The Pyrolysis-Bioenergy-Biochar Pathway to Carbon-Negative Energy

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Abstract

Avoiding irreversible climate change requires >50% reduction in anthropogenic greenhouse gas (GHG) emissions by the year 2050 and the net removal of GHGs from the atmosphere by the end of the 21st century. This challenge is particularly daunting given that energy derived from fossil fuels is at the core of all modern economies and some sectors of the economy, such as transportation, will be almost impossible to completely decarbonize. To address this challenge, we are investigating the integrated pyrolysis-bioenergy-biochar platform (PBBP) to determine whether this system can produce economically viable carbon-negative energy products. Use of the biochar co-product as a soil amendment is the key to transforming bio-oil and other energy products produced by fast-pyrolysis of biomass from near carbon neutral to carbon negative. This is so because the half-life of biochar C in soil environments is approximately 1000 years.

Major accomplishments during the first two years of our project include the design and development of a biochar module within the Agricultural Production Systems Simulator (APSIM), a widely used and publically available cropping systems model. The APSIM Biochar Model provides for the first time a means of systematically investigating complex soil-biochar-crop-climate-management interactions, and critically a means of estimating the agronomic and environmental impacts of soil biochar applications. Much effort during the second year of the project was focused on quantifying and developing a mechanistic understanding of how biochar influences nitrogen dynamics and bioavailability in soil environments. Sorption of nitrate and ammonium by biochar were shown to be strongly dependent on pH and peak pyrolysis production temperature. We also focused on developing a rapid method for determining the size and properties of the labile and recalcitrant biochar fractions, as these are needed to accurately parametrize “biochar quality” within the APSIM Biochar Model. And, we made substantial progress in calibrating and validating the APSIM Biochar Model using literature data from globally diverse field and laboratory experiments.

Techno-economic analysis (TEA) of the PBBP was used to determine the minimum fuel selling price (MFSP) and lifecycle GHG emissions for a 1000 dry ton per day fast pyrolysis plant. Both MFSP and GHG emissions were shown to be strongly dependent on the ash content and O/C ratio of the biomass feedstock. The results indicate a trade-off between economic and environmental benefits based on feedstock selection. The MFSP for 346 different feedstocks range from $2.3/gal to $4.8/gal of liquid fuels in the diesel/gasoline range. The TEA demonstrated that the PBBP has the potential to produce carbon negative energy products even when indirect land use and synergistic agronomic and environmental effects of soil biochar applications are discounted.

During the third year of the project we will focus on completing on-going laboratory and field studies designed to improve and validate the APSIM Biochar Model and on integrating output from the APSIM Biochar Model with econometric, TEA, and lifecycle assessments of the economic viability and environmental impact of the PBBP for three case studies; the upper Mississippi River basin, California, and the U.S. Southeast.
Introduction

Avoiding irreversible climate change requires >50% reduction in anthropogenic greenhouse gas (GHG) emissions by the year 2050 and the net removal of GHGs from the atmosphere by the end of the 21st century [1]. To address the need to remove GHG from the atmosphere, we are investigating the integrated pyrolysis-bioenergy-biochar platform (PBBP) for the production of carbon-negative energy (Figure 1). Bio-oil and non-condensable gases produced by fast pyrolysis of biomass are sources of potentially viable liquid transportation fuels, heat, power, bio-asphalt, and other products that can offset fossil fuels [2]. Biochar, the condensed aromatic carbon-rich solid co-product of biomass pyrolysis, is a soil amendment that is effective for sequestering carbon for centuries, if not millennia, while improving soil quality and reducing leaching of nutrients [3, 4]. The key challenge for scaling up the PBBP industry is the identification of economically-viable markets for both the bioenergy and biochar co-products.

Figure 1: The integrated pyrolysis-bioenergy-biochar platform has the potential to provide carbon negative energy products and multiple ecosystem services.

The overall goals of our project are: 1) To advance basic understanding of the impacts of biochar on agroecosystems; 2) to assess the technical and economic viability of an integrated pyrolysis-bioenergy-biochar industry in the Upper Mississippi River Basin (UMRB), California, and U.S. Southeast; 3) to assess regional and global impacts of an integrated pyrolysis-bioenergy-biochar industry on indirect land use and net GHG emissions; and 4) to build a foundation for the development of a vanguard economically-viable carbon-negative integrated pyrolysis-bioenergy-biochar industry. The proposed research systematically builds capacity to achieve these goals through the following specific objectives:
1) Develop, parameterize, and validate a biochar module for the *Agricultural Production Systems sIMulator* (APSIM).

2) Quantify the public and private benefits accrued from integrating biochar into pyrolysis-based bioenergy production systems for three case studies.

3) Use techno-economic analysis to assess the economic performance of pyrolysis plants producing bioenergy and biochar co-products and use life cycle assessments to determine the net GHG emissions from an integrated pyrolysis-bioenergy-biochar production facility.

4) Estimate carbon credits for indirect land use avoidance and compare system production costs.

**Background**

**Political:** The outcome of the 2016 US presidential and congressional elections have resulted in a shift in US political priorities, which have dimmed the prospects for large scale commercialization of the PBBP in the US in the near future. As long as the environmental costs associated with fossil fuels are externalized and the environmental benefits associated with the PBBP are discounted, it will be difficult for the PBBP to compete with fossil fuels on the large scale. However, the small scale biochar industry is still growing rapidly in the US; entrepreneurs are primarily targeting niche high-value markets for biochar in horticulture, land reclamation, and organic agriculture. Most of the small biochar production facilities use slow pyrolysis or gasification and are either not capturing the bioenergy co-products or are producing process heat and/or electricity rather than liquid biofuel products. The industry is also targeting feedstocks which can be obtained for little or no cost, such as orchard trimmings and bark beetle killed tress harvested to suppress fire in the intermountain west.

On a global scale, the Paris Climate Agreement, which went into effect in October 2016, highlighted the need for carbon negative systems to offset GHG emissions from sectors of the global economy that will be extremely difficult to de-carbonize. While there are many opportunities to reduce GHG emissions through improved energy efficiency, there are relatively few identified opportunities for industrial scale systems that on net remove CO₂ from the atmosphere. The two most prominent carbon negative systems are Bioenergy Carbon Capture and Sequestration (BECCS), where biomass is burned directly or co-fired with fossil fuel to generate electricity and the emitted CO₂ is captured and geologically sequestered, and PBBP (also called bioenergy-biochar systems; BEBCS). A recent paper published in Science [5] compared the economic prospects for PBBP with BECCS and concluded that PBBP is economically more viable for carbon prices below $1000 Mg⁻¹ C. Hence, when policy makers finally choose to seriously address climate change, the PBBP is poised to assume a prominent role in that effort.

China is emerging as a global leading for biochar research (Figure 2) and is likely to be the first country with wide-spread commercialization of the PBBP. China has severe air quality problems stemming in part from the widespread practice of burning crop residues. China also has severe soil contamination problems, a critical need to improve nutrient and water use efficiency in agricultural production, and a rapidly growing demand for both food and energy. All of these issues can be partially addressed through PBBP [6].
Various biorenewable energy production technologies have been investigated in order to reduce the country’s dependence on foreign energy, enhance energy security, utilize excess agricultural resources and mitigate environmental concerns [7]. Biorenewable resources can be converted into bioenergy, transportation fuels, chemicals and fibers through biochemical and thermochemical conversion technologies. Here we focus on pyrolysis, the thermochemical conversion of biomass feedstocks in the absence of oxygen into various gas (non-condensable gases), liquid (bio-oil), and solid (biochar) co-products. Although it has a relatively low energy density, the non-condensable gas can be combusted to generate heat and/or power. Bio-oil, a viscous and dark-brown fluid with water content of 15-20%, can be refined to produce liquid fuels and other products [9]. Biochar is primarily used as a soil amendment because it has the potential to sequester carbon, improve soil quality, and increase plant productivity.

Pyrolysis technologies are broadly categorized, based on different reaction conditions, as fast pyrolysis, slow pyrolysis, catalytic pyrolysis, and autothermal fast pyrolysis. Fast pyrolysis is a rapid (~2s) thermochemical conversion technology operating at moderate temperatures (typically ~ 500°C) [8]. Fast pyrolysis systems are optimized for the production of bio-oil. Production of bio-oil is maximized (up to 75 wt%) under fast pyrolysis temperatures of around 500°C. Slow Pyrolysis has a lower heating rate of 0.1-1°C/s compared to fast pyrolysis (10-200°C/s) [8], and higher yield of biochar around 25-35 wt % [10]. The autothermal fast pyrolysis operates by inserting oxygen into the pyrolysis reactor at equivalence ratios of about 0.05 to provide heat for the endothermic pyrolysis decomposition reactions by partially oxidizing the biomass. Autothermal fast pyrolysis could reduce operating cost and increase commercialization feasibility because it does not require external heat supply [11–13].

Raw bio-oil has several undesirable properties, such as high water content, high viscosity, high ash content, high oxygen content and high corrosiveness [8], which make it less...

