

Final Technical Report for

***Adding value to ethanol production byproducts
(dried distillers grain) through production
of biochar and bio-oil***

8/31/2010 through 8/31/2012

Prepared for:

Minnesota Corn Growers Association

Minnesota Corn Research & Promotion Council

Institute for Renewable Energy & the Environment (IREE)

Project # 58-3640-1-456

Team Leader

Kurt Spokas (USDA-ARS; St. Paul, MN)

Co Principal Investigators

Roger Ruan and Robert Morrison (University of Minnesota; St. Paul, MN)

August 2012

Executive Summary of Project:

In this project, we investigated the potential to increase the value of ethanol co-products (distillers grain) by demonstrating how these biomass feedstocks can be used to produce additional renewable energy resources (bio-oil) and also be recycled through a proposed mechanism of land application as biochar. In this report we document the conversion utilizing microwave assisted pyrolysis (MAP) of five mixing ratios of corn stover and dried distillers grain (with solubles: DDGS) (100:0, 75:25, 50:50, 25:75, and 0:100), as well as the initial impacts of the MAP produced biochar on three typical soils from Minnesota by examining impact on soil fertility and net greenhouse gas production potentials following biochar soil addition.

We have demonstrated that MAP is a promising process to create additional value added products of bio-oil and biochar from various mixtures of corn stover and DDGS. MAP conversion of the DDGS does provide the opportunity to generate additional renewable energy resources (bio-oil and syngas), with the MAP process nearly matching the bio-oil yield of traditional fast pyrolysis techniques. The produced biochar does possess additional soil nutrient value compared to the biochar produced by traditional pyrolysis, as a majority of the soil nutrients present in the DDGS/stover are concentrated into the biochar product by MAP. The major benefit of the MAP conversion is the concentration of the N nutrient value of the DDGS into the biochar product. Despite the fact that this initial data is promising, additional research is needed into the chemical composition of the bio-oil products and the long-term implications of the biochar soil addition before a final economic assessment of the feasibility of this conversion can be determined.

Section 1. Background

1.1 Overview of Pyrolysis

“Pyrolysis” is the thermal/chemical degradation of a carbon source (biomass) in the absence of oxygen [Bridgwater *et al.*, 1999]. This alteration converts biomass into various products, which are chemically and physically different than the original material [Bridgwater *et al.*, 1999]. This process is graphically illustrated in Figure 1. These products are broadly grouped into three classifications based on their physical states:

- 1) Solids (biochar),
- 2) Liquids (bio-oil, heavy molecular weight compounds that condense when cooled down or trapped) and
- 3) Gaseous products (syngas, light molecular weight gases which do not condense after cooling).

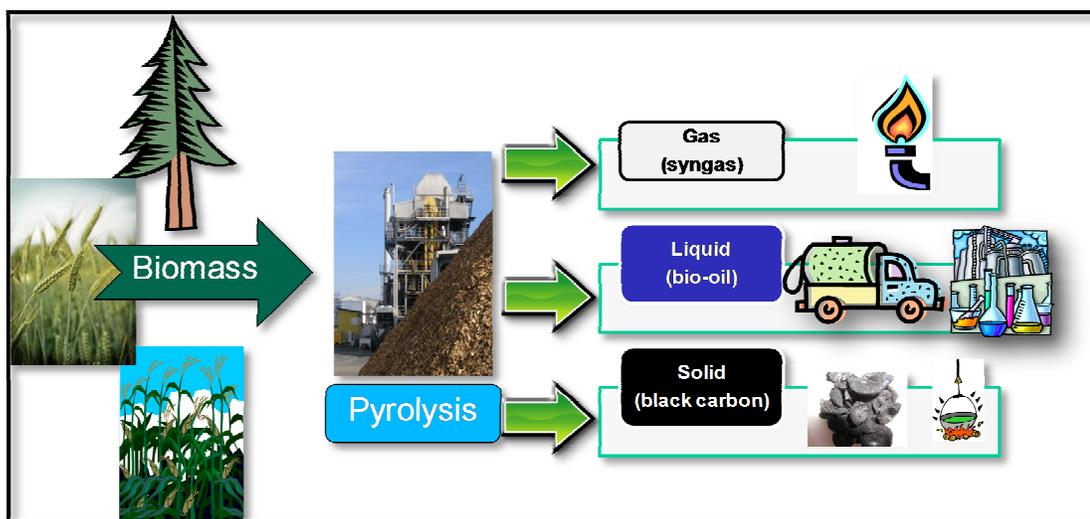


Figure 1. Overview of biomass conversion through pyrolysis

The pyrolysis process is highly variable, which results in differences in both the chemical properties and distribution of these product groupings. These differences are both a function of the feedstock as well as the pyrolysis reactions [Ayache *et al.*, 1990; Butuzova *et al.*, 1998; Gray *et al.*, 1985; Minkova *et al.*, 1991; Mok and Antal, 1983; Shafizadeh, 1968; Williams and Besler, 1996; Williams and Nugranad, 2000]. As of yet, there is no unified model to allow the prediction of the chemical composition or distribution of these pyrolysis products across the various platforms [i.e. Bradbury *et al.*, 1979; Navarro *et al.*, 2012]. Although, advancements have occurred in lab scale units to improve the reproducibility of the pyrolysis process [e.g. K Cantrell *et al.*, 2007; K B Cantrell and Martin, 2012a; b; Lin *et al.*, 2012]. Therefore, there is hope with added research to unveil the factors that influence these aspects of variability.

We have utilized pyrolysis of biomass in the past for energy and chemical production [Hawley, 1926], and there is even reference of its use for production of a soil amendment [Lefroy, 1883]. However, due to its energy value, it has not been economically favorable to apply in the past to fields since the the yield gain would not offset the cost of the amendment [K A Spokas *et al.*, 2012]. However, recent technology enhancements allow additional process controls which were not possible in these past efforts, which establishes more control of the pyrolysis reaction conditions and hence the product distribution and chemistry. The overall renaissance in biomass pyrolysis research is largely connected to the search for renewable energy options [McKendry, 2002]. Biomass pyrolysis is one option which has been cited as being capable of providing future energy resources [Yaman, 2004].

There are many different styles of pyrolysis which differ in the residence time of the material in the reactor. These different reactor times are given the names of slow (hours to days), fast (seconds to minutes), or flash (seconds) as indications of the relative time differences. In addition to the time in the reactor, there are differences in how heat is generated for the reactor. The traditional pyrolysis reactor utilize thermal heat, which is produced by electricity [Q Zhang *et al.*, 2007]. However, new advancements have also focused on utilizing microwave energy [Miura *et al.*, 2004; Yu *et al.*, 2007], plasma [Shuangning *et al.*, 2005], or hydrothermal [Libra *et al.*, 2011], which is a combination of steam and pressure in the reactor cell to achieve the thermal transformations. All of these methods have corresponding advantages and disadvantages [L Zhang *et al.*, 2010].

The option selected in this project was the use of a microwave assisted pyrolysis (MAP). This choice was based on the fact that MAP can process the distillers grain and corn stover in a fast, uniform, and efficient way [Wan *et al.*, 2009; Yu *et al.*, 2007], which makes the processing method appealing economically since the costs and fossil fuel use for drying are significantly reduced or eliminated.

1.2 Introduction of Microwave Assisted Pyrolysis (MAP)

Microwave-assisted pyrolysis is an innovative technique of utilizing “microwave dielectric heating” for rapid and efficient heating of biomass materials [Yin, 2012]. Similar to the revolution of the microwave as a kitchen appliance in the late 1970’s, the microwave has also impacted organic chemical synthesis [Cresswell and Haswell, 2001; Kappe, 2004].

One of the characteristics of MAP, is the fact that heating directions are reversed when compared to conventional thermal pyrolysis reactions. As shown in Figure 2, the conventional thermal pyrolysis (non-microwave assisted), the material heats from the outside towards the inside. Whereas, MAP the heat and charring progress from the inside to the outside of the material (Fig. 2c). Therefore, in MAP the visual appearance of a charred surface, typically indicates that the material is completely charred. On the other hand, in conventional pyrolysis the charred outside of the material cannot be used as a measure of the completeness of pyrolysis, since the charring would progress from the outside to the inside.

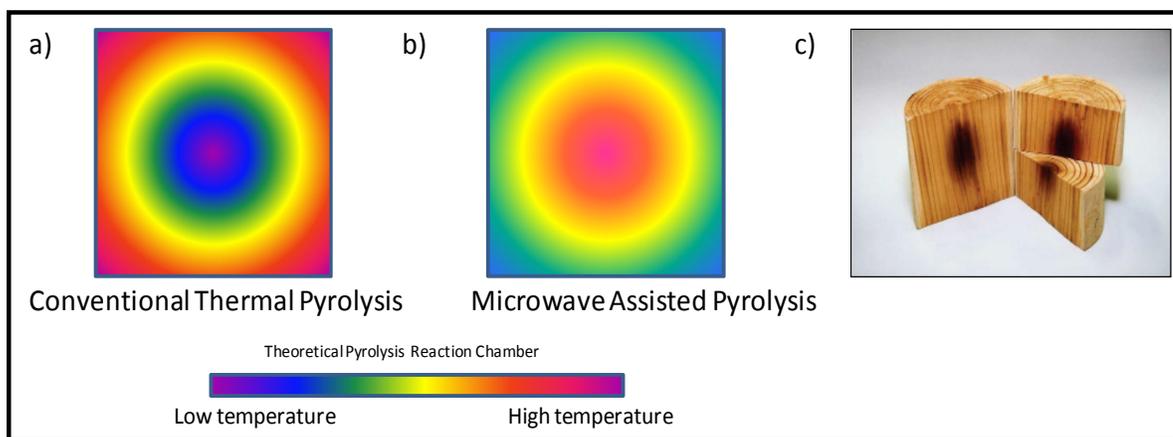


Figure 2. Examples of modeled temperature profiles in the pyrolysis reactor for a) conventional thermal heating and b) microwave assisted pyrolysis [modeled after Fernandez et al. (2011)]. Also in c) is a picture of charred wood achieved through MAP [photo taken from Miura et al. [2004]], which clearly shows the inward charring occurring during MAP processing.

1.3 Overview of biochar

The name “biochar” has been receiving increased public attention, and is being hyped as a potential game changing soil amendment [Atkinson *et al.*, 2010; K A Spokas *et al.*, 2012]. However, there are layers of undiscovered history and science that are behind the term *biochar*.

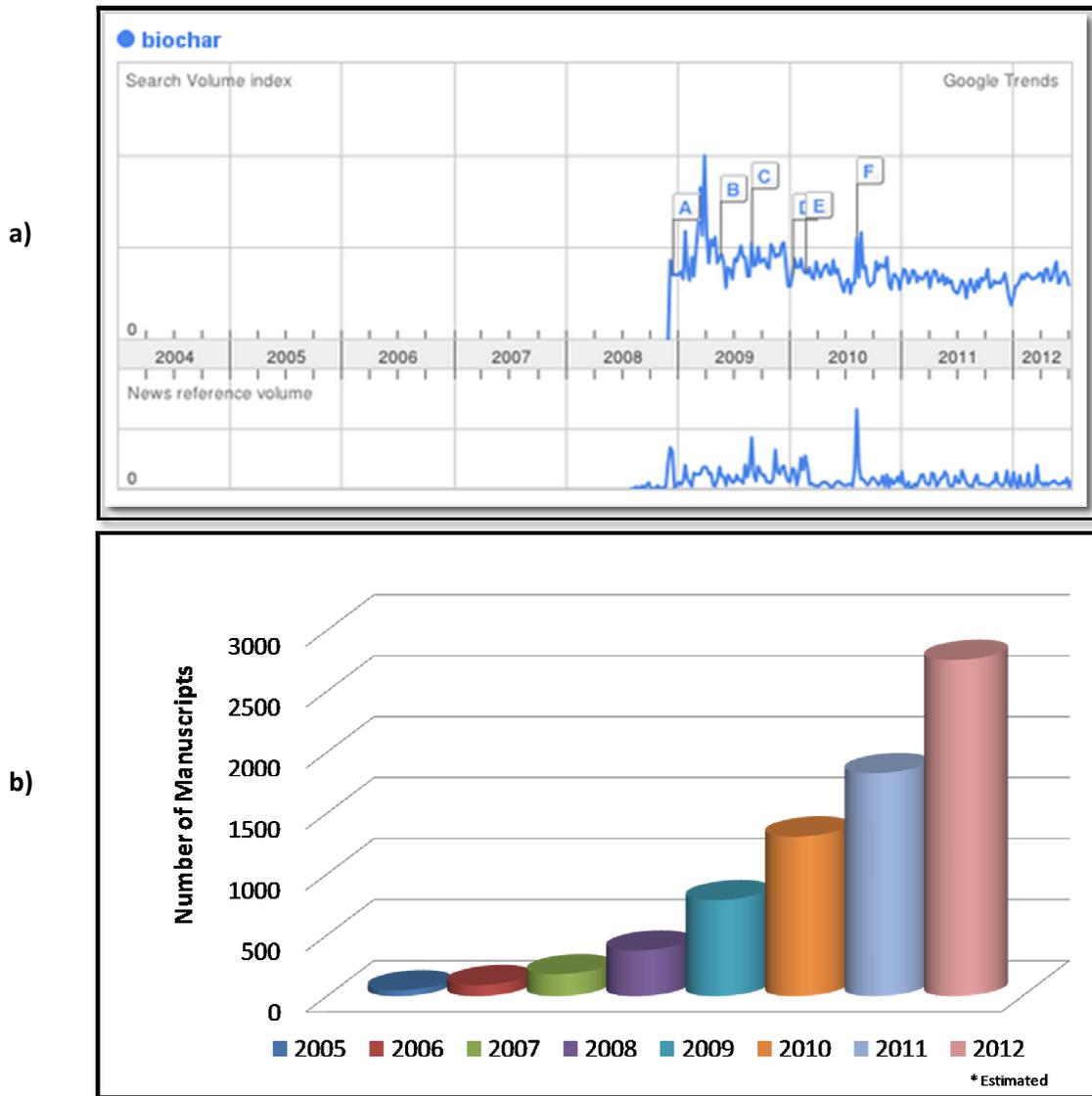


Figure 3. a) Google™ search index trends for *biochar* and b) the number of scientific publications which include the term *biochar* in the recent eight years (Data from Google Scholar™).

When one examines the Google™ trends, we see that the biochar search trend has two distinct phases (Figure 3). A pre-2008 phase, with is characterized by an insignificant number of searches being conducted, resulting in no detectable search volume (volume index = 0). Then, a late 2008-2009 spike is followed by a sustained search intensity that is continued to the current day, as represented by the continual volume of Google™ search queries (Figure 3a). This sudden appearance onto the global stage for the “biochar” term occurred simultaneously with the release of an Associated Press (AP) news story

summarizing the research of Christoph Steiner (from the University of Georgia at the time) on the potential of biochar to be both a climate mitigation mechanism and a potential soil improvement agent. Accompanying this growth in popular searches of biochar, have been an accompanying increase in the number of scientific publications including the term “biochar”, growing from less than 10 manuscripts in 2005, to over 2700 so far in 2012 (Figure 3b, through Aug. 24, 2012; data from Google™ Scholar).

However, all of this public attention and growth of *biochar* has also resulted in some misinformation and confusion surrounding biochar. One example of this is in the difficulty of defining biochar. The name biochar is given to the conversion of easily degradable carbon (biomass) into a more stable form for the purpose of carbon sequestration. However, there was a study published by Abdullah and Wu [2009], that was focused on the use of *biochar as a fuel source*. Granted burning biochar is a source of renewable energy (bio-coal), but this full combustion fails to maintain the carbon sequestering purpose, since the carbon will be released and returned to the atmosphere. Therefore, **biochar** should not be used to describe material that will eventually be used as fuel, since the focus is on the creation of a carbon sequestration benefit. Overall, biochar has generated significant interest, primarily due to three reasons:

1. Potential mitigation mechanism for combating climate change,
2. Increasing soil fertility, and
3. Bioenergy resource.

First, biochar is a form of carbon sequestration. But unlike the graph shown in Figure 3, the use of biochar as a carbon sequestration agent did not start in 2008. This notion can be traced back in the scientific literature to the early 1980's, with the work of Goldberg [1985] and Kuhlbusch and Crutzen [1995]. The hypothesis at that time was that the conversion of the biomass into a more stable charred product (biochar) could aid in the mitigation of increasing atmospheric CO₂ levels. This notion has been validated in the various laboratory studies on the stability of biochar [e.g. Harvey *et al.*, 2012; Smith *et al.*, 2010; Andrew R. Zimmerman *et al.*, 2011]. The most important aspect of biochar is that the name refers to this carbon sequestration purpose. Therefore, the name biochar does not refer to the actual chemical composition or physical properties [Mukherjee *et al.*, 2011; K A Spokas *et al.*, 2012], but rather to the purpose of the creation. Since different pyrolysis conditions infers different product chemical properties, different biochars are chemically unique and possessing different resistances to microbial mineralization [Kurt A. Spokas, 2010].

Soil fertility increases have been observed following some biochar soil additions [Adams, 1991; Agblevor *et al.*, 2010; Jeffery *et al.*, 2011; Vaccari *et al.*, 2011]. Although the exact mechanisms behind these yield improvements still require study [Atkinson *et al.*, 2010; Lehmann *et al.*, 2011], the observations to date support the continued examination into potential benefits from biochar, even if niche or more specialized markets need to be pursued for economic viability [K A Spokas *et al.*, 2012].

Lastly, biochar can be a co-product of renewable bioenergy production. This does translate into lower overall conversion efficiencies for bioenergy production, since some energy is left in the solid char. There are many factors influencing the agricultural commodities market, but according to the OECD/FAO Agricultural outlook for 2012-2021,

“...higher oil prices are a fundamental factor behind the higher agricultural commodity price projections, affecting not only oil-related costs of production but also increasing the demand for biofuels and the agricultural feedstocks used in their production” [OECD/FAO, 2012].

This statement highlights the direct linkage of agricultural commodities and energy prices as one of the new sources of agricultural price volatility [Gouel, 2012]. Therefore, indicating that the price fluctuations will be tied to energy prices for the immediate future and will directly impact the economics of both ethanol production as well as the reuse of co-products (e.g. biochar and bio-oil production). Thereby, we need to maximize effective strategies for biofuel production in order to meet both the food as well as energy demands of the growing global society. The production of bioethanol globally has increased from 4 billion gallons (17.25 billion L) in 2000 to more than 12 billion gallons (46 billion L) in 2007 [Balat and Balat, 2009]. With this increased bioethanol production both in operation and future planned plants, there is an increase in the production of co-products, which may create a surplus of DDGS that cannot be meet directly by animal feed uses [Rausch and Belyea, 2006].

