedstock nutrient}}$ is the mass of nutrient in feedstock in mg.

To calculate nutrient mass in bio-char, the product of dissolution volume (0.1 L) and nutrient concentration (mg L^{-1}), and bio-char subsample mass of each pyrolysis run (mg) was divided by the mass of the bio-char subsample that was ashed (mg). For the NCG mass, the nutrient concentration (expressed in mg L^{-1}) was multiplied by 0.2 L (dissolution volume). For mass of the feedstock nutrient, the concentration (expressed in mg L^{-1}) was multiplied by the input mass of feedstock used during the pyrolysis repetition. Co-product nutrient concentrations are provided in Tables 11 and 12.

Table 11. Concentrations of nutrients in bio-char, bio-oil, and NCG.

Species	P	Std Dev	K	Std Dev	Ca	Std Dev	Mg	Std Dev
mg kg^{-1}								
Bio-char co-product								
Corn stover	2044b[†]	89.4	240.3E+02a	109.6	102.8E+02b	572.3	4380a	71.4
Switchgrass	4534a	16.1	2011c	145.3	131.1E+02a	526.7	2658b	59.4
HES	4042a	56.7	4285c	73.5	111.2E+02ab	328.5	2030b	85.8
Rice Biomass	2693b	21.9	9821b	67.9	3448c	129.3	2197b	42.4
Bio-oil co-product								
Corn stover	15.9b	5.9	327.7b	19.6	292.3b	13.5	817.0a	3.9
Switchgrass	50.1a	7.2	321.6b	20.4	5913ab	430.1	647.8a	9.2
HES	52.6a	8.0	413.3ab	19.8	8027a	27.6	1053a	6.0
Rice Biomass	27.2ab	5.1	510.9a	28.8	474.4b	31.5	1147a	5.4
NCG co-product								
Corn stover	0.1c	0.1	1.3b	0.4	6.0b	0.1	0.1b	0.1
Switchgrass	1.6a	1.1	4.1a	1.0	20.9a	0.9	3.5a	0.6
HES	1.0b	1.0	2.2b	1.7	23.1a	0.4	3.3a	0.4
Rice Biomass	0.1c	0.1	1.0b	0.3	9.0b	0.1	0.1b	0.1

[†] Means within a column followed by the same letter (separated by co-product) do not significantly differ (0.05 level).

Table 12. Concentrations of micronutrients in bio-char, bio-oil, and NCG.

Species	Na	Std Dev	Zn	Std Dev	Fe	Std Dev	Cu	Std Dev	Mn	Std Dev
mg kg^{-1}										
Bio-char co-product										
Corn stover	1409a[†]	43.5	82.3a	5.7	1948c	89.8	27.8c	13.9	157.9c	8.2
Switchgrass	1570a	25.5	30.7c	6.6	146.7E+02b	37.4	100.1b	36.9	383.3b	24.5
HES	143a	44.4	62.7b	1.5	229.9E+02a	21.3	228.1a	63.1	712.5a	31.2
Rice Biomass	1447a	48	35.7c	4.6	1797c	25.4	20.7c	8.0	471.0b	30.5
Bio-oil co-product										
Corn stover	1367ab	68.4	2243ab	22.8	259.4b	9.3	1173ab	15.0	2.0c	2.6
Switchgrass	249.1c	68.2	1465b	24.3	4022a	11.7	485.6b	35.7	128.4b	22.5
HES	667.9bc	9.3	2387ab	19.4	4579a	41.3	1033b	35.2	304.5a	19.2
Rice Biomass	1712a	63.6	3152a	31.5	236.7b	26.4	2505a	82.3	2.6c	1.6
NCG co-product										
Corn stover	3.3b	0.6	0.7b	0.1	4.0a	1.0	7.0ab	0.2	0.1a	0.1
Switchgrass	55.7a	8.3	6.6a	1.0	2.6a	1.8	4.0ab	0.2	0.1a	0.1
HES	58.7a	5.1	4.1ab	0.5	2.4a	1.3	3.1b	0.4	0.1a	0.1
Rice Biomass	4.1b	3.5	0.1b	0.1	3.4a	2.4	7.6a	0.1	0.1a	0.1

†Means within a column followed by the same letter (separated by co-product) do not significantly differ (0.05 level).

Phosphorus concentration in bio-char varied among species. Switchgrass and HES bio-chars had similar and the higher P concentrations then corn stover or rice biomass. Concentration of K in bio-chars varied among species. The most K was found in corn stover bio-char. A smaller concentration of K was found in rice biomass and concentrations were lower and similar in switchgrass and HES than in rice biomass. Variation among species was detected for Ca concentration in bio-char. Switchgrass had the highest concentration of Ca. Concentrations of Ca found in HES, corn and rice biomass were lower than switchgrass. Magnesium concentration in bio-char varied among species. The highest concentration of Mg was found in corn stover. Similar, yet smaller concentrations of Mg were found in switchgrass, HES, and rice biomass.

Potassium concentration in corn stover bio-char was noticeably much higher than the biomass of each species. Such high K concentrations can be attributed to soil contamination caused by the raking of the corn stover from the soil surface. The most K was found in rice biomass. The next highest K concentrations were found in HES and switchgrass and corn stover.

Concentrations of P in bio-oil varied among species. The highest amount of P was found in similar concentrations in switchgrass and HES bio-oils. Smaller and similar concentrations of P were found in corn and rice biomass bio-oils. Potassium concentration in bio-oil varied among species. The most K was found in rice biomass bio-oil. A lowest concentration of K was found in HES. Corn stover and switchgrass contained the least amount of K in similar concentrations. Calcium concentration in bio-oil varied among species. The highest concentration of Ca was found in HES. Lower concentrations of Ca were found in switchgrass. The least amount of Ca was found in corn and rice biomass in similar concentrations. Magnesium concentration in bio-oil did not vary among species.

Macronutrients in NCG's were low. However, variation among species was detected for each macronutrient.

Sodium concentration in bio-char did not vary among species (Table 12). However, variation among species was found for Zn, Fe, Cu, and Mn in bio-char. High-energy sorghum bio-char contained significantly more Fe, Cu, and Mn than the other species. This could be due to contamination from metal alloys released from reactor piping during pyrolysis and needs further investigation.

Variation among species was detected for each micronutrient in bio-oil (Table 12). Rice biomass bio-oil contained significantly higher concentrations of Na, Zn, and Cu. Studies have documented these minerals are some of the main constituents in rice biomass ash, which could have contaminated the bio-oil (Schultz et al., 1984).

Sodium, Zn, and Cu concentrations in NCG's varied among species. No differences were detected in Fe and Mn concentrations in NCG's. Switchgrass and HES NCG's contained high concentrations of Na. This could have been due to the formation of salts during pyrolysis that were swept out and captured in the HCl solution.

Compared to slow-pyrolysis bio-chars from peanuts and other dicotyledoneous species, concentrations for macro-nutrients were relatively high in bio-char of corn stover and sorghum, switchgrass, and rice biomass. For example, mean concentrations were 585.8 mg kg^{-1} of P, 6384 mg kg^{-1} of K, and 1181 mg kg^{-1} of Ca in peanut hull bio-char (Gaskin et al., 2007). Yet, high nutrient levels in bio-chars derived from grasses as opposed to legumes could have been due to soil nutrient status, growing conditions, harvest times, fertilizer application rate, regional climate, and other environmental factors.

Mean percent recovery of nutrients from the fixed-bed, slow pyrolysis experiment is given in Tables 13 and 14.

Table 13. Mean percent recovery of nutrients from fixed-bed, slow pyrolysis reactor.

Species	P	Std Dev	K	Std Dev	Ca	Std Dev	Mg	Std Dev
%								
Bio-char co-product								
Corn stover	49.9c[†]	20.5	30.1a	12.8	60.8a	26.7	61.5b	26.1
Switchgrass	159.8a	64.9	10.7c	2.8	67.0a	8.0	83.1a	20.1
HES	90.5b	20.3	4.8d	1.8	55.9a	12.6	38.3c	12.2
Rice Biomass	52.1c	3.4	18.4b	0.9	40.7b	2.8	45.1c	2.5
Bio-oil co-product								
Corn stover	0.1b	0.1	0.1b	0	0.3b	0.1	1.7a	1.5
Switchgrass	0.3a	0.4	0.26a	0.16	4.5ab	8.8	3.0a	2.5
HES	0.2ab	0.2	0.1b	0	5.6a	5.7	2.8a	2.0
Rice Biomass	0.1b	0.1	0.1b	0.05	0.6b	0.4	2.4a	1.6
NCG co-product								
Corn stover	0.2b	0.1	0.1b	0	2.1b	0.6	0.1c	0
Switchgrass	3.4a	2.3	1.3a	0.9	6.5a	1.5	6.6a	1.1
HES	1.0b	1.2	0.1b	0.1	5.4a	3.2	2.9b	1.4
Rice Biomass	0.1b	0.1	0.1b	0	4.3ab	4.2	0.1c	0.1
Co-products combined								
Corn stover	50.1c	20.5	30.3a	12.8	63.2b	26.6	63.3b	25.4
Switchgrass	163.5a	64.5	12.3c	2.9	78.1a	8.2	92.8a	21.7
HES	91.6b	20.0	5.0d	1.8	66.9ab	11.3	44.0c	13.1
Rice Biomass	52.2c	3.4	18.6b	1.0	45.6c	5.7	47.6c	3.2

†Means within a column followed by the same letter (separated by co-product) do not significantly differ (0.05 level).

Table 14. Mean percent recovery of micronutrients from fixed-bed, slow pyrolysis reactor.

Species	Na	Std Dev	Zn	Std Dev	Fe	Std Dev	Cu	Std Dev	Mn	Std Dev
%										
Bio-char co-product										
Corn stover	265.3a†	102.0	65.9a	28.0	765.4b	545.8	104.8c	55.6	76.1c	32.5
Switchgrass	275.2a	100.5	31.3b	7.9	272.1E+02b	118.8E+02	487.6b	217.5	295.5b	171.9
HES	285.1a	94.0	68.5a	30.8	167.5E+03a	469.6E+02	115.3E+02a	435.0	750.9a	316.3
Rice Biomass	148.3b	11.0	38.8b	6.3	165.3E+02b	117.9E+02	82.4c	33.5	69.4c	5.2
Bio-oil co-product										
Corn stover	38.1a	26.9	267.2a	241.0	15.2b	21.2	649.3ab	594.1	0.1c	0.1
Switchgrass	6.6b	15.1	225.1a	205.7	110.7b	88.4	351.4b	460.5	14.6b	13.9
HES	18.6b	25.3	359.4a	294.9	466.0a	309.8	723.2ab	864.4	44.1a	28.6
Rice Biomass	17.9b	15.2	348.4a	240.7	22.0b	7.1	101.4E+02a	112.0E+02	0.1c	0.0
NCG co-product										
Corn stover	37.2b	29.3	21.8b	75.4	95.1a	70.2	154.9E+02a	112.8E+02	1.5a	0.8
Switchgrass	584.4a	87.7	404.5a	744.2	28.7b	20.0	114.7E+02a	180.7E+02	1.1b	0.0
HES	543.3a	258.9	204.2ab	316.6	79.8ab	59.6	715.6a	920.5	1.1b	0.5
Rice Biomass	17.2b	14.4	179.2b	78.8	126.4a	91.6	123.5E+02a	840.4	0.2c	0.1
Co-products combined										
Corn stover	340.6b	109.0	354.8a	231.2	875.7b	492.3	2303.9a	1301.9	77.7c	32.0
Switchgrass	866.2a	130.6	660.9a	907.2	2860.5b	1250.8	1986.2a	2122.5	311.1b	300.7
HES	847.0a	285.9	632.1a	477.9	17301.8a	4979.3	2592.3a	1810.6	796.1a	181.7
Rice Biomass	183.4c	23.0	387.2a	237.9	1801.6b	1215.7	2331.9a	1420.5	69.6c	5.2

†Means within a column followed by the same letter (separated by co-product) do not significantly differ (0.05 level).

Variation among species was detected for recovery of each macronutrient in bio-char. More than 90% of feedstock P was recovered in HES bio-char and greater than 83% of feedstock Mg was recovered in switchgrass bio-char. Additionally, more than 150% of feedstock P was recovered in switchgrass bio-char and needs further investigation.

Recovery of feedstock macronutrients in bio-oil was low. Variation among species was detected for the recovery of each feedstock macronutrient except Mg. Recovery of feedstock macronutrients in NCG's was low and varied among species. Variation among species was also detected for the recovery of each feedstock macronutrient when co-products are combined.

Mean recoveries of nutrients, expressed as the percentage in biomass, varied among nutrients and biomass species for each co-product of slow pyrolysis. Macronutrient recovery in switchgrass co-products was high for P, Ca, and Mg and most likely due to contamination and needs further investigation. For HES, mean percent recovery of P in bio-char was high when compared to a 34% recovery of feedstock P from auger-fed, slow pyrolysis of sorghum (Schnell, 2011). Similarly, recovery of K in HES bio-char was high when compared to a recovery of 6.8% of K in sorghum bio-char found in the same study (Schnell, 2011). In contrast, recoveries P and K in HES bio-char were low in relation to high recoveries of P (~95%) and K (~90%) from sorghum bio-char that were found using the same slow pyrolysis, auger-fed reactor (Husmoen, 2011). Phosphorus and K in corn stover, HES, and rice biomass bio-chars were also low when compared to recoveries of P (60 to 100%) and K (60 to 110%) in bio-char produced from the pyrolysis of pine chips, poultry litter and peanut hulls (Gaskin et al., 2008).

Recoveries of macronutrients in bio-char (with the exception of switchgrass) were low. High recovery of P from HES bio-char was most likely due to nutrient-rich tar and oil re-condensing on the bio-char during the long vapor residence time associated with fixed-bed, slow pyrolysis systems. Bio-chars from this experiment were ashed (800°C) for ICP analysis of nutrient concentrations in HCl solution used to solubilize ash. Ashing temperatures above 760°C may have contributed to vaporization losses of P and K (Knicker, 2007). However, using the same ashing analysis method as the current study, such vaporization losses were not observed by Husmoen (2011). A study on the fate of ash particulate in gaseous emissions from residential biomass combustion revealed that K can be lost as KCl and K_2SO_4 at temperatures above 500°C (Boman, 2005). Hence, it is possible for K to be swept out with fine particulate matter along with other NCG's. In a study of gasified coal, research has suggested that K loss during pyrolysis was prevented through use of a catalyst to create hydroxyl and carboxyl groups that provide anchoring sites (Gorrini et al., 1990).