Figure 2: Numbers of refereed publications listed in the Web of Science database identified by the topic word “biochar”. Red indicates the number of publications originating from the USA, green from China, and blue from the rest of the world. Web of Science accessed 5-3-17.
competitive relative to petroleum. Several studies, which have investigated bio-oil upgrading to biofuels, focused mainly on hydrotreating, hydrocracking, and fluid catalytic cracking (FCC) [14]. Catalytic pyrolysis is a combination of fast pyrolysis and catalytic upgrading processes. Biomass is decomposed and hydrotreated in the same reactor in the presence of catalysts or the pyrolysis vapor can be catalytically upgraded to less reactive compounds subsequently [15-17]. Therefore, it can be grouped as *in-situ* and *ex-situ* catalytic pyrolysis, depending on whether catalytic upgrading takes place within or following the pyrolysis reactor. Autothermal fast pyrolysis is a relatively new technology. Bio-oil can be upgraded into transportation fuels, chemicals, heat and power with physically, chemically and catalytically upgrading processes.

Techno-economic analysis (TEA) studies of fast pyrolysis of biomass to produce different products have been conducted for several years. Wright et al. [2] evaluated the MFSP of converting corn stover to naphtha- and diesel-range stock fuel via fast pyrolysis as $3.09/gal and $2.11/gal for the hydrogen production and hydrogen purchase scenarios, respectively. The capital cost for the nth plant for the hydrogen production scenario is estimated as $287 million, while for the hydrogen purchase scenario capital cost is assessed as $200 million. Pacific Northwest National Laboratory (PNNL) has done a TEA study to evaluate the economic cost of the fast pyrolysis conversion of lignocellulosic biomass to hydrocarbon fuels [18]. The MFSP is evaluated as $3.34/gal for gasoline blendstock and the capital investment for the whole pyrolysis and upgrading process is calculated as $700 million. A study of producing biofuels, biochemical and hydrocarbon chemicals via fast pyrolysis of red oak has compared the economic performance among different products scenarios [19]. The MPSPs for biofuel production, biochemical production and hydrocarbon chemicals production have been estimated as $3.09/gal, $433.7/MT and $773.5/MT, respectively. Dang et al. [20] investigated the economic and environmental performance of producing ultra-low carbon emissions by co-firing bio-oil with coal. The economic results from this study suggests a minimum carbon price of $67.4 ± 13 per metric ton of CO2-eq could make the bio-oil co-firing fuel commercially viable and competitive.

Production, characteristics and potential applications for biochar from various feedstock have been widely studied. Biochar derived from six waste biomass sources: pine sawdust, paunch grass, broiler litter, sewage sludge, dewatered pond sludge and dissolved air-floatation sludge were recently analyzed and compared [21]. All six kinds of biochar contained low levels of heavy metals, which indicate their feasibility of being used as soil amendments. Biochar from pine sawdust was recommended due to its high surface area, high aromaticity, high carbon content, and low ash content. Biochar produced from commercially cultivated seaweed has also been investigated [22]. Seaweed biochar contains low carbon content and surface area, but high yield, essential mineral nutrients (N, P, and K), and exchangeable cations. The pH of seaweed biochars ranges from 7 to 11. The study concluded that blending seaweed biochar with lignocellulosic biochar might have the most potential to improve the soil quality. Another study [23] compared the profitability of biochar production via slow and fast pyrolysis. Producing biochar via slow pyrolysis is not profitable although it produces more biochar compared to fast pyrolysis. The profitability depends not only on the biochar yields, but also the value of the main energy product. The two main products of slow pyrolysis are pyrolysis gas
(64% of dry biomass) and biochar (36%), while fast pyrolysis mainly produces bio-oil (53%) and biochar (26%). This study estimated capital costs for slow pyrolysis and fast pyrolysis as $132MM and $200MM, respectively. Minimum product selling price for biofuel and biochar were estimated as $2.68/gal (with a biochar value of $20/t) and $346/t for fast pyrolysis case.

Much of the current understanding of physical and chemical properties of biochar and the impact of biochar applications on soil properties, environmental outcomes, and crop productivity was summarized in the 2015 edition of *Biochar for Environmental Management*, edited by J. Lehmann and S. Joseph [24]. In brief, agronomic research has shown that soil biochar amendments commonly increase agricultural production on marginal and degraded lands but may have little or no yield impact on well-managed, high-quality soils. Laboratory and field research in soil science has identified some of the mechanisms by which biochar enhances soil quality, and hence crop productivity. For example, biochar has been shown to reduce soil bulk density and increase soil porosity, both of which improve the rooting environment and hence stimulate plant growth. Biochar has also been shown to increase nutrient- and water-holding capacity of most soils and especially sandy, low-organic matter, and otherwise degraded soils. The literature also shows that soil biochar amendments are effective means of sequestering carbon and reducing N$_2$O emissions, although the nature of interactions between biochar and biogenic soil organic matter (soil humus) remains controversial. Although much of the scientific literature has reported positive agronomic and environmental outcomes, there are also reports finding no effect and even adverse outcomes from the use of biochar. Understanding and predicting positive and negative outcomes resulting from soil biochar applications is made difficult by the diversity of biochar physical and chemical properties, changes in the properties of biochar that occur with time (biochar aging), and complex soil-biochar-crop-climate-management interactions.

**Results**

*Objective 1: Develop, parameterize, and validate a biochar module for the Agricultural Production Systems sIMulator (APSIM).*

*Building the APSIM Biochar model:* We reported last year on the development of a mechanistic biochar model within the APSIM simulation platform [25]. This is the first worldwide comprehensive simulation model for biochar that can concurrently evaluate biochar impacts on soil properties such as bulk density, plant available water content, soil processes such soil organic carbon dynamics and N cycling, greenhouse gas emissions (N$_2$O and CO$_2$), and crop yield (Figure 3).
This year we report on our continuing efforts to update, calibrate, and validate the biochar model and an initial report on develop of a new stochastic model, which will allow users to identify the probability of obtaining a positive crop yield response from biochar applications.

Inorganic nitrogen adsorption by biochars: The capacity of biochars to adsorb NH$_4^+$ and NO$_3^-$ in soil environments will influence plant available N, N leaching and fertilizer N use efficiency in cropping systems and hence is a critical component of the APSIM biochar model. Here we quantified NH$_4^+$ and NO$_3^-$ sorption by acid-washed biochars produced from red oak and corn stover at three pyrolysis temperatures (400, 500 and 600°C; see Table 1), over a range of sorbate solution pHs (3.5-7.5); we furthermore examine sorption mechanisms by concurrent quantification of NH$_4^+$ and NO$_3^-$ sorption and Ca$^{2+}$ and Cl$^-$ displacement for corn stover biochars. Solution pH curves showed that NH$_4^+$ sorption was highest (0.9-1.0 mg N g$^{-1}$) for low temperature (400°C) biochars at high solution pHs (7.0-7.5) (Figure 4), whereas NO$_3^-$ sorption was highest (1.2-1.3 mg N g$^{-1}$) for high temperature (600°C) biochars at low solution pHs (3.5-4) (Figure 5). Compared with the biochar production temperature effects on sorption, feedstock effects were minimal. The

**Figure 3:** A simplified diagram illustrating APSIM’s soil carbon (top left panel), soil nitrogen (bottom left panel), soil water (top right panel) and crop (bottom right panel) modules. Boxes are state variables, solid arrows are rate variables and indicate material flow (e.g. carbon), broken arrows indicate information flow (e.g. priming), and circles are intermediate variables. Driving variables for the system (green circles at the top) include weather, soil, crop, and management. Shown in red are the state, rate, and intermediate variables that we hypothesize to be influenced by biochar amendments. RES, surface residue; FOM, fresh organic matter; BIOM, microbial pool; HUM, humic pool; INERT, inert pool; SAT, saturation point; DUL and LL, drained upper and lower limits; KL, parameter defining the ability of the roots to take up water; CEC, cation exchange capacity; and BD, soil bulk density. Figure from Archontoulis et al., [25].
Langmuir model provided the best fits on average for both NH$_4^+$ (pH 7) and NO$_3^-$ (pH 3.7) sorption isotherms of the corn stover biochars ($r^2 = 0.90-0.99$), suggesting that biochars contain a finite number of sorption sites that are progressively filled as solution concentration increases (Figure 6). The adsorption of NH$_4^+$ and NO$_3^-$ are accompanied by displaced Ca$^{2+}$ and Cl$, respectively, from CaCl$_2$-saturated corn stover biochars, suggesting solution electrolyte competition for adsorption sites (Figure 7). The combined evidence from pH curves, Langmuir isotherms, and ion displacement studies supports a predominantly electrostatic adsorption mechanism for both NH$_4^+$ and NO$_3^-$, and demonstrates that both cation and anion sorption sites are pH dependent. Overall results emphasize the importance of solution pH, solution ion concentration and biochar pyrolysis temperature while highlighting trade-offs between NH$_4^+$ and NO$_3^-$ sorption. The results also demonstrate that it is possible to engineer biochars with high NH$_4^+$ and NO$_3^-$ sorption capacities.

### Table 1 Biochar abbreviations, feedstocks, slow pyrolysis temperatures, element percentages (by mass) and element ratios (molar).