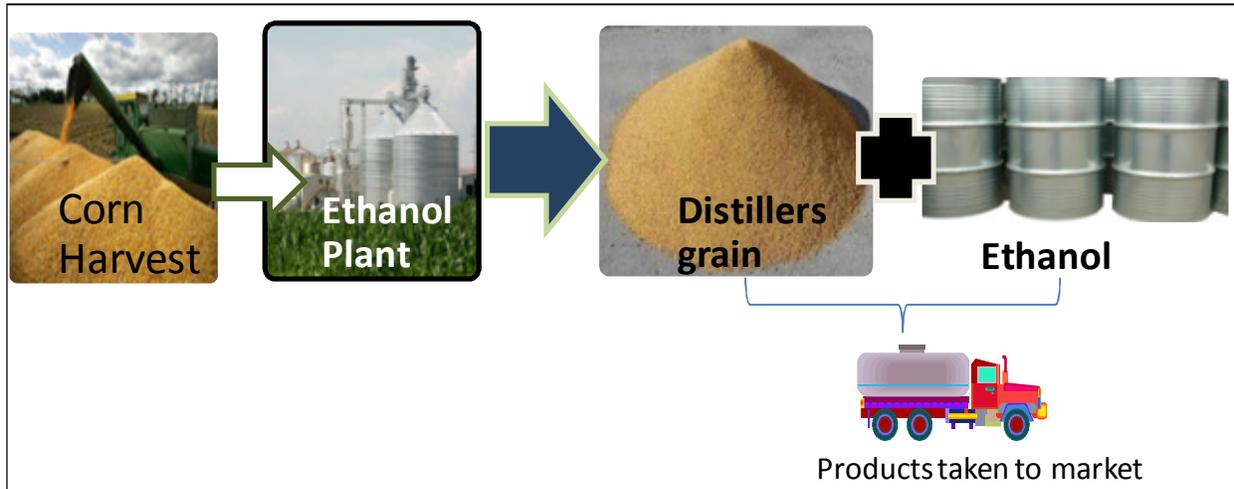
1.4 Project Objectives

The fundamental objectives of this project can be highlighted in Figure 4. The current simplified synopsis of ethanol production is shown in Figure 4a. The corn is harvested and brought to the ethanol plant, where through fermentation the co-products of distillers grain and ethanol are produced. This current system is a one way process, with nothing being returned to the fields from this process.

This project is the first step along the path for a new processing system, which is illustrated in Figure 4b. The same grain is brought to the ethanol plant, but instead of the distillers grain being sold to the market directly, a portion or all of this initial co-product will be the feedstock for a secondary process of microwave assisted pyrolysis (MAP). This process will transform the distillers grain, into 3 additional value added products. The first being the solid residue (biochar), which will be returned to the farmers field to aid in closing the soil nutrient loop. In other words, instead of the production of bioenergy being a one-way loss of nutrients through the grain export from the field, this new processing system will enable some of the soil nutrients in the grain to be returned to the fields to improve the sustainability of agricultural production. By returning this biochar in the empty grain trucks to the farms, the transport cost hurdle will be reduced since these trucks are returning to the farm already. The other product is a syngas, which is a source of energy and can be used to supplement natural gas use at the plant, thereby reducing the overall fossil fuel consumption at the plant. The last product is a liquid (bio-oil) that is envisioned to provide additional bioenergy resources (i.e. boiler fuel) or even the possibility of being refined into even high value products (e.g. chemicals, diesel fuel).

However, before this vision can become a reality, the feasibility of each step needs to be assessed. This evaluation was initiated in this project. The goals of this project were to (1) assess the initial yields of syngas, bio-oil, and biochar by MAP as impacted by different feedstock ratios of distillers grain and corn stover mixtures, and (2) to examine the initial short-term impacts (1 year) of this biochar on three different soil types in Minnesota.

a) Existing process



b) Proposed process

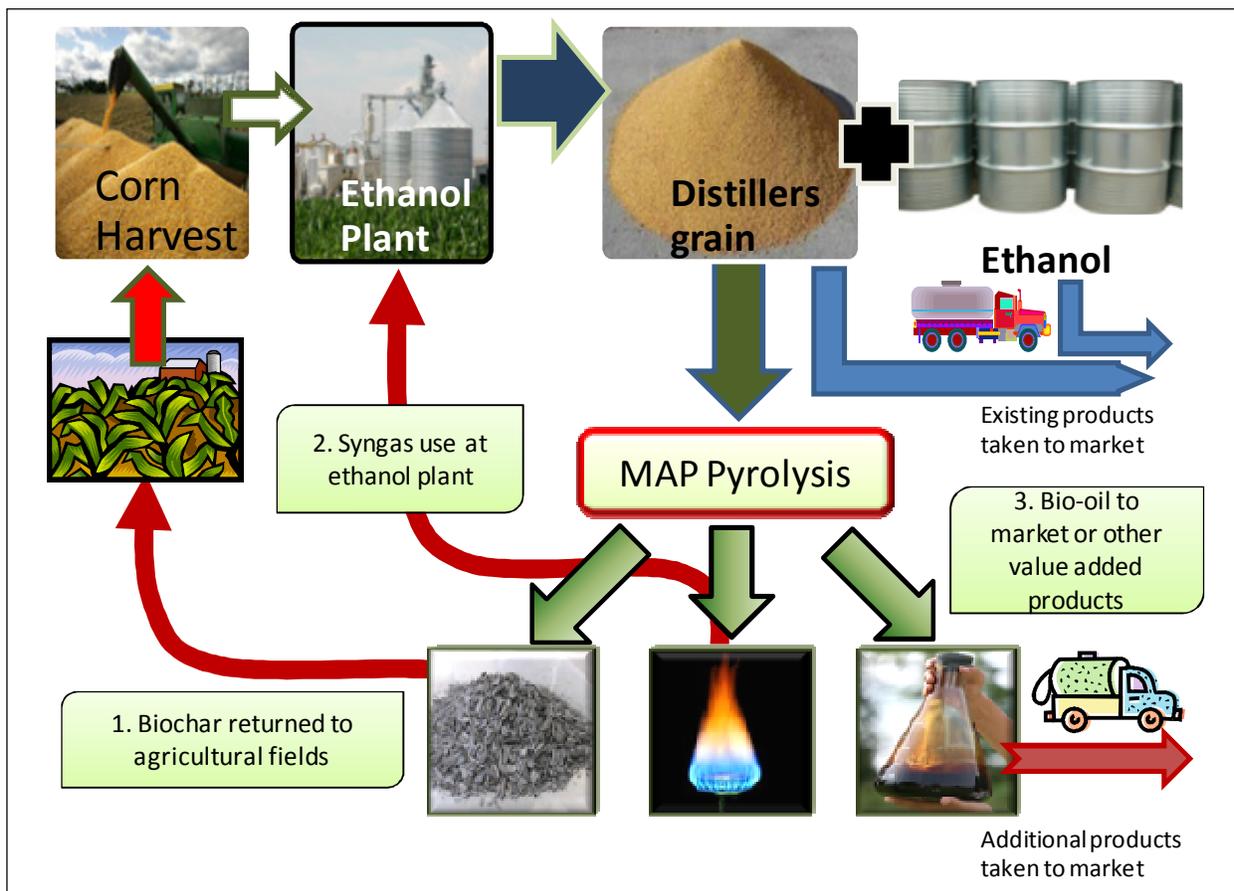


Figure 4. Illustration of a) existing methanol processing diagram and b) the proposed new process which generates additional bioenergy resources as well as biochar for soil application.

Section 2. Detailed Accomplishments of MAP Pyrolysis Conversion

2.1 Microwave Assisted Pyrolysis (MAP): Product Distribution

The pyrolysis of dried distillers grain solids (DDGS) and corn stover pellets was carried out in a microwave oven with the incident power of 1000 W at a frequency of 2450 MHz. DDGS and corn stover were mixed with mass ratios of 100:0, 0:100, 50:50, 25:75, and 75:25, respectively. After the sample preparation, about 150 g of the mixture was placed in a 1000 mL quartz flask each time, which was then subjected to microwave assisted pyrolysis treatment. The condensable volatiles were continuously collected by five sequential condensers with cooling water temperature 0-2 °C (Figure 5). The reaction time was set at 20 min, since no detectable volatile gases were observed after that. This lack of gas production was taken as the endpoint of the pyrolysis reactions, as has been done in other pyrolysis research studies. The solid and liquid fraction yields were calculated from the weight of each fraction, while the gas yield was calculated by the mass balance.



Figure 5. Illustration of the bench-scale microwave assisted pyrolysis unit at the University of Minnesota – Bioproducts and Biosystems Engineering Department. The liquid condensate columns are shown in the red box.

Catalytic pyrolysis with Pyroprobe

To evaluate the effects of catalysts on the quality of bio-oil, catalytic pyrolysis experiments were performed using an analytical pyrolyzer coupled with a GC-MS (Py-GC-MS). About 0.5 mg of DDGS and 1.5 mg HZSM-5 zeolite was filled into a quartz tube, inserted into a platinum coil, and pyrolyzed in a CDS2000 pyrolyzer (Figure 6). Samples were heated at a heating rate of 1000 °C/s to 500 °C and then isothermally for 30 s to ensure complete pyrolysis. Upon pyrolysis, the pyrolysis vapors were directly swept into the GC-MS with a DB-5MS (30 m × 0.25 m × 0.25 μm) column. An injector temperature of 250 °C and a split ration of 1:100 were used. The initial oven temperature was 40 °C. After 3 min, the temperature was increased to 250 °C at a rate of 5 °C /min, and held at 250 °C for 10 min.



Figure 6. Catalytic pyrolysis probe with catalysts (zeolite powder in the vial)

Analysis

The components of the liquid product were specified using an Agilent 7890-5975C gas chromatography/ mass spectrometer with a HP-5 MS capillary column. All experiments were performed in duplicate and average values were reported. There was no analysis of the produced gas phase, which was vented. This gaseous phase consisted of the volatile compounds not trapped in the liquid condensers (non-condensable gases).

Results

The pyrolysis of DDGS and corn stover yielded three fractions of products, namely biochars, bio-oil, and syngas. The biochars and bio-oil were collected and the syngas was flared off. The fractional yields were determined. The biochars were sent to our collaborators for their work, and bio-oil was characterized using GC-MS.

In this project, the bio-oil varied from a two-phases system (water and organic) to a single system (mixed fraction) as shown in Table 1. As shown in Figure 7, the amounts of bio-oil generated was related to the feedstock ratio, with the 100% distiller's grain and 75% distillers grain mixtures producing the maximum observed bio-oil yields of 46%. These were also the two samples that possessed the dual liquid phases. The amount of bio-oil produced decreased with increasing amounts of the corn stover additions (Table 1). The presence of the organic phases in the high percentage DDGS feedstocks could aid in reducing the distillation costs, since dewatering is one of the expensive steps in the upgrading of the bio-oil product [e.g. *Junming et al.*, 2008]. However, these aspects require additional research into the potential use of the various components and chemicals observed in the various fractions.

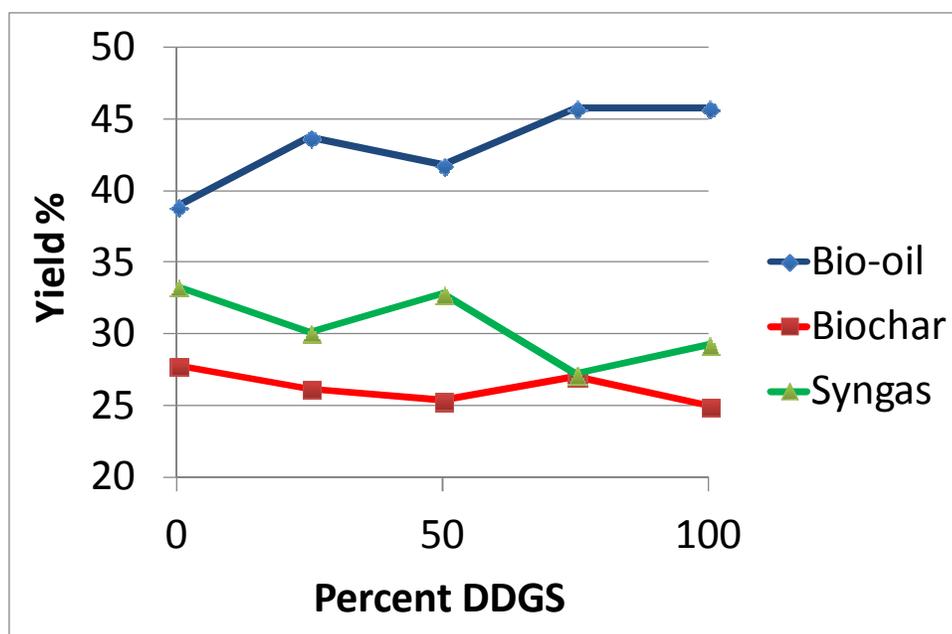


Figure 7. Product distribution from the MAP processing as a function of feedstock mixing ratios.

Table 1. Distribution of products from the microwave assisted pyrolysis of varying feedstock compositions.

Feedstock	Char (%)	Liquid		Gas (%)
		Organic Phase (%)	Water Phase (%)	
100% DDGS *	25.0	18.3	27.5	29.2
DDGS: Corn stover 75:25 *	27.0	17.2	28.6	27.2
DDGS: Corn stover 50:50	25.4	41.8		32.8
DDGS: Corn stover 25:75	26.2	43.7		30.1
100% Corn stover	27.8	38.9		33.3
<i>Values From Other Literature Sources</i>				
Hydrothermal Conversion of DDGS				
[Mansur <i>et al.</i> , 2012]	30	45		NR
[Mørup <i>et al.</i> , 2012] 300-350 °C	3 to 4	17 to 23		NR
Slow Thermal Pyrolysis DDGS				
[Kern <i>et al.</i> , 2012] 550 °C	30	20		50
Fast Thermal Pyrolysis DDGS				
[Sanna <i>et al.</i> , 2011] 460 °C	20	40		40
540 °C	15	40		45
Fast pyrolysis of corn stover				
[Mullen <i>et al.</i> , 2010]	17	62		22

*Since phase separation was observed for pure DDGS and DDGS: Corn stover 75:25, yields of oil (organic) and water phase were reported individually.

NR = not reported.

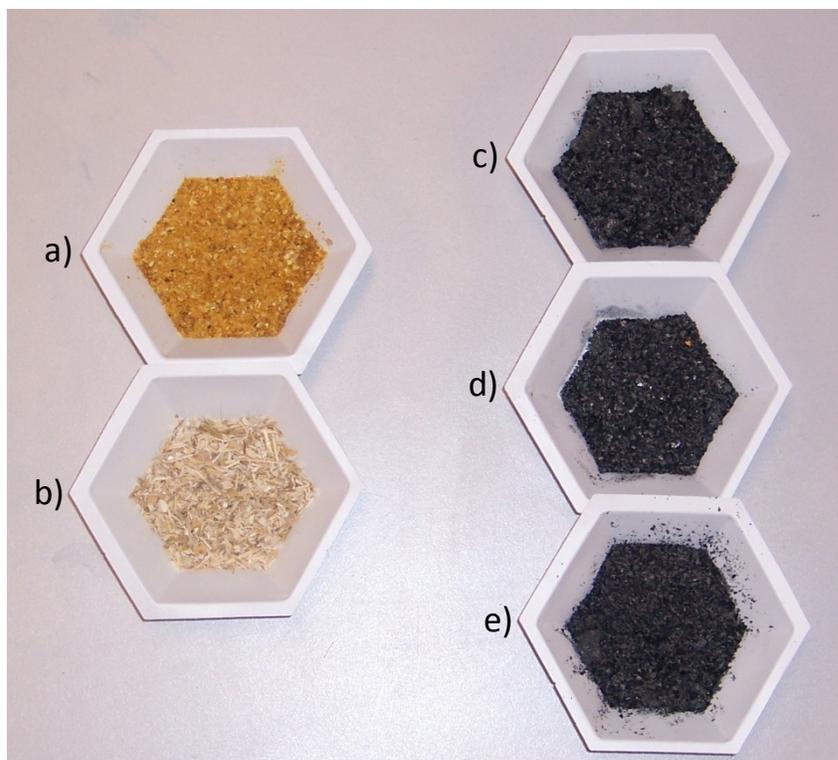


Figure 8. Illustrations of the original biomass feedstocks used in this project for the a) dried distillers grain and b) corn stover as well as the produced biochars from c) 100% DDGS , d) 50-50 DDGS:corn stover, and 3) 100% corn stover.

As shown in Table 1, the MAP process does produce more char product than fast pyrolysis (Figure 8). Fast pyrolysis produces about 15-20% char (Table 1), whereas the slow pyrolysis optimizes char production at about 30% of the original material, which is slightly more than the MAP char yield of 25-28% (Table 1). However, MAP is very competitive in terms of mass yield of char compared to the other thermal forms of pyrolysis, out yielding both fast and hydrothermal pyrolysis, and virtually matching the highest conversion into char observed in slow pyrolysis.

For bio-oil, the MAP process produces approximately double the amount of bio-oil as compared to slow pyrolysis. Fast pyrolysis, which has been optimized for bio-oil production, has high yields of bio-oil (40-60%). These values are higher than the MAP process (39-46%), but only by 10-15%. However, this difference is seen as very promising, **since we can double the production of the solid residual through MAP, while still converting a significant portion of the biomass into a renewable energy liquid product.**

Therefore, the MAP process is increasing the amount of char produced while maintain a high conversion of the biomass into bio-oil. This was one of the goals of the project, demonstrating that MAP was a feasible methodology for the production of secondary bio-energy based products from ethanol byproducts. Although requiring additional research and understanding of the potential market forces, the MAP conversion is seen as being more favorable in regards to the net economics. One of the most

significant hurdles in the biorefinery model is the transportation of the biomass feedstock to the plant [Kaylen *et al.*, 2000; Overend, 1982]. In our vision for the ethanol plants, the feedstock for the pyrolysis is already at the plant (DDGS) and all the equipment to handle the biomass preparation is already in place. In addition, the grain trucks which brought the grain to the plant would be filled with the biochar to return to the fields. In this fashion, these significant economic barriers of biomass transport are substantially reduced.

2.2 Bio-Oil Analysis

The total ion chromatograms of bio-oil obtained from the five bio-oils produced in this project are shown in the Appendix of this report as Figures A1 through A5, and the identified compounds with peak area percentage larger than 1% (corresponding to major compounds) are shown in Tables A1-A5. There were no significant differences observed in the density of the bio-oil as a function of the feedstock ratio as shown in Figure 9.

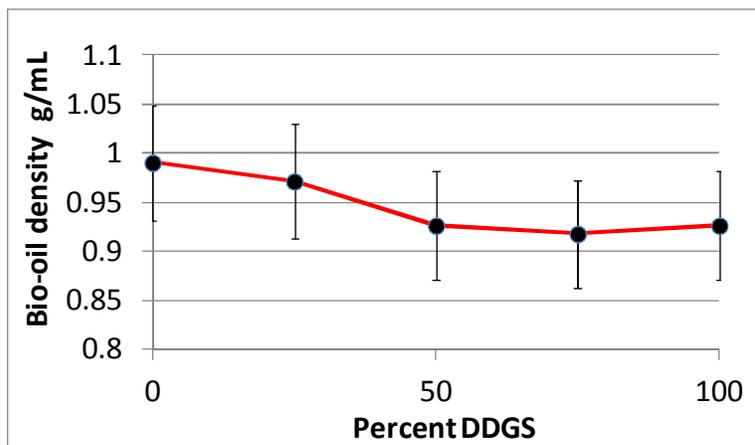


Figure 9. Alteration of the bio-oil density as a function of the feedstock ratio

As seen in the Appendix, the composition of the bio-oil does change in response to the mixed feedstock percentages. DDGS contains amino acids and lipids which were converted into long chain fatty acids and hydrocarbons during pyrolysis. The presence of these organic compound mixtures were a function of the feedstock ratios. More importantly, modifying the feedstock ratio allows the tailoring of the generating bio-oil to generate more hydrocarbon compounds. As these bio-oil compounds are highly non-polar, they are mainly located in the oil (organic) phase of the bio-oil. These hydrocarbon compounds are highly desirable products economically, since they can be upgraded (distilled and refined) into sources of renewable fuels, which are the core concepts behind the new “biorefineries” [Sharara *et al.*, 2012]. Because of the existence of proteins and amino acids in DDGS, nitrogen containing compounds were detected in the bio-oil of DDGS (i.e., pyridine). On the other hand, since corn stover is a lingo-cellulosic material, it was converted to mainly polar compounds, including organic acids, phenolics, aldehyde, and furfural. Some economic analyses of proposed biorefineries have included furfural [Kaylen *et al.*, 2000], as well as other of these identified organic components as value added products.