With the exception of Zn in bio-char, recovery of all feedstock micronutrients was high (>100%) and needs further investigation. For bio-oil, recoveries for each nutrient varied amongst feedstocks except for Zn (Table 14). Elevated (>100%) recoveries of Fe in corn stover co-products can be attributed to soil getting attached to feedstock during harvest. High-energy sorghum, switchgrass, and rice biomass were harvested as standing biomass and dried on tarps in greenhouse. In contrast, corn stover was raked from the soil surface before chopping and piling in the field. Elevated levels of Cu and Zn were most likely a result of alloys being released from reactor piping during pyrolysis.

3.2.3. Fixed-Bed Reactor Mass and Energy Closure

Reactor energy and mass balances (with respect to bio-char and bio-oil co-products) were calculated to determine reactor biomass-to-co-product and energy conversion efficiency. The results are presented in Table 15 as mean percent mass recovery and energy efficiency.

Table 15. Mean percent mass and energy efficiency of fixed-bed, slow pyrolysis reactor.[1]

Species	Mass	Std Dev	Energy	Std Dev
%				
Corn stover	29.0b†	2.7	27.9b	2.9
HES	35.6a	6.1	27.8b	4.8
Switchgrass	39.3a	5.7	44.7a	6.2
Rice Biomass	36.9a	2.0	27.3b	2.0

†Means within a column followed by the same letter do not significantly differ (0.05 level).

[1] Calculations do not include NCG's.

Mass recovery in co-products was low for all species compared to published data for slow pyrolysis of similar feedstocks (Brown, 2009; Ketterings et al., 2007). Mean mass recovery was lower for corn stover than the other biomass species. In most cases, greater than 50% of feedstock mass was unaccounted for. In contrast, researchers achieved a mass conversion efficiency of 53% from the fixed-bed slow pyrolysis of Turkish oil shale (Snape, 1993). Poor mass conversion efficiency of biomass could have been a result of fluctuations in reactor temperature during sample changing and mass lost as NCG's and fine particulate matter.

Energy efficiency for all feedstocks was also low. Efficiencies varied statistically with switchgrass being the highest followed by lower and similar efficiencies for corn stover, HES, and rice biomass. Reactor efficiencies were especially low when compared to the energy efficiencies (~50%) of slow pyrolysis systems intended solely for the production of bio-char (Bridgwater and Cottam, 1992). In a study of switchgrass, corn stover and other feedstocks , slow pyrolysis systems optimized for bio-char production generally see a reduction in energy output (Gaunt and Lehmann, 2008). Similar to mass conversion, low energy efficiencies are due in part to the inability to measure and quantify NCG mass and energy. Other potential reasons for low mass conversion and energy efficiency could be due to system design and collection methods for the co-products, bio-oil in particular. Reactor system design may have contributed to the loss of some of the initial biomass due to inert gas flow at the beginning of pyrolysis. A noticeable amount of "coke" or a hardened tar-like substance was seen in reactor piping during disassembly for cleaning, which could have contributed to mass conversion and energy losses. Smaller mass conversion and energy could also be due to small system leaks that were periodically observed during pyrolysis.

In all, mass and energy balances were low. Most of the reasons are listed above and should be noted for improvements for future experiment replication. This experiment was ideal to learn how to assemble, from the ground-up, a laboratory scale fixed-bed, slow pyrolysis system to evaluate co-products. This system generated bio-char with average yields and bio-oil with below average yields. In bio-char, bio-oil, and the NCG acid trap contents, nutrient recovery was low for macronutrients and high for micronutrients. Mass conversion and energy efficiency gave insight into low recovery of feedstock nutrients and yields from the co-products.

3.2.4. Correlation Analysis

Correlation analysis was completed for each feedstock to determine the existence of any potential linear relationship among mass and energy recovery, feedstock composition (NDF, ADF, ADL (DM), ADL (OM), ash, cellulose, hemicellulose, and soluble sugars), and macro and micronutrient recovery. The scatter plot matrix between reactor mass and energy for feedstocks pyrolyzed using fixed-bed, slow pyrolysis is shown in Figure 6.

Figure 6 can be read as an inverse plot. For instance, the upper right hand quadrant can be read as “Mass efficiency (%)” on the “y” axis with the percentage range listed to the left of the axis label and “Energy efficiency (%)” on the “x” axis with the percentage range listed below the axis label. The bottom left hand quadrant can be read in a similar manner.

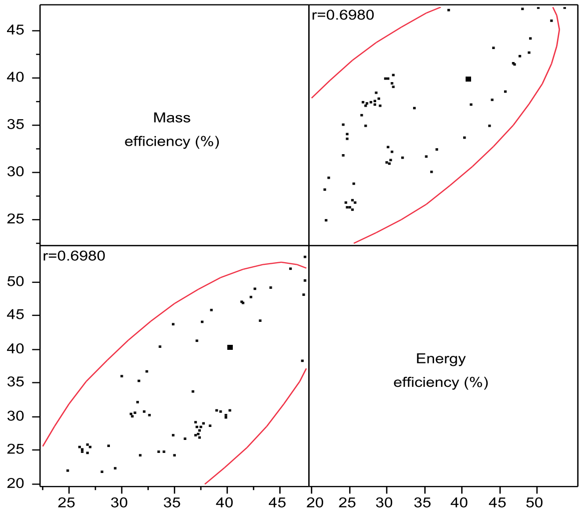

Figure 6. Scatter plot matrix for correlation between mass and energy efficiency across feedstocks for fixed-bed, slow pyrolysis.

Figure 6 showed high correlations between mass and energy efficiencies. The significant Pearson's correlation coefficient (r) also suggests a linear relationship between reactor mass and energy efficiency. Correlations between fiber composition and nutrient recovery were low (often less than r=0.6). Low correlations suggest that the potential for a linear relationship between the variables is low. Results for correlation analysis between feedstock fiber properties and nutrient recovery are given in Tables B-1 through B-8 of Appendix B.

Correlations between mass, energy and nutrient recovery were evaluated to determine the degree of linear relationships between the three dependent variables (Table 16).

Table 16. Correlations between mass, energy and nutrient recovery across feedstocks.

Variable	%Total P	%Total K	%Total Ca	%Total Mg
Mass Efficiency (%)	0.5104	-0.3247	0.154	0.33
Energy Efficiency (%)	0.7254	-0.1319	0.4558	0.7227

Correlations between mass efficiency and recovery of nutrients were low (<r=0.6). This implies that mass efficiency and nutrient recovery neither increases nor decreases proportionally. Low correlations also indicate a low probability of a linear relationship between the two variables. Energy efficiency and the recovery of P and Mg were moderately correlated (~r=0.7). Such correlations indicate that as energy efficiency increases, so does the recovery of P and Mg. The Pearson's correlation coefficients also indicate that linear relationships between energy efficiency and recovery of P and Mg are likely.

3.2.5. Regression Analysis

Simple linear regression analysis was performed to evaluate relationships among variation of mass and energy (combined bio-char and bio-oil).

For the mass vs. energy model, the hypothesis was;

- H_0: Mass efficiency is independent of energy efficiency; therefore the slope is equal to zero.
- H_a: There is some dependence.

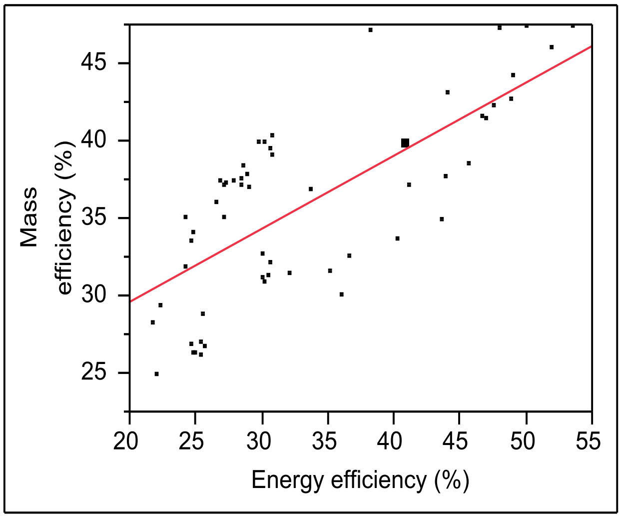

Figure 7. Linear fit for mass and energy efficiency across feedstocks for fixed-bed, slow pyrolysis.

The linear relationship between variation of mass and energy recoveries in pyrolysis co-products was;

$$\text{Mass Efficiency} = 20.02 + 0.4753*\text{Energy Efficiency}, (R^2=0.69).$$

Table 17. Parameter estimates for mass vs. energy efficiency regression.

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	20.02	2.374	8.43	<.0001
Energy	0.4753	0.0719	6.61	<.0001

The relationship between variation of recoveries of mass and energy in pyrolysis co-products was linear (Figure 7). To insure that the model was acceptable, parameter estimates (Table 17) were generated and produced a p-value (Prob>|t|) of less than 0.05 which meant that with 95% certainty that H_0 could be rejected. By accepting H_a, this indicated that mass efficiency increases proportionally with energy efficiency. Meaning, mass conversion is known for a given energy efficiency.

For the energy vs. nutrient recovery model, the hypothesis was;

- H_0: Energy efficiency is independent of nutrient recovery; therefore the slope is equal to zero.
- H_a: There is some dependence.

The linear fit between energy efficiency and recovery of P and Mg is shown in Figure 8 and their parameter estimates in Table 18.

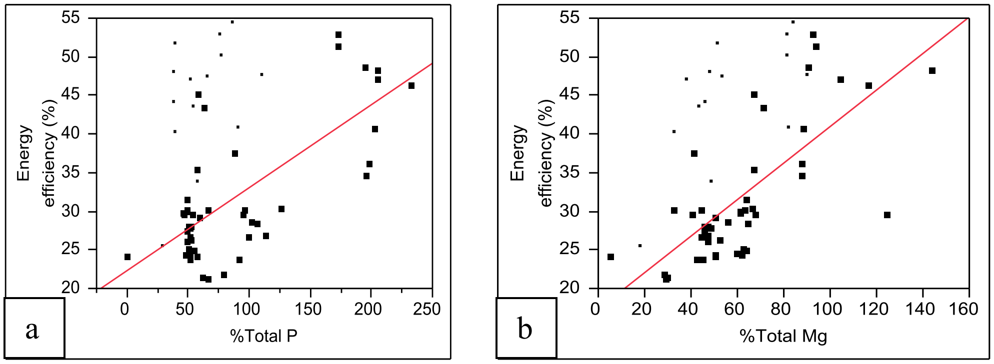

Figure 8. Linear fits for mass and recovery of a) P and b) Mg across feedstocks.

The linear relationships between variation of energy and nutrient recovery of P and Mg were found to be;

$$\text{Energy efficiency} = 22.31 + 0.1075*\text{Total P}, (R^2=0.56),$$

$$\text{Energy efficiency} = 17.27 + 0.2364*\text{Total Mg}, (R^2=0.52).$$

Table 18. Parameter estimates for energy efficiency vs. recovery of P and Mg regression.

%Total P				
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	22.31	1.594	13.99	<.0001
%Total P	0.1075	0.01504	7.15	<.0001
%Total Mg				
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	17.27	2.237	7.72	<.0001
%Total Mg	0.2364	0.0333	7.09	<.0001

From the data in Table 18, it is clear that the slope for each linear relationship is not zero. Additionally, the p-values (Prob>|t|) ensure that the linear assumptions is valid and thus, the H_a was rejected and H_0 was accepted. However, P and K only accounted for 56% and 52% o the variation in energy efficiency.

To evaluate the relationship between variation of feedstock composition and mean percent total nutrient recovery, a simple linear model was not sufficient. In this case, variation of Total P recovery (%) was analyzed using multiple regression analysis of several covariate terms. Covariate terms of feedstock composition included concentrations of NDF, ADF, ADL (DM), ADL (OM), ash, cellulose, hemicellulose, and soluble sugars. The model was multiply regressed with only variation of ADL (DM) and ash concentrations accounting for 57% (R^2=0.569) of variation of Total P recovery in co-products. The hypothesis was;

- H_0: Variation of %Total P in co-products was independent of feedstock composition; therefore the slope is equal to zero.
- H_a: There is some dependence.

Table 19. Summary of fit table for %Total P terms.

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-74.31	22.32	-3.33	0.0017
ADL(DM)	1.365	0.2299	5.94	<.0001
Ash	0.6684	0.1929	3.46	0.0012

The estimated expression for variation of %Total P was found to be;

$$\%\text{Total P} = -74.31 + 1.37 * \text{ADL (DM)} + 0.67 * \text{Ash}, (R^2 = 0.569).$$

Using p-values from the summary of fit table (Table 19), the null hypothesis was rejected. The estimated expression for %Total P was dependent on two terms and was found to be linear.

Regression analysis proved to be a useful tool to evaluate relationships among variation of dependent and independent variables. However, when more covariates are involved, multiple linear regressions were used to evaluate relationships. The multiple linear regression model only explained 57% of the data in predicting %Total P in which only ash and ADL (DM) statistically contributed to the model. This implies that more information should be added to the regression model in addition to feedstock properties. Future investigations such as the addition of covariates such a moisture and elemental compositions of ash could potentially contribute to explain variation of the %Total P. Multiple linear regression equations for the remaining macronutrients were found to be linear. The relationships all depended on several feedstock compositions ADL (DM), cellulose, hemicellulose, and soluble sugars for K and NDF for Ca and soluble sugars for Mg. The equations are presented in B-9 of Appendix B.

3.3. Fluidized-bed, Fast Pyrolysis

Fast pyrolysis is characterized by rapid heating rates (300-500°C min^{-1}), very short vapor residence times (<1 sec), and a temperature range of 500 to 700° within the reactor (S. Capareda, personal communication, August 2010). The primary goal of fast pyrolysis is the production of bio-oil and syngas. If the purpose is to maximize the yield of bio-oil, a moderate temperature (≤650°C), a high heating rate, and a short vapor residence time would be required. For targeted syngas production, a high temperature (≥650°C), low heating rate, and long vapor residence time is preferred (Bridgwater et al., 1999).