<table>
<thead>
<tr>
<th>Biochar</th>
<th>Feedstock</th>
<th>Pyrolysis Temperature</th>
<th>%C</th>
<th>%N</th>
<th>%H</th>
<th>%S</th>
<th>C:N</th>
<th>H:C</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO4s</td>
<td>Red oak</td>
<td>400°C</td>
<td>79.1 ±1.1</td>
<td>0.22 ±0.02</td>
<td>4.07 ±0.03</td>
<td>0.08 ±0.05</td>
<td>431 ±33</td>
<td>0.617 ±0.005</td>
</tr>
<tr>
<td>RO5s</td>
<td>Red oak</td>
<td>500°C</td>
<td>86.1 ±0.8</td>
<td>0.25 ±0.01</td>
<td>3.26 ±0.03</td>
<td>0.02 ±0.01</td>
<td>409 ±22</td>
<td>0.454 ±0.004</td>
</tr>
<tr>
<td>RO6s</td>
<td>Red oak</td>
<td>600°C</td>
<td>91.6 ±0.5</td>
<td>0.3 ±0.05</td>
<td>2.49 ±0.03</td>
<td>0.01 ±0.01</td>
<td>370 ±68</td>
<td>0.326 ±0.003</td>
</tr>
<tr>
<td>CS4s</td>
<td>Corn stover</td>
<td>400°C</td>
<td>73.2 ±0.5</td>
<td>1.2 ±0.01</td>
<td>4.14 ±0.04</td>
<td>0.1 ±0.06</td>
<td>71 ±1</td>
<td>0.678 ±0.003</td>
</tr>
<tr>
<td>CS5s</td>
<td>Corn stover</td>
<td>500°C</td>
<td>78.7 ±0.2</td>
<td>1.15 ±0.01</td>
<td>3.13 ±0.03</td>
<td>0.06 ±0.01</td>
<td>78 ±3</td>
<td>0.476 ±0.003</td>
</tr>
<tr>
<td>CS6s</td>
<td>Corn stover</td>
<td>600°C</td>
<td>82.2 ±0.7</td>
<td>1.06 ±0.05</td>
<td>2.31 ±0.03</td>
<td>0.05 ±0.01</td>
<td>90 ±4</td>
<td>0.338 ±0.003</td>
</tr>
</tbody>
</table>

**Figure 4**: Ammonium sorption from a 10 ppm NH$_4^+$-N solution by a) red oak biochars (RO) and b) corn stover (CS) biochars per g of biochar (pH adjusted by addition of Ca(OH)$_2$). Numbers in the biochar names indicate peak slow (S) pyrolysis temperatures: 4s = 400°C, 5s = 500°C, and 6s = 600°C.
Figure 5: Nitrate sorption from a 10 ppm NO₃⁻-N solution by a) red oak biochars (RO) and b) corn stover (CS) biochars per g of biochar (pH adjusted by addition of Ca(OH)₂). Numbers in the biochar names indicate peak slow (s) pyrolysis production temperatures: 4s = 400°C, 5s = 500°C, and 6s = 600°C.

Figure 6: Langmuir sorption isotherms showing sorption (Q) of a) NH₄⁺ and b) NO₃⁻ to corn stover biochars as a function of initial concentration (C).

Figure 7: Displacement of a) Ca²⁺ by NH₄⁺ from corn stover 400°C (CS4s) biochar at pH 7 (see Figure 3a for sorption isotherm), and b) displacement of Cl⁻ by NO₃⁻ from corn stover 600°C (CS6s) biochar at pH 3.7 (see Figure 3b for sorption isotherm).
Results of this study indicate that soil pH and biochar production temperature have a large influence on the ability of biochar to adsorb NO$_3^-$ and NH$_4^+$. The results further indicate that biochars produced at high temperatures (~600°C) may have a high agronomic value because of their ability to retain NO$_3^-$. Nitrogen fertilizer is the largest annual input cost for corn production and a major input cost for many other cropping systems. The inefficient use of N fertilizer by cropping systems is a major economic loss to farmers and the cause of serious environmental problems, such as the hypoxic or “dead zone” in the Gulf of Mexico. The results of this study indicate the potential to engineer biochars that will increase soil retention of NO$_3^-$ and/or NH$_4^+$ and thereby improve N fertilizer use efficiency by crops.

Updates for an ongoing study designed to determine the effects of biochar on nitrogen mineralization and nitrification: Understanding the capacity of biochar to adsorb NO$_3^-$ and NH$_4^+$ is critical; however to improve N use efficiency in crop production it is also necessary to understand how biochar additions influence N cycling in soils. Here we report on the results of an on-going study which is evaluating the impact of various types of biochar on N mineralization and nitrification in soils.

Interactions between soil type, biochar type, and biochar aging may influence N cycling in soils. To gain a better understanding of biochar impacts on N mineralization and nitrification (gross N transformation process), a $^{15}$N tracer study in combination with numerical data analysis has been employed using both fresh and laboratory-aged fast pyrolysis biochars and three soil types (sand, silt, and clay). Soils were incubated with biochars (1% w/w) and sub-samples were taken at day 0. Those sub-samples were then incubated with isotopically labeled N-fertilizer ($^{15}$NH$_4$Cl; application rate of 170 lbs-N/acre) for 0, 3, 7, 14, 35, 63, and 98 days. Moisture content was maintained at field capacity (-0.33 bar matric potential) during the incubation. Measurements of NH$_4^+$ and NO$_3^-$ concentrations and $^{15}$N:$^{14}$N ratios are being used to assess the impact of biochar on both gross and net N mineralization and nitrification rates in the soils.

Preliminary findings show that the NH$_4$-N pool decreased significantly (P<0.05) within 7 d for all fertilizer treated soil-biochar mixtures (Fig. 8). For the sandy soil with fertilizer addition, a paired t test indicated no significant difference (Pearson correlation = 0.998 for HF, 0.998 for SF, and 0.994 for CF) between any of the fresh and laboratory aged biochar pairs, nor was there a significant biochar effect (Pearson correlation ≥ 0.997 for all cases) on ammonification considering the whole 98 d incubation. For the sandy soil without fertilizer, the same trend was observed as fertilizer treated soil with no significant difference for biochar age and biochar addition treatments (Pearson correlation ≥ 0.95 for all cases). The NH$_4$-N pool in the loam soil decreased rapidly within the first 7 days of the incubation and remained stable thereafter at low levels for the remainder of the incubation. The NH$_4$-N pool in the clay soil behaved differently; the NH$_4$-N pool initial decreased until day 14 and thereafter there were periodic increases in the NH$_4$-N pool which varied by treatment, indicating higher rates of N mineralization. The NO$_3$-N pool increased significantly (P<0.05) through day 7 of the incubation for all fertilizer treated systems, and then stabilizing at ~60 mg-N kg$^{-1}$ for the remainder of the incubation.
Based on a paired t test, no significant differences (Pearson correlation $\geq 0.995$ for all cases) were found for the biochar aging effect or the biochar addition effect for the sandy soils, however the hardwood fast pyrolysis biochar (HF) increased the NO$_3$-N pools ($P<0.05$) for the fertilizer treated loam and clay soils. For the loam soil, the HF-LA treatment had $\sim 22\%$ more NO$_3$-N than the HF-F on day 0 and this difference increased to $\sim 28\%$ by day 14, and then declined to $\sim 7\%$ by the end of incubation. Similarly, for clay soil, the HF-LA treatment had $\sim 7.5\%$, $27\%$, and $4.5\%$ more NO$_3$-N than the HF-F treatment on day 0, day 14, and at the end of the incubation, respectively. For soil-biochar systems incubated without fertilizer the size of the NO$_3$-N pool was strongly influenced by soil type with the biochar treatments having differential effects.

Based on the data we have so far (dynamics of the total NO$_3$-N and NH$_4$-N pools), we see a substantial soil texture effect, but little biochar or biochar age effect, on N-dynamics. The samples from this incubation study are currently being analyzed to determine $^{15}$N:$^{14}$N ratios. The results of the isotope analysis will allow us to distinguish between net and gross N mineralization. We hypothesize that the biochar treatments will have a larger influence on gross N mineralization. Agronomically the results of this study are critical as they will allow us to predict the impact of biochar amendments on N-dynamics in soil systems, which will impact N fertilization recommendations and the economic viability of biochar applications. When the study is complete the results will be factored into the APSIM biochar model.

**Figure 8:** Effects of biochar additions and biochar age on dynamics of the total soil NO$_3$-N and NH$_4$-N pools with and without fertilizer additions. Treatment abbreviations: LA=lab aged, F=fresh, ammon=NH$_4$, nit=NO$_3$. Biochar abbreviations: HF=hardwood fast pyrolysis, SF=soybean fast pyrolysis, CF=corn stover fast pyrolysis, Control=no biochar amendment.

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**Update on assessment of biochar labile and recalcitrant C pools:** The new biochar module in the APSIM cropping systems model assumes that biochar C and N are divided into labile and recalcitrant fractions (or pools). Currently, volatile matter and fixed carbon as determined by proximate analysis are used to estimate the size of the labile and
recalcitrant pools, respectively. We are assessing the validity of using proximate analysis to quantify the size of the biologically labile and recalcitrant biochar pools and developing a means of determining the C:N ratio of the biologically labile fraction. The specific goal of this study is to evaluate various chemical fractionation schemes for biochars, which allow the C:N ratio of the labile fraction to be rapidly determined, and compare the results of the chemical fractionations with results for proximate analysis and biological incubations.

Nine biochars produced from five biomass feedstocks (hardwood, corn stover, soybean stover, switchgrass and macadamia nut shells) using four thermochemical techniques (gasification, slow pyrolysis, fast pyrolysis, and autothermal fast pyrolysis) were used in the study. The inorganic C fraction of biochar was determined by measuring CO₂-C released on reaction with 1M HCl. Acid and base labile organic C was progressively extracted in seven steps using hot water, 0.05M, 0.5M, 1M, 2M, 3M, and 6M of either H₂SO₄ or NaOH. The fraction of biochar C oxidized with 15% H₂O₂ and 0.33M KMnO₄ (pH 7.2) was also determined. All extracted solutions were analyzed for dissolved organic carbon and nitrogen and the residues were evaluated separately by proximate and ultimate analysis. Volatile matter as determined by proximate analysis was compared with the amounts of organic C extracted using hot water and the various acid, base, and oxidation treatments.