In general, bio-oil is a highly heterogeneous mixture of various components and it also contains a higher concentration of oxygenated components (which leads to viscosity and thermal breakdown issues) compared to its analog of crude oil. These two differences are the key problems behind the higher economic costs of reforming bio-oil compared to crude oil [Vagia and Lemonidou, 2008; Wang *et al.*, 1996]. Due to the lack of an actual bio-oil it has been assumed that in a target cost of bio-oil of \$3.00 per gallon, \$0.84 is actual production costs and the remainder is refining/upgrading costs [Badger *et al.*, 2011]. However, others have speculated that upgrade costs on the order of \$8.00 per gallon of bio-oil are possible [Wright *et al.*, 2010], due to unknown technological challenges which still have not been fully

accounted for. However, looking at the range in potential upgrade costs, one can appreciate the difficulty that currently faces economic assessments.

The distribution of these organics in the bio-oil are important, since the types of organic components will influence the net economic value as well as dictate clean-up/refining steps that are necessary for eventual end uses of the bio-oil fraction. However, the process and technological hurdles of this improvement is largely unknown, due to the absence of full-scale (commercial) plants [*Dale et al.*, 2011; *Wright et al.*, 2010]. Therefore, current extrapolations of economic viability are hampered by this lack of knowledge into the economics of the scale-up operations.

Catalytic pyrolysis

The addition of catalysts greatly changed the profile of the pyrolysis products from DDGS by deoxygenation and denitrogenation. With catalysts, the pyrolytic products are dominated with aromatic hydrocarbons, which accounted for 74% yield based on DDGS dry weight (Figure 10; Table 2).

The pyrolytic vapors were upgraded in-situ with the catalysts without influencing the properties of biochars. These aromatics could be used as gasoline and diesel additives or directly as more valuable industrial chemicals. They are much more valuable than the pyrolytic products without catalysts, which could only be used for boiler fuels without expensive upgrading. A previous study estimated that only 62-wt% of the available bio-oil could be upgraded to transportation fuels in a stand-alone facility [Wright *et al.*, 2010]. However, one could envision with the correct catalyst selection that this could also be optimized, but this still requires further investigation.

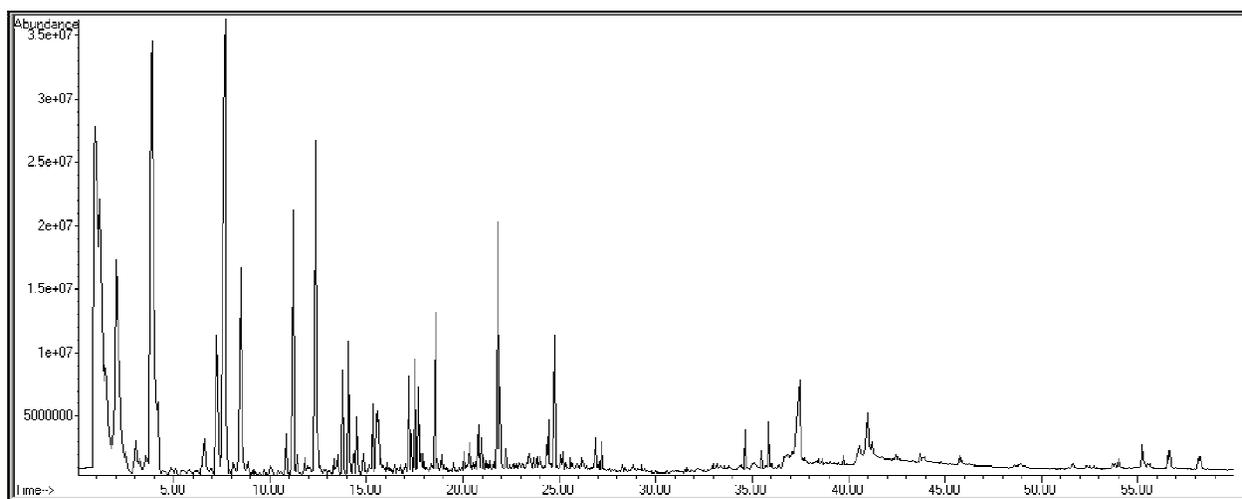


Figure 10. GC-MS chromatogram of bio-oil from catalytic MAP of DDGS (3 parts DDGS to 1part catalyst)

Table 2. Relative proportions (area%) of bio-oil compounds from catalytic pyrolysis of DDGS

Retention Time	Area Percentage	Library/ID
3.8771	12.4928	Toluene
0.9291	10.9392	Gas peak (CO, CO ₂ , etc.)
7.6789	9.8403	Benzene, 1,3-dimethyl-
1.1671	8.0415	Methacrolein
2.0387	7.4854	Benzene
12.3909	4.4224	Benzene, 1,2,3-trimethyl-
11.2456	3.5311	Benzene, 1-ethyl-2-methyl-
8.5029	3.3549	Benzene, 1,3-dimethyl-
1.4587	3.2812	(E)-2-Pentenenitrile
7.2416	2.7968	Ethylbenzene
21.8299	2.349	Naphthalene, 1-methyl-
37.4712	2.1276	n-Hexadecanoic acid
24.7719	1.4024	Naphthalene, 2,7-dimethyl-
18.5814	1.2471	Naphthalene
40.9993	1.0963	Octadecanoic acid
14.0925	1.0957	Indene

(*) Aromatic constituents are highlighted in yellow.

2.3 Biochar Physical Characterization

The five biochars were analyzed through a variety of analyses as highlighted below. Each analysis will be presented separately.

2.3.1. Proximate/Ulimate Analyses

The five biochars were analyzed by proximate and ultimate analyses. Ultimate analysis evaluates the elemental composition (sulfur, carbon, nitrogen, and oxygen), and proximate analysis determines the amount of fixed carbon (FC), volatile matter (VM) and ash within the sample. These results are shown in Table 3 below.

Table 3. Proximate and Ultimate Analysis of the MAP Biochars

Feedstock Ratios (wt %)										
Corn Stover	DDGS	Ash	Sulfur	Carbon	Hydrogen	Nitrogen	Oxygen	Ash	VM	FC
		% Dry Weight Basis								
0	100	17.4	0.6	73.1	1.1	6.7	1.2	17.4	15.1	67.5
25	75	21.2	0.5	71.5	1.0	4.8	1.0	21.2	14.2	64.7
50	50	24.6	0.4	70.0	0.7	2.8	1.6	24.6	7.5	67.8
75	25	25.1	0.3	69.9	0.7	2.1	1.9	25.1	7.2	67.7
100	0	26.3	0.1	68.4	0.7	1.0	3.5	26.3	9.7	64.0

As seen in Table 3, the feedstock mixing ratios influence the resulting chemical properties of the produced biochar, particularly for the total C, N, H, S, and ash. This correlation can be seen graphically in Figure 11. This variability could be an important facet for tailoring biochar properties. Low O:C ratios (<0.2) have been demonstrated to indicate a more stable carbon form against microbial mineralization (Spokas, 2010), or in other words a lower O:C ratio is a better material for soil carbon sequestration purposes. An interesting observation was that the O:C ratio of the biochars were related to the feedstock ratios (Figure 12), with higher concentrations of DDGS leading to lower O:C ratios in the biochar. This would suggest that the 100% DDGS biochar would be the most stable biochar form for carbon sequestration purposes.

However, not all properties were well correlated with the feedstock ratios. Some of these were the fixed carbon (Figure 11f) and the volatile matter (Figure 11e). The fact that the fixed carbon ratio is not directly correlated to the feedstock ratio like total carbon, does suggest that the stability of the produced

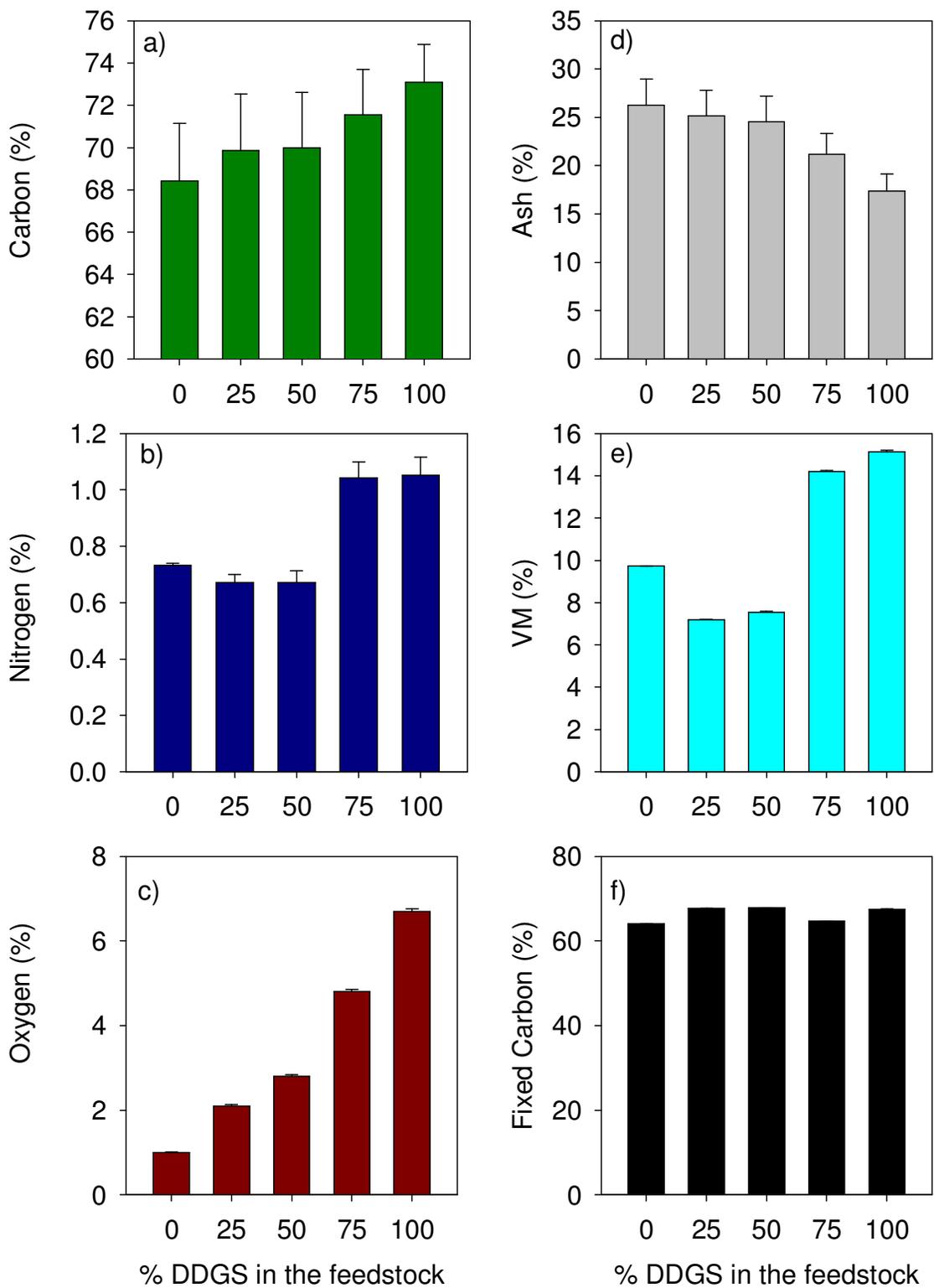


Figure 11. The variability of the composition of the biochar as a function of feedstock ratios is shown for a) carbon, b) nitrogen, c) oxygen, d) ash, e) volatile matter (VM), and f) fixed carbon.

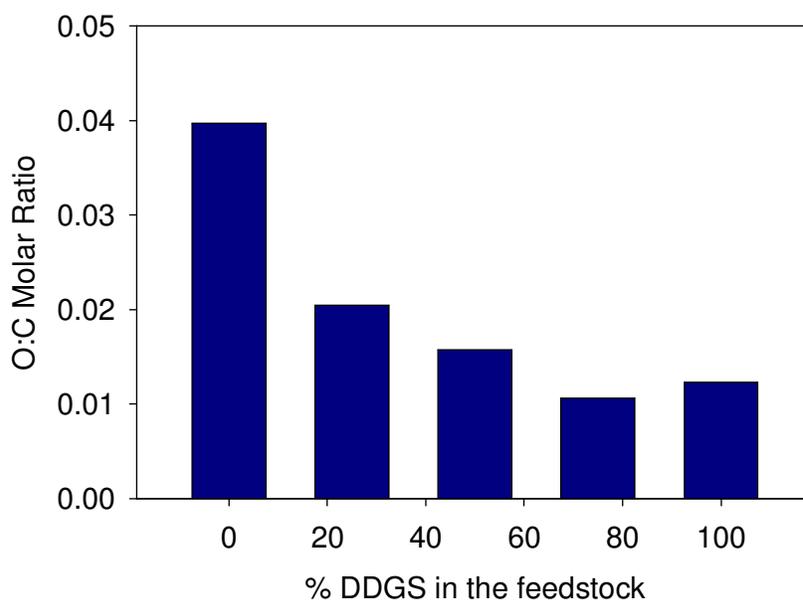


Figure 12. Oxygen to carbon (O:C) molar ratio of the produced biochar as a function of feedstock mixing ratio.

carbon in the biochar is also a function of other factors (i.e., cooling rate, cooling conditions) rather than solely determined by the composition of the feedstock.

The other observation from Table 3 is the high nitrogen content of the produced biochar from the pure DDGS biochar (N = 6.7% w/w). This is one advantage of the microwave assisted pyrolysis technique, since there is a reduction in the volatile loss of important plant nutrients (N, P, and K) compared to other production techniques (i.e., traditional kiln or fluidized bed reactors). These nutrients are typically lost through volatilization in thermally produced biochars. For the MAP, the nitrogen content is enriched compared to the original DDGS feedstock (original DDGS; N = 5.3% w/w).

The ability to increase N content in biochar was first reported by Radleim et al. (1987). In their work, a patented technique was developed to produce a nitrogen rich-slow release fertilizer from biomass pyrolysis products. This was accomplished by exposing the formed biochar with N-rich products to create a slow release fertilizer, primarily through sorption of the N containing compounds. As further studies have shown, this was a critical basis for slow release fertilizers creation from biochar [González et al., 1992; Khan et al., 2008]. Ammonia exposed to black carbon surfaces is known to react with surface oxygen groups leading to the formation of amines and amides under ambient (<100 °C) conditions [Seredych and Badosz, 2007; K Spokas et al., 2012]. Further investigation of these N-sorption mechanisms has shown that some of the sorbed N is bio-available [Taghizadeh-Toosi et al., 2011]. The use of DDGS as a biochar feedstock offers unique opportunities to further allow optimization of the soil N delivery/fertilization and reduce the environmental impacts of agricultural production.

Figure 13 illustrates the alteration in energy content (heating values) of the original biomass compared to the charred biomass as observed from the 100% feedstock MAP conversions. There was a

significant increase in the energy content of the corn stover biochar, which signifies a densification of the energy, which has been known to occur during low-temperature pyrolysis reactions or torrefaction [Bridgeman *et al.*, 2008]. The energy value for the two pure feedstock biochars (26.2 MJ kg⁻¹ for the DDGS and 23.9 MJ kg⁻¹ for the corn stover) are in line with other energy values for biochars created from a variety of biomass feedstocks (8 to 34 MJ kg⁻¹) [Parikh *et al.*, 2005]. As mentioned above (Section 1.3), the purpose for the creation of biochar is for carbon sequestration and not for direct energy production. However, these comparative energy contents are critical, since biochar will compete with energy generation [OECD/FAO, 2012].

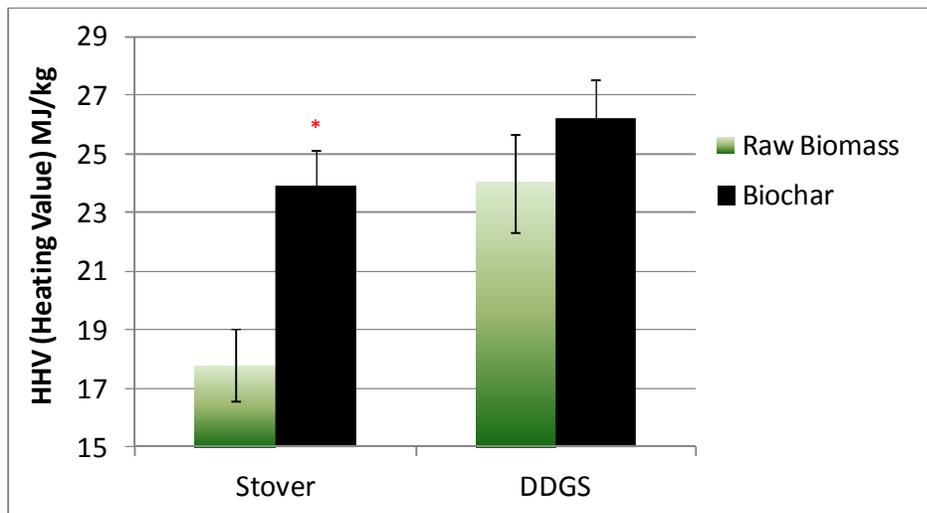


Figure 13. The energy content of the char residuals created by MAP compared to the original feedstocks.

2.3.2 Sorbed volatile organic profiles

Biochar has been observed to contain a variety of sorbed organics [see [K.A. Spokas *et al.*, 2011]]. The MAP biochars created here possessed lower levels of sorbed organics compared to thermally prepared counterparts. This could be an important facet in their interactions with the soil and plant systems (see Section 3). The sorbed volatile organic chromatograms collected from these biochars are presented in Figure 14, with the major compounds identified presented in Table 4.