For both fast pyrolysis experiments (College Station, TX and Wyndmoor, PA), three feedstocks (switchgrass, corn stover, and HES) were pyrolyzed. Pyrolysis conditions and data collected from both reactors are listed in Table 1.

3.3.1. Fluidized-bed Pyrolysis Bio-char and Bio-oil Characterization

After pyrolysis, both bio-char and bio-oil co-products were collected and weighed. From these weights and the weight of the initial amount of input biomass pyrolyzed, bio-char and bio-oil yields were calculated. The bio-char and bio-oil yields for both reactors are expressed as yield kg^{-1} feedstock and presented in Table 20.

Table 20. Mean yields of bio-char and bio-oil kg^{-1} feedstock for both fluidized-bed, fast pyrolysis experiments.

Species	Bio-char	Std Dev	Bio-oil	Std Dev
g kg^{-1}				
College Station, TX				
Corn stover	179.8a[†]	10.6	280.2a	32.8
Switchgrass	122.6b	10.5	243.5a	58.1
HES	193.2a	22.2	229.2a	36.7
Wyndmoor, PA				
Corn stover	237.3a	35.6	331.0a	46.0
Switchgrass	154.7b	7.5	413.4a	20.3
HES	253.8a	18.4	213.6b	72.0

†Means within a column and location followed by the same letter (separated by location) do not significantly differ (0.05 level).

Bio-char yield kg^{-1} feedstock varied for both reactors. For locations, HES and corn stover produced similar and the highest bio-char kg^{-1} feedstock, followed by a lower bio-char yield for switchgrass. Bio-oil kg^{-1} feedstock varied for the Wyndmoor location but not for the College Station location. For the Wyndmoor reactor, corn stover and switchgrass had the highest and similar yields of bio-oil kg^{-1} feedstock. High-energy sorghum produced the least amount of bio-oil kg^{-1} feedstock at the Wyndmoor location. For the Wyndmoor reactor, higher bio-char yields could have been a result of a more efficient bio-char collection system and higher bio-oil yields could have been related to the existence of 4 in-series oil collection canisters followed by an electrostatic precipitator (ESP).

Corn stover pyrolyzed at Wyndmoor, PA, bio-char kg^{-1} feedstock was higher and bio-oil kg^{-1} feedstock was lower compared to respective bio-char and bio-oil yields of 170 and 616 g kg^{-1} feedstock from corn stover pyrolyzed under similar conditions (Mullen et al., 2010). Similarly, respective bio-char yields from fast pyrolysis of fresh corn stover, switchgrass, and hybrid poplar were 155, 210, and 140 g kg^{-1} and bio-oil yields were 605, 625, and 622 g kg^{-1}(Agblevor et al., 1995). Another study investigating the fast pyrolysis of switchgrass found respective bio-char and bio-oil yields of 150 and 610 g kg^{-1} biomass (Boateng, 2007). Research on fast pyrolysis of rice biomass reported a bio-oil mean yield kg^{-1} of 417 g kg^{-1}(Chen et al., 2011b). Of the three feedstocks tested, the aforementioned yield was only comparable to switchgrass in the present study. Similarly, bio-char and bio-oil yields of 152 and 410 g kg^{-1} were generated from the fast pyrolysis of pine saw dust (Chen et al., 2010). Similarly, fast pyrolysis of sugarcane residue at 500°C yielded respective bio-char and bio-oil of 274 and 523 g kg^{-1} of biomass (Xu et al., 2011). Similarly, respective bio-char and bio-oil yields ranged from 160 to 210 g kg^{-1} and 420 to 500 g kg^{-1} in a study on the fast pyrolysis of barley stover

(Mullen et al., 2009). These yields were similar to bio-char yields in Table 20, but bio-oil yields were higher than those in the current study (Table 20).

When both locations are compared, the Wyndmoor, PA reactor produced higher bio-char and bio-oil yields kg^{-1} feedstock in most cases. Higher yields of bio-char may have been a result of the more sophisticated bio-char collection system. Higher bio-oil yields kg^{-1} feedstock could have been a result of the presence of electrostatic precipitators on the Wyndmoor, PA reactor which optimized the collection of bio-oil.

For each location, proximate and ultimate analyses were performed on the bio-char generated by each reactor (Tables 21 and 22). For the College Station location, bio-char water kg^{-1} feedstock and ash kg^{-1} bio-char did not vary amongst feedstocks but VCM, fixed C, HHV kg^{-1} bio-char did vary (Table 21). For feedstocks pyrolyzed at the Wyndmoor location, variation in water and HHV's kg^{-1} bio-char were detected amongst feedstocks, but no variation was found for VCM, fixed C, and ash kg^{-1} bio-char. Water in corn stover and HES were higher for the Wyndmoor location and switchgrass was higher at the College Station location. Higher water contents in corn stover and HES for the Wyndmoor location could have been due to reactions within pipes and cyclone separators after bio-char exited the pyrolysis reactor and needs further investigation. No variation in ash kg^{-1} bio-char was detected for either location.

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Table 21. Proximate analyses of fluidized-bed, fast pyrolysis bio-chars.

Species	Moisture	Std Dev	VCM	Std Dev	Fixed C	Std Dev	Ash	Std Dev	HHV	Std Dev
g kg^{-1}									MJ kg^{-1}	
College Station, TX										
Corn stover	35.8a†	7.0	408.6ab	74.1	296.4ab	70.5	294.9a	72.6	21.7a	2.0
HES	46.0a	6.8	488.5a	64.1	144.9b	98.2	366.6a	68.7	22.4a	5.7
Switchgrass	35.2a	11.9	298.5b	75.7	312.7a	51.9	388.8a	31.0	19.8b	8.6
Wyndmoor, PA										
Corn stover	52.7a	6.9	411.5a	27.6	237.2a	50.2	351.3a	51.2	19.2ab	3.2
HES	46.5b	27.3	416.9a	26.7	232.8a	41.7	350.3a	21.3	17.5b	6.0
Switchgrass	34.1c	15.8	415.0a	44.2	238.5a	57.1	346.5a	44.6	19.3a	13.7

†Means within a column and location followed by the same letter (separated by location) do not significantly differ (0.05 level).

Table 22. Ultimate analyses of fluidized-bed, fast pyrolysis bio-chars.

Species	N	Std Dev	C	Std Dev	H	Std Dev	S	Std Dev	O	Std Dev
g kg^{-1}										
College Station, TX										
Corn stover	9.3a†	1.0	601.7a	54.3	35.9a	3.6	2.7b	0.5	350.4b	58.8
Sorghum	6.8b	1.1	445.2b	88.9	27.1a	7.0	3.0ab	0.6	517.8a	47.3
Switchgrass	5.1b	0.1	569.8ab	36.6	35.2a	3.9	3.8a	0.5	386.1ab	36.5
Wyndmoor, PA										
Corn stover	11.2a	1.0	533.0a	36.5	33.3a	3.5	1.8a	0.6	422.8a	39.9
Sorghum	6.8b	0.5	532.5a	30.0	32.3a	1.8	2.3a	0.5	473.5a	30.9
Switchgrass	4.8c	0.4	485.0a	54.2	31.2a	1.7	1.5a	0.1	427.9a	55.4

†Means within a column and location followed by the same letter (separated by location) do not significantly differ (0.05 level).

In a study of fast pyrolysis of switchgrass, investigators found bio-char proximate analysis values of: water - 37.85g kg^{-1} bio-char, VCM - 283.75g kg^{-1} bio-char, fixed C – 420.5g kg^{-1} bio-char, ash - 258.5g kg^{-1} bio-char and HHV - 19.4 MJ kg^{-1} bio-char (Boateng et al., 2007). These values were inconsistent with proximate analysis of switchgrass in Table 21 (with the exception of water and HHV). Research on the fast pyrolysis by Brewer et al. (2009) found values of: water - 10.05g kg^{-1} bio-char, VCM – 149.5g kg^{-1} bio-char, fixed C – 344.5g kg^{-1} bio-char, ash - 497g kg^{-1} bio-char and an HHV of 13.8 MJ kg^{-1} bio-char in corn stover bio-char. When compared to proximate analysis results for corn stover bio-chars in Table 21, these values were low with the exception of fixed C and ash.

Research done on fast pyrolysis of barley stover by Mullen et al. (2010) discovered bio-char water and ash values of 19.25g kg^{-1} bio-char and 356.3g kg^{-1} bio-char and a HHV of 18 MJ kg^{-1} bio-char. Ash and HHV kg^{-1} bio-char values from the aforementioned study are similar to bio-char ash and HHV values in Table 21 for both locations, however, water was not. Proximate analyses for the two fast pyrolysis systems in the present study were different. Mean water concentrations were higher for bio-char at the Wyndmoor location, but HHV were higher for the College Station location. However, ash, VCM, and fixed C concentrations were similar for both locations. Similarities can be attributed to the same feedstock being used for both locations and relatively similar sample handling and analysis procedures. Additionally, similar pyrolysis temperatures were used at both locations.

Variation amongst species in N kg^{-1} bio-char was detected for both locations (Table 22). Carbon, H, S, and O kg^{-1} bio-char did not vary amongst feedstocks pyrolyzed at the Wyndmoor location. However, variation amongst species was detected for C, S, and O kg^{-1} bio-char for the College Station location. Ultimate analysis for fast pyrolysis corn stover and switchgrass bio-chars in the present study were similar to that of Brewer et al. (2009) for H, N, and S kg^{-1} bio-char, but C kg^{-1} bio-char was higher for bio-chars generated at both locations presented in Table 22. Ultimate analysis results for corn stover bio-char produced at the Wyndmoor location was similar to corn stover bio-char investigated by Mullen et al. (2010), but not similar to the corn stover bio-char produced at the College Station location. A publication by Chen et al (2010) revealed concentrations of: C - 781.4, H - 33.4, and N - 3.0g kg^{-1} bio-char for bio-char from fast pyrolysis of sawdust. These values were similar to N and S kg^{-1} bio-char for bio-chars produced at both locations, but C kg^{-1} bio-char in sawdust bio-char was higher.

Ultimate analysis results varied by species and, in most cases, by reactor location. Differences among species can be attributed to similar reasons as listed for proximate analysis.

3.3.2. Mineral Nutrient Recovery from Fluidized-bed, Fast Pyrolysis Co-products

Corn stover, HES, and switchgrass were pyrolyzed using fluidized-bed reactors in College Station, TX and Wyndmoor, PA. Pyrolysis conditions are listed in Table 1. However, for these experiments, bio-char nutrients were determined by modified Kjeldahl digestion. Bio-oil nutrients were determined using the ashing method.

The initial macro and micronutrient concentrations in the feedstock can be found in Tables 6 and 7. Bio-char and bio-oil macro and micronutrient concentrations for each reactor location are listed in Tables 23 and 24.

Table 23. Bio-char and bio-oil nutrient concentrations for both locations.

Species	P	Std Dev	K	Std Dev	Ca	Std Dev	Mg	Std Dev
mg kg^{-1}								
Bio-char co-product (College Station, TX)								
Corn stover	1870c†	96.2	445.1E+02b	596.6	139.3E+02a	301.1	5307a	211.7
Switchgrass	2689b	157.8	150.0E+02c	574.8	151.6E+02a	648.3	2750c	171.3
HES	3511a	315.5	580.1E+03a	341.7	145.4E+02a	117.7	4010b	203
Bio-oil co-product (College Station, TX)								
Corn stover	26.9a	3.3	458.5ab	28.8	262.0b	12.6	75.1a	10.9
Switchgrass	21.2a	5.1	175.7b	10.3	116.0c	23.0	35.3b	8.3
HES	39.3a	4.3	932.4a	41.7	455.3a	19.3	85.6a	6.2
Bio-char co-product (Wyndmoor, PA)								
Corn stover	3550a†	72.2	562.5E+02b	110	141.3E+02b	122.2	5464a	13.4
Switchgrass	3607a	71.4	209.8E+02c	102.7	191.4E+02a	108.9	3012c	82.5
HES	3368a	43.7	626.8E+02a	229	142.5E+02b	91.1	3730b	45.4
Bio-oil co-product (Wyndmoor, PA)								
Corn stover	34.4a	6.2	654.9a	32.3	188.5a	12.1	176.6a	8.5
Switchgrass	35.4a	3.5	365.7a	27.8	196.4a	11.7	123.9a	6.9
HES	39.6a	9.7	482.3a	37.1	185.8a	11.4	157.8a	7.0

†Means within a column and location followed by the same letter (separated by co-product) do not significantly differ (0.05 level).

Table 24. Bio-char and bio-oil micronutrient concentrations for both locations.

Species	Na	Std Dev	Zn	Std Dev	Fe	Std Dev	Cu	Std Dev	Mn	Std Dev
mg kg^{-1}										
Bio-char co-product (College Station, TX)										
Corn stover	311.4a†	3.6	136.8a	9.6	139.5a	9.6	43.9a	7.2	139.7a	15.7
Switchgrass	321.5a	8.7	88.4b	1.9	151.2a	8.1	35.0a	8.1	107.3a	8.1
HES	311.2a	2.8	73.1c	2.4	126.4a	8.2	37.5a	8.0	73.5b	8.1
Bio-oil co-product (College Station, TX)										
Corn stover	253.1a	24.4	21.4b	5.5	502.2a	23.3	4.9a	1.3	23.4a	1.2
Switchgrass	195.6a	22.1	8.5b	3.4	245.8b	17.1	4.1a	2.0	11.1b	1.8
HES	251.8a	11.1	53.8a	5.7	544.1a	17.1	3.2a	1.5	17.0ab	5.8
Bio-char co-product (Wyndmoor, PA)										
Corn stover	286.7a†	6.7	102.1a	4.1	267.6a	6.3	21.6a	5.3	159.7a	9.5
Switchgrass	289.4a	8.0	100.6a	2.5	187.4b	2.5	13.8b	0.7	112.3b	5.3
HES	291.0a	4.6	62.8b	7.6	78.0c	3.4	11.9b	1.0	61.8c	8.9
Bio-oil co-product (Wyndmoor, PA)										
Corn stover	699.4a	17.3	15.7a	1.2	1331a	17.7	41.0a	7.4	39.5a	4.9
Switchgrass	487.9a	8.0	6.1a	1.8	205.1a	14.4	11.9a	3.9	8.5a	0.6
HES	696.2a	22.4	17.8a	0.7	1967a	16.2	39.2a	2.2	34.7a	2.1

†Means within a column and location followed by the same letter (separated by co-product) do not significantly differ (0.05 level).