The amount of C extracted, oxidized, or volatilized from the biochars by the various treatments ranged from 0.06 to 76% of total C (Fig. 9). The KMnO₄ treatment was the most effective, removing on average 51.8% of total C from the studied biochars. A trend of decreasing C removal with increasing base concentration was observed for all samples except the HA biochar. By contrast, the effect of acid strength on the amount of extractable C was inconsistent. The amount of C oxidized with KMnO₄ was significantly correlated with the amount of C extracted with hot water (R²=0.687; P < 0.05) but not with the amount of C removed by any of the other treatments (P > 0.05). No significant correlation (P > 0.05) was found between the amount of C volatilized by the thermal treatment and the amount of C extracted or oxidized by any other treatments. In general, fast pyrolysis biochars had more chemically extractable or oxidizable C than the slow pyrolysis biochars; however no consistent pattern is evident among feedstocks for C removed. The amount of N extracted, oxidized or volatilized from the studied biochars by the various acid, base, hot water, oxidation, and thermal treatments ranged from 6.6 to 92.6% of total N (Fig. 9). The largest fraction of total N was removed by the KMnO₄ treatment (average 63.6%) followed by the hot water, 0.05 M acid, and H₂O₂ treatments, which averaged 41.1, 40.5, and 37.0% of total N, respectively. In general, fast pyrolysis biochars had more chemically extractable or oxidizable N than the slow pyrolysis biochars, however, no clear trend relative to feedstock was evident for the fraction of total N removed. These results indicate that the various acid and base extractions, oxidation, and thermal volatilization treatments differentially extract C and N from the various biochars.

The ash-free mass extracted, oxidized or volatilized from the studied biochars by the various acid, base, hot water, oxidation, and thermal treatments ranged from -14.9 to
67.2% of total ash-free mass (Fig. 9). The largest average mass loss was for KMnO₄, 0.05 M base, and H₂O₂ treatments, which averaged 37.5, 30.9, and 26.7%, respectively; while the least mass loss was associated with the 1 M and 3 M base treatments, which averaged 14.8 and 7.5%, respectively. The ash-free mass loss for the KMnO₄ treatment was significantly correlated with the ash-free mass loss for the hot water, H₂O₂, and thermal treatments ($r² = 0.884, 0.788,$ and 0.561, respectively), but not with ash-free mass loss for any of the acid or base extractions.

These results suggest that addition reactions occur under both acidic and basic conditions, which would preclude the use of acid or base extractions for assessing the mass of the chemically labile fraction of biochars. Proximate analysis preferentially removes O and H from the biochars relative to C. The KMnO₄ treatment preferentially removes C from the biochars and the amount of C removed from the biochars by the H₂O₂ treatment was not correlated with the mass loss. The 1:1 relationship between the C extracted and ash-free mass loss observed for the hot water treatment (Fig. 9), indicates that the hot water treatment conservatively extracts a fraction of total biochar C. In general, N was enriched in the extracts relative to the original biochars, suggesting that high N biochars could be a slow release source of N fertility.

Our goal in this research is to develop a rapid chemical or thermal assay that can be used to a priori predict the size and properties (C:N ratio and stability) of the biologically labile and recalcitrant biochar fractions, because these are critical biochar quality input parameters in the APSIM biochar model. Thus we are also conducting a long-term incubation study to quantify the size and properties of the biologically labile and thermally labile and recalcitrant biochar fractions (Fig. 9) discussed above.

The on-going long-term incubation study is using the same nine biochars that were used to assess the chemically and thermally labile and recalcitrant biochar fractions. The biochars are being incubated in a sand matrix with a moisture content held at field capacity. Initially all necessary nutrients were added except C (biochar C is the only source of C), however to stimulate biologically activity periodically $^{13}$C labeled glucose is being added to the systems. By using labeled glucose we are able to differentiate CO₂-C coming from biochar $^{12}$C and glucose $^{13}$C. During the first 30 days following addition

**Figure 9:** Relationship between the percent of total C and total N removed by the various hot water, acid, base, oxidation, and thermal treatments and the amount of ash-free mass lost during the treatments.
of glucose, biochar type affected both biochar C mineralized and glucose C mineralized (Fig. 10). The most biochar C was mineralized from the fast pyrolysis biochars (1.2-5.1 mg CO₂-C per g of biochar-C), whereas the least amount of C was mineralized from slow pyrolysis biochars (0.6-0.8 mg CO₂-C/g biochar-C). By comparison, the autothermal hardwood biochar (HA) lost slightly less C than the hardwood fast pyrolysis biochar (1.3 mg CO₂-C/g biochar-C compared with 1.6 mg CO₂-C/g biochar-C). The gasification switchgrass biochar (GG) lost about the same amount of C as the slow pyrolysis switchgrass biochar (GS) (0.6-0.7 mg CO₂-C/g biochar-C). In most cases, a similar or greater amount of glucose-C was lost as CO₂ compared with biochar C (equivalent to 8-34% of glucose C added) (Fig. 10). An exception was the macadamia nut shell biochar (MF), for which >2x more glucose C was respired than biochar C. Among fast pyrolysis biochars, biochar C mineralized increased in the order MF<HF<CF<SF, whereas glucose C respired increased in the order HF<CF~MF<SF (feedstock had a minimal effect among slow pyrolysis biochars). These feedstock differences were likely due to differences in biochar physical structure and labile C:N ratios.

**Figure 10:** Mineralization of biochar-C and added glucose-C during the first 30 days of the long-term incubation study designed to determine the fractions of biologically labile and recalcitrant C in biochars.

Preliminary results from the long-term (one year) incubation study suggest that biochars produced by fast pyrolysis contain the more labile C than biochars produced by slow pyrolysis and gasification. The preliminary results also indicate that mineralized glucose C and mineralized biochar C are correlated and that a large amount of the added glucose C was immobilized in the biochar amended systems. The long-term incubation study is scheduled for completion during the summer of 2017. After completion we will relate the biologically labile and recalcitrant C and N to the various measures of chemically and thermally labile C and N, and prepare a manuscript document the findings.

**Impact of biochar amendments on soil organic C and N concentrations and N dynamics under field conditions:** Laboratory incubations do not always correspond quantitatively with field observations; hence it is also important to assess the influence of biochar on soil C and N dynamics under field conditions. To this end, we maintain long-term biochar field trials on the Agronomy and Agricultural Engineering Research Farm (Field 70/71), the ISU Sorenson Farm (long-term rotation plots), the ISU Boyd Farm (Biochar
rate trials), and the ISU Armstrong Research and Demonstration Farm (Bioenergy cropping systems trials).

The long-term rotation plots on the ISU Sorenson Farm are assessing the effects of various bioenergy cropping systems on biomass and grain productivity and the impacts of the cropping systems and biochar amendments on soil quality and carbon sequestration. The plots were established in 2006 and biochar was applied following a corn phase in split plots after the first complete 6-year rotation cycle. The crop rotations include: continuous no-tillage corn (Rot 1), alternating corn-soybean (Rot 2), corn soybean-triticale/soybean-corn-soybean-triticale/soybean (Rot 3), corn-corn-corn/switchgrass switchgrass-switchgrass-switchgrass-switchgrass (Rot 4), and continuous switchgrass (Rot 5). All above ground corn stover, switchgrass and triticale biomass has been harvested (simulated biomass harvesting for bioenergy production). Soil samples were collected at time zero (2006) and again after 10 years (2016) to quantify the long-term effects of the cropping systems and biochar amendments on soil organic C and N levels (Fig. 11).

Figure 11: Total soil C (left) and N (right) by rotation measured in 2006 and 2016 for biochar and no-biochar treatments. Values are the averages of four field replicates with standard error bars. Different letters indicate significant differences between biochar and no-biochar treatments within a rotation (P < 0.05). Significant differences between rot. 5 and the no-biochar plots from 2006 and 2016 are indicated by an asterisk (*). Rot 1: continuous corn, Rot 2: alternating corn-soybean, Rot 3: corn soybean-triticale/soybean-corn-soybean-triticale/soybean, Rot 4: corn-corn-corn/switchgrass switchgrass-switchgrass-switchgrass-switchgrass, Rot 5: continuous switchgrass.

The Armstrong bioenergy cropping systems research trials are comparing the effects of biochar and cropping systems, continuous no-tillage corn (Corn), low diversity prairie (LD), high diversity prairie (HD) and bioenergy (Liberty) switchgrass (SG), on biomass production, GHG emissions, and soil quality. The LD and HD prairies were seeded in 2012, however drought in 2012 delayed stand establishment. The LD prairie was well established by 2015, while the HD prairie is still struggling with weed completion. Because of the 2012 drought, the Liberty switchgrass had to be reseeded in 2013 and good stands were achieved by 2015. Here we report on the effects of these systems on N dynamics.
Averaged across three years (2014-2016), which includes 2014 before the perennial crops were fully established, there is no effect of biochar on KCl extractable NO$_3^-\text{-N}$ and NH$_4^+\text{-N}$ (0-15 cm) concentrations, while biochar had a marginally significant ($P<0.06$) effect on potentially mineralizable nitrogen (PMN; Table 2). By 2016 growing season, the SG and LD systems were well established while the HD system was still developing. For the fall 2016 sampling, biochar significantly ($p<0.05$) decreased soil NH$_4^+\text{-N}$ concentrations and increased PMN under the LD plant community; the same pattern was observed for the HD community but the differences were not significant (Fig. 12). These results indicate substantial cropping system (plant community) by biochar interactions. Specifically these results indicate negative priming – the buildup of the readily mineralizable organic N pool – in biochar amended soils under the LD and HD polycultures but show no evidence for the buildup of this pool under the maize or switchgrass monocultures.