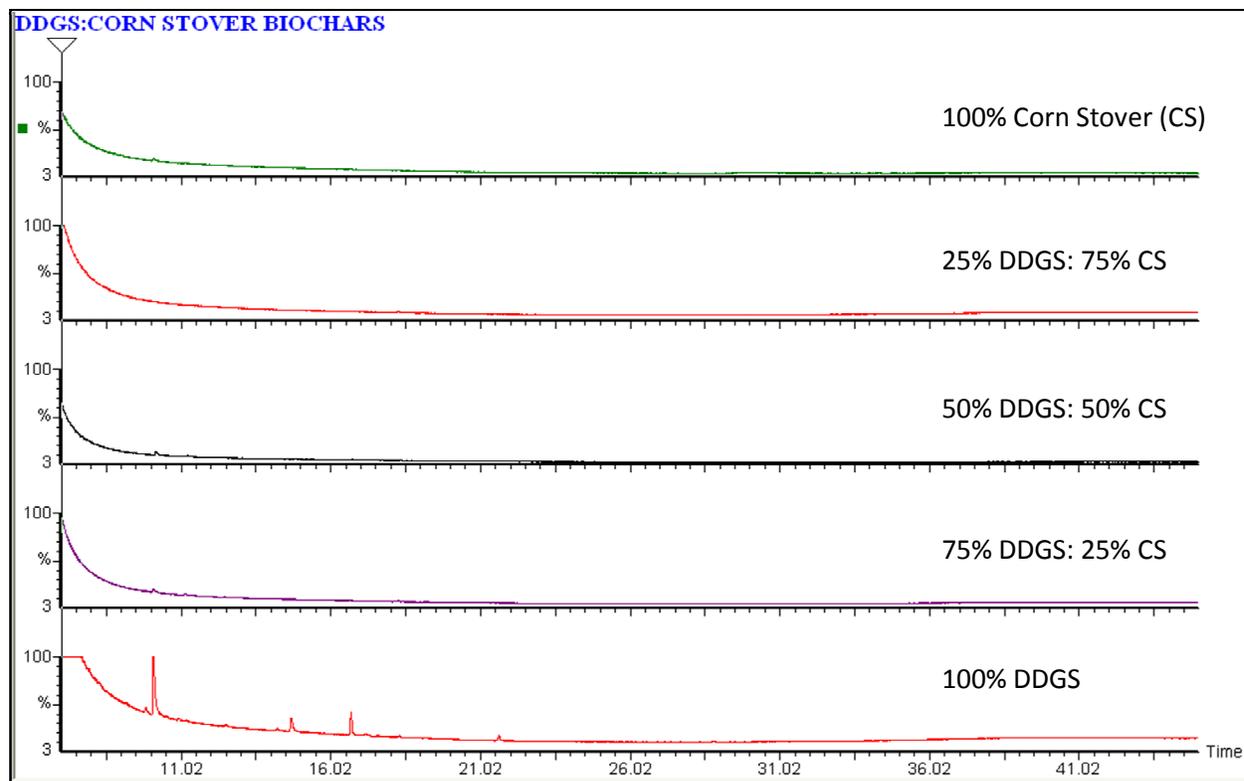


Figure 14. Thermal desorption total ion chromatograms collected from the 5 biochars as indicated in the figure. All axes are scaled equally for comparison.

The alteration in the sorbed species is a function of the feedstock mixing ratios; particularly for the volatile N-containing species (i.e., acetonitrile, mercrylate, and methylisocyanide). These N containing compounds are hypothesized to result from the proteins/amino acids in the DDGS, since their appearance is correlated to the DDGS feedstock percentage. Other researchers have observed that different amino acids produce compounds with drastically different chemistries as a function of the pyrolysis [Choi and Ko, 2011], which is being used as an analytical tool in the identification of amino acids [i.e. Richmond-Aylor *et al.*, 2007].

Table 4. Identified compounds sorbed to the various biochars

Feedstock Ratios (wt %)		Compounds in the highest amounts sorbed to the biochars		
Corn Stover	DDGS			
0	100	2-butanone	mercrylate (C ₅ H ₅ NO ₂)	methylisocyanide/acetonitrile
25	75	2-butanone	acetonitrile	benzene
50	50	2-butanone	acetonitrile	benzene
75	25	acetone	benzene	2-butanone
100	0	acetone	benzene	2-butanone

In this research, we observed that the production of bio-oil and biochar was achieved through microwave assisted pyrolysis (MAP), and the yields were similar across different mixing ratios of feedstocks (i.e. the same % char, % liquid, and an assumed % gases). The char itself was a highly porous structure when viewed under an electron microscope (Figure 15), with spots of visible precipitates and/or discolorations. These are a combination of both mineral and organic compounds that are sorbed to the surface of the char particle.

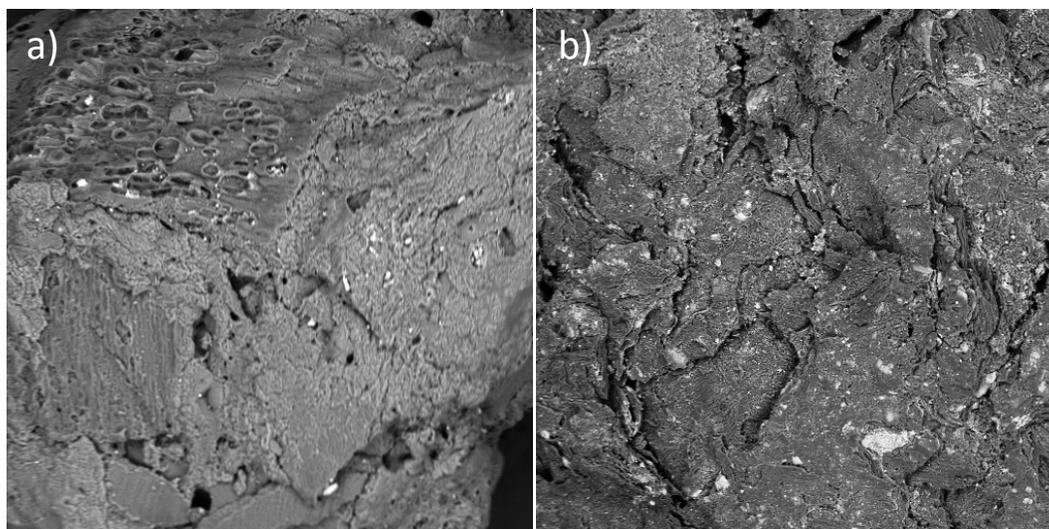


Figure 15. Scanning electron micrographs of the produced biochars: a) 100% corn stover biochar and b) 100% DDGS biochar. Images were collected by Aspex Corporation (Delmont, PA).

Section 3 Soil Amended with DDGS/Stover and MAP Biochars

Alteration in soil chemistry with the addition of MAP biochar

The use of DDGS as a biochar feedstock offers unique opportunities to further allow optimization of the soil N delivery/fertilization and reduce the environmental impacts of agricultural production. There have been a relatively few studies that have examined the direct use of DDGS as a soil fertilizer. A greenhouse based study which utilized DDGS as a potential herbicidal treatment, observed some weed suppression when DDGS was used as a broadcast application for horticultural use at rates exceeding 0.8 kg m⁻² [Boydston *et al.*, 2008]. In addition, Boydston *et al.* [2008] observed some plant injury and growth suppression to some horticulture crops (i.e. roses, phlox) when 20% DGGs (w/w) was mixed with the potting soil. They also noted that this suppression continued even after methanol rinsing of the DGGs. Nelson *et al.* [2009] reported on the observations of utilizing DGGs as a direct N-fertilizer addition. In that study, they observed the similar yields of corn with DDGS applied N and inorganic fertilizer N (urea and anhydrous ammonia), when applied at equivalent total N values. This was the same result observed by Shroyer *et al.* [2011] in Kansas. The Shroyer *et al.* (2011) study also examined charcoal (they did not directly state what the source material or conversion style of the charcoal), but noted lower yields due to the lower nitrogen availability in the charcoal amended plots.

Soil was amended with each of the 5 different biochars at 1% (w/w) and then analyzed for soil nutrients (A&L Laboratories, Memphis, TN). As seen in Figure 16, there were some significant effects on the soil chemistry as a result of the various types of biochar that were amended to a Rosemount, MN soil (Waugekan silt loam). Unlike the linear trends observed in the biochar chemistry, the biochar did increase the total organic carbon of the mixture compared to the original soil (red line in figure panels, Figure 16a). However, the amount detected was not directly equivalent (even though the amount of total C added was virtually identical). The increased organic matter appears to be a function of the feedstock ratio, with the mixtures providing more organic carbon to the soil than the pure biochars (Figure 16a). However, the exact cause of this was not determined and could be a function of the automated sample preparation at the contract laboratory (i.e. preferentially removing charcoal pieces as non-soil particles). A similar trend was seen in the pH (Figure 16b) with the mixtures causing an increase in the pH of the soil mixture (liming), and the 100% pure corn stover having no effect and the 100% DGGs biochar decreasing the pH of the mixture (acidifying) (Figure 16b).

The alterations in CEC were also dependent on whether the biochar was from a mixed feedstock (decreased CEC) or if it was the pure feedstock (increased CEC) (Figure 16c). Again, the exact cause of the alteration in the CEC is not known. On the other hand, the impact on phosphorus (Figure 16e), sulfur (Figure 16f), and nitrate (Figure 16d) availability was universal across the five biochars. Biochar addition resulted in higher available sulfur levels in the amended soil compared to the un-amended control. In addition, phosphorus was also increased across the 5 biochars. The complicating factor is the amount of the increases is not correlated with the added amounts, due to unknown causes.

Biochar additions also reduced the availability of nitrate (Figure 16d), which when properly managed can reduce leaching and losses of nitrate from agricultural soils [Laird *et al.*, 2010], but if improperly managed could be the reason for the lack of yield improvements and even yield suppressions in some biochar amendment experiments [Shroyer *et al.*, 2011; K A Spokas *et al.*, 2012].

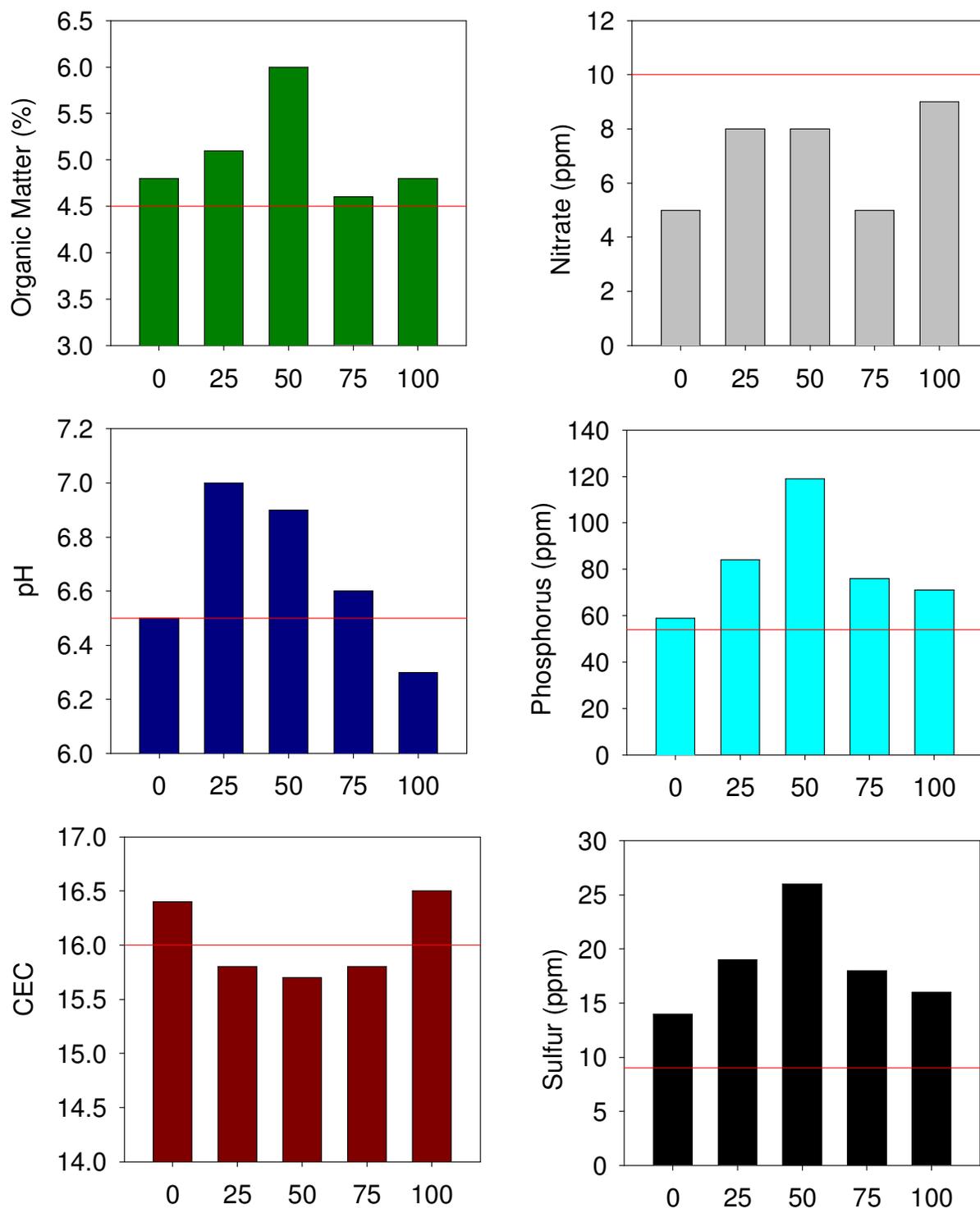


Figure 16. Illustration of the alteration of the soil chemistry in a Rosemount, MN (Waukegan silt loam soil) as a function of the biochar addition as a function of the DGGS content of the feedstock (0-100%). The red line in the graph is the value for the un-amended control soil.

Section 4 – Greenhouse Gas (GHG) Production Impacts

4.1 Production of Greenhouse Gas Production Potential Following Biochar Addition

Each of the produced biochars (5) were then utilized in triplicate greenhouse gas incubation studies, which were similar in design to those performed by Spokas *et al.* (2009) as given below:

1. 5 g Soil + 0.75 mL deionized (DI) water (*soil control – field capacity*),
2. 5 g Soil + 5 mL deionized (DI) water (*soil control - saturated*),
3. 0.5 g Biochar (*biochar dry control*),
4. 0.5 g Biochar + 0.75 mL DI water (*biochar field capacity control*)
5. 0.5 g Biochar + 5 mL DI water (*biochar saturated control*)
6. 0.5 g Biochar + 5 g soil + 0.75 mL DI water.
7. 0.5 g Biochar + 5 g soil + 5 mL DI water.

The above incubations were carried out at field capacity (-33 kPa) and saturated conditions (5 g soil: 5 mL water) and on each of the 5 different biochars added to the 3 different MN soil types. Biochar was not mechanically ground prior to the incubations. Soil and biochar were manually mixed in the serum bottle prior to the moisture addition. Triplicate sub-samples were placed in clean and sterilized 125 ml serum vials (Wheaton Glass, Millville, NJ) and sealed with red butyl rubber septa (Grace, Deerfield, IL). The incubations were pre-incubated for 7 d to allow reestablishment of steady-state conditions, since the production of GHG after moisture and amendment addition is highly variable [i.e. Cabrera, 1993; Franzluebbers *et al.*, 1996; Lamparter *et al.*, 2009]. Following the pre-incubation, periodic headspace gas samples were withdrawn from the incubations for analysis on a gas chromatographic system (GC-FID/TCD/ECD), that was previously described in Spokas and Bogner (2011) to quantify gas production over the 100-d incubation period. The individual gases analyzed were oxygen, nitrogen, carbon dioxide, nitrous oxide, and methane. The GC system was calibrated for the above gases using multiple traceable gas tank mixtures (Minneapolis Oxygen, Minneapolis, MN). If the O₂ level dropped below 15% during the incubation, the incubation was stopped and the rates of production were calculated up to that point to maintain comparison of aerobic conditions across all incubations. This aeration limit does not impact the rate calculation since the observed production rates were linear ($R^2 > 0.85$) for the 300 d incubation period. The linearity of the GHG production was further ensured due to the pre-incubation period (7 d), which does not account for the variable pulse of CO₂ resulting from rewetting soil samples (i.e., Fierer & Schimel, 2003) and initial biochar degassing/production (Zimmerman *et al.*, 2011). Total GHG production/consumption for the soil and the soil + biochar incubations was calculated as shown below:

$$\text{Total GHG Production Rate} = \frac{[(\text{GHG}_{\text{Soil+Biochar}}) - (\text{GHG}_{\text{Biochar Control}})]}{5 \text{ g soil}}, \quad (\text{Eq. 1})$$

where $\text{GHG}_{\text{Soil+Biochar}}$ is the total production/consumption rate of the particular GHG in the soil + biochar treatment (see Eq. 2), and $\text{GHG}_{\text{Biochar Control}}$ is the total production rate of the gas in the biochar control treatment (if applicable). In this fashion, the production/consumption of the biochar is accounted for in the estimated net impact on the GHG production (Spokas *et al.*, 2009, Zimmerman, 2010). The total

production rate of a particular GHG from the incubations can be estimated by the following formula (assuming 25 °C and 1 atm):

$$\text{GHG Production Rate (g d}^{-1}\text{)} = \frac{\text{slope (ppmv d}^{-1}\text{)}}{V_{\text{molar}}} (\text{MW})(\chi) \left(\frac{120 \text{ mL}}{1000 \text{ mL L}^{-1}} \right), \quad (\text{Eq. 2})$$

where the slope is the change in GHG concentration in the headspace per day (fitted with a linear regression on the periodic headspace gas concentrations), MW is the molecular weight of the gas of interest, and χ is the ratio of the molar mass of C or N to molecular weight of the gas (i.e., 12/44 for CO₂, 28/44 for N in N₂O; 12/16 for CH₄), V_{molar} is the molar volume of a gas (22.414 L mole⁻¹), and finally the last term is the conversion of volume units and accounting for the headspace volume of the serum bottle (120 mL).

Results for the GHG production/consumption activities were arithmetic means of triplicate samples. Linear regression analysis was conducted over the 300 d period to calculate the rate of change in headspace concentration per day (Eq. 2). This linear extrapolation has been performed in other studies (Spokas *et al.*, 2009), and is justified based on observed linear changes in the concentrations over the 100 d incubation period ($R^2 > 0.85$). Data were analyzed using an analysis of variance (ANOVA) procedure for independent samples to test for statistically significant differences using MINITAB (Minitab, Inc., State College, PA) between the paired fresh and weathered biochars as well as between biochar amended and control incubations. If significant differences existed among the factors, as indicated by the F-ratio, the Tukey's Honest Significant Difference (HSD) test was performed to determine which pair-wise interactions were significantly different at the $P < 0.05$ levels.

Results

The typical CO₂ production curve, as illustrated by the cumulative CO₂ produced during the course of the laboratory incubations is shown in Figure 17a. This is the characteristic curve that a number of laboratory studies on biochar additions have shown (e.g.), which has been used to hypothesize the presence of a rapidly degradable carbon source [A. R. Zimmerman, 2010; Andrew R. Zimmerman *et al.*, 2011]. However, if the initial 7 day period is dropped from the data set, due to the fact that there is irreproducible CO₂ production resulting from water and amendment additions to the soil incubations, as discussed elsewhere [Cabrera, 1993; Klein and Schimel, 1994; Fierer and Schimel, 2003; Groffman and Tiedje, 1988; Lamparter *et al.*, 2009], the resulting CO₂ production curve is shown in Figure 17b. Since we are interested in the long-term (chronic) alterations, for all the incubations conducted in this project we used a 7d pre-incubation period to allow the microbial population to adapt to the new conditions before starting the laboratory assessments [Franzluebbers *et al.*, 1996].