For the College Station location, P, K, and Mg concentrations in bio-char varied among species but Ca did not (Table 23). For the Wyndmoor location, K, Ca, and Mg concentrations in bio-char varied among species, however, no variation in P was detected. For bio-oil, variation among species was detected in K, Ca, and Mg concentrations but not for P for the College Station location. No variation among species was detected for macronutrient concentrations in bio-oil produced at the Wyndmoor location.

For the College Station location, variation among species was detected in bio-char Zn and Mn concentrations but not for Na, Fe, or Cu (Table 24). Variation among species was detected for every bio-char micronutrient concentration except for Na at the Wyndmoor location. Zinc, Fe, and Mn concentrations in bio-oil varied among species, however, Cu and Na did not (College Station). No variation among species was found for micronutrient concentrations in bio-oil produced at the Wyndmoor location.

Corn stover bio-chars produced at both reactor locations had low P concentration in bio-char when compared to 12940 mg kg^{-1} of P in corn stover bio-char found by Mullen et al. (2010). Agblevor et al. reported P concentrations of 1.2 and 1 mg kg^{-1} in bio-oil made from fresh and stored corn stover. These values are low in comparison to P concentrations in bio-oil in Table 24. However, P concentration in switchgrass bio-char was low for samples pyrolyzed at both locations compared to a concentration of 2700 mg kg^{-1} of P in bio-char from stored switchgrass (Agblevor et al., 1995). Phosphorus concentrations in switchgrass bio-oils in the present study were high for both locations when compared to concentrations of 3.4 and 3.5 mg kg^{-1} of P in bio-oil produced from fresh and stored switchgrass feedstock (Agblevor et al., 1995). For corn stover, bio-char

K concentrations in the current study were low for both locations when compared to Mullen et al. (2010) who found 23450 mg kg^{-1} of K in corn stover bio-char generated by fast pyrolysis. Agblevor et al. (1995) found a K concentration of 24000 mg kg^{-1} in bio-char produced from stored switchgrass, which is a higher K concentration than switchgrass bio-chars produced at in fast pyrolysis systems at College Station and Wyndmoor in the present study (Table 23). A study by Agblevor et al. (2010) revealed K concentrations of 115 and 158 mg kg^{-1} in bio-oil produced from fresh and stored switchgrass. These were lower than K concentrations in switchgrass bio-oil produced at both College Station and Wyndmoor locations. Mullen et al. (2010) found a concentration of 2013 mg kg^{-1} of Ca in corn stover bio-char. This Ca concentration is higher than any Ca concentration in bio-chars that were produced at College Station and Wyndmoor locations in the present study. Calcium concentrations of the current study were lower than concentrations of 3.1 and 5.6 mg kg^{-1} reported by Agblevor et al. (1995) in bio-oil generated from fresh and stored corn stover. The same publication revealed a Ca concentration of 7300 mg kg^{-1} in stored switchgrass bio-char, which is lower than either P concentration in switchgrass bio-char reported in Table 23. Meanwhile for bio-oil, Agblevor et al. (1995) found Ca concentrations of 8.2 and 6.9 mg kg^{-1}. These values are well below related concentrations in bio-oil in Table 23.

Mullen et al. (2010) reported a Na concentration in corn stover bio-char of 1070 mg kg^{-1}, which is low when compared to bio-char derived from during fast pyrolysis for College Station and Wyndmoor systems (Table 24). The same fast pyrolysis reactor produced samples presented in Mullen et al. (2010) and the Wyndmoor location of the current study. Therefore, variation among sample nutrient concentrations can be attributed differences in feedstock source. The same reason for differences can be attributed to variation in nutrient concentrations for samples pyrolyzed using the College Station reactor. Additionally, reactor design could have contributed to variations for the College Station reactor as well. Sodium concentrations in corn stover bio-oil in the current study were high when compared to concentrations of 12.2 and 22.2 mg kg^{-1} of Na found by Agblevor et al. (1995) in bio-oil produced from fresh and stored corn stover. Concentrations of Na in switchgrass bio-oil in the present study were also low when compared to fresh and stored bio-oil concentrations of 8.2 and 6.9 mg kg^{-1} published by Agblevor et al. (1995). Concentrations of 15950 and 650 mg kg^{-1} of Fe and Mn in corn stover bio-char have been reported by Mullen et al. (2010). Iron and Mn concentrations in corn stover bio-chars derived from samples pyrolyzed at using the Wyndmoor and College Station locations are far lower than the aforementioned concentrations.

Differences in nutrients could also have been due to reactor conditions. The inert-gas flow rate for the College Station reactor was ~40 L min^{-1} whereas the flow rate for the Wyndmoor reactor was operated at ~70 L min^{-1}. However, no distinct pattern in bio-char or bio-oil macro and micronutrient concentration was observed to conclude that inert-gas flow rate had an influence. The Wyndmoor reactor contained four in-series condensers followed by an electrostatic precipitator (ESP). This also may have contributed to differences in bio-oil macro and micronutrient concentrations amongst species for both locations.

The recovery of nutrients for both fluidized-bed, fast pyrolysis reactor locations are given in Tables 25 and 26.

Table 25. Mean percent recovery of nutrients from fluidized-bed, fast pyrolysis reactors.

Species	P	Std Dev	K	Std Dev	Ca	Std Dev	Mg	Std Dev
%								
Bio-char co-product (Wyndmoor, PA)								
Corn stover	65.4a†	16.8	53.1a	3.9	63.2a	10.6	57.8a	3.0
HES	56.5a	9.7	54.0a	8.3	57.9a	8.2	36.0b	5.3
Switchgrass	30.1b	6.7	8.9b	1.2	38.5b	5.8	14.3c	1.4
Bio-oil co-product (Wyndmoor, PA)								
Corn stover	5.2a	2.0	2.1a	0.7	5.3a	1.3	7.7a	2.0
HES	2.0a	2.0	0.9a	0.6	2.3a	1.9	3.3a	1.7
Switchgrass	5.5a	4.4	2.1a	1.5	6.1a	4.7	7.7a	4.5
Bio-char and bio-oil combined (Wyndmoor, PA)								
Corn stover	70.8a	14.8	55.1a	3.3	68.5a	17.7	65.5a	7.1
HES	58.6a	8.5	54.8a	8.0	60.2a	4.7	39.3b	3.6
Switchgrass	35.5b	5.5	11.0b	1.7	44.6b	5.7	22.0c	1.0
Bio-char co-product (College Station, TX)								
Corn stover	37.8a†	0.8	46.64a	1.4	61.1a	3.2	47.2a	2.6
HES	49.9a	19.1	46.48a	21.5	40.5a	18.4	38.9a	18.9
Switchgrass	47.6a	7.9	38.72a	3.8	41.6a	6.3	37.0a	5.4
Bio-oil co-product (College Station, TX)								
Corn stover	0.9a	0.2	0.75a	0.2	1.8a	0	1.0a	0.1
HES	0.8a	0.4	1.10a	0.8	1.8a	0.3	1.2a	0.4
Switchgrass	0.8a	0.7	0.96a	0.8	0.7a	0.3	1.0a	0.7
Bio-char and bio-oil combined (College Station, TX)								
Corn stover	38.6a	1.0	47.4a	1.5	62.9a	3.2	48.3a	2.7
HES	50.8a	19.5	47.6a	22.3	42.3a	18.2	40.0a	19.1
Switchgrass	48.4a	8.2	39.7a	3.8	42.3a	6.3	38.0a	5.4

†Means within a column followed by the same letter (separated by co-product location) do not significantly differ (0.05 level).

Table 26. Mean percent recovery of micronutrients from fluidized-bed, fast pyrolysis reactor (Wyndmoor, PA).

Species	Na	Std Dev	Zn	Std Dev	Fe	Std Dev	Cu	Std Dev	Mn	Std Dev
%										
Bio-char co-product										
Corn stover	40.6a[†]	3.1	61.7a	5.8	79.7a	12.1	61.1a	18.1	57.9a	0.3
HES	37.6a	5.6	34.7b	6.2	21.1b	2.2	30.6b	4.6	20.4b	2.6
Switchgrass	18.4b	1.8	27.2b	2.4	25.0b	6.2	17.5b	2.4	18.3b	1.7
Bio-oil co-product										
Corn stover	272.8a	51.8	22.4a	16.4	656.6a	73.1	224.7a	142.6	30.4a	21.3
HES	252.2a	61.5	15.8a	2.7	803.5a	33.4	132.3a	41.5	19.0a	7.2
Switchgrass	147.0a	47.0	15.6a	4.9	178.3a	85.0	99.4a	5.2	15.0a	9.3
Bio-char and bio-oil combined										
Corn stover	223.5a	29.2	96.6a	5.2	770.6ab	85.2	276.0a	145.5	99.6a	25.8
HES	181.6a	43.7	88.5a	11.2	123.7E+02a	214.0	221.5a	61.1	98.9a	3.3
Switchgrass	242.3a	9.6	87.8a	6.2	120.4b	73.6	183.1a	11.7	76.2a	6.1

†Means within a column followed by the same letter (separated by co-product) do not significantly differ (0.05 level).

Tablel 27. Mean percent recovery of micronutrients from fluidized-bed, fast pyrolysis reactor (College Station, TX).

Species	Na	Std Dev	Zn	Std Dev	Fe	Std Dev	Cu	Std Dev	Mn	Std Dev
%										
Bio-char co-product										
Corn stover	4.1a[†]	0.3	76.9a	5.04	28.7a	16.8	112.4a	12.2	51.5a	3.7
HES	3.3a	1.5	37.9b	16.0	22.7a	5.2	106.5a	62.4	38.3a	14.2
Switchgrass	2.7a	0.2	44.3b	4.6	20.3a	12.3	107.3a	15.5	48.5a	8.3
Bio-oil co-product										
Corn stover	5.2a	0.5	18.4a	2.2	164.8a	17.0	19.4a	4.4	13.5a	1.5
HES	3.9a	1.9	38.9a	15.6	148.4a	21.9	11.9a	4.9	12.5a	2.7
Switchgrass	3.3a	0.9	8.2a	2.4	67.5a	36.4	25.7a	13.4	10.0a	2.9
Bio-char and bio-oil combined										
Corn stover	9.3a	0.3	95.2a	4.6	193.5a	31.7	131.8a	10.7	65.0a	5.0
HES	7.2a	3.1	76.7b	11.4	171.1a	17.8	118.4a	59.6	50.8a	11.6
Switchgrass	5.9a	0.9	52.5c	2.5	87.8a	33.2	132.9a	16.3	58.5a	11.0

[†] Means within a column followed by the same letter (separated by co-product) do not significantly differ (0.05 level).

Recovery of macronutrients in bio-char varied among species for the Wyndmoor location, but not for the College Station location (Table 25). Variation among species was not detected for recovery of macronutrients in bio-oil for either location. When bio-char and bio-oil are combined (combined co-products), recovery of macronutrients varied among species for the Wyndmoor location, however, no variation among species was found for the College Station location.

Recovery of micronutrients in bio-char varied among species for the Wyndmoor location (Table 26). For the College Station location, only recovery of Zn in bio-char varied among species. Recovery of micronutrients in bio-oil did not vary among species for either location. However, elevated levels of Na, Fe, and Cu were recovered in select bio-oils generated at the Wyndmoor location. This could have been due to the more efficient bio-oil collection system. This system, which had and electrostatic precipitator (ESP), could have condensed metal alloys released in the bio-oil from stainless steel reactor tubing during pyrolysis. However, this needs further investigation. For combined co-products, only recovery of Fe varied among species for the Wyndmoor location and only recovery of Zn for the College Station location (Tables 26 and 27).

For the College Station location, corn stover bio-char conserved more feedstock K, Ca, and Mg than HES or switchgrass, but the most P was conserved in HES bio-char. No more than 7.7% of any macronutrient was recovered in bio-oils produced at the Wyndmoor location and less than 2% of macronutrients were recovered from bio-oil produced at the College Station location (Tables 26 and 27). Recovery of macronutrients in corn stover bio-char was low when compared to Mullen et al. (2010) who reported recoveries of >100% of P and >87% of K. This was likely due to differences in nutrient analysis methods. Recovery of macronutrients in switchgrass bio-char was also low when compared work done by Agblevor et al. (1995).

For the Wyndmoor location, recoveries of P, K, Ca, and Mg in bio-char varied among species, but not in bio-oil.

For the College Station reactor, recoveries of P, K, Ca, and Mg in combined co-products were low. Low recovery of macronutrients could have been due to several factors such as; low feedstock nutrient concentrations and volatilization during pyrolysis.

For the Wyndmoor location, recoveries of micronutrients in bio-chars varied amongst species (Table 26). Recoveries of feedstock Na, Zn, Cu, and Mn did not vary among combined co-product species, however, Fe did vary.

For the College Station location, recovery of Fe in bio-char and in combined co-products varied among species. Recovery of micronutrients in bio-oil was low and did not vary among species (Table 27). However, recovery of Cu was elevated (>100%) for all three species and needs further investigation.

Potential causes for high recoveries of Cu in bio-char and Fe in bio-oil could be a result of alloys released from reactor piping during pyrolysis. Low recovery of Na in bio-char and bio-oil could have due to the formation of Na-containing salts during combustion reactions that were swept out with NCG’s (Lindner and Wall, 1991).

3.3.3. Fluidized-Bed Reactor Mass and Energy Closure

Mass and energy balances with respect to bio-char and bio-oil co-products (i.e. NCG's were not included) for both systems were calculated to determine reactor biomass-to-co-product conversion and energy efficiencies. The results for both reactors are presented as mean percent mass conversion and energy efficiency.