Table 2: Mixed model analysis output, p values for the effects of cropping system (Crop), year (2014-2016), soil depth (0-5 and 5-15 cm), and biochar application (Char) on soil on NO$_3^-\text{N}$, and NH$_4^+\text{-N}$ concentrations and potentially mineralizable N (PMN).

<table>
<thead>
<tr>
<th></th>
<th>Nitrater-N mg kg$^{-1}$</th>
<th>Ammonium-N mg kg$^{-1}$</th>
<th>PMN mg kg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crop</td>
<td>0.5</td>
<td>0.02</td>
<td>0.2</td>
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<tr>
<td>Year</td>
<td>0.08</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Depth</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Char</td>
<td>0.7</td>
<td>0.67</td>
<td>0.06</td>
</tr>
<tr>
<td>Crop*year</td>
<td>0.0003</td>
<td>0.0002</td>
<td>0.01</td>
</tr>
<tr>
<td>Depth*Year</td>
<td>0.52</td>
<td>&lt;0.0001</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Figure 12: Impact of biochar and cropping systems on concentrations of NO$_3^-\text{N}$ and NH$_4^+\text{-N}$ (0-15 cm) and potentially mineralizable N (PMN) for soils (0-15 cm) collected from the Armstrong research plots in fall 2016, 6 years after biochar applications. The cropping systems in this study are continuous corn (Corn), low diversity prairie (LD), high diversity prairie (HD) and bioenergy switchgrass (SG). PMN is determined by the difference in KCl extractable mineral N before and after a 28 aerobic incubation at 30°C. Error bar represents standard errors of means for the individual treatments.

Overall the field data is consistent with the laboratory incubation studies in indicating the potential for biochar to significantly increase soil organic C and N levels and provides evidence that biochar is catalyzing the formation and stabilization of new biogenic humic substances (new soil organic matter). These findings indicate that biochar amendments
are highly effective for sequestering C and building soil quality, but also suggest that biochar amendments may require an increase in the rate of N fertilization during the first few years after application to compensate for increased N immobilization.

*Calibration, validation, and application of the APSIM biochar model:* We performed a number of activities to calibrate, validate and apply the APSIM biochar model and to answer key systems-level research questions that are impossible to address through traditional field plot research.

First, we extensively reviewed the international literature to identify suitable datasets for model calibration and validation (Table 3). We identified 15 published papers that met requirements for modeling; seven of those papers were lab incubation experiments and eight were field experimental studies from all over the world. The majority of these experiments have been analyzed using the APSIM-biochar model (see status column in Table 2). We found that in general the newly developed biochar model perform well in terms of simulation accuracy of soil and crop processes. Some specific examples are provided below. We also improved some functions (algorithms) within the model to further increase the accuracy of the model under certain conditions (e.g. low soil pH).

<table>
<thead>
<tr>
<th>Number</th>
<th>Reference [26]-[40]</th>
<th>Focus</th>
<th>Data / Process tested</th>
<th>Duration</th>
<th>Treatments</th>
<th>Modeling Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fidel, 2015a. Lab</td>
<td>N2O, CO2</td>
<td>180 days</td>
<td>soil types, biochar types</td>
<td>80%</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Rogovska et al., 2014 Field</td>
<td>Yield, BD, SOC, Biomass, pH</td>
<td>2 years</td>
<td>biochar rates</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ameloot et al., 2013 Lab</td>
<td>N2O, CO2</td>
<td>120 days</td>
<td>biochar rates</td>
<td>99%</td>
<td></td>
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<tr>
<td>4</td>
<td>Ding et al., 2010 Lab</td>
<td>NH4 adsorption</td>
<td>70 days</td>
<td>control, fertilization, biochar and fertilization x biochar</td>
<td>99%</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Zheng et al., 2010 Field</td>
<td>Maize yield and biomass</td>
<td>5 months</td>
<td>biochar types</td>
<td>80%</td>
<td></td>
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<tr>
<td>6</td>
<td>Güereña et al. 2013 Field</td>
<td>Yield, pH, NO3 by depth</td>
<td>4 years</td>
<td>Biochar rates, nitrogen fertilizer rates</td>
<td>65%</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Strubel et al. 2011 Lab</td>
<td>pH, water holding capacity, N-mineralization, CO2 emissions</td>
<td>200 days</td>
<td>biochar rates, soil types, biochar types</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Zimmerman et al., 2011 Lab</td>
<td>C mineralization only</td>
<td>505 days</td>
<td>biochar types, pyrolysis temperature, soil types</td>
<td>99%</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Laird et al. 2010. Lab</td>
<td>pH, BD, ECEC, N leaching</td>
<td>69 weeks</td>
<td>biochar rates, manure rates</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Rogovska et al. 2016. Field</td>
<td>SOC, pH, BD, Plant N uptake, yield</td>
<td>5 years</td>
<td>biochar rates, residue removal practices</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Fidel, 2015b. Both</td>
<td>N2O, CO2</td>
<td>150 days</td>
<td>cropping systems</td>
<td>80%</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Cross and Sohi, 2011. Lab</td>
<td>CO2 mineralization</td>
<td>2 weeks</td>
<td>biochar types, soil types</td>
<td>99%</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Major et al., 2010. Field</td>
<td>Yield, pH, plant nutrient uptake</td>
<td>4 years</td>
<td>biochar rates</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Jones et al. 2012. Field</td>
<td>Biomass, Grain N%, denitrification</td>
<td>3 years</td>
<td>biochar rates</td>
<td>20%</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Laird et al., 2016. Field</td>
<td>Yields, SOC, biomass</td>
<td>&gt;5 years</td>
<td>5 sites, many years</td>
<td>50%</td>
<td></td>
</tr>
</tbody>
</table>
Secondly, we ran two multi-factorial simulation experiments to see how the model behaves under a range of management practices. The simulation experiments included different factors such as biochar types, biochar rates, soil types, locations, residue removal, nitrogen fertilizer and 35 weather years. This massive simulation analysis provided results on crop yields, N leaching, N₂O emissions, and soil organic carbon (Figs. 13-17), which were forwarded to economists (Objective 2) for further analysis.

Figure 13: Simulated versus measured temporal changes in soil NH₄-N concentration at different depths (Calibration dataset # 4, see Table 3).

Figure 14: Simulated versus measured temporal changes in soil NO₃-N leaching (Calibration dataset # 9, see Table 3).
Figure 15: Simulated versus measured percent differences in plant available water content (PAWC) across multiple soils and biochar application rates and types (Calibration dataset # 7, see Table 3).

Figure 16: Simulated versus measured corn yields over 5 years and multiple biochar x residue removal treatments in central Iowa (Calibration dataset # 10, see Table 3).

Figure 17: Scenario analysis using the calibrated APSIM-biochar model for a Colombian savanna Oxisol (Calibration dataset # 13, see Table 3). During calibration we improved the pH-nitrification modifier.
Developing a stochastic model to predict probability of a positive crop yield response to biochar applications: Because of the complexity of biochar-soil-crop-climate-management interactions, the long term effects of, and agronomic implications of, biochar applications are not well understood by the general public. Laboratory and field experiments results are necessarily limited by both time and scale and they are not well suited to explore the impacts of biochar applications at regional scales. Prediction models enable us to deal with this complexity and help to refine our understanding of the relationships between the factors involved.

We have developed a Bayesian Belief Network (BBN), a powerful statistical model, which uses probabilistic graphical models to address a wide range of environmental problems. We built a predictive BBN model to estimate the biochar response for a wide range of soil and biochar properties. We are currently building a large training dataset for the biochar statistical model, but in the meantime we are using data previously collected form a meta-analysis study published in 2013. This study originally contained 15 relevant variables and 935 observations from 87 studies from all around the world. Our BBN model was developed using the training dataset within the R environment using software called “Bayes Server”. BNN model consist of two main components: 1) A graphical model or representation of how the variables are statistically dependent on each other, and 2) the estimated BN parameters of (conditional probability distribution of nodes given their parents) variables specified in the graphical model. The joint distributions are estimated using the training dataset. The model estimates the mean yield response to biochar in the mathematical form of RR:

\[ RR = \log\left(\frac{\text{Yield}_{\text{Biochar}}}{\text{Yield}_{\text{Control}}}\right) \]

This allows us to estimate the probability of positive yield response to biochar applications over a wide range of soil and management scenarios. Accuracy of the response is limited by the size, accuracy, and relevance of the training dataset; the more observations available, the higher the degree of model accuracy.