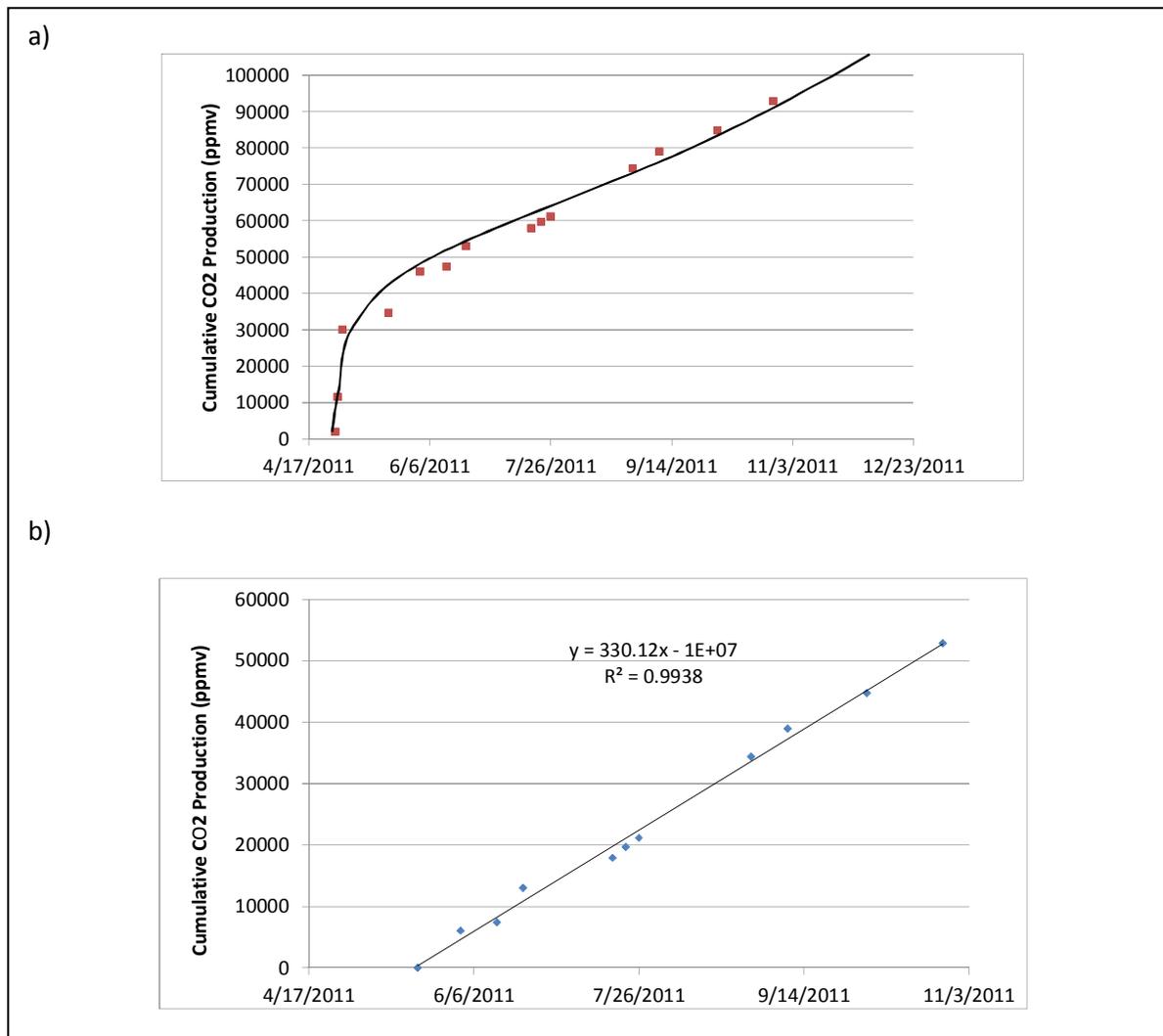


Figure 17. The total CO₂ production from a biochar amended laboratory incubation from a) the entire incubation period and b) after the 7 day pre-incubation period. For the data presented here, only the post pre-incubation production rates (b) were used in the analyses.

The results of the greenhouse gas production potentials for the biochar additions to the Rosemount, Morris, and Becker soils are shown in Figures 18, 19, and 20, respectively. The addition of the five different biochars did cause alterations in the observed CO₂ production. For the Rosemount soil (Figure 18), 4 of the 5 cases at field capacity these increases were significantly higher than the control, indicating a higher respiration activity in these soils. Under saturated conditions, 4 out of the 5 biochars created no significant impacts on the CO₂ respiration, and only the 100% corn stover biochar stimulated CO₂ respiration under these conditions. However, we did not determine the source of the respiration in this study (whether it is the soil organic matter or biochar material itself). The assumption here is that it is the biochar material. However, the response in the other two soils was more predictable. With all 5 biochars stimulating CO₂ production in the Morris soil (Figure 19) as well as the Becker soil (Figure 20), under both field capacity and saturated conditions.

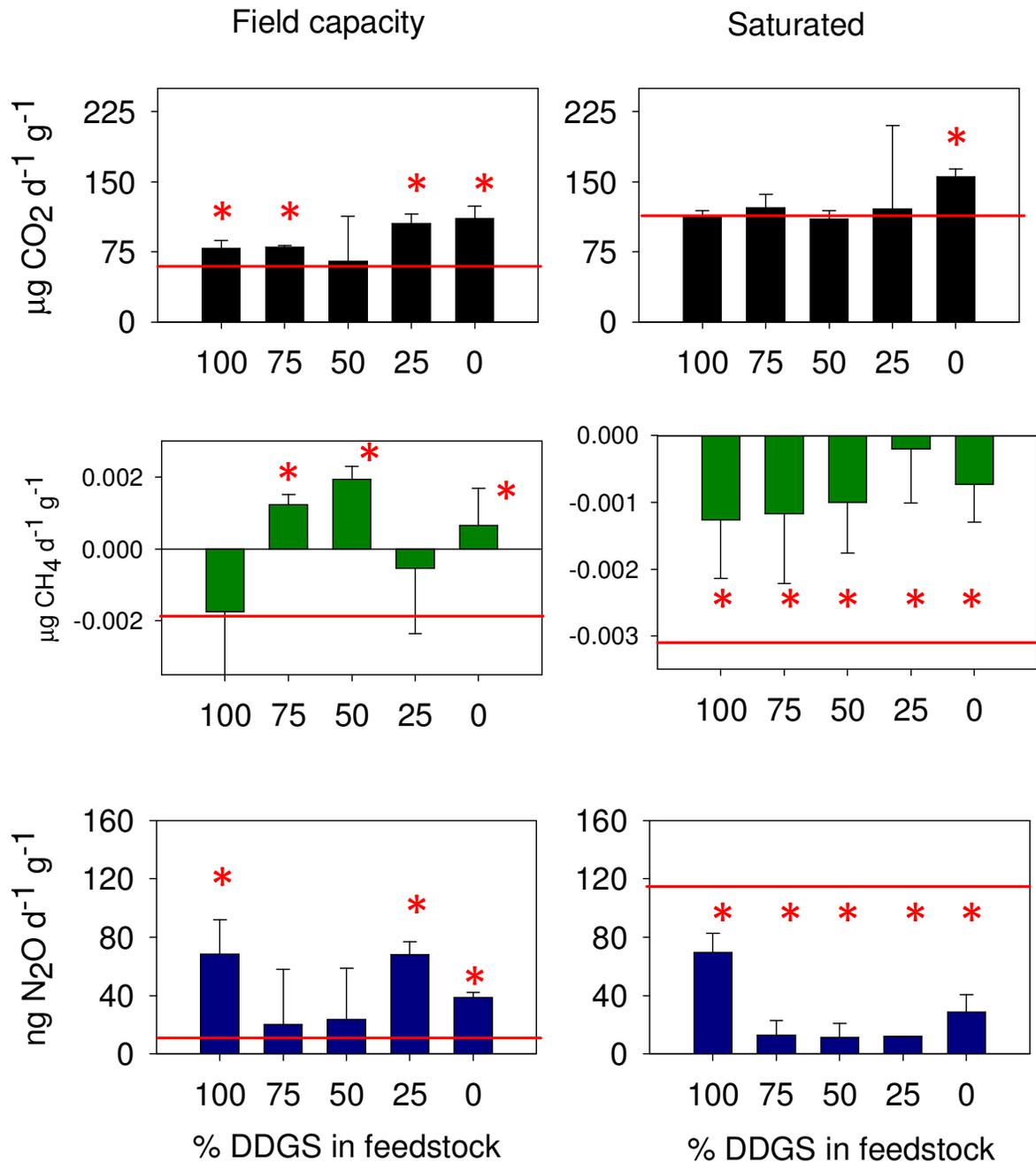


Figure 18. Impact of various biochar addition on the CO_2 , CH_4 , and N_2O production profiles over the 300 day incubation on the Rosemount, MN soil (Waukegan silt loam). The un-amended (control) soil is shown by the red line on each graph. The three graphs on the left side are at field capacity, and the three graphs on the right side are at saturated conditions. The asterisk indicate which additions were statistically different than the control (at $p < 0.05$).

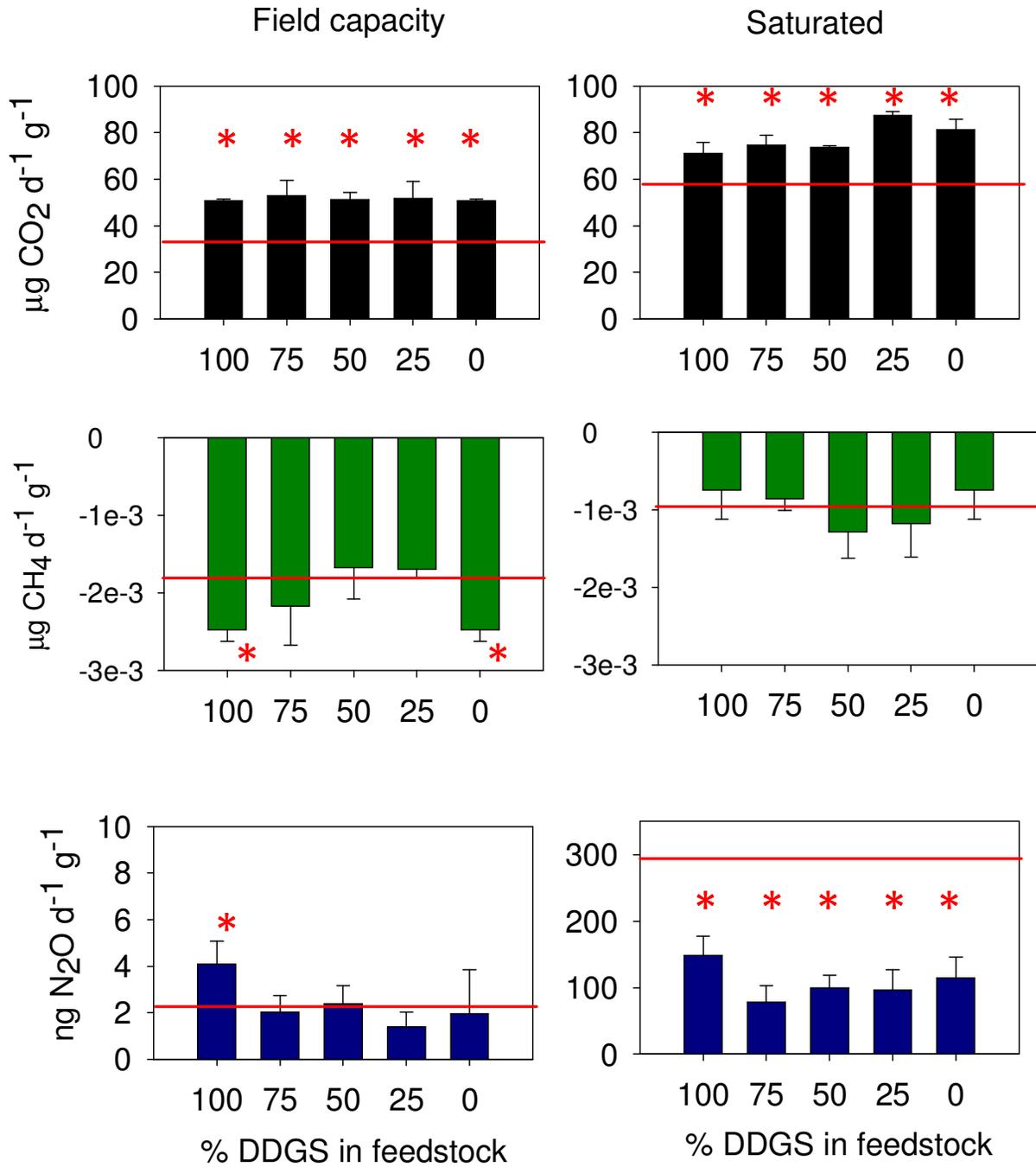


Figure 19. Impact of various biochar addition on the CO_2 , CH_4 , and N_2O production profiles over the 300 day incubation on the Morris, MN soil (Barnes loam). The un-amended (control) soil is shown by the red line on each graph. The three graphs on the left side are at field capacity, and the three graphs on the right side are at saturated conditions. The asterisk indicate which additions were statistically different than the control (at $p < 0.05$).

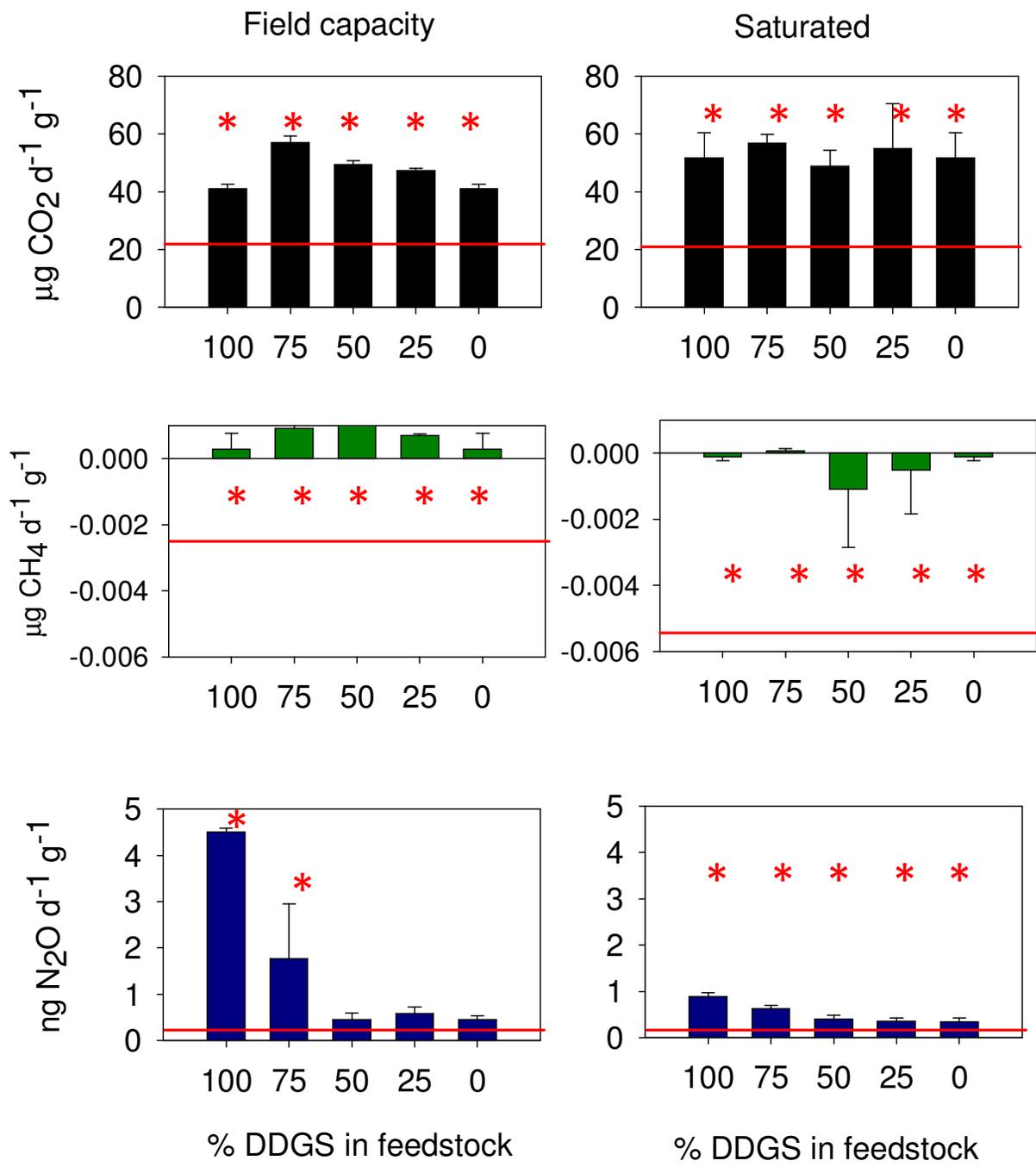


Figure 20. Impact of various biochar addition on the CO_2 , CH_4 , and N_2O production profiles over the 300 day incubation with the Becker, MN soil (Hubbard loamy sand). The un-amended (control) soil is shown by the red line on each graph. The three graphs on the left side are at field capacity, and the three graphs on the right side are at saturated conditions. The asterisk indicate which additions were statistically different than the control (at $p < 0.05$).

For methane, the addition of biochar reduced soil methanotrophic activity for 3 of the 5 biochars at field capacity and all 5 biochars reduced observed CH₄ oxidation activity in the saturated soils (Figure 18). In the Morris soil, there were no reductions in the oxidation capacity at either soil moisture condition for any biochar addition (Figure 19). Instead, there were two biochars (100% DDGS and 100% corn stover) which increased the observed rate of CH₄ oxidation higher than the soil control. Under saturated conditions, the biochar had no significant impact for the Morris soil. However, in the Becker soil (Figure 20), the biochar addition universally suppressed the native CH₄ oxidation capacity both at field capacity and under saturated conditions. In the case of field capacity, the biochar additions altered the soil from net methane oxidizing to net emitting (or methane producing) following the biochar addition.

For nitrous oxide, the addition of biochar at field capacity stimulated the production of N₂O in the Rosemount, with nearly increasing N₂O production by 5 fold over the control with the 100% DDGS biochar. However, under saturated conditions the biochar amendments did cause a significant decrease in the N₂O production by 38-89% compared to the soil control. The 100% DDGS biochar did possess the highest N-content and thereby typically had the highest stimulating effect on the soil following incorporation. However, the reductions under saturated conditions are very significant and noteworthy. In the Morris soil, the addition of biochar had the same trends as those observed in the Rosemount soil. At field capacity, there was a general tendency for the biochars to increase N₂O production, again with the 100% DDGS biochar having the highest stimulating effect (Figure 19). All 5 biochars also decreased the observed N₂O production under saturated conditions in the Morris soil, ranging from 48 to 73% reduction compared to the saturated control soil. In the Becker soil, the biochar addition also stimulated N₂O production at field capacity by almost 20 times, with the 100% DDGS having the highest stimulating effect. Under saturated conditions, unlike the other two soils, biochar amendments had a stimulating effect, increasing the N₂O production by 5-fold again with the 100% DDGS biochar addition.

Therefore, from this data it would appear that the biochars stimulate microbial activity in lower activity soils. These three soils examined here varied in the estimated microbial population from the Rosemount soil having the highest microbial density (63 mg C_{mic} kg⁻¹), then the Morris soil (44 mg C_{mic} kg⁻¹), and finally the Becker soil (7 mg C_{mic} kg⁻¹). The biochar stimulation effect is not as consistent when biochar is added to a high microbial activity soils (i.e. Rosemount). This is also the same pattern for N-cycling, with higher N-activity soils (Morris and Rosemount) having a corresponding negative or no effect on the overall N-cycle. Whereas, in the lower N-activity soil the biochar addition greatly enhanced the level of activity since it was very low to begin with (0.23 ng N₂O d⁻¹ g⁻¹ compared with 2 and 13 ng N₂O d⁻¹ g⁻¹ in the Morris and Rosemount soil, respectively). However, when we look at the total inorganic N at the end of the laboratory incubations (Figure 19) we see a different pattern. Overall, all the biochar additions universally across all three soil types reduced the amount of extractable nitrate assessed at the conclusion of the incubation (day 375). This is important since even in the incubations with increased N₂O production (Becker soil), there was still overall decrease in extractable nitrate, indicating that the biochar does indeed interact with the microbial N-cycling either by slowing the nitrate production or by reacting with the nitrate outside of the microbial cycle. However, these mechanisms still require further investigation.