Table 28. Mean percent mass and energy efficiency for both fluidized-bed, fast pyrolysis reactors.

Species	Mass	Std Dev	Energy	Std Dev
%				
College Station, TX				
Corn stover	46.0a[†]	2.6	47.9a	3.8
HES	38.9a	7.4	43.6a	4.0
Switchgrass	36.6a	4.2	35.5a	3.3
Wyndmoor, PA				
Corn stover	56.8a	3.3	51.3b	3.3
HES	46.7b	6.2	48.5b	6.9
Switchgrass	56.8a	2.6	67.1a	4.2

†Means within a column followed by the same letter (separated by location) do not significantly differ (0.05 level).

Mass efficiency for the College Station reactor was below 50% for all feedstocks. For the Wyndmoor location, mass efficiency was over 50% for corn stover and switchgrass and just below 50% for HES. Energy efficiency was also below 50% for the College Station reactor, whereas the reactor at the Wyndmoor location was above 50% for corn stover and switchgrass and just below 50% for HES.

Energy efficiencies for corn stover were low for both reactors in comparison to an energy efficiency of ~70% (combination of bio-char and bio-oil) found by Mullen et al. (2010) for pyrolysis of corn stover. This could be due to bio-char unaccounted for that was left mixed in with bed sand. In a related study, when all pyrolysis co-products were accounted for, an energy efficiency of 90% was reached from the fast pyrolysis of high-biomass soybean (Boateng et al., 2010). Mass and energy losses for both systems could have been attributed to not taking into account NCG's and heat and energy losses in the condenser systems. Mullen et al. (2010) concluded similar findings on potential energy losses. Higher mass and energy efficiencies imply that a higher percentage of the input feedstock is accounted for, which narrows the possible reasons for low recoveries of nutrients. More efficient reactor heating, biomass feeding, reactor degassing, and biomass fluidization could improve mass and energy efficiency. More research is needed to investigate mass and energy losses during fast pyrolysis of corn stover, HES, and switchgrass.

3.3.4. Correlation Analysis

Results for correlation analysis between mass and energy for both fluidized-bed, fast pyrolysis systems (Wyndmoor, PA and College Station, TX) are presented in Figure 9.

Figure 9 can be read as an inverse plot. For instance, the upper right hand quadrant can be read as “Mass efficiency (%)” on the “y” axis with the percentage range listed to the left of the axis label and “Energy efficiency (%)” on the “x” axis with the percentage range listed below the axis label. The bottom left hand quadrant can be read in a similar manner.

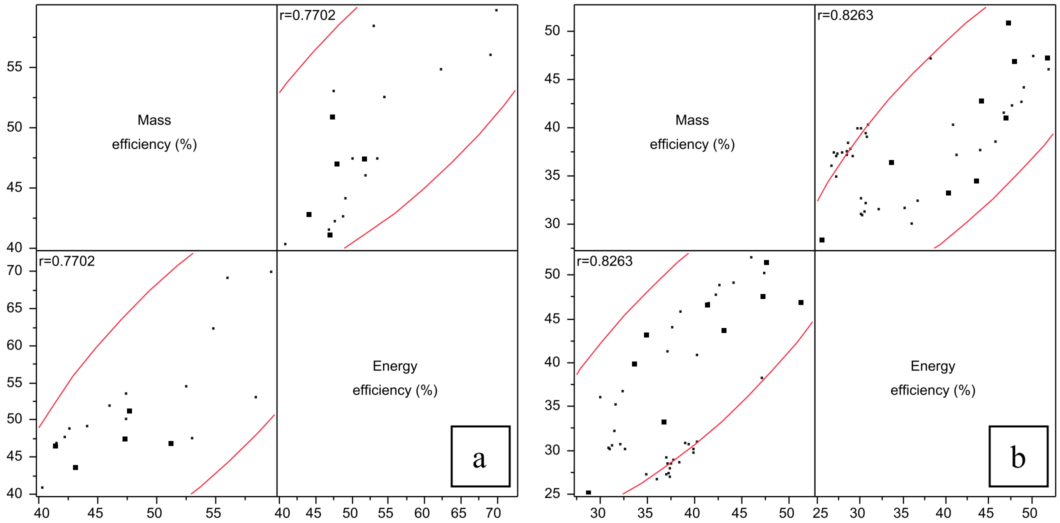

Figure 9. Scatter plot matrix for correlation between reactor mass vs. energy efficiency across feedstocks for a) Wyndmoor and b) College Station.

Correlation between mass and energy was moderate for each location. Pearson’s correlation coefficient for the Wyndmoor reactor was (r=0.7702) and (r=0.8.63) for the

College Station reactor. High correlations ($r \geq 0.7$) indicate a linear relationship between mass and energy efficiency of both the Wyndmoor and College Station reactor.

On an individual feedstock basis, correlations between feedstock fiber properties and the recovery of nutrients were mixed for both reactor locations. For the most part, Pearson's correlation coefficient was low ($r \leq 0.6$). However, for select feedstocks, moderate ($0.6 \leq r \leq 0.7$) and high ($r \geq 0.8$) positive and negative correlations were found. This indicates possible linear relationships between select nutrients and feedstock fiber properties for both reactor locations. This implies that feedstock fiber properties either increase or decrease proportionally with the recovery of nutrients. However, only three data points (3 pyrolysis replications for each feedstock) for each feedstock and needs to be further investigated with more data points, as was the case with slow pyrolysis experiments in Fixed-bed, Slow Pyrolysis section of this dissertation. The correlation tables are presented in Tables C-1 through C-9 of Appendix C.

Correlation analysis between mass efficiency and nutrient recovery and between energy efficiency and nutrient recovery for the feedstocks pyrolyzed using the Wyndmoor reactor were low ($r<0.6$). This indicates that the probability of a linear relationship between the two variables is low. However for feedstocks pyrolyzed using the College Station reactor, select correlation between mass and energy efficiency and nutrient recoveries were higher ($0.7<r< 0.9$). Correlations between mass efficiency and the recoveries of K, Ca, and Mg were 0.77, 0.87, and 0.83, respectively. Correlations between energy efficiency and the recoveries of Ca and Mg were 0.81 and 0.74, respectively. This suggests that mass and energy increases proportionally with nutrient recovery.

3.3.5. Regression Analysis

Simple linear regression analysis was performed to determine the linear relationships between variation of reactor mass and energy efficiency.

The hypothesis for the mass vs. energy model for both fluidized-bed, fast pyrolysis systems were;

- H_0: Mass efficiency is independent of energy efficiency; therefore the slope is equal to zero.
- H_a: There is some dependence.

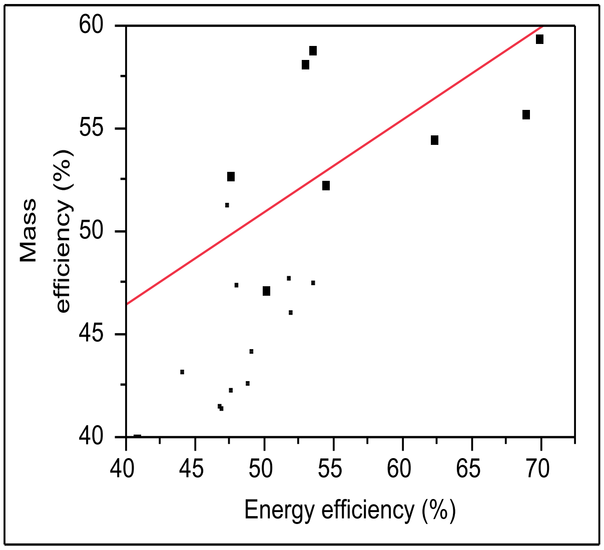

Figure 10. Linear fit for mass and energy efficiency across feedstocks (Wyndmoor, PA).

The relationship between mass and energy was found to be;

$$\text{Mass} = 28.474259 + 0.4490239*\text{Energy}$$

Table 29. Parameter estimates for mass and energy efficiency regression (Wyndmoor, PA).

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	28.47	9.873	2.88	0.0235
Energy	0.4490	0.1750	2.56	0.0373

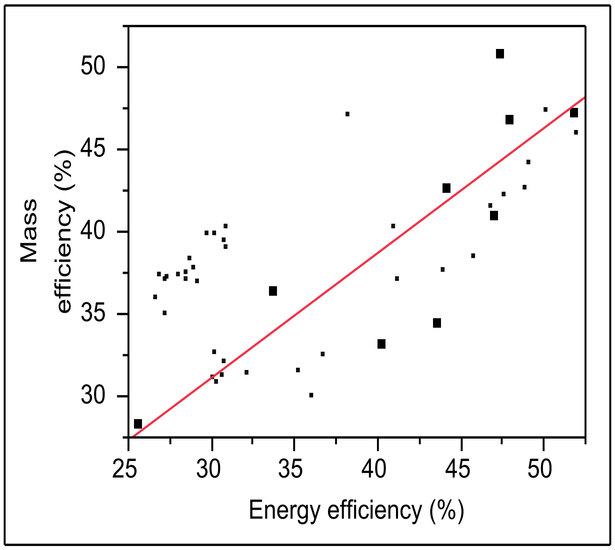

Figure 11. Linear fit for mass and energy efficiency across feedstocks (College Station, TX).

The relationship between mass and energy was found to be;

$$\text{Mass} = 8.3259979 + 0.7598098 * \text{Energy}$$

Table 30. Parameter estimates for mass and energy efficiency regression (College Station, TX).

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	8.325	8.428	0.99	0.3562
Energy	0.7598	0.1957	3.88	0.006

The second entry in the "estimate" column in Tables 29 and 30 both reveal non-zero slopes, which indicates acceptable linear regression models. The null hypothesis was rejected for both reactor locations.

Similar to the fixed-bed system, multiple linear regression analysis was done for both fluidized-bed systems. Analysis was done to determine the linear relationship between feedstock composition and percent total nutrient recovery.

For P, the hypothesis for both fluidized-bed systems was;

- H_0: %Total P is independent of feedstock composition; therefore the slope is equal to zero.
- H_a: There is some dependence.

The relationship between %Total P and feedstock composition for the Wyndmoor reactor was found to be;

%Total P = -908.8 + 0.63*NDF + 1.96*ADF + 0.66*ADL (DM) – 4.92*ADL (OM) – 1.54*ash, R^2=0.47.

The relationship between %Total P and feedstock composition for the College Station reactor was found to be;

%Total P = 234.1E+04 – 66.20*NDF+71.16*ADF – 43.20*ADL (DM) + 8.45*ADL (OM) – 11.72*ash – 26.55*Cellulose + 45.39*Hemicellulose – 24.10*Sugars, R^2=0.47

Parameter estimates results for the two above relationships indicated bias, which means a clear linear relationship between the two variables could not be determined. Typically, this indicates that another model should be used. However, the least squares fit will still give the best linear predictor of the response variable %Total P, but the estimates of the coefficients will be biased by inconsistencies and variance within data points. Similar relationships and inconsistencies were found for Ca and Mg for both reactor locations (C-9 and C-10 of Appendix C). Additionally, the remaining R^2-values for Ca and Mg of the two locations revealed less than 50% of the variation in recovery of Ca and Mg was explained by the covariates. To obtain a more accurate model, a more advanced method must be used and should be further investigated.

3.4. Mineral Nutrient Recovery Comparison between Fixed and Fluidized-Bed Reactors

Both fluidized-bed systems and the fixed-bed system were compared to each other to determine effectiveness in the recovery of macro and micronutrients (Tables 31 and 32).

Table 31. Mean percent recovery of macronutrients for each reactor (combined co-products).

Species	P	Std Dev	K	Std Dev	Ca	Std Dev	Mg	Std Dev
%								
Fixed-Bed (College Station, TX)								
Corn stover	50.1c†	20.5	30.3a	12.8	63.2b	26.6	63.3b	25.4
Switchgrass	163.5a	64.5	12.3c	2.9	78.1a	8.2	92.8a	21.7
HES	91.6b	20.0	5.0d	1.8	66.9ab	11.3	44.0c	13.1
Rice stover	52.2c	3.4	18.6b	1.0	45.6c	5.7	47.6c	3.2
Fluidized-Bed (Wyndmoor, PA)								
Corn stover	70.8a	14.8	55.1a	3.3	68.5a	17.7	65.5a	7.1
HES	58.6a	8.5	54.8a	8.0	60.2a	4.7	39.3b	3.6
Switchgrass	35.5b	5.5	11.0b	1.7	44.6b	5.7	22.0c	1.0
Fluidized-Bed (College Station, TX)								
Corn stover	38.6a	1.0	47.4a	1.5	62.9a	3.2	48.3a	2.7
HES	50.8a	19.5	47.6a	22.3	42.3a	18.2	40.0a	19.1
Switchgrass	48.4a	8.2	39.7a	3.8	42.3a	6.3	38.0a	5.4

†Means within a column followed by the same letter (separated by reactor type) do not significantly differ (0.05 level).

Table 32. Mean percent recovery of micronutrients for each reactor (combined co-products).

Species	Na	Std Dev	Zn	Std Dev	Fe	Std Dev	Cu	Std Dev	Mn	Std Dev
%										
Fixed-Bed (College Station, TX)										
Corn stover	340.6b	109.0	354.8a	231.2	875.7b	492.3	2304a	1302	77.7c	32.0
Switchgrass	866.2a	130.6	660.9a	907.2	2861b	1251	1986a	2123	311.1b	300.7
HES	847.0a	285.9	632.1a	477.9	173.0E+02a	4979	2592a	1811	796.1a	181.7
Rice stover	183.4c	23.0	387.2a	237.9	1802b	1216	2332a	1421	69.6c	5.2
Fluidized-Bed (Wyndmoor, PA)										
Corn stover	223.5a	29.2	96.6a	5.2	770.6ab	85.2	276.0a	145.5	99.6a	25.8
HES	181.6a	43.7	88.5a	11.2	1238a	214	221.5a	61.1	98.9a	3.3
Switchgrass	242.3a	9.6	87.8a	6.2	120.4b	73.6	183.1a	11.7	76.2a	6.1
Fluidized-Bed (College Station,TX)										
Corn stover	9.3a	0.3	95.2a	4.6	193.5a	31.7	131.8a	10.7	65.0a	5.0
HES	7.2a	3.1	76.7b	11.4	171.1a	17.8	118.4a	59.6	50.8a	11.6
Switchgrass	5.9a	0.9	52.5c	2.5	87.8a	33.2	132.9a	16.3	58.5a	11.0

†Means within a column followed by the same letter (separated by reactor type) do not significantly differ (0.05 level).