The new BN model was run for the state of Iowa using 6 different soil properties (Sand, Silt, Clay, OC, pH, and CEC) with the aim of finding the most agronomically and/or economically plausible soils (agricultural fields) for application of biochar. Using our limited training dataset, preliminary results show that the model reproduces the known variable response of different soil properties to biochar applications. For example, the model showed that there is a lower chance of a biochar response in the Des Moines Lobe area (a region dominated by young high fertility soils) compared to the southern part of the state (a region dominated by older soils with low water and nutrient holding capacity). In some areas, sharp changes in the model predictions were found along political boundaries. These artifacts come from inconstancies in the structure of SSURGO soils database, which is an input for the model. Although imperfect, the SSURGO database is the best available and most widely used soil database in the United States. Currently the predictive power of the model suffers from an insufficient number of observations in the initial training dataset. This limitation is being address as we are
building an expand biochar database. Our goal is to prepare an application for public distribution after the model has been updated and validated with the larger database.

**Objective 2:** Quantify the public and private benefits accrued from integrating biochar into pyrolysis-based bioenergy production systems for three case studies.

**Introduction:** The overall objective of our work is to estimate the private economic value of biochar. We have taken several perspectives going from micro to macro. Most of the analysis is at the micro level. The first step in meeting this objective was to apply an appropriate conceptual framework to explain how land owners/managers would view adoption of land application of biochar. The framework we adopted was a micro-level choice model where the decision maker chooses whether to adopt biochar, and if the answer is yes, then the percentage of land to received biochar is then determined.

The task is to simulate and evaluate the economic feasibility and cost effectiveness of biochar production and application. For example, we hypothesize that spatially targeted applications of biochar on marginal land with acidic and otherwise low-quality soils would have substantial benefits in terms of carbon sequestration and crop yield enhancement.

**Figure 13:** Estimated probability of a positive crop yield response to biochar applications across the state of IOWA using a BBN model.
Another objective is to analyze how to develop a supply chain to expand the use of biochar, and this analysis is more conceptual.

**Impact of Biochar at the micro-level**

*Methods:* We have assembled a database using APSIM Biochar Model simulations for major crops grown on representative soils and under both historic and projected climates for the Upper Mississippi River Basin, California, and U.S. Southeast. Assessing biochar impacts for these three regions will be part of the iterative calibration and validation process for the APSIM Biochar Model.

We hired two master students in the Department of Agronomy at Iowa State, Garrett Lies and Isaiah Huber, to run APSIM Biochar Model simulations to investigate whether and how biochar affect agronomic and environmental characteristics such as runoff, soil organic carbon, nitrogen leaching and crop yields. In particular, we run these simulations for six different soil types (Canisteo, Clarion, Estherville, Nicollet, Webster, and Zenor soil), different residual removal rates, biochar types and biochar application rates.

*Results:* Effects on yield: The analysis indicates that biochar applications have only small effects maize yields (<3% for the studied systems), and with positive, neutral and negative yield responses observed depending on complex soil by biochar type interactions.

Figure 18 shows that biochar applications have heterogeneous impacts on crop yields depending on soil type and biochar type. In particular, for the Estherville and Zenor soils, biochar increased yields, and there are sometimes slight increases in yields for the Nicollet and Webster soils, however for the Clarion and Canisteo soils biochar decreased yields. The GCB2 biochar consistently had a higher yield response than GCB3 biochar, indicating that biochar quality is an important consideration.

Effects on DUL (drained upper limit, defined as the amount of water that a particular soil holds after drainage has practically ceased): Figure 19 below shows that the APSIM biochar model predicts an overall increase in DUL for all of the studied soil-biochar systems with biochar application rate. The Webster soil sees a decrease in DUL for the 10 Mg/ha application rate. This prediction is consistent with measured data for field and greenhouse studies which typically show increases in soil moisture retention due to biochar applications for coarse and medium textured soils and decreases in moisture retention for fine textured soils.

Effects of biochar application on nitrate leaching: the APSIM model predicts (Figure 20) decreases in nitrate leaching as biochar application rates increase, which applies to all of the studied soil types. In particular, biochar application at higher levels (20 Mg/ha or above) would decrease nitrate leaching. Field and laboratory studies have found mixed results, but generally decreased nitrate leaching in course textured soils and no effect or even a slight increase in nitrate leaching for fine textured soils.

Effects of biochar on soil organic carbon: the simulations reveal that biochar application always result in an increase in soil organic carbon, and the effect increases linearly as
biochar application rate increases. In particular, figure 21 shows that every 10 Mg/ha application of biochar roughly leads to a 5-8% increase in soil organic carbon. These model predictions are consistent with field studies, laboratory incubations, and known recalcitrant nature of the condensed aromatic carbon in biochars.

**Figure 18:** Effects of biochar application rate on corn yields estimated using the APSIM biochar model.

**Figure 19:** Effects of biochar application rate on ‘field capacity’, the ability of soils to hold water against gravity drainage, estimated using the APSIM biochar model. Within APSIM field capacity is references as drainage upper limit (DDL).
**Figure 20:** Effects of biochar application rate on nitrate (NO$_3$-N) leaching estimated using the APSIM biochar model.

**Figure 21:** Effects of biochar application rate on nitrate on soil organic C estimated using the APSIM biochar model.
Macro and supply chain analysis

Much of our analysis has been conceptual. The literature on adoption recognizes that new technologies are adopted in areas where they are most profitable, but that has to take into account gains for the producers, as well as costs of the technology. When it comes to biochar, the distance between users and buyers matters, and therefore biochar is more likely to be used on low quality land that needs it in locations that are closer to the source of the biochar. We are developing conceptual models that incorporate transportation costs and infrastructure between sources and uses. Furthermore, producers of biochar, which may originate from forest products or crop residue, need to develop a supply chain that will make it profitable to engage in biochar activities.

Zilberman et al. (forthcoming) develop a framework that emphasizes the development of supply chain to implement innovation. At the basic level, supply chains have three elements – a feedstock (e.g., a crop, forest product, residue), processing facility, and shipping/marketing activity. In the case of biochar, the feedstock is crop residue or forest product and the physical process of converting it to biochar, followed by an element of marketing. A key question is if we expect biochar producers to be vertically integrated, who own feedstock and produce biochar and other products, or to be individual firms who establish facilities and contract to suppliers. The decision of whether to engage in each type of activity depends on credit availability and risk considerations [41]. With economies of scale in production of biochar, or when the demand is significant, and the processor faces financial constraints in addition to relatively available feedstock, we may see more contractual-based operations. In other cases, when biochar financing is more easily obtained, we expect to see more vertically integrated operations, where farmers will process their own feedstock. This suggests that as we aim to introduce biochar activities, we need to be concerned with the cost of processing the biochar and the willingness to pay for it.

Objective 3: Use techno-economic analysis to assess the economic performance of pyrolysis plants producing bioenergy and biochar co-products and use life cycle assessments to determine the net GHG emissions from an integrated pyrolysis-bioenergy-biochar production facility.

Regression model: We have gathered data from North Carolina State University and Iowa State University for fast pyrolysis experiments conducted under similar experimental conditions using 12 different feedstocks (Table 4). Table 4 shows data for fast pyrolysis product yields including bio-oil organics, water content, NCG, and biochar on a dry basis, as well as ultimate analysis data for the 12 feedstocks. The selected feedstocks include wood residues, crop residues and grasses. We employ a prediction function from Mathematica 11.0 software to build correlations between the fast pyrolysis yields and the biomass properties [42]. Ash content and the oxygen to carbon ratio (O:C) of biomass are selected to represent the biomass properties. To build the model, three outlier data points were eliminated (feedstocks of outliers were beech bark, sweetgum and acacia). We compared the experimental pyrolysis yields and prediction yields from the regression models, as shown in Figure 22. Percent error is calculated as the absolute difference
between the experimental and prediction pyrolysis yields divided by the experimental yields. All calculated percent errors for different pyrolysis yields are under 10 %, which indicates that our regression model works well to predict pyrolysis yields from ash content and oxygen to carbon ratio of biomass within the range of the provided experimental feedstock.

**Table 4.** Ultimate analysis (on a dry basis) and experimental pyrolysis yield data for 12 different feedstocks

<table>
<thead>
<tr>
<th>Ultimate analysis (% dry basis)</th>
<th>Sweetgum</th>
<th>Beech Bark</th>
<th>Acacia</th>
<th>Acacia Bark</th>
<th>Corn Stover</th>
<th>Red Oak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>46.4</td>
<td>44.5</td>
<td>48.4</td>
<td>49.9</td>
<td>43.2</td>
<td>49.6</td>
</tr>
<tr>
<td>Oxygen</td>
<td>48.4</td>
<td>50.2</td>
<td>46.5</td>
<td>44.0</td>
<td>49.4</td>
<td>44.3</td>
</tr>
<tr>
<td>Ash</td>
<td>0.8</td>
<td>7.4</td>
<td>0.6</td>
<td>3.3</td>
<td>8.1</td>
<td>0.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pyrolysis yield (wt. %)</th>
<th>Sweetgum</th>
<th>Beech Bark</th>
<th>Acacia</th>
<th>Acacia Bark</th>
<th>Corn Stover</th>
<th>Red Oak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organics</td>
<td>55.1</td>
<td>29.2</td>
<td>43.9</td>
<td>33.8</td>
<td>27.7</td>
<td>43.4</td>
</tr>
<tr>
<td>Char</td>
<td>9.0</td>
<td>24.6</td>
<td>10.7</td>
<td>21.7</td>
<td>21.7</td>
<td>13.5</td>
</tr>
<tr>
<td>NCG</td>
<td>25.4</td>
<td>19.8</td>
<td>32.5</td>
<td>25.5</td>
<td>26.9</td>
<td>23.3</td>
</tr>
<tr>
<td>Water</td>
<td>10.5</td>
<td>26.4</td>
<td>12.9</td>
<td>19.0</td>
<td>23.8</td>
<td>19.8</td>
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</table>