Figure 22 illustrates the observed trends in the GHG production as a function of gravimetric soil moisture for an amended and control Rosemount soil. As shown in Figure 22a, there was negligible impact on the CO₂ respiration as a function of the soil moisture (10% w/w of 100% DDGS biochar).

However, for the N₂O suppression we see that the percent suppression increases as a function of the soil moisture, which suggests that water is involved in the mechanistic interaction of the suppression. This data supports that dissolved N forms interact with the biochar, since as soil moisture is increasing these interactions could also be increasing. However, more detailed isotopic labeled experiments are needed to fully elucidate this reaction.

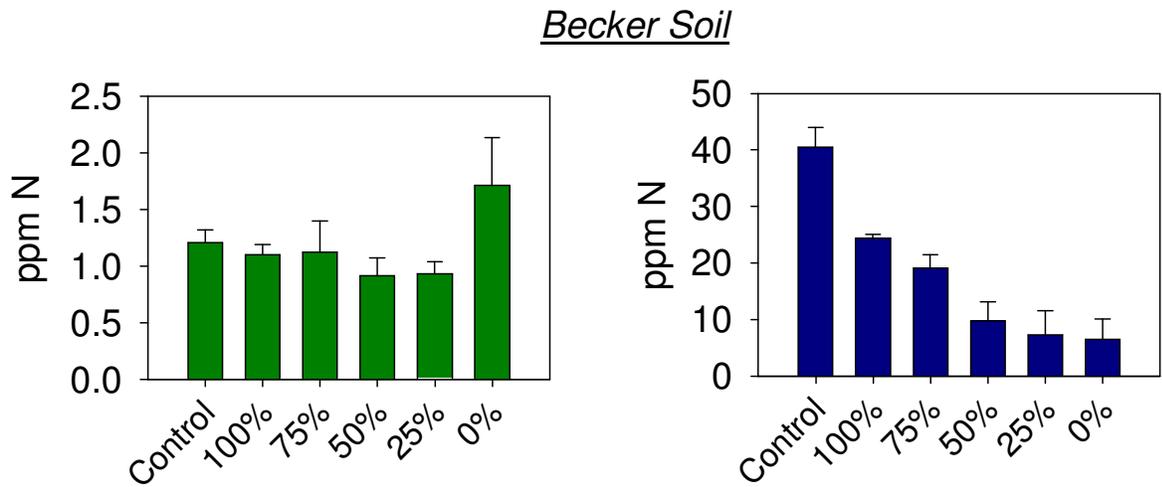
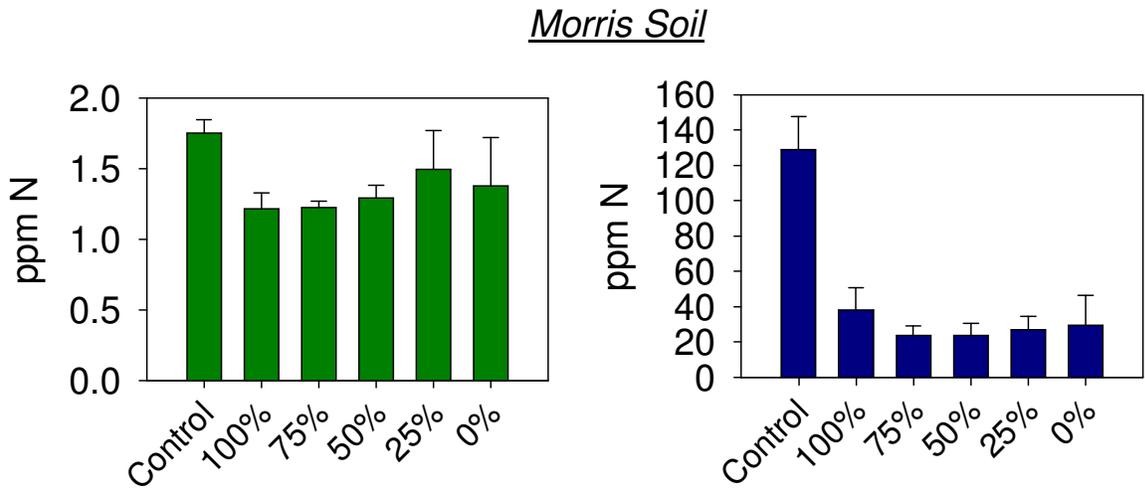
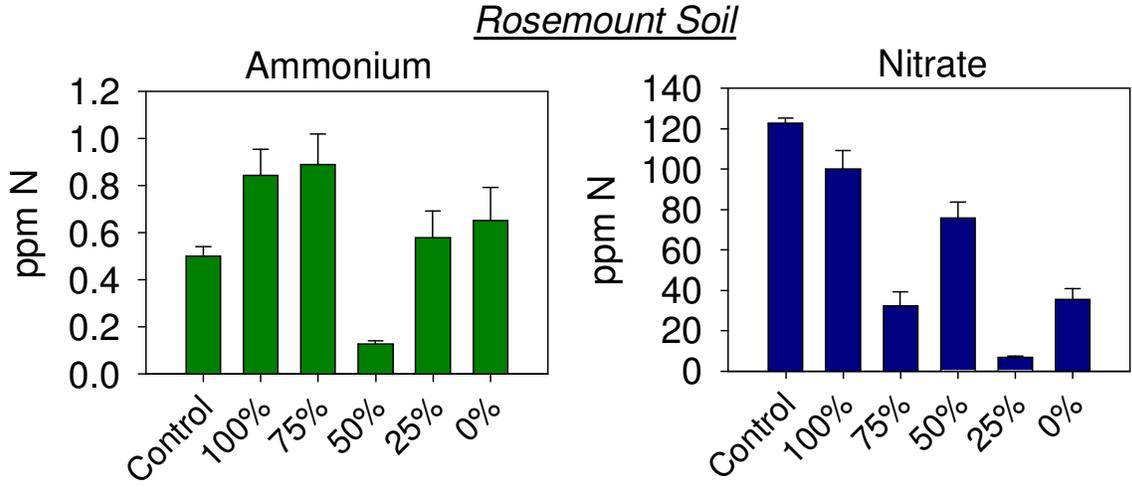


Figure 21. Quantification of inorganic N-forms (ammonium and nitrate) in the three different Minnesota soils at the conclusion of the 375 day laboratory incubation. The asterisk indicate which additions were statistically different than the control (at $p < 0.05$).

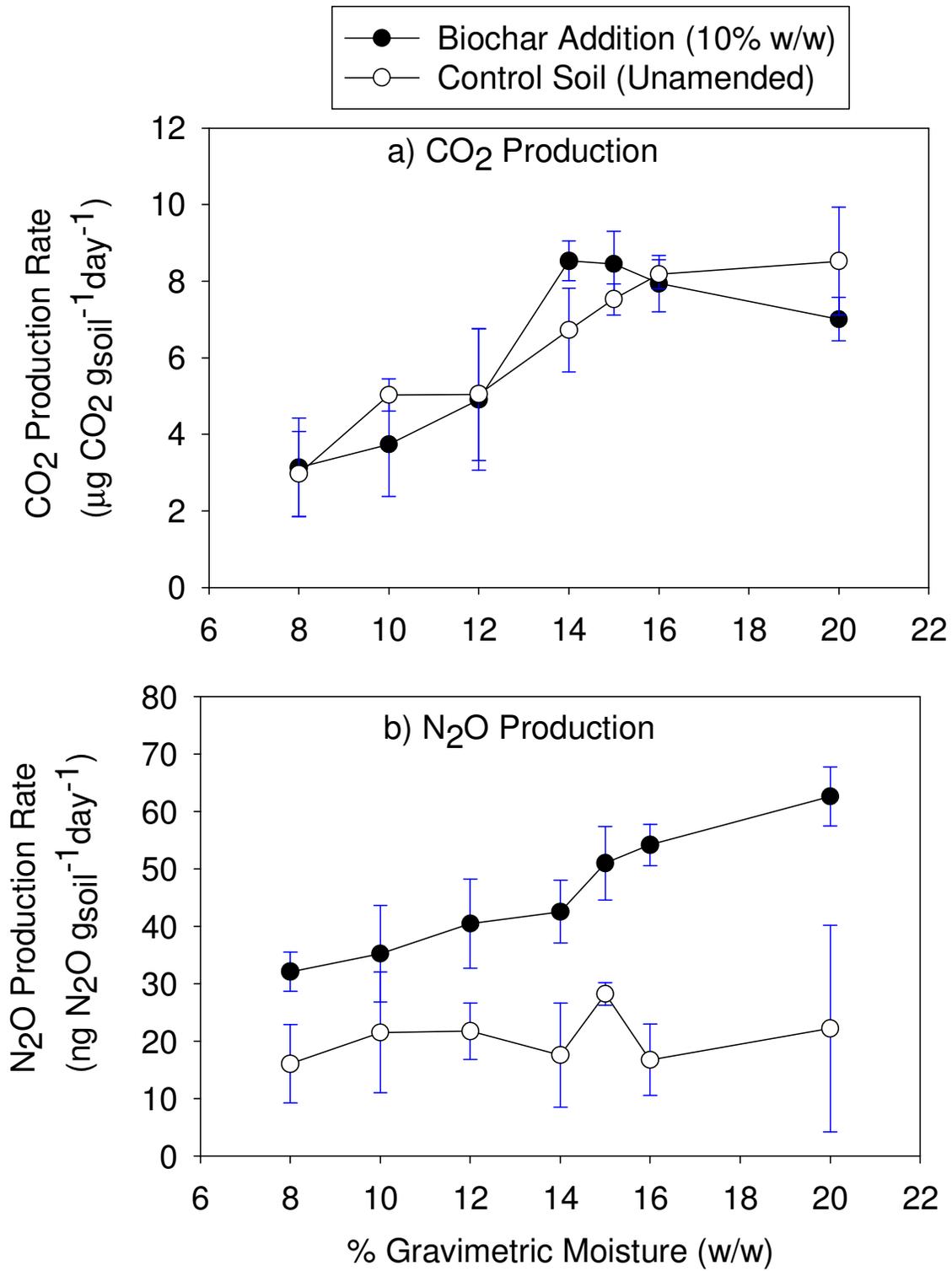


Figure 22. The observed production of a) CO₂ and b) N₂O from a 0.5% w/w addition of 1005 DDGS biochar as a function of soil moisture compared to the control Rosemount soil. Error bars represent the standard deviation of the triplicate measurements.

Section 5. Impact of MAP biochar addition on soil microbial system

The use of glucose induced respiration has been a fundamental method used to assess the differences in the functionality and the relative size of soil microbial biomass through laboratory incubations, since the method was proposed in 1973 [Anderson and Domsch, 1973]. An assessment of the microbial biomass was made utilizing the method of West and Sparling [1986]. Briefly, 5 g (dry-basis) of soil was placed in a sealed 125 mL serum bottle. A glucose solution was added to the soil to achieve a final glucose concentration of 10 mg g_{soil}⁻¹ and 60% water holding capacity. Substrate-induced respiration (SIR), a measure of active microbial biomass, was measured by analyzing for the production rate of CO₂ during the first 24 hr period after the glucose addition. The soil microbial biomass was estimated from the equation of Anderson and Domsch [1978], where

$$C_{mic} = 40.4 * C_{CO_2Rate} + 0.37, \quad (Eq. 3)$$

where C_{CO₂Rate} is the rate of CO₂ evolution (ml CO₂ 100 g⁻¹ dry soil h⁻¹) and C_{mic} is the microbial biomass (mg microbial C 100 g⁻¹ dry soil). These conversion factors do vary, with some being as high as 81.9 [Nakamoto and Wakahara, 2004]. In this study, since we were solely comparing the differences across different treatments, the absolute value of this factor is less important.

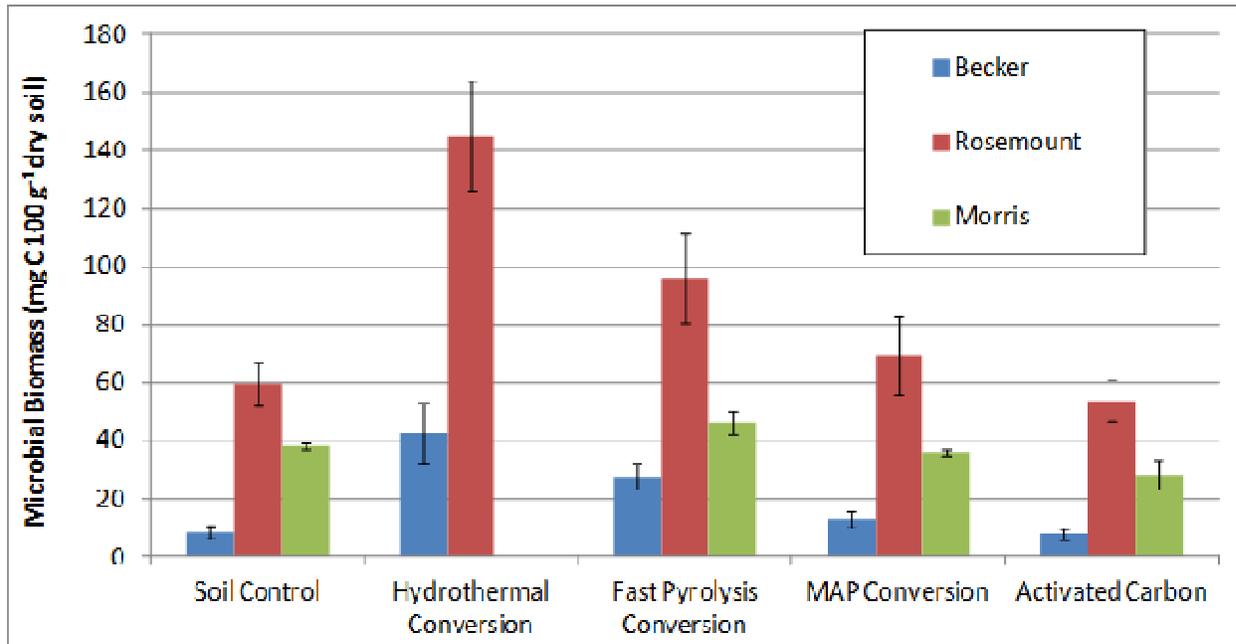


Figure 23. Impact of pyrolysis type on corn stover biochar addition on the net soil microbial population after 100 days of soil incubation for the three Minnesota soil types.

We compared the impacts of the style of pyrolysis (hydrothermal, fast thermal pyrolysis, MAP versus an activated carbon) on the soil microbial community. From this data (Figure 23), we see that the response of the microbial community is a function of the type of pyrolysis that was used for the corn

stover. The conversion that stimulated the microbial population the most was the hydrothermal conversion (lower overall C stability) and the fast pyrolysis biochar also resulted in net stimulation of the microbial population over a 100 d period. This does suggest a pool of liable carbon that was able to supply nutrients for a larger microbial population than the original soil organic matter.

There was no significant alteration observed in the estimated microbial density at 100 days in either the MAP biochar or the active charcoal addition (AC) ($P > 0.05$). The traditional pyrolysis biochar stimulated the activity of the soil microbial community from 1.2 to 3 times as a function of the soil type. In the Becker soil (Sandy loam), which possessed the lowest native microbial activity ($0.86 \text{ mg C}_{\text{microbial}} \text{ kg}^{-1}$), the traditional corn stover BC increased the microbial population by 2.9x, the Morris soil (Barnes-Arnstad silt loam) was stimulated 1.2x, and the Rosemount soil (Waukegan silt loam) was enhanced by 1.6x. This does indicate that the response of the microbial community will be variable as a function of soil type (as well as biochar type), which agrees with the existing data on biochar soil additions (Spokas and Receisoky, 2009) and the data presented above on the GHG production from these same biochars.

As seen in Figure 23, the addition of the thermal pyrolysis biochar did significantly increase the production observed of CO_2 above the soil control incubations. Similar results have been observed in other studies examining soil amendment quality [Chen *et al.*, 2002; Pennanen *et al.*, 2004], where the size of the enhancement in the microbial population is related to the quality of the amendment. However, the interconnections between microbe-soil-plant and the soil organic pool are complex and highly variability [Ponge, 2012], which limits overarching conclusions across soil types. Recent studies have examined the impact of fresh DDGS on the soil system and have observed even higher stimulation of CO_2 production compared to the un-amended soil control [Cayuela *et al.*, 2010], which suggests a more easily degraded substrate in the non-converted DDGS.

There have been numerous hypotheses put forward regarding the interaction of biochar with the soil microbial community [Joseph *et al.*, 2010; Lehmann *et al.*, 2011; Yao *et al.*, 2012]. However, the data collected during this project does suggest the addition of an inert black carbon back bone (MAP and activated charcoal) does not result in an alteration of the soil microbial community. However, the addition of the fast pyrolysis biochar, which contains higher amounts of sorbed organic compounds and the hydrothermal converted corn stover (lower aromatic character and higher O:C ratio for the carbonized material) are more easily degraded and correspondingly stimulates the activity of the soil microbial community due to the addition of the new food source. From the data collected in this study, the MAP biochar does appear to have a lower mineralization potential compared to the hydrothermal and fast pyrolysis conversion biochars. In other words, the biochar produced by MAP is more stable than corresponding biochar produced by hydrothermal or fast pyrolysis techniques.

Conclusions:

This project has demonstrated that DDGS and corn stover can be converted utilizing MAP for production of secondary renewable energy products (bio-oil/syngas) and the production of a solid residual biochar, which could have uses as a soil amendment and carbon sequestration purposes. This biochar was shown to impact soil microbial processes involving N-cycling in three different Minnesota soils. The most prominent observation was the reduction in available nitrate in the soil system (Figure 21), along with suppression of N₂O production in soils under saturated conditions (Figure 18 and 19). However, more research is needed to fully comprehend how this material will or can fit into an innovative fertilizer management program. The data does support continued research into these mechanisms as well as the use of catalysts during the pyrolysis process to produce a higher quality bio-oil than is possible without their use.

Recently, the use of corn stover biochar from thermal pyrolysis has already been shown to be a viable replacement for carbon black during the production of styrene-butadiene rubber composite materials [Peterson, 2012]. This is one example where the value of the char product could be greatly enhanced above its value currently for animal feed, energy, or soil fertilization. Incidentally, since this process is still maintaining the integrity of the carbon sequestration value of biochar, the product can be referred to as a biochar. From the data collected in this project, the MAP biochar would also be capable to fulfilling this end use.