Between all three reactors, the highest recovery of P was obtained from the fixed-bed, slow pyrolysis of HES. The next highest recoveries of P were obtained from the fluidized-bed, fast pyrolysis of corn stover and HES at the Wyndmoor location. Elevated (>100%) recovery of P from slow pyrolysis of switchgrass was unusual and needs further investigation.

Potassium recovery was low (≤30%) for all feedstocks pyrolyzed using the fixed-bed system. However, more than 45% of feedstock K was recovered using both fluidized-bed systems. Recovery of corn stover Ca was consistent for all three reactor types. The most switchgrass Ca was recovered by using the fixed-bed reactor. The highest recovery of HES Ca was similar for the fixed-bed system and Wyndmoor fluidized-bed reactor with a slightly lower recovery of Ca using the College Station fluidized-bed system.

Fixed-bed, slow pyrolysis of switchgrass produced the highest recovery of Mg. The next highest recoveries of Mg were obtained from the pyrolysis of corn stover using the Wyndmoor reactor. The lowest recovery of feedstock Mg was obtained from the slow pyrolysis of corn stover. From this analysis, the data in can be summarized;

1. Recovery of macronutrients varied by reactor design, and furthermore
2. Recovery of appreciable amounts (>90%) of P is potentially dependant on reactor design, and
3. Recovery of feedstock K was low for all feedstocks and reactor designs, and
4. Recovery of feedstock Ca is similar for corn stover, regardless of reactor design.

Recovery of Na was low for all feedstocks pyrolyzed using the College Station fluidized-bed reactor. However, elevated levels (>100%) of Na were recovered from each feedstocks' co-products that were pyrolyzed using the Wyndmoor reactor and the fixed-bed system. Recovery of Zn was elevated for all feedstocks that were pyrolyzed using the fixed-bed reactor. However, relatively high recoveries of feedstock Zn were obtained using both fluidized-bed systems. Recovery of feedstock Fe and Cu were elevated (>100%) for all three reactor types. Recovery of switchgrass and HES Mg using slow pyrolysis were also elevated.

Feedstocks pyrolyzed at the Wyndmoor location produced higher percentages of recoverable feedstock Mg than the College Station location. Elevated recoveries of micronutrients were assumed to be due to contamination and need further investigation. From this analysis, the data can be summarized;

1. Recovery of micronutrients are unpredictable and varied by reactor design, and
2. Recovery of select micronutrients were consistently elevated (>100%) and may be due to contamination, and
3. Distribution of bio-char to soil may be an option for soils with micronutrient deficiencies.

3.5. Fluidized-Bed, Fast Pyrolysis Bio-char Surface Area Study

Prior to measuring particulate surface area of bio-char, an acetone wash was used to remove residual tars, oils, resins, and other debris. The acetone wash was expected to increase bio-char surface area and potential bio-oil yield. Bio-chars with higher surface areas have been reported to have higher cation exchange capacities (CEC), which leads to higher nutrient retention capacity in soils over time. Bio-chars with high surface areas also have higher water holding capacities (Thies and Rillig, 2009).

Surface area data for acetone washed and unwashed bio-chars were collected for all bio-char species for both fluidized-bed systems. The collected data comprised three replications of each bio-char species for both reactors with and without the acetone wash. The results of the study are presented in Table 33.

For the College Station location, surface area differences were only found between washed and unwashed switchgrass bio-chars. For the Wyndmoor location, variation among treatments was only detected for corn stover bio-char.

For both locations, mean surface area of bio-char derived from one species increased after the acetone wash. This suggests the solvent wash was effective in making more surface area available due to removal of some of the residual oils, tars, resins, and other debris from the porous bio-char surface which comprises macro and micropores.

Table 33. Surface area for acetone-washed and unwashed bio-chars (both locations).

Treatment	Surface area	Std Dev
	$m^2\ g^{-1}$	
	College Station, TX	
	Corn stover	
Washed	10.8a†	4.9
Unwashed	5.1a	8.7
	HES	
Washed	12.4a	4
Unwashed	10.6a	2.9
	Switchgrass	
Washed	10.2a	4.7
Unwashed	1.5b	1.6
	Wyndmoor, PA	
	Corn stover	
Washed	12.3a	7.8
Unwashed	2.4b	1.5
	HES	
Washed	6.0a	2.5
Unwashed	4.4a	2.8
	Switchgrass	
Washed	17.7a	9.2
Unwashed	4.7a	2.8

†Means within a column followed by the same letter (separated by species) do not significantly differ (0.05 level).

Surface areas for unwashed corn stover and switchgrass bio-chars from both reactors were low compared to surface areas of 21.9 and 7 $m^2\ g^{-1}$ for fast pyrolysis corn stover and switchgrass bio-chars (Brewer et al., 2009). Additionally, surface areas of unwashed corn stover bio-chars from both reactors were low compared to a reported corn stover bio-char surface area of 12 $m^2\ g^{-1}$ also generated by fast pyrolysis (Lee et al., 2010). Surface areas from both reactors and treatments were well below activated carbon (486 $m^2\ g^{-1}$), which is chemically similar to bio-char (Koutcheiko et al., 2007).

The surface area of bio-char is important because it affects retention of water, cations, and anions in amended soils. The use of a solvent wash to remove surface-adhered organics has the potential to increase bio-oil yield and improve bio-char physical properties such as porosity and surface area, which makes biomass pyrolysis a much more efficient means of energy conversion and bio-char a more suitable option for use as a soil enhancer.

4. CONCLUSIONS AND FUTURE WORK

For biomass conversion systems such as pyrolysis to thrive they must provide sustainable uses for not only the liquid and gaseous fuels, but also for the solid fuel as well. One way to meet this goal is to recycle biomass nutrients back to the soil by land application of bio-char. Yet, until the current study, relatively little published data exists concerning the quantification of the recovery macro and micronutrients from pyrolysis co-products. This study investigated a fixed-bed pyrolysis system and two fluidized-bed systems. Four biomass species were pyrolyzed and their co-products were chemically and physically characterized and analyzed for recovery of nutrients, on a biomass basis.

4.1. Feedstock Characterization

Initial characterization of the feedstocks in this study revealed variation among species. Feedstock fiber properties varied among species. In most cases, feedstock fiber properties were similar to related fiber properties in publications. Similarly, feedstock ultimate and proximate analyses varied among species and agreed well with published studies. Nutrient concentrations varied by species. Review of literature revealed low initial feedstock nutrient concentrations compared to published research on similar feedstocks. Future studies should attempt to relate fiber properties to recovery of nutrients and bio-char yield.

4.2. Fixed-bed, Slow Pyrolysis

Recovery of macro and micronutrients varied among feedstocks. Although various temperatures and inert-gas flow rate were used, statistics proved that effect of pyrolysis conditions on recoveries were inconsistent and inconclusive. More than 90% of feedstock P and greater than 66% of feedstock Ca was recovered in HES co-products. The highest amount of feedstock Mg was recovered in corn stover co-products. Recovery of feedstock K was relatively low for co-products produced by slow pyrolysis. If the goal is to recycle soil P, Ca, Mg and minimal K, HES and corn stover bio-chars could be recycled back to production fields. Correlation analyses revealed high correlations and linear relationships between total recoveries of feedstock macronutrients and nutrient mass loss in bio-char. This proved that the majority of feedstock nutrients are concentrated within the bio-char. High correlation and a linear relationship was found between reactor mass and energy efficiency. Additionally, multiple linear regression analysis revealed linear relationships between feedstock fiber properties and total recoveries of macronutrients.

Recoveries of feedstock micronutrients varied among species and were found to be elevated (>100%) for all micronutrients. Future investigations should study why, in most cases, micronutrients are created rather than lost during conversion. Return of soil micronutrients through bio-char could potentially be more effective than return of macronutrients. However, micronutrients are required by soil in smaller amounts than P, K, Ca, and Mg and the introduction of additional micronutrients, even in small amounts could disturb soil equilibrium and lead to subsurface water contamination from leaching in susceptible soils - future studies could investigate these effects.

4.3. Fluidized-bed, Fast Pyrolysis

Recoveries of macronutrients varied among species for the Wyndmoor reactor, but not for the College Station reactor. Between the two reactors, corn stover performed the best. More than 70% of feedstock P, 55% of feedstock K, 68% of feedstock Ca, and 65% of feedstock Mg was recovered. For the recovery of feedstock macronutrients, the Wyndmoor reactor had slightly higher recoveries than the College Station reactor with the exception of switchgrass. Similar to the fixed-bed experiment, high correlations and linear relationships between total recoveries of feedstock macronutrients and nutrient mass loss in bio-char and between reactor mass and energy efficiencies were found. Relationships were also found between feedstock fiber properties and total recovery of macronutrients. However, due to the complex nature of these relationships, future studies should investigate whether a linear model is appropriate for fluidized-bed pyrolysis.

The majority of recoveries of micronutrients did not vary by species for either location. Elevated recoveries for each species were found for Na, Fe and Cu and relatively high recoveries were found for Zn and Mn for the Wyndmoor reactor. For the College Station reactor, low recovery of Na was found along with elevated recoveries of Fe, and Cu. Future work should investigate these inconsistencies.

The bio-char solvent wash experiment revealed higher BET surface areas after washing. Yet, surface areas were very low compared to activated charcoal. The likelihood of positive impacts on CEC or surface charge densities of soil particles is low. The use of the solvent removed residual oils, tars, resins, and other debris and increased surface area. The increased surface area would allow for increased bio-char CEC which would increase its nutrient holding capacity and water holding capacity. Future studies could investigate how solvent-washed bio-char effects soil nutrient status and moisture content after application.

4.4. Ultimate Research Findings

This study lays the foundation for future investigations for the recovery of mineral nutrients from pyrolysis co-products of various feedstocks generated from different reactor types and designs. The ultimate findings of new knowledge that this dissertation brings to the scientific community can be summarized as;

1. The recovery of mineral nutrients varies depending on feedstock,
2. The recovery of mineral nutrients varies depending on specific reactor design,
3. The recovery of mineral nutrients is correlated to mass efficiency,
4. The recovery of mineral nutrients is correlated to energy efficiency,
5. The recovery of mineral nutrients is correlated to feedstock fiber properties, and
6. Reactor design and construction may contaminate pyrolysis co-products resulting in elevated (>100%) recoveries of select nutrients.

When the initial hypotheses of this research were revisited, the null hypothesis was rejected and the alternative hypothesis was accepted. Meaning, the recovery of mineral nutrients depends on and is related to feedstock fiber properties, mass and energy efficiency, and reactor design.

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APPENDIX A

A-1. Interactions table for mean percent recovery of macronutrients from fixed-bed, slow pyrolysis.[1, 2]

Effect	P	K	Ca	Mg
%				
Bio-char co-product				
Species	**	**	**	**
Rep	*	**	**	**
Species*Rep	**	**	**	**
Temp	**	N/A	*	*
Species*Temp	**	N/A	**	**
Species*Temp*Rep	**	**	**	**
Flow	**	**	**	*
Temp*Flow	**	*	**	**
Species*Flow	*	**	**	**
Species*Temp*Flow	**	**	**	**
Bio-oil co-product				
Species	**	**	**	N/A
Rep	N/A	N/A	N/A	N/A
Species*Rep	N/A	*	N/A	N/A
Temp	**	N/A	**	N/A
Species*Temp	**	*	**	*
Species*Temp*Rep	N/A	N/A	N/A	N/A
Flow	*	N/A	**	N/A
Temp*Flow	**	N/A	**	N/A
Species*Flow	**	N/A	**	N/A
Species*Temp*Flow	N/A	N/A	**	**
NCG co-product				
Species	**	N/A	**	**
Rep	N/A	N/A	N/A	N/A
Species*Rep	N/A	*	N/A	N/A
Temp	N/A	N/A	*	**
Species*Temp	N/A	N/A	*	**
Species*Temp*Rep	N/A	N/A	N/A	N/A
Flow	N/A	*	*	**
Temp*Flow	N/A	*	N/A	**

Species*Flow	*	**	N/A	**
Species*Temp*Flow	N/A	**	*	**
<u>All co-products combined</u>				
Species	**	**	**	**
Rep	*	*	**	**
Species*Rep	**	**	**	**
Temp	**	N/A	*	**
Species*Temp	**	N/A	**	**
Species*Temp*Rep	**	**	**	**
Flow	*	**	N/A	*
Temp*Flow	**	*	**	**
Species*Flow	*	**	**	**
Species*Temp*Flow	**	**	**	**

[1] * and ** indicates significance at the 0.05 and 0.10 levels.

[2] N/A indicates no significance at either the 0.05 or 0.10 levels.