<table>
<thead>
<tr>
<th>Switchgrass</th>
<th>Sourwood</th>
<th>Yellow Poplar</th>
<th>Red Maple</th>
<th>Beech</th>
<th>Loblolly Pine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>46.6</td>
<td>46.9</td>
<td>47.1</td>
<td>47.4</td>
<td>48.2</td>
</tr>
<tr>
<td>Oxygen</td>
<td>48.0</td>
<td>48.0</td>
<td>47.8</td>
<td>47.5</td>
<td>46.3</td>
</tr>
<tr>
<td>Ash</td>
<td>1.4</td>
<td>0.5</td>
<td>0.6</td>
<td>0.3</td>
<td>0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Switchgrass</th>
<th>Sourwood</th>
<th>Yellow Poplar</th>
<th>Red Maple</th>
<th>Beech</th>
<th>Loblolly Pine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organics</td>
<td>51.4</td>
<td>58.0</td>
<td>52.3</td>
<td>53.5</td>
<td>54.0</td>
</tr>
<tr>
<td>Char</td>
<td>9.5</td>
<td>6.3</td>
<td>7.4</td>
<td>7.0</td>
<td>10.6</td>
</tr>
<tr>
<td>NCG</td>
<td>25.3</td>
<td>27.5</td>
<td>30.2</td>
<td>30.5</td>
<td>25.2</td>
</tr>
<tr>
<td>Water</td>
<td>13.8</td>
<td>8.2</td>
<td>10.1</td>
<td>9.0</td>
<td>10.2</td>
</tr>
</tbody>
</table>
**Process modeling:** We have modeled the fast pyrolysis and upgrading process to convert biomass into transportation fuel and produce biochar as a byproduct in Aspen Plus™. We assume a 2000 metric tons of biomass per day (MT/d) biorefinery plant has been built. The block flow diagram for converting biomass to gasoline and diesel range of transportation fuels is shown in Figure 23. The whole process is modeled as biomass pretreatment, fast pyrolysis, bio-oil fractionation, stabilization, upgrading, hydrogen production and steam generation. We first chop and grind biomass into less than 3mm-diameter fine particles. A series of dryers are used to reduce the biomass moisture content to less than 10 wt. %. Pretreated biomass is then decomposed into bio-oil, biochar and non-condensable gases in a fluidized bed reactor operated at 500 °C and 1 atm. We model the bio-oil compositions based on the previous fast pyrolysis study [43], while the pyrolysis product yields are predicted by the regression model, which is based on experimental pyrolysis data.

A five-stage fractionation system developed by Iowa State University, which mainly includes electrostatic precipitators (ESPs) and condensers, is employed to recover the pyrolysis vapor into five stage fractions with distinctive characteristics. The heavy and middle bio-oil stage fractions (SF1-4), which includes water-soluble sugars and water-insoluble phenols, are deoxygenated into stable oil using a two-stage hydrotreating process. A subsequent upgrading process further hydrocracks and distills the stable oil into gasoline and diesel range fuels.
The light stage fraction of bio-oil (SF5) consist of light oxygenated compounds such as acids, ketones, and furans. SF5 is reformed with make-up natural gas, pyrolysis off gases and water to produce H\textsubscript{2} in a steam reforming reactor and a subsequent water-gas shift reactor. We assume a steam to carbon ratio of 2.5 to determine the water required in the H\textsubscript{2} production system based on other studies [44]. NCG, off gases and merchant natural gas are combusted to produce steam for heat and fluidize the pyrolysis reactor. Biochar is separated from the pyrolysis vapor and used as a soil amendment to improve the soil quality, sequester carbon and further increase the crop yields.

The Phyllis2 database created by the Energy Research Center of Netherland (ECN) is a properties database for various biomass samples. We collected ultimate analysis data (on a dry basis) of 2000 different biomass samples from the Phyllis2 database and downsized them to 346 kinds of biomass based on the O/C ratio and ash content range of the selected experimental feedstocks. Figure 24 shows the O/C and H/C ratio for all 346 biomass samples, which could be grouped into untreated wood, treated wood, straw (stalk/cob/ear), grass/plant, organic residue/product and husk/shell/pit categories. An Aspen Simulation Workbook (ASW) imports these 346 biomass properties datasets and runs the process model for all 346 scenarios to predict pyrolysis yields for different feedstocks. The O/C ratio of the selected biomass feedstocks ranges from 0.88 to 1.12, while the H/C ratio varies from 0.09 to 0.15.

**Figure 23:** Block flow diagram of fast pyrolysis to gasoline and diesel production process.
Figure 25 shows the impacts of ash content and O/C ratio of the biomass feedstock on biochar and biofuel yields. As shown in Figure 25A, higher ash content of biomass has the potential to increase biochar output for all investigated types of feedstock. Biochar output ranges from 12.5-15.5 wt. % of dry biomass. Figure 25B shows that fuel output decreases with higher ash content of biomass. The annual biofuel output could decrease from 64 to 30 MM gallons for different ash content values. The impact of ash content of biomass on the fuel and char yields are consistent across a large number of experimental studies [45]–[47]. It shows that high ash content of biomass leads to greater biochar formation and has a negative impact on the fuel yield. High ash content of biomass also has a negative impact on bio-oil quality and could cause problems with process operation. However, these impacts were not investigated in this study.

The impacts of O/C ratio of biomass on the biofuel and biochar yields have also been investigated. Instead of grouping feedstocks by their categories, we grouped all different biomass into 6 groups with different ash content levels (ash 0-1%, ash 1-2%, ash 2-3%, ash 3-4%, ash 4-5% and ash 5-8%) to isolate ash content impacts. As shown in Figure 25C, higher O/C ratio of biomass decreases biochar yield and increases biofuel yield within the same ash content level. Lower O/C ratio of biomass might be attributed to higher lignin content, which requires more serious conditions to decompose and trends to decrease biofuel yield. The impact trend for high ash content biomass (ash 5-8%) is more scattered both for char and fuel yields, compared to other ash content levels in biomass (ash 0-5%).
**Economic analysis:** We evaluate the economic performance of the pyrolysis-bioenergy-biochar platform by considering three main categories: capital cost, operating cost and minimum fuel selling price (MFSP). Capital cost is a one-time investment spent for all process equipment purchase and installation, including different reactors, condensers, and heat exchangers and so on. Aspen Plus Economic Analyzer (APEA) calculates the equipment purchase cost based on estimates and public data. We also compare our economic estimates for some special units with previous TEA studies of fast pyrolysis technology. The equipment installation cost is calculated by multiplying installation factors with the purchase cost. Peters and Timmerhaus’s book provides recommended installation factors for various kinds of equipment [48].

Operating costs represent expenditures to keep the process in operation on an annual basis. The cost and benefit break-even point price (referred as minimum fuel selling price MFSP) is calculated based on a discounted cash flow rate of return (DFROR) spreadsheet. MFSP is calculated as the fuel price required for the net present value (NPV) to equal zero under an internal rate of return (IRR) of 10%. The equity is assumed as 40% and the remaining 60% debt is assumed to be loaned at an interest rate of 10% for 10 years. Contingency accounting for all unexpected events is assumed as 9.5% of the total purchase and installation equipment costs. All costs are presented on a 2011-year dollar basis. Table 5 lists major financial assumptions for this economic analysis.

**Figure 25:** A. The impact of ash content of biomass on biochar and fuel output (Biomass are separated into six feedstock type categories); B. The impact of O/C ratio of six biomass ash content groups on biochar and fuel output.
Table 5. Financial Assumptions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Assumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal rate of return</td>
<td>10%</td>
</tr>
<tr>
<td>Equity</td>
<td>40%</td>
</tr>
<tr>
<td>Plant life</td>
<td>30 years</td>
</tr>
<tr>
<td>Income tax rate</td>
<td>35%</td>
</tr>
<tr>
<td>Interest rate for debt financing</td>
<td>7.5% annually</td>
</tr>
<tr>
<td>Term for debt financing</td>
<td>10 years</td>
</tr>
<tr>
<td>Working capital cost</td>
<td>15% of fixed capital cost</td>
</tr>
<tr>
<td>Depreciation schedule</td>
<td>7-years MACRS schedule</td>
</tr>
<tr>
<td>Construction period</td>
<td>3 years</td>
</tr>
<tr>
<td>Plant salvage value</td>
<td>0</td>
</tr>
<tr>
<td>Startup time</td>
<td>0.5 year</td>
</tr>
<tr>
<td>Revenue and costs during startup</td>
<td>revenue: 50%</td>
</tr>
<tr>
<td>(% of normal)</td>
<td>variable costs: 75%</td>
</tr>
<tr>
<td></td>
<td>fixed cost: 100%</td>
</tr>
<tr>
<td>On-stream factor</td>
<td>90%</td>
</tr>
</tbody>
</table>

A few economic assumptions have been made in this study. First, we assume a common delivered feedstock cost of $83/MT for all 346 kinds of feedstock, including logistics and feedstock cost. Feedstock costs vary from their types, plant & harvest method, market, locations, and other relevant regulations. Although the feedstock cost plays a significant role in the final product selling price, our data sources did not include matching delivery prices for the feedstock. Therefore, we chose a baseline feedstock cost based on Department of Energy cost targets at this stage. Second, we assume to process all biomass in the same facility under similar conditions without considering any process modifications. Optimal operating conditions might differ for different feedstocks. However, optimizing the operation condition to decompose different feedstocks is not within the scope of this study. Future work could investigate and compare biomass properties’ impact including consideration of process design modification for various feedstocks. According to a 2013 report by the International Biochar Initiative (IBI), biochar retail price varies with biochar quality and market demand. In this study, biochar is assumed to be sold as $20/MT, which is a highly discounted price.