A study by Brown *et al.* [2011] demonstrated that with the same input assumptions, the slow pyrolysis of corn stover would not be economically profitable in 2015, whereas the fast pyrolysis could be profitable in 2015, largely *due to the sale of the refined bio-oil fraction resulting from the fast pyrolysis*. Even though the exact extrapolations are uncertain and cannot be made with the data currently available, the conclusion that can be made at this time is that the MAP conversion of DDGS does appear to be economically favorable, largely due to the following factors:

1. Reduced energy (fossil fuel) due to the reduced need for drying the DDGS
2. Increased value of the potential bio-oil byproducts – which could yield higher profits than the sale of the current DDGS, which is at \$285-300 /ton (<http://agebb.missouri.edu/dairy/byprod/bplist.asp>) or the estimated \$22 a ton as a direct energy source. The economic value of DDGS directly as an energy source was estimated to be approximately \$22 per ton, with the assumption that the energy value would be directly related to the BTU value compared to coal (\$33/ton for 13,000 btu/lb) [Lory *et al.*, 2008].
3. MAP pyrolysis also yields a substantially greater amount of the bio-oil, compared to slow pyrolysis. Bio-oil has been shown to be one of the determining factors in the economic returns of a proposed pyrolysis plant operation [e.g. Brown *et al.*, 2011].
4. MAP pyrolysis through the use of catalysts can provide an improved bio-oil quality (with increased aromatic content) compared to the conversion without catalysts.
5. The economic value of biochar is still uncertain. However, as demonstrated recently with slow pyrolysis corn stover biochar, soil is not the only end use of the biochar product [Peterson, 2012; K A Spokas *et al.*, 2012]. When examining history, one finds that the application of charcoal to soils has always had questionable economic value, since the value for charcoal for energy far out-weighs the current soil fertilization value. However, these

past conclusions are based on broadcast (full field application). With the advancement of GPS and precision agriculture, we can now apply soil amendments precisely into the row or position them in the respective layer of soil for where they are needed. The other possibility is with the given situation of the lack of productive farm land for expansion, if biochar is capable of reclaiming deteriorated lands, this could drastically impact the economics of biochar.

Appendix

Individual Chromatograms of Bio-Oil Analyses

and

Tables of Identified Compounds

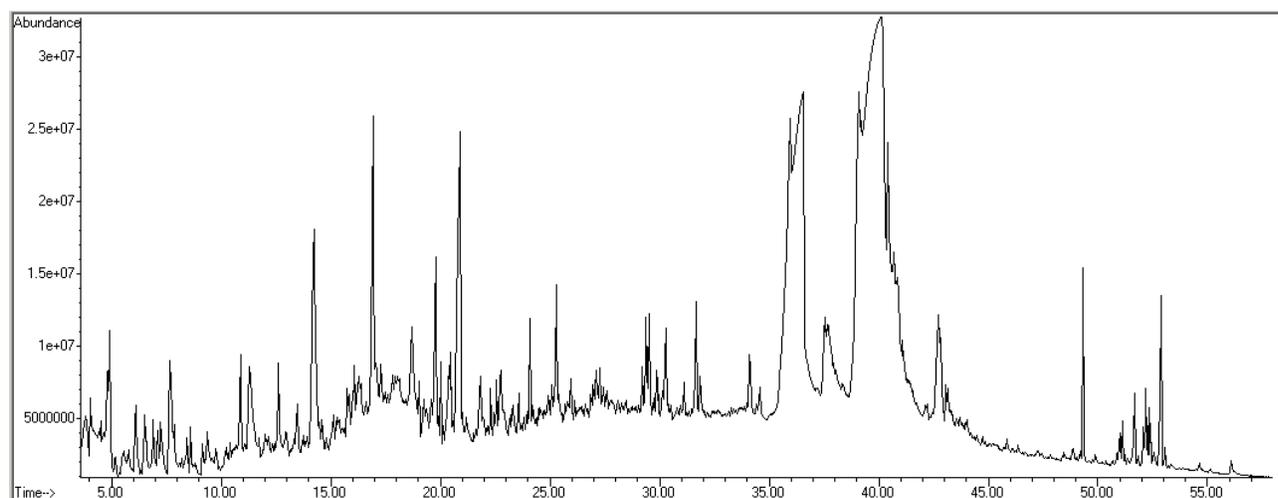


Figure A1. GC-MS chromatogram of bio-oil from pure DDGS

Table A1. Relative proportions (area%) of the main compounds of bio-oil from pure DDGS

Retention Time	Area Percentage	Library/ID
39.9149	8.6151	9,12-Octadecadienoic acid (Z,Z)-
36.5582	6.4315	n-Hexadecanoic acid
35.9739	4.511	Octadecanoic acid
39.1057	3.2508	Linoleic acid ethyl ester
40.1428	2.3608	9,17-Octadecadienal, (Z)-
20.9197	2.0735	2-Methoxy-4-vinylphenol
40.0551	2.004	9,12-Octadecadienoic acid (Z,Z)-
40.4145	1.9461	Hexadecanamide
14.2384	1.713	Phenol, 4-methyl-
16.932	1.5189	Naphthalene
39.167	1.061	9,12-Octadecadienoic acid (Z,Z)-
40.8352	1.0539	(R)-(-)-14-Methyl-8-hexadecyn-1-ol

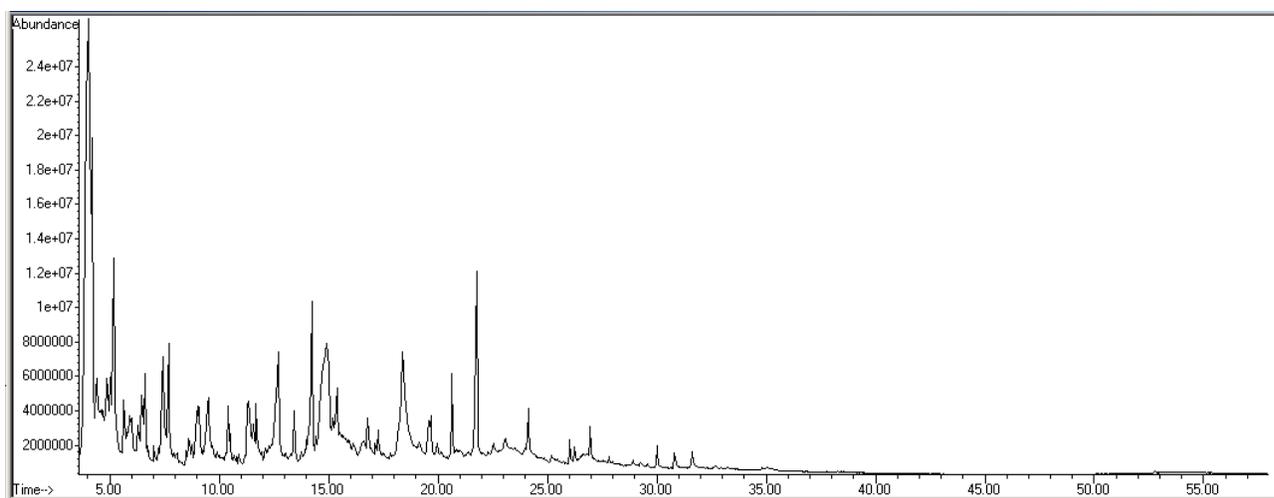


Figure A2. GC-MS chromatogram of bio-oil from pure corn stover

Table A2. Relative proportions (area%) of the main compounds of bio-oil from pure corn stover

Retention Time	Area Percentage	Library/ID
4.0366	9.7648	Acetic acid
3.949	8.087	Acetic acid
18.3926	6.304	Benzofuran, 2,3-dihydro-
14.9161	5.5625	2-Propenamide
4.2002	4.4697	2-Propanone, 1-hydroxy-
12.7016	3.5458	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
21.7814	3.326	Phenol, 2,6-dimethoxy-
14.7525	3.0068	1,3-Propanediamine, N-methyl-
7.4284	2.6	2-Furanmethanol
14.2383	2.4439	Phenol, 2-methoxy-
9.5055	2.2295	1,3-Cyclopentanedione
5.1731	2.0659	1-Hydroxy-2-butanone
7.6972	1.9256	2-Propanone, 1-(acetyloxy)-
4.8692	1.7209	Pyridine
11.3198	1.7141	Phenol
15.3923	1.5564	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
4.1184	1.4792	Acetic acid
9.0147	1.4142	Butyrolactone
5.0358	1.3586	1-Hydroxy-2-butanone
4.4018	1.3225	Formic acid, ethyl ester
5.1993	1.2591	1-Hydroxy-2-butanone
6.6133	1.0314	2-Cyclopenten-1-one
11.6966	0.9715	Butanoic acid, (tetrahydro-2-furanyl)methyl ester

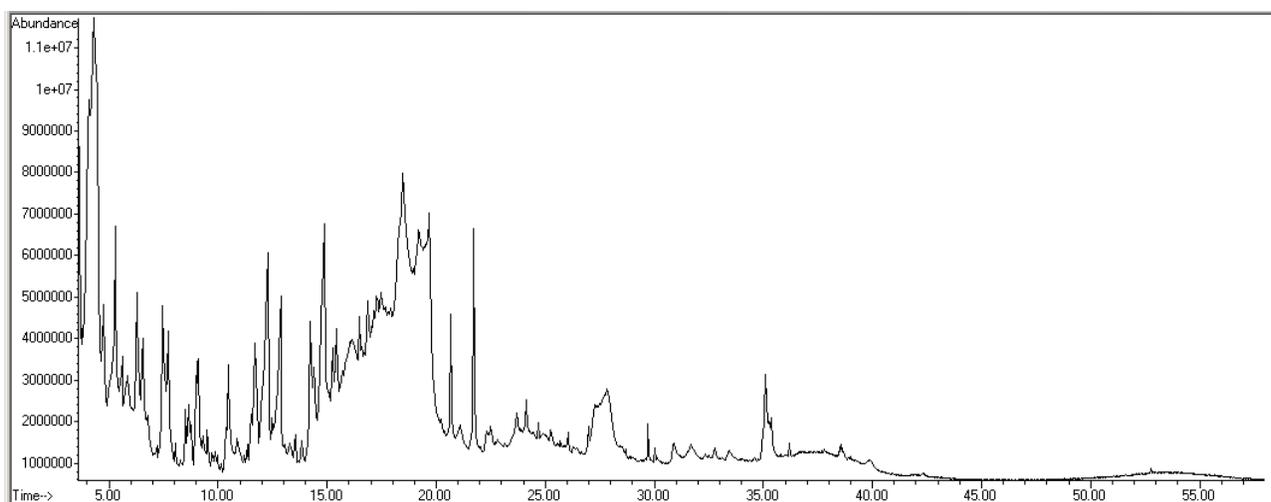


Figure A3. GC-MS chromatogram of bio-oil from a mixture of corn stover and DDGS (50:50)

Table A3. Relative proportions (area%) of the main compounds from 50:50 mixture

Retention Time	Area Percentage	Library/ID
12.2986	7.0979	2,4-Dimethyl-2-oxazoline-4-methanol
18.4658	5.9008	Glycerin
14.8549	5.6307	2-Butanamine, 3-methyl-
4.3085	4.9058	Acetic acid
12.88	3.4962	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
5.2872	2.9214	1-Hydroxy-2-butanone
4.2822	2.8489	Acetic acid
7.4607	2.4025	2-Furanmethanol
7.7178	2.3483	2-Propanone, 1-(acetyloxy)-
21.7349	2.3453	Phenol, 2,6-dimethoxy-
14.2151	2.0954	Phenol, 2-methoxy-
19.684	2.0785	Glycerin
6.2659	1.8319	1,3-Dimethyl-pyridinium chloride
27.8436	1.7783	1,6-Anhydro-.beta.-D-glucopyranose (levoglucosan)
11.6822	1.6828	Phenol
9.0383	1.6586	Butyrolactone
35.0858	1.5853	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a;1',2'-d]pyrazine
4.475	1.547	Acetic acid
10.4552	1.5121	2-Cyclopenten-1-one, 3-methyl-
14.3904	1.4399	Triethylenediamine
27.2885	1.393	1,6-Anhydro-.beta.-D-glucopyranose (levoglucosan)
15.4246	1.3769	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
9.1084	1.2567	2(5H)-Furanone
27.6566	1.183	1,6-Anhydro-.beta.-D-glucopyranose (levoglucosan)

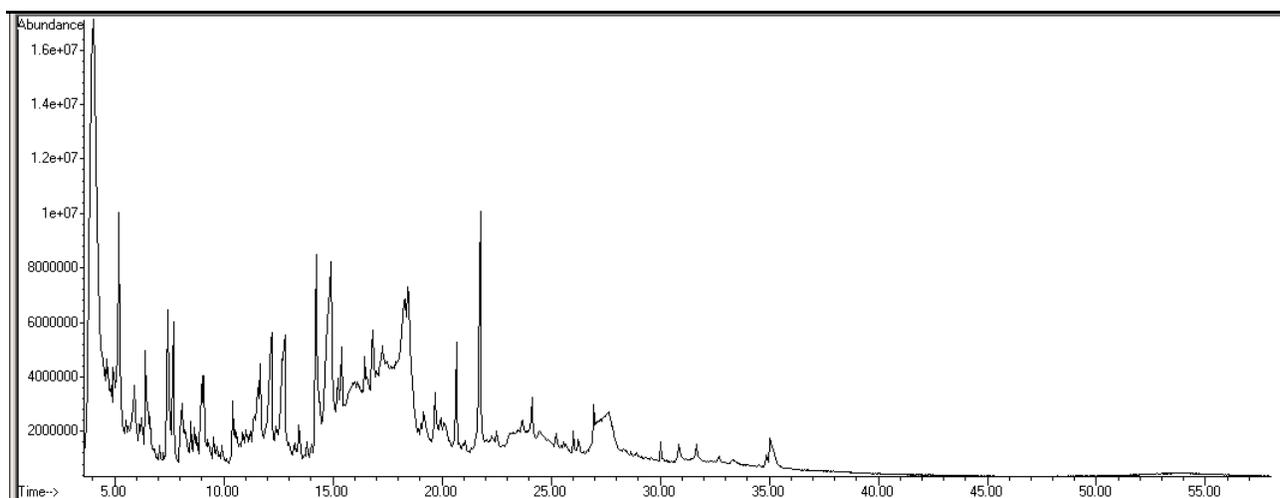


Figure A4 GC-MS chromatogram of bio-oil from a mixture of corn stover and DDGS (75:25)

Table A4. Relative proportions (area%) of the main compounds of bio-oil from a mixture of corn stover and DDGS (75:25)

Retention Time	Area Percentage	Library/ID
4.0337	13.4718	Acetic acid
14.9219	6.8394	2(3H)-Furanone, dihydro-4-hydroxy-
3.9782	5.1859	Acetic acid
5.2081	4.5439	1-Hydroxy-2-butanone
3.8818	4.128	Acetic acid
18.2933	3.3332	Glycerin
21.7581	3.227	Phenol, 2,6-dimethoxy-
12.1991	3.1062	2,4-Dimethyl-2-oxazoline-4-methanol
18.4481	2.8617	Benzofuran, 2,3-dihydro-
14.2295	2.673	Phenol, 2-methoxy-
7.4489	2.3772	2-Furanmethanol
12.798	2.1007	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
12.6753	1.6418	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-
11.6733	1.4697	3-Hexanone, 2-methyl-
9.0148	1.3805	Butyrolactone
11.5447	1.2967	Phenol
7.6972	1.2865	2-Propanone, 1-(acetyloxy)-
8.0887	1.1474	2,4-Dimethyl-2-oxazoline-4-methanol
4.8313	1.0275	Acetic acid, methoxy-
5.9122	1.0003	2,3-Butanediol

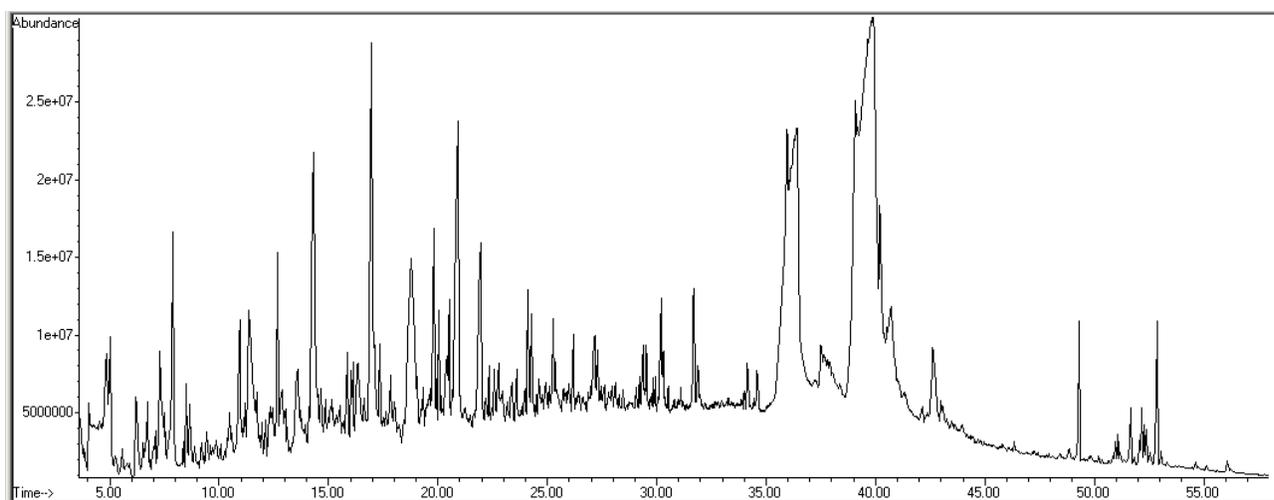


Figure A5. GC-MS chromatogram of bio-oil from a mixture of corn stover and DDGS (25:75)

Table A5. Relative proportions (area%) of the main compounds of bio-oil from a mixture of corn stover and DDGS (25:75)

Retention Time	Area Percentage	Library/ID
35.9592	4.3391	Octadecanoic acid
39.0822	3.381	Linoleic acid ethyl ester
18.787	3.1764	Benzofuran, 2,3-dihydro-
39.5175	3.0388	9,12-Octadecadienoic acid (Z,Z)-
14.3289	2.944	Phenol, 4-methyl-
20.943	2.8419	2-Methoxy-4-vinylphenol
16.9728	2.7099	Naphthalene
39.8798	2.4347	9,17-Octadecadienal, (Z)-
11.3665	2.0481	Phenol
39.3334	1.7775	9,12-Octadecadienoic acid (Z,Z)-
36.1666	1.7693	n-Hexadecanoic acid
39.7366	1.7448	9,12-Octadecadienoic acid (Z,Z)-
40.2011	1.7075	Tetradecanamide
21.9714	1.6901	Phenol, 2,6-dimethoxy-
36.4179	1.4589	n-Hexadecanoic acid
39.6373	1.4469	9,12-Octadecadienoic acid (Z,Z)-
7.8871	1.3508	Styrene
36.3507	1.2806	n-Hexadecanoic acid
39.8593	1.1869	9,17-Octadecadienal, (Z)-
36.2601	1.1581	n-Hexadecanoic acid
39.8009	1.1382	9,12-Octadecadienoic acid (Z,Z)-
4.8371	1.1035	Pyridine
10.9429	1.0195	Benzonitrile
9.829	1.008	Phenol, 4-ethyl-2-methoxy-