A-2. Interactions table for mean percent recovery of micronutrients from fixed-bed, slow pyrolysis.[1, 2]

Effect	Na	Zn	Fe	Cu	Mn
%					
Bio-char co-product					
Species	N/A	**	N/A	**	N/A
Rep	N/A	**	**	**	N/A
Species*Rep	N/A	**	**	**	N/A
Temp	N/A	**	*	**	N/A
Species*Temp	N/A	**	N/A	**	N/A
Species*Temp*Rep	N/A	**	**	**	N/A
Flow	N/A	**	**	**	N/A
Temp*Flow	N/A	**	N/A	**	N/A
Species*Flow	**	**	**	**	N/A
Species*Temp*Flow	**	N/A	**	**	N/A
Bio-oil co-product					
Species	**	**	N/A	N/A	**
Rep	**	N/A	N/A	N/A	**
Species*Rep	**	N/A	N/A	N/A	**
Temp	**	N/A	**	N/A	**
Species*Temp	*	N/A	**	N/A	**
Species*Temp*Rep	**	N/A	**	N/A	**
Flow	**	N/A	**	N/A	**
Temp*Flow	**	**	**	N/A	**
Species*Flow	**	**	**	N/A	N/A
Species*Temp*Flow	*	**	**	**	N/A
NCG co-product					
Species	N/A	N/A	N/A	N/A	N/A
Rep	N/A	N/A	N/A	**	N/A
Species*Rep	N/A	N/A	N/A	N/A	N/A
Temp	N/A	N/A	N/A	N/A	N/A
Species*Temp	N/A	N/A	N/A	N/A	N/A
Species*Temp*Rep	N/A	N/A	N/A	N/A	N/A
Flow	N/A	N/A	N/A	N/A	N/A
Temp*Flow	N/A	N/A	N/A	N/A	N/A
Species*Flow	N/A	N/A	N/A	N/A	N/A
Species*Temp*Flow	N/A	N/A	*	N/A	N/A
All co-products combined					

Species	**	*	N/A	**	N/A
Rep	**	**	N/A	**	N/A
Species*Rep	**	**	N/A	**	N/A
Temp	**	N/A	*	N/A	N/A
Species*Temp	N/A	**	**	**	N/A
Species*Temp*Rep	N/A	**	**	**	N/A
Flow	N/A	**	**	*	N/A
Temp*Flow	N/A	**	**	N/A	N/A
Species*Flow	N/A	N/A	**	**	N/A
Species*Temp*Flow	N/A	N/A	**	**	N/A

[1] * and ** indicates significance at the 0.05 and 0.10 levels.

[2] N/A indicates no significance at either the 0.05 or 0.10 levels.

APPENDIX B

B-1. Correlations table between feedstock properties and mean percent recovery of nutrients (fixed-bed, slow pyrolysis of corn stover).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1.00	0.61	-0.36	0.37	-0.42	0.20	0.17	0.25
ADF	0.61	1.00	0.17	0.81	-0.08	0.02	0.04	0.31
ADL(DM)	-0.36	0.17	1.00	0.42	0.42	0.20	0.33	0.41
ADL(OM)	0.37	0.81	0.42	1.00	0.19	0.26	0.33	0.63
Ash	-0.42	-0.08	0.42	0.19	1.00	-0.06	0.02	0.31
Cellulose	0.20	0.02	0.20	0.26	-0.06	1.00	0.95	0.59
Hemicellulose	0.17	0.04	0.33	0.33	0.02	0.95	1.00	0.66
Sugars	0.25	0.31	0.41	0.63	0.31	0.59	0.66	1.00
%P	0.39	-0.14	-0.46	-0.09	-0.14	0.42	0.38	0.41
%K	0.37	-0.16	-0.48	-0.09	-0.14	0.43	0.38	0.40
%Ca	0.37	-0.15	-0.48	-0.12	-0.10	0.41	0.37	0.37
%Mg	0.36	-0.17	-0.51	-0.14	-0.12	0.39	0.34	0.35

B-2. Correlations table between feedstock properties and mean percent recovery of nutrients (fixed-bed, slow pyrolysis of HES).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1.00	-0.22	-0.01	-0.07	-0.31	-0.02	0.09	-0.27
ADF	-0.22	1.00	0.79	0.81	-0.45	0.33	0.17	0.06
ADL(DM)	-0.01	0.79	1.00	0.92	-0.82	-0.04	0.25	-0.05
ADL(OM)	-0.07	0.81	0.92	1.00	-0.84	0.18	0.33	-0.21
Ash	-0.31	-0.45	-0.82	-0.84	1.00	0.06	-0.29	0.37
Cellulose	-0.02	0.33	-0.04	0.18	0.06	1.00	0.62	0.20
Hemicellulose	0.09	0.17	0.25	0.33	-0.29	0.62	1.00	0.51
Sugars	-0.27	0.06	-0.05	-0.21	0.37	0.20	0.51	1.00
%P	-0.01	0.17	0.22	0.22	-0.19	0.20	0.40	0.25
%K	-0.45	-0.58	-0.47	-0.61	0.56	-0.42	-0.21	0.36
%Ca	-0.06	0.42	0.49	0.52	-0.49	0.22	0.32	0.02
%Mg	0.23	0.19	0.28	0.27	-0.33	0.18	0.33	0.07

B-3. Correlations table between feedstock properties and mean percent recovery of nutrients (fixed-bed, slow pyrolysis of rice biomass).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1.00	0.91	-0.29	-0.24	-0.09	0.86	0.45	-0.96
ADF	0.91	1.00	-0.14	-0.47	-0.06	0.87	0.12	-0.88
ADL(DM)	-0.29	-0.14	1.00	0.02	0.39	-0.53	-0.55	0.18
ADL(OM)	-0.24	-0.47	0.02	1.00	0.48	-0.52	0.06	0.10
Ash	-0.09	-0.06	0.39	0.48	1.00	-0.44	-0.62	-0.19
Cellulose	0.86	0.87	-0.53	-0.52	-0.44	1.00	0.44	-0.72
Hemicellulose	0.45	0.12	-0.55	0.06	-0.62	0.44	1.00	-0.26
Sugars	-0.96	-0.88	0.18	0.10	-0.19	-0.72	-0.26	1.00
%P	0.41	0.33	-0.13	-0.19	-0.25	0.38	0.38	-0.33
%K	0.13	-0.03	0.21	0.25	-0.03	-0.09	0.33	-0.12
%Ca	-0.15	-0.28	0.34	0.53	0.24	-0.40	0.04	0.08
%Mg	0.06	-0.01	0.35	0.17	-0.01	-0.11	0.14	-0.06

B-4. Correlations table between feedstock properties and mean percent recovery of nutrients (fixed-bed, slow pyrolysis of switchgrass).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1.00	0.90	0.27	0.77	0.08	0.11	0.67	0.48
ADF	0.90	1.00	0.42	0.91	0.04	0.19	0.49	0.20
ADL(DM)	0.27	0.42	1.00	0.59	-0.15	0.28	-0.05	-0.34
ADL(OM)	0.77	0.91	0.59	1.00	-0.01	0.26	0.38	-0.10
Ash	0.08	0.04	-0.15	-0.01	1.00	0.44	0.20	-0.03
Cellulose	0.11	0.19	0.28	0.26	0.44	1.00	-0.40	-0.55
Hemicellulose	0.67	0.49	-0.05	0.38	0.20	-0.40	1.00	0.72
Sugars	0.48	0.20	-0.34	-0.10	-0.03	-0.55	0.72	1.00
%P	-0.12	0.00	0.62	-0.01	0.18	0.25	-0.19	-0.27
%K	0.06	0.27	0.37	0.24	0.32	0.04	0.18	-0.17
%Ca	0.17	0.29	0.56	0.55	-0.13	0.12	0.06	-0.47
%Mg	-0.32	-0.19	0.36	-0.16	0.12	-0.08	-0.11	-0.22

B-5. Correlations table between feedstock properties and mean percent recovery of micronutrients (fixed-bed, slow pyrolysis of corn stover).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1	0.61	-0.36	0.37	-0.42	0.2	0.17	0.25
ADF	0.61	1	0.17	0.81	-0.08	0.02	0.04	0.31
ADL(DM)	-0.36	0.17	1	0.42	0.42	0.2	0.33	0.41
ADL(OM)	0.37	0.81	0.42	1	0.19	0.26	0.33	0.63
Ash	-0.42	-0.08	0.42	0.19	1	-0.06	0.02	0.31
Cellulose	0.2	0.02	0.2	0.26	-0.06	1	0.95	0.59
Hemicellulose	0.17	0.04	0.33	0.33	0.02	0.95	1	0.66
Sugars	0.25	0.31	0.41	0.63	0.31	0.59	0.66	1
%Na	0.52	0.16	-0.53	0.07	0.06	0.09	0.1	0.27
%Zn	-0.47	-0.29	-0.17	-0.56	-0.11	-0.38	-0.41	-0.59
%Fe	0.48	0.17	-0.27	0.13	0.3	0.18	0.21	0.35
%Cu	-0.65	-0.32	0.06	-0.26	0.28	-0.36	-0.35	-0.1
%Mn	0.53	0.01	-0.47	0.03	0.01	0.41	0.39	0.47

B-6. Correlations table between feedstock properties and mean percent recovery of micronutrients (fixed-bed, slow pyrolysis of HES).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1	-0.22	-0.01	-0.07	-0.31	-0.02	0.09	-0.27
ADF	-0.22	1	0.79	0.81	-0.45	0.33	0.17	0.06
ADL(DM)	-0.01	0.79	1	0.92	-0.82	-0.04	0.25	-0.05
ADL(OM)	-0.07	0.81	0.92	1	-0.84	0.18	0.33	-0.21
Ash	-0.31	-0.45	-0.82	-0.84	1	0.06	-0.29	0.37
Cellulose	-0.02	0.33	-0.04	0.18	0.06	1	0.62	0.2
Hemicellulose	0.09	0.17	0.25	0.33	-0.29	0.62	1	0.51
Sugars	-0.27	0.06	-0.05	-0.21	0.37	0.2	0.51	1
%Na	-0.29	0.63	0.51	0.47	-0.26	-0.3	-0.57	-0.35
%Zn	0.15	0.4	0.33	0.27	-0.12	0.18	0.26	0.25
%Fe	-0.35	0.51	0.61	0.59	-0.42	-0.2	0.07	0.06
%Cu	-0.09	0.39	0.54	0.44	-0.33	-0.21	0.09	0.08
%Mn	-0.29	0.42	0.61	0.56	-0.46	-0.27	0.03	-0.02

B-7. Correlations table between feedstock properties and mean percent recovery of micronutrients (fixed-bed, slow pyrolysis of rice biomass).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1	0.91	-0.29	-0.24	-0.09	0.86	0.45	-0.96
ADF	0.91	1	-0.14	-0.47	-0.06	0.87	0.12	-0.88
ADL(DM)	-0.29	-0.14	1	0.02	0.39	-0.53	-0.55	0.18
ADL(OM)	-0.24	-0.47	0.02	1	0.48	-0.52	0.06	0.1
Ash	-0.09	-0.06	0.39	0.48	1	-0.44	-0.62	-0.19
Cellulose	0.86	0.87	-0.53	-0.52	-0.44	1	0.44	-0.72
Hemicellulose	0.45	0.12	-0.55	0.06	-0.62	0.44	1	-0.26
Sugars	-0.96	-0.88	0.18	0.1	-0.19	-0.72	-0.26	1
%Na	-0.09	-0.07	0.6	0.44	0.54	-0.39	-0.36	-0.06
%Zn	-0.52	-0.5	0.59	0.37	0.04	-0.6	-0.2	0.5
%Fe	0.08	0.3	-0.27	-0.42	-0.07	0.35	-0.3	-0.06
%Cu	-0.61	-0.48	0.43	0.24	0.01	-0.53	-0.37	0.6
%Mn	0.18	0.26	-0.17	-0.07	0.04	0.26	-0.1	-0.19

B-8. Correlations table between feedstock properties and mean percent recovery of micronutrients (fixed-bed, slow pyrolysis of switchgrass).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1	0.9	0.27	0.77	0.08	0.11	0.67	0.48
ADF	0.9	1	0.42	0.91	0.04	0.19	0.49	0.2
ADL(DM)	0.27	0.42	1	0.59	-0.15	0.28	-0.05	-0.34
ADL(OM)	0.77	0.91	0.59	1	-0.01	0.26	0.38	-0.1
Ash	0.08	0.04	-0.15	-0.01	1	0.44	0.2	-0.03
Cellulose	0.11	0.19	0.28	0.26	0.44	1	-0.4	-0.55
Hemicellulose	0.67	0.49	-0.05	0.38	0.2	-0.4	1	0.72
Sugars	0.48	0.2	-0.34	-0.1	-0.03	-0.55	0.72	1
%Na	-0.29	-0.26	0.48	-0.13	-0.25	-0.2	-0.21	-0.24
%Zn	-0.48	-0.42	0.1	-0.33	-0.17	-0.28	-0.23	-0.2
%Fe	0.16	0.27	-0.02	0.14	0.48	0.35	0.24	-0.05
%Cu	-0.41	-0.34	0.2	-0.28	-0.09	-0.16	-0.21	-0.2
%Mn	0.14	0.24	-0.06	0.1	0.4	0.3	0.25	-0.02

B-9. Multiple linear regression equations for K, Ca, and Mg for fixed-bed, slow pyrolysis.

Potassium: %Total K= 48.28 - 0.27*ADL(DM) - 0.12*Cellulose - 0.20*Hemicellulose - 0.06*Sugars, (R^2=0.36).

Calcium: %Total Ca = -72.89 + 0.18*NDF, (R^2=0.53).

Magnesium: %Total Mg = 37.18 – 0.18*Sugars, (R^2=0.47).