Figure 26(A) shows the installed equipment cost distribution for the pyrolysis-biochar-bioenergy platform. The total installed equipment cost is estimated as $277 million (MM). Pretreatment and pyrolysis are the major contributors of the total installed equipment cost due to expensive costs of a series of dryers and pyrolysis reactors. Hydrogen generation also takes a big percentage of the total installed equipment cost. Capital cost for hydrogen generation process are scaled up based on SRI 2007 Yearbook.
and is comparable to Jones et al. (2013) [49]. The total fixed capital investment is assessed as $364 MM including direct costs and indirect costs accounting for engineering, construction, contractor fees and contingency. Operating costs vary with different feedstocks. We decide to calculate the average operating cost for each category of biomass. As shown in Figure 26(B), biomass cost is the major contributor to the total operating cost, taking 28%-34% of the total operating cost, followed by average return on investment and fixed cost. The average operating cost varies from $2.99/gal for woody biomass to $3.76/gal for straw biomass.

![Figure 26](image)

**Figure 26:** A. Total installed equipment costs of the pyrolysis-bioenergy-biochar platform; B. Average operating cost distribution for five types of biomass
We calculate the MFSPs for all 346 feedstocks based on the capital and operating costs shown above. Figure 27 shows how biomass properties affect MFSP. As the results indicates, higher ash content of biomass has the potential to increase MFSP, while higher O/C ratio of biomass has the potential to decrease MFSP within the same ash content level. The MFSPs for 346 different feedstocks range from $2.3/gal to $4.8/gal. The impacts of biomass properties on MFSPs is consistent with the influence on the biofuel yields even though there are other parameters impacts. Higher biofuel yields are predicted with lower ash content and higher O/C ratio of biomass, which leads to better economic performance.

**Figure 27:** A. The impact of ash content of biomass on minimum fuel-selling price (Biomass are categorized into six feedstock types); B. The impact of O/C of six biomass ash content groups on minimum fuel-selling price

*Life cycle analysis:* Life cycle analysis is a widely-used methodology for evaluating the emissions to the environment through a product’s life. In this study, we use GREET (Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation) developed by Argonne National Laboratory to evaluate the GHG emissions for the pyrolysis-bioenergy-biochar platform. Figure 28 shows the system boundary for the pyrolysis-bioenergy-biochar platform process. This study sequesters biochar into the soil as a soil amendment. Merchant natural gas from shale gas and conventional recovery are combusted to produce heat and power for the pyrolysis system. The functional unit is chosen as 1MJ of fuel produced to simplify comparison with other studies. A higher
heating value (HHV) of pyrolysis fuel of 41.31 MJ/kg is chosen by the GREET software [50]. GHG emissions from biofuels combustion are assumed to be compensated by biogenic CO₂ absorbed via biomass photosynthesis.

![Diagram of fast pyrolysis process]

**Figure 28**: Life-cycle analysis system boundaries for the fast pyrolysis bio-oil stabilization process.

Primary GHG emission sources for this process are fertilizers and petroleum fuels used for feedstock production and collection, natural gas required for H₂ production, natural gas required for heat and power production, petroleum fuels for transporting and distributing biochar and biofuels. Biomass production GHG emissions differ for different types of biomass due to varying fertilization requirements, and planting and harvest methods. However, the feedstock production emission database is very limited. Therefore, we decided to choose one representative biomass with available biomass production emission data to represent each category of feedstock as summarized in Table 6. The biomass production emission data come from GREET and SimaPro 7.

<table>
<thead>
<tr>
<th>Feedstock type</th>
<th>Representative</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>Forest Residue</td>
<td>GREET 2015</td>
</tr>
<tr>
<td>Straw</td>
<td>Corn Stover</td>
<td>GREET 2015</td>
</tr>
<tr>
<td>Grass</td>
<td>Switchgrass</td>
<td>GREET 2015</td>
</tr>
<tr>
<td>Organic Residue</td>
<td>Bagasse (from Sweet Sorghum)</td>
<td>SimaPro 7</td>
</tr>
<tr>
<td>Husk</td>
<td>Palm Kernel</td>
<td>SimaPro 7</td>
</tr>
</tbody>
</table>

Table 7 compiles the GHG emissions per kg input and their sources. Feedstock production emissions for forest residue, corn stover and switchgrass come from the GREET database. The forest residue production emission does not require any fertilizers. Feedstock production GHG emission might vary significantly within different allocation methods for these feedstock that is not specifically grown as an energy crop. Three based allocation methods include mass, energy, and economic basis are broadly discussed.
Murphy et al. (2013) discussed details of the life cycle inventory of corn/stover production using different allocation methods. He concluded a corn grain to stover allocation ratio of 7:3 using an energy based allocation method and a ratio of 8.5:1.5 when using an economic allocation method [51]. Some studies separate corn stover harvesting from the corn production process. They only assigned a GHG emission for harvesting & transporting stover and supplementing fertilizers [51]. In GREET, the GHG emission for corn stover production consists of supplemental rates of N, P, K fertilizer, diesel fuel for collection and transportation. The nutrient supplemental rates are calculated based on the nutrients contained in corn stover. Switchgrass production emissions also derive from the required fertilizer, herbicides, diesel fuel for harvest and transportation [9]. SimaPro 7 provides production emission data for Bagasse from sweet sorghum gathered at distilleries, and palm kernel [52]. Allocation methods vary with the end use of bagasse from sweet sorghum. Mass allocation is preferred when bagasse is used for animal feed, while energy allocation is commonly used when fuel or electricity is produced from bagasse [53]-[55]. Palm kernel is one of the byproduct of crude palm oil and mass allocation is commonly used for partitioning the byproducts. Subramaniam et al. (2012) allocated the crude palm oil, palm kernel and palm shell by 61%, 25% and 14% [56]. Palm kernel production emissions from SimaPro are extremely high compared to other feedstocks. The main emission sources for palm kernel production are: fossil fuel for palm kernel transportation, electricity for kernel-crushing, N₂O emission from fertilizer, biogas release from anaerobic digestion of palm oil mill effluent in pond and CO₂ emission from peat decay [57]-[58]. Subramaniam et al. 2010 suggests that integrating kernel-crushing with the palm oil mill, capturing biogas and collecting palm fruit bunches from a plantation with 50-years cultivation history to avoid indirect land use change could minimize the GHG emissions [59].

Table 7. GHG emissions per kg input and their sources.

<table>
<thead>
<tr>
<th>LCA Input</th>
<th>GHG Emission g CO₂/kg input</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest Residue</td>
<td>45</td>
<td>GREET 2015</td>
</tr>
<tr>
<td>Corn Stover</td>
<td>85</td>
<td>GREET 2015</td>
</tr>
<tr>
<td>Switchgrass</td>
<td>140</td>
<td>GREET 2015</td>
</tr>
<tr>
<td>Bagasse (Sweet Sorghum)</td>
<td>6</td>
<td>SimaPro 7</td>
</tr>
<tr>
<td>Palm Kernel</td>
<td>1400</td>
<td>SimaPro 7</td>
</tr>
<tr>
<td>NG for Heat Production</td>
<td>2944</td>
<td>GREET 2015</td>
</tr>
<tr>
<td>NG for H₂ Production</td>
<td>2790</td>
<td>GREET 2015</td>
</tr>
<tr>
<td>Fuel Transportation</td>
<td>30</td>
<td>GREET 2015</td>
</tr>
<tr>
<td>Biochar Sequestration</td>
<td>-1492</td>
<td>GREET 2015</td>
</tr>
</tbody>
</table>

We gathered GHG emissions per unit of other main sources besides feedstock production from GREET. Natural gas for H₂ production emits GHG emissions starting from natural gas production, transportation, steam reforming reactions, while natural gas combustion for heat and power consists of emissions from natural gas production, distribution and combustion. GHG emissions from fossil fuel come from transporting biofuel from
integrated pyrolysis facility to the bulk terminal via barge, pipeline and rail, then finally distributing to refueling station via heavy-duty truck.

Biochar sequestration might have multiple impacts on the soil, for example, increasing soil organic carbon (SOC), fertilization efficiency, net primary productivity, crop yields, decreasing soil bulk density and so on. The impacts of biochar on soil vary with feedstock categories, soil types, weather conditions, which will further affect the GHG emission results. However, in this study, we only focus on the biochar impacts on the carbon sequestration without accounting the indirect land use change impacts. GHG emissions related to biochar consist of biochar transportation and GHG emission credits from biochar carbon sequestration. We assume a biochar transportation distance of 40 miles [50]. The fraction of carbon in biochar remaining in the soil varies with biochar type and climate. As assessed by Roberts et al. 2010, 80% of carbon is assumed to stay in the soil over 100 years [42]. We calculate GHG emissions for all 346 different biomass cases by combining product yields data from Aspen Plus™ model with the per unit input GHG emission table to evaluate impacts of biomass properties on the environment performance.

Figure 29 shows the correlation between ash content of biomass