References Cited

- Abdullah, H., and H. W. Wu (2009), Biochar as a Fuel: 1. Properties and Grindability of Biochars Produced from the Pyrolysis of Mallee Wood under Slow-Heating Conditions, *Energy Fuel.*, 23(8), 4174-4181.
- Adams, M. D. (1991), The mechanisms of adsorption of $\text{Hg}(\text{CN})_2$ and HgCl_2 on to activated carbon, *Hydrometallurgy*, 26(2), 201-210.
- Agblevor, F. A., S. Beis, S. S. Kim, R. Tarrant, and N. O. Mante (2010), Biocrude oils from the fast pyrolysis of poultry litter and hardwood, *Waste Manage.*, 30(2), 298-307.
- Anderson, J. P. E., and K. H. Domsch (1973), Quantification of bacterial and fungal contributions to soil respiration, *Archives of Microbiology*, 93(2), 113-127.
- Anderson, J. P. E., and K. H. Domsch (1978), A physiological method for the quantitative measurement of microbial biomass in soils, *Soil Biol. Biochem.*, 10(3), 215-221.
- Atkinson, C., J. Fitzgerald, and N. Hipps (2010), Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: a review, *Plant Soil*, 337(1), 1-18.
- Ayache, J., A. Oberlin, and M. Inagaki (1990), Mechanism of carbonization under pressure, part II: Influence of impurities, *Carbon*, 28(2-3), 353-362.
- Badger, P., S. Badger, M. Puettmann, P. Steele, and J. Cooper (2011), Techno-economic analysis: preliminary assessment of pyrolysis oil production costs and material energy balance associated with a transportable fast pyrolysis system, *Bioresources*, 6(1), 34-47.
- Balat, M., and H. Balat (2009), Recent trends in global production and utilization of bio-ethanol fuel, *Applied Energy*, 86(11), 2273-2282.
- Boydston, R. A., H. P. Collins, and S. F. Vautghn (2008), Response of weeds and ornamental plants to potting soil amended with dried distillers grains, *HortScience*, 43(1), 191-195.
- Bradbury, A. G. W., Y. Sakai, and F. Shafizadeh (1979), A kinetic model for pyrolysis of cellulose, *J. Appl. Polym. Sci.*, 23(11), 3271-3280.
- Bridgeman, T. G., J. M. Jones, I. Shield, and P. T. Williams (2008), Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties, *Fuel*, 87(6), 844-856.
- Bridgwater, A. V., D. Meier, and D. Radlein (1999), An overview of fast pyrolysis of biomass, *Org. Geochem.*, 30(12), 1479-1493.
- Brown, T. R., M. M. Wright, and R. C. Brown (2011), Estimating profitability of two biochar production scenarios: slow pyrolysis vs fast pyrolysis, *Biofuels, Bioproducts and Biorefining*, 5(1), 54-68.
- Butuzova, L., M. Razvigorova, A. Krzton, and V. Minkova (1998), The effect of water on the yield and structure of the products of brown coal pyrolysis and hydrogenation, *Fuel*, 77(6), 639-643.
- Cabrera, M. L. (1993), Modeling the flush of nitrogen mineralization caused by drying and rewetting soils, *Soil Sci. Soc. Am. J.*, 57, 63-66.
- Cantrell, K., K. Ro, D. Mahajan, M. Anjom, and P. G. Hunt (2007), Role of thermochemical conversion in livestock waste-to-energy treatments: Obstacles and opportunities, *Ind. Eng. Chem. Res.*, 46(26), 8918-8927.
- Cantrell, K. B., and J. H. Martin (2012a), Stochastic state-space temperature regulation of biochar production. Part II: Application to manure processing via pyrolysis, *J. Sci. Food Agric.*, 92(3), 490-495.
- Cantrell, K. B., and J. H. Martin (2012b), Stochastic state-space temperature regulation of biochar production. Part I: Theoretical development, *J. Sci. Food Agric.*, 92(3), 481-489.
- Cayuela, M. L., O. Oenema, P. J. Kuikman, R. R. Bakker, and J. W. Van Groenigen (2010), Bioenergy by-products as soil amendments? Implications for carbon sequestration and greenhouse gas emissions, *GCB Bioenergy*, 2(4), 201-213.
- Chen, S.-K., S. Subler, and C. A. Edwards (2002), Effects of agricultural biostimulants on soil microbial activity and nitrogen dynamics, *Applied Soil Ecology*, 19(3), 249-259.

Choi, S.-S., and J.-E. Ko (2011), Analysis of cyclic pyrolysis products formed from amino acid monomer, *J. Chromatogr.*, 1218(46), 8443-8455.

Clein, J. S., and J. P. Schimel (1994), Reduction in microbial activity in Birch litter due to drying and rewetting event, *Soil Biol. Biochem.*, 26(3), 403-406.

Cresswell, S. L., and S. J. Haswell (2001), Microwave Ovens—Out of the Kitchen, *J. Chem. Educ.*, 78(7), 900.

Dale, V. H., K. L. Kline, L. L. Wright, R. D. Perlack, M. Downing, and R. L. Graham (2011), Interactions among bioenergy feedstock choices, landscape dynamics, and land use, *Ecol. Appl.*, 21(4), 1039-1054.

Fierer, N., and J. P. Schimel (2003), A proposed mechanism for the pulse in carbon dioxide production commonly observed following the rapid rewetting of a dry soil, *Soil Sci. Soc. Am. J.*, 67(3), 798-805.

Franzluebbers, A. J., R. L. Haney, F. M. Hons, and D. A. Zuberer (1996), Determination Of Microbial Biomass And Nitrogen Mineralization Following Rewetting Of Dried Soil, *Soil Sci. Soc. Am. J.*, 60(4), 1133-1139.

Goldberg, E. D. (1985), *Black Carbon in the Environment: Properties and Distribution*, 216 pp., John Wiley & Sons Inc, New York.

González, C., R. Alvarez, and J. Coca (1992), Waste kraft black liquors as raw material for the production of nitrogenous humic fertilizers by an oxidation-ammoniation process, *Nutrient Cycling in Agroecosystems*, 33(3), 279-285.

Gouel, C. (2012), AGRICULTURAL PRICE INSTABILITY: A SURVEY OF COMPETING EXPLANATIONS AND REMEDIES, *Journal of Economic Surveys*, 26(1), 129-156.

Gray, M. R., W. H. Corcoran, and G. R. Gavalas (1985), Pyrolysis of a wood-derived material. Effects of moisture and ash content, *Industrial & Engineering Chemistry Process Design and Development*, 24(3), 646-651.

Groffman, P. M., and J. M. Tiedje (1988), Denitrification hysteresis during wetting and drying cycles in soil, *Soil Sci. Soc. Am. J.*, 52(6), 1626-1629.

Harvey, O. R., L.-J. Kuo, A. R. Zimmerman, P. Louchouart, J. E. Amonette, and B. E. Herbert (2012), An index-based approach to assessing recalcitrance and soil carbon sequestration potential of engineered black carbons (biochars), *Environ. Sci. Technol.*, 46(3), 1415-1421.

Hawley, L. F. (1926), Fifty years of wood distillations, *Industrial & Engineering Chemistry*, 18(9), 929-930.

Jeffery, S., F. G. A. Verheijen, M. van der Velde, and A. C. Bastos (2011), A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis, *Agriculture, Ecosystems & Environment*, 144(1), 175-187.

Joseph, S. D., et al. (2010), An investigation into the reactions of biochar in soil, *Aust. J. Soil Res.*, 48(6-7), 501-515.

Junming, X., J. Jianchun, S. Yunjuan, and L. Yanju (2008), Bio-oil upgrading by means of ethyl ester production in reactive distillation to remove water and to improve storage and fuel characteristics, *Biomass Bioenergy*, 32(11), 1056-1061.

Kappe, C. O. (2004), Controlled microwave heating in modern organic synthesis, *Angewandte Chemie - International Edition*, 43(46), 6250-6284.

Kaylen, M., D. L. Van Dyne, Y. S. Choi, and M. Blase (2000), Economic feasibility of producing ethanol from lignocellulosic feedstocks, *Bioresour. Technol.*, 72(1), 19-32.

Kern, S., M. Halwachs, G. Kampichler, C. Pfeifer, T. Pröll, and H. Hofbauer (2012), Rotary kiln pyrolysis of straw and fermentation residues in a 30 MW pilot plant – Influence of pyrolysis temperature on pyrolysis product performance, *J. Anal. Appl. Pyrolysis*, 97(0), 1-10.

Khan, M., K.-W. Kim, W. Mingzhi, B.-K. Lim, W.-H. Lee, and J.-Y. Lee (2008), Nutrient-impregnated charcoal: an environmentally friendly slow-release fertilizer, *The Environmentalist*, 28(3), 231-235.

Kuhlbusch, T. A. J., and P. J. Crutzen (1995), Toward a global estimate of black carbon in residues of vegetation fires representing a sink of atmospheric CO₂ and a source of O₂, *Global Biogeochem. Cycles*, 9(4), 491-501.

Laird, D., P. Fleming, B. Wang, R. Horton, and D. Karlen (2010), Biochar impact on nutrient leaching from a Midwestern agricultural soil, *Geoderma*, 158(3-4), 436-442.

Lamparter, A., J. Bachmann, M. O. Goebel, and S. K. Woche (2009), Carbon mineralization in soil: Impact of wetting–drying, aggregation and water repellency, *Geoderma*, 150(3–4), 324-333.

Lefroy, J. H. (1883), Remarks on the Chemical Analyses of Samples of Soil from Bermuda, edited, p. 35, Royal Gazette Office, Hamilton, UK.

Lehmann, J., M. Rillig, J. Thies, C. A. Masiello, W. C. Hockaday, and D. Crowley (2011), Biochar effects on soil biota - A review, *Soil Biol. Biochem.*, 43, 1812-1836.

Libra, J. A., et al. (2011), Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis, *Biofuels*, 2(1), 71-106.

Lin, Y., J. Cho, J. M. Davis, and G. W. Huber (2012), Reaction-transport model for the pyrolysis of shrinking cellulose particles, *Chem. Eng. Sci.*, 74(0), 160-171.

Lory, J. A., R. E. Massey, C. D. Fulhage, M. C. Shannon, R. L. Belyea, and J. M. Zulovich (2008), Comparing the feed, fertilizer, and fuel value of distiller's grains, *Crop Management, Online*, 7.

Mansur, D., M. Shimokawa, K. Oba, Y. Nakasaka, T. Tago, and T. Masuda (2012), Conversion of ethanol fermentation stillage into aliphatic ketones by two-step process of hydrothermal treatment and catalytic reaction, *Fuel Process. Technol.*, In Press(0).

McKendry, P. (2002), Energy production from biomass (part 2): Conversion technologies, *Bioresour. Technol.*, 83(1), 47-54.

Minkova, V., M. Razvigorova, M. Goranova, L. Ljutzkanov, and G. Angelova (1991), Effect of water vapour on the pyrolysis of solid fuels. 1. Effect of water vapour during the pyrolysis of solid fuels on the yield and composition of the liquid products, *Fuel*, 70(6), 713-719.

Miura, M., H. Kaga, A. Sakurai, T. Kakuchi, and K. Takahashi (2004), Rapid pyrolysis of wood block by microwave heating, *J. Anal. Appl. Pyrolysis*, 71(1), 187-199.

Mok, W. S. L., and M. J. Antal (1983), Effects of pressure on biomass pyrolysis. II. Heats of reaction of cellulose pyrolysis, *Thermochim. Acta*, 68(2-3), 165-186.

Mørup, A. J., P. R. Christensen, D. F. Aarup, L. Dithmer, A. Mamakhel, M. Glasius, and B. B. Iversen (2012), Hydrothermal liquefaction of dried distillers grains with solubles: A Reaction temperature study, *Energy & Fuels*, In Press.

Mukherjee, A., A. R. Zimmerman, and W. Harris (2011), Surface chemistry variations among a series of laboratory-produced biochars, *Geoderma*, 163(3-4), 247-255.

Mullen, C. A., A. A. Boateng, N. M. Goldberg, I. M. Lima, D. A. Laird, and K. B. Hicks (2010), Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis, *Biomass and Bioenergy*, 34(1), 67-74.

Nakamoto, T., and S. Wakahara (2004), Development of substrate induced respiration (SIR) method combined with selective inhibition for estimating fungal and bacterial biomass in humic Andosols, *Plant Production Science*, 7(1), 70-76.

Navarro, M. V., J. D. Martínez, R. Murillo, T. García, J. M. López, M. S. Callén, and A. M. Mastral (2012), Application of a particle model to pyrolysis. Comparison of different feedstock: Plastic, tyre, coal and biomass, *Fuel Process. Technol.*, 103(0), 1-8.

Nelson, K. A., P. P. Motavalli, and R. L. Smoot (2009), Utility of dried distillers grain as a fertilizer source for corn, *J. Agric. Sci.*, 1(1), 12.

OECD/FAO (2012), *OECD - FAO Agricultural Outlook 2012-2021*, 286 pp., OECD Publishing and FAO, Paris, France.

Overend, R. P. (1982), The average haul distance and transportation work factors for biomass delivered to a central plant, *Biomass*, 2(1), 75-79.

Parikh, J., S. A. Channiwala, and G. K. Ghosal (2005), A correlation for calculating HHV from proximate analysis of solid fuels, *Fuel*, 84(5), 487-494.

Pennanen, T., S. Caul, T. J. Daniell, B. S. Griffiths, K. Ritz, and R. E. Wheatley (2004), Community-level responses of metabolically-active soil microorganisms to the quantity and quality of substrate inputs, *Soil Biology and Biochemistry*, 36(5), 841-848.

Peterson, S. C. (2012), Evaluating corn starch and corn stover biochar as renewable filler in carboxylated styrene-butadiene rubber composites, *Journal of Elastomers and Plastics*, 44(1), 43-54.

Ponge, J.-F. (2012), Plant-soil feedbacks mediated by humus forms: A review, *Soil Biology and Biochemistry*, In press.

Rausch, K., and R. Belyea (2006), The future of coproducts from corn processing, *Appl. Biochem. Biotechnol.*, 128(1), 47-86.

Richmond-Aylor, A., S. Bell, P. Callery, and K. Morris (2007), Thermal degradation analysis of amino acids in fingerprint residue by pyrolysis GCMS to develop new latent fingerprint developing reagents, *Journal of Forensic Sciences*, 52(2), 380-382.

Sanna, A., S. Li, R. Linforth, K. A. Smart, and J. M. Andrésen (2011), Bio-oil and bio-char from low temperature pyrolysis of spent grains using activated alumina, *Bioresour. Technol.*, 102(22), 10695-10703.

Seredych, M., and T. J. Bandosz (2007), Mechanism of ammonia retention on graphite oxides: Role of surface chemistry and structure, *J. Phys. Chem. C*, 111(43), 15596-15604.

Shafizadeh, F. (1968), Pyrolysis and Combustion of Cellulosic Materials, in *Advances in Carbohydrate Chemistry*, edited by L. W. a. R. S. T. Melville, pp. 419-474, Academic Press.

Sharara, M. A., E. C. Clausen, and D. J. Carrier (2012), *An overview of biorefinery technology*, 321 pp., John Wiley & Sons Ltd., West Sussex, UK.

Shroyer, K. J., S. A. Staggenborg, and J. L. Propheter (2011), Utilization of dry distillers grains and charcoal as nitrogen fertilizer in corn, *Agron. J.*, 103(5), 1321-1328.

Shuangning, X., Y. Weiming, and B. Li (2005), Flash pyrolysis of agricultural residues using a plasma heated laminar entrained flow reactor, *Biomass Bioenergy*, 29(2), 135-141.

Smith, J. L., H. P. Collins, and V. L. Bailey (2010), The effect of young biochar on soil respiration, *Soil Biol. Biochem.*, 42(12), 2345-2347.

Spokas, K., J. Novak, and R. Venterea (2012), Biochar's role as an alternative N-fertilizer: Ammonia capture, *Plant Soil*, 350(1), 35-42.

Spokas, K. A. (2010), Review of the stability of biochar in soils: predictability of O:C molar ratios, *Carbon Management*, 1(2), 289-303.

Spokas, K. A., J. M. Novak, C. E. Stewart, K. B. Cantrell, M. Uchimiya, M. G. duSaire, and K. S. Ro (2011), Qualitative analysis of volatile organic compounds on biochar, *Chemosphere*, 85(5), 869-882.

Spokas, K. A., et al. (2012), Biochar: A synthesis of its agronomic impact beyond carbon sequestration, *Journal of Environmental Quality*, In press.

Taghizadeh-Toosi, A., T. Clough, R. R. Sherlock, and L. M. Condon (2011), Biochar adsorbed ammonia is bioavailable, *Plant and Soil*, In press.

Vaccari, F. P., S. Baronti, E. Lugato, L. Genesio, S. Castaldi, F. Fornasier, and F. Miglietta (2011), Biochar as a strategy to sequester carbon and increase yield in durum wheat, *European Journal of Agronomy*, 34(4), 231-238.

Vagia, E. C., and A. A. Lemonidou (2008), Thermodynamic analysis of hydrogen production via autothermal steam reforming of selected components of aqueous bio-oil fraction, *Int. J. Hydrogen Energy*, 33(10), 2489-2500.

Wan, Y., P. Chen, B. Zhang, C. Yang, Y. Liu, X. Lin, and R. Ruan (2009), Microwave-assisted pyrolysis of biomass: Catalysts to improve product selectivity, *J. Anal. Appl. Pyrolysis*, 86(1), 161-167.

Wang, D., D. Montané, and E. Chornet (1996), Catalytic steam reforming of biomass-derived oxygenates: Acetic acid and hydroxyacetaldehyde, *Applied Catalysis A: General*, 143(2), 245-270.

West, A. W., and G. P. Sparling (1986), Modifications to the substrate-induced respiration method to permit measurement of microbial biomass in soils of differing water contents, *J. Microbiol. Methods*, 5(3-4), 177-189.

Williams, P. T., and S. Besler (1996), The influence of temperature and heating rate on the slow pyrolysis of biomass, *Renewable Energy*, 7(3), 233-250.

Williams, P. T., and N. Nugranad (2000), Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks, *Energy*, 25(6), 493-513.

Wright, M. M., D. E. Daugaard, J. A. Satrio, and R. C. Brown (2010), Techno-economic analysis of biomass fast pyrolysis to transportation fuels, *Fuel*, 89, Supplement 1(0), S2-S10.

Yaman, S. (2004), Pyrolysis of biomass to produce fuels and chemical feedstocks, *Energy Convers. Manage.*, 45(5), 651-671.

Yao, Y., B. Gao, M. Zhang, M. Inyang, and A. R. Zimmerman (2012), Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil, *Chemosphere*, In press.

Yin, C. (2012), Microwave-assisted pyrolysis of biomass for liquid biofuels production, *Bioresour. Technol.*, 120(0), 273-284.

Yu, F., S. Deng, P. Chen, Y. Liu, Y. Wan, A. Olson, D. Kittelson, and R. Ruan (2007), Physical and chemical properties of bio-oils from microwave pyrolysis of corn stover, *Appl Biochem Biotechnol*, 137-140, 957-970.

Zhang, L., C. Xu, and P. Champagne (2010), Overview of recent advances in thermo-chemical conversion of biomass, *Energy Convers. Manage.*, 51(5), 969-982.

Zhang, Q., J. Chang, T. Wang, and Y. Xu (2007), Review of biomass pyrolysis oil properties and upgrading research, *Energy Convers. Manage.*, 48(1), 87-92.

Zimmerman, A. R. (2010), Abiotic and microbial oxidation of laboratory-produced black carbon (biochar), *Environ. Sci. Technol.*, 44(4), 1295-1301.

Zimmerman, A. R., B. Gao, and M.-Y. Ahn (2011), Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils, *Soil Biol. Biochem.*, 43(6), 1169-1179.