APPENDIX C

C-1. Correlations table between feedstock properties and percent recovery of nutrients (fluidized-bed, fast pyrolysis of HES at Wyndmoor, PA).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1.00	-0.64	0.90	0.98	-0.97	0.76	0.97	0.93
ADF	-0.64	1.00	-0.24	-0.79	0.81	-0.99	-0.82	-0.88
ADL(DM)	0.90	-0.24	1.00	0.78	-0.77	0.40	0.76	0.67
ADL(OM)	0.98	-0.79	0.78	1.00	-1.00	0.88	1.00	0.99
Ash	-0.97	0.81	-0.77	-1.00	1.00	-0.89	-1.00	-0.99
Cellulose	0.76	-0.99	0.40	0.88	-0.89	1.00	0.90	0.95
Hemicellulose	0.97	-0.82	0.76	1.00	-1.00	0.90	1.00	0.99
Sugars	0.93	-0.88	0.67	0.99	-0.99	0.95	0.99	1.00
%P	-0.57	1.00	-0.16	-0.74	0.75	-0.97	-0.76	-0.84
%K	-0.45	0.97	-0.01	-0.63	0.65	-0.92	-0.66	-0.75
%Ca	-0.63	1.00	-0.23	-0.79	0.80	-0.98	-0.81	-0.88
%Mg	0.39	0.46	0.75	0.17	-0.15	-0.31	0.14	0.01

C-2. Correlations table between feedstock properties and percent recovery of nutrients (fluidized-bed, fast pyrolysis of switchgrass at Wyndmoor, PA).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1.00	0.97	0.89	0.78	-0.98	1.00	-0.66	0.93
ADF	0.97	1.00	0.98	0.91	-0.89	0.97	-0.83	-0.88
ADL(DM)	0.89	0.98	1.00	0.98	-0.77	0.89	-0.93	0.67
ADL(OM)	0.78	0.91	0.98	1.00	-0.62	0.78	-0.99	0.99
Ash	-0.98	-0.89	-0.77	-0.62	1.00	-0.98	0.49	-0.99
Cellulose	1.00	0.97	0.89	0.78	-0.98	1.00	-0.66	0.95
Hemicellulose	-0.66	-0.83	-0.93	-0.99	0.49	-0.66	1.00	0.99
Sugars	-0.99	-1.00	-0.95	-0.87	0.93	-0.99	0.78	1.00
%P	-0.78	-0.92	-0.98	-1.00	0.64	-0.79	0.98	-0.84
%K	0.23	-0.03	-0.24	-0.43	-0.43	0.23	0.58	-0.75
%Ca	0.31	0.04	-0.17	-0.37	-0.50	0.30	0.51	-0.88
%Mg	0.32	0.06	-0.15	-0.35	-0.52	0.32	0.50	0.01

C-3. Correlations table between feedstock properties and percent recovery of micronutrients (fluidized-bed, fast pyrolysis of HES at Wyndmoor, PA).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1.00	-0.64	0.90	0.98	-0.97	0.76	0.97	0.93
ADF	-0.64	1.00	-0.24	-0.79	0.81	-0.99	-0.82	-0.88
ADL(DM)	0.90	-0.24	1.00	0.78	-0.77	0.40	0.76	0.67
ADL(OM)	0.98	-0.79	0.78	1.00	-1.00	0.88	1.00	0.99
Ash	-0.97	0.81	-0.77	-1.00	1.00	-0.89	-1.00	-0.99
Cellulose	0.76	-0.99	0.40	0.88	-0.89	1.00	0.90	0.95
Hemicellulose	0.97	-0.82	0.76	1.00	-1.00	0.90	1.00	0.99
Sugars	0.93	-0.88	0.67	0.99	-0.99	0.95	0.99	1.00
%Na	1.00	-0.61	0.92	0.97	-0.96	0.73	0.96	0.91
%Zn	-0.76	0.99	-0.41	-0.89	0.90	-1.00	-0.90	-0.95
%Fe	-0.14	-0.67	-0.55	0.08	-0.11	0.54	0.12	0.25
%Cu	-0.67	-0.14	-0.93	-0.49	0.47	-0.03	-0.46	-0.35
%Mn	0.49	-0.98	0.06	0.67	-0.68	0.94	0.69	0.78

C-4. Correlations table between feedstock properties and percent recovery of micronutrients (fluidized-bed, fast pyrolysis of switchgrass at Wyndmoor, PA).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1.00	0.97	0.89	0.78	-0.98	1.00	-0.66	-0.99
ADF	0.97	1.00	0.98	0.91	-0.89	0.97	-0.83	-1.00
ADL(DM)	0.89	0.98	1.00	0.98	-0.77	0.89	-0.93	-0.95
ADL(OM)	0.78	0.91	0.98	1.00	-0.62	0.78	-0.99	-0.87
Ash	-0.98	-0.89	-0.77	-0.62	1.00	-0.98	0.49	0.93
Cellulose	1.00	0.97	0.89	0.78	-0.98	1.00	-0.66	-0.99
Hemicellulose	-0.66	-0.83	-0.93	-0.99	0.49	-0.66	1.00	0.78
Sugars	-0.99	-1.00	-0.95	-0.87	0.93	-0.99	0.78	1.00
%Na	-0.16	0.10	0.31	0.50	0.36	-0.16	-0.64	-0.01
%Zn	-0.94	-1.00	-0.99	-0.94	0.85	-0.94	0.88	0.99
%Fe	-1.00	-0.98	-0.91	-0.81	0.97	-1.00	0.70	0.99
%Cu	1.00	0.94	0.84	0.71	-0.99	1.00	-0.59	-0.96
%Mn	-0.91	-0.77	-0.62	-0.44	0.98	-0.91	0.29	0.82

C-5. Correlations table between feedstock properties and percent recovery of macronutrients (fluidized-bed, fast pyrolysis of corn stover at College Station, TX).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1.00	0.87	-0.24	0.69	-0.65	-0.46	-0.48	1.00
ADF	0.87	1.00	0.27	0.96	-0.19	-0.84	-0.85	0.91
ADL(DM)	-0.24	0.27	1.00	0.54	0.90	-0.75	-0.73	-0.15
ADL(OM)	0.69	0.96	0.54	1.00	0.11	-0.96	-0.97	0.75
Ash	-0.65	-0.19	0.90	0.11	1.00	-0.38	-0.36	-0.57
Cellulose	-0.46	-0.84	-0.75	-0.96	-0.38	1.00	1.00	-0.54
Hemicellulose	-0.48	-0.85	-0.73	-0.97	-0.36	1.00	1.00	-0.56
Sugars	1.00	0.91	-0.15	0.75	-0.57	-0.54	-0.56	1.00
%P	-0.20	-0.66	-0.90	-0.85	-0.62	0.96	0.95	-0.29
%K	-0.63	-0.93	-0.60	-1.00	-0.18	0.98	0.98	-0.70
%Ca	0.64	0.18	-0.90	-0.12	-1.00	0.39	0.37	0.56
%Mg	0.21	-0.30	-1.00	-0.56	-0.88	0.77	0.75	0.12

C-6. Correlations table between feedstock properties and percent recovery of macronutrients (fluidized-bed, fast pyrolysis of HES at College Station, TX).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1.00	0.01	-0.96	-0.75	1.00	-0.63	0.92	-1.00
ADF	0.01	1.00	-0.31	-0.67	-0.04	0.77	-0.37	0.00
ADL(DM)	-0.96	-0.31	1.00	0.91	-0.94	0.38	-0.77	0.95
ADL(OM)	-0.75	-0.67	0.91	1.00	-0.71	-0.04	-0.44	0.74
Ash	1.00	-0.04	-0.94	-0.71	1.00	-0.67	0.94	-1.00
Cellulose	-0.63	0.77	0.38	-0.04	-0.67	1.00	-0.88	0.65
Hemicellulose	0.92	-0.37	-0.77	-0.44	0.94	-0.88	1.00	-0.93
Sugars	-1.00	0.00	0.95	0.74	-1.00	0.65	-0.93	1.00
%P	0.98	-0.19	-0.88	-0.60	0.99	-0.78	0.98	-0.98
%K	0.98	-0.17	-0.88	-0.62	0.99	-0.76	0.98	-0.99
%Ca	0.97	-0.24	-0.85	-0.56	0.98	-0.81	0.99	-0.97
%Mg	0.96	-0.26	-0.84	-0.54	0.98	-0.82	0.99	-0.97

C-7. Correlations table between feedstock properties and percent recovery of macronutrients (fluidized-bed, fast pyrolysis of switchgrass at College Station, TX).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1.00	0.97	0.89	0.78	-0.98	1.00	-0.66	-0.99
ADF	0.97	1.00	0.98	0.91	-0.89	0.97	-0.83	-1.00
ADL(DM)	0.89	0.98	1.00	0.98	-0.77	0.89	-0.93	-0.95
ADL(OM)	0.78	0.91	0.98	1.00	-0.62	0.78	-0.99	-0.87
Ash	-0.98	-0.89	-0.77	-0.62	1.00	-0.98	0.49	0.93
Cellulose	1.00	0.97	0.89	0.78	-0.98	1.00	-0.66	-0.99
Hemicellulose	-0.66	-0.83	-0.93	-0.99	0.49	-0.66	1.00	0.78
Sugars	-0.99	-1.00	-0.95	-0.87	0.93	-0.99	0.78	1.00
%P	-0.32	-0.55	-0.72	-0.84	0.11	-0.32	0.92	0.48
%K	-0.10	-0.35	-0.54	-0.70	-0.12	-0.10	0.81	0.27
%Ca	-0.33	-0.57	-0.73	-0.85	0.13	-0.33	0.93	0.49
%Mg	0.07	-0.20	-0.40	-0.58	-0.28	0.07	0.70	0.11

C-7. Correlations table between feedstock properties and percent recovery of micronutrients (fluidized-bed, fast pyrolysis of corn stover at College Station, TX).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1.00	0.87	-0.24	0.69	-0.65	-0.46	-0.48	1.00
ADF	0.87	1.00	0.27	0.96	-0.19	-0.84	-0.85	0.91
ADL(DM)	-0.24	0.27	1.00	0.54	0.90	-0.75	-0.73	-0.15
ADL(OM)	0.69	0.96	0.54	1.00	0.11	-0.96	-0.97	0.75
Ash	-0.65	-0.19	0.90	0.11	1.00	-0.38	-0.36	-0.57
Cellulose	-0.46	-0.84	-0.75	-0.96	-0.38	1.00	1.00	-0.54
Hemicellulose	-0.48	-0.85	-0.73	-0.97	-0.36	1.00	1.00	-0.56
Sugars	1.00	0.91	-0.15	0.75	-0.57	-0.54	-0.56	1.00
%Na	0.37	0.78	0.81	0.93	0.47	-0.99	-0.99	0.45
%Zn	-0.48	-0.85	-0.74	-0.97	-0.36	1.00	1.00	-0.56
%Fe	0.99	0.92	-0.14	0.76	-0.56	-0.55	-0.57	1.00
%Cu	0.81	0.42	-0.76	0.13	-0.97	0.14	0.12	0.76
%Mn	0.82	0.43	-0.75	0.15	-0.97	0.13	0.10	0.77

C-8. Correlations table between feedstock properties and percent recovery of micronutrients (fluidized-bed, fast pyrolysis of HES at College Station, TX).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1.00	0.01	-0.96	-0.75	1.00	-0.63	0.92	-1.00
ADF	0.01	1.00	-0.31	-0.67	-0.04	0.77	-0.37	0.00
ADL(DM)	-0.96	-0.31	1.00	0.91	-0.94	0.38	-0.77	0.95
ADL(OM)	-0.75	-0.67	0.91	1.00	-0.71	-0.04	-0.44	0.74
Ash	1.00	-0.04	-0.94	-0.71	1.00	-0.67	0.94	-1.00
Cellulose	-0.63	0.77	0.38	-0.04	-0.67	1.00	-0.88	0.65
Hemicellulose	0.92	-0.37	-0.77	-0.44	0.94	-0.88	1.00	-0.93
Sugars	-1.00	0.00	0.95	0.74	-1.00	0.65	-0.93	1.00
%Na	0.96	0.30	-1.00	-0.91	0.94	-0.38	0.77	-0.95
%Zn	0.54	0.85	-0.76	-0.96	0.50	0.31	0.18	-0.53
%Fe	-0.92	0.38	0.76	0.43	-0.94	0.89	-1.00	0.92
%Cu	1.00	0.02	-0.96	-0.75	1.00	-0.63	0.92	-1.00
%Mn	0.97	-0.24	-0.85	-0.56	0.98	-0.81	0.99	-0.97

C-8. Correlations table between feedstock properties and percent recovery of micronutrients (fluidized-bed, fast pyrolysis of switchgrass at College Station, TX).

Parameter	NDF	ADF	ADL(DM)	ADL(OM)	Ash	Cellulose	Hemicellulose	Sugars
NDF	1.00	0.97	0.89	0.78	-0.98	1.00	-0.66	-0.99
ADF	0.97	1.00	0.98	0.91	-0.89	0.97	-0.83	-1.00
ADL(DM)	0.89	0.98	1.00	0.98	-0.77	0.89	-0.93	-0.95
ADL(OM)	0.78	0.91	0.98	1.00	-0.62	0.78	-0.99	-0.87
Ash	-0.98	-0.89	-0.77	-0.62	1.00	-0.98	0.49	0.93
Cellulose	1.00	0.97	0.89	0.78	-0.98	1.00	-0.66	-0.99
Hemicellulose	-0.66	-0.83	-0.93	-0.99	0.49	-0.66	1.00	0.78
Sugars	-0.99	-1.00	-0.95	-0.87	0.93	-0.99	0.78	1.00
%Na	-0.88	-0.97	-1.00	-0.98	0.75	-0.88	0.94	0.95
%Zn	0.29	0.03	-0.19	-0.38	-0.49	0.29	0.53	-0.12
%Fe	-0.52	-0.72	-0.85	-0.94	0.32	-0.52	0.98	0.66
%Cu	-1.00	-0.94	-0.85	-0.73	0.99	-1.00	0.61	0.97
%Mn	-0.61	-0.80	-0.91	-0.97	0.43	-0.61	1.00	0.74

C-9. Multiple linear regression equations for K, Ca, and Mg (Wyndmoor, PA).

Potassium: %Total K= -396.53 + 0.20*NDF + 0.86*ADF + 0.60*ADL (DM) – 1.67*ADL (OM) – 0.32*ash, (R^2=0.35).

Calcium: %Total Ca = -383.43 + 0.26*NDF + 1.09*ADF + 0.05*ADL (DM) – 2.52*ADL (OM) – 0.94*ash, (R^2=0.42).

Magnesium: %Total Mg = -356.22 + 0.27*NDF + 0.67*ADF + 0.49*ADL (DM) – 1.51*ADL (OM) – 0.32*ash, (R^2=0.51).

C-10. Multiple linear regression equations for K, Ca, and Mg (College Station, TX).

Potassium: %Total K= -46328.09 – 129.69*NDF + 138.69*ADF – 85.85*ADL (DM) + 17.62*ADL (OM) – 22.68*ash – 51.34*Cellulose + 87.13*Hemicellulose – 46.87*Sugars, (R^2=0.21).

Calcium: %Total Ca = 16216.36 – 146.13*NDF + 49.33*ADF – 31.19*ADL (DM) + 6.93*ADL (OM) – 8.05*ash – 18.12*Cellulose + 32.26*Hemicellulose – 16.87*Sugars, (R^2=0.18).

Magnesium: %Total Mg = 15229.22 – 43.46*NDF + 46.31*ADF – 29.26*ADL (DM) + 6.75*ADL (OM) – 7.61*ash – 16.90*Cellulose + 30.62*Hemicellulose – 16.01*Sugars, (R^2=0.23).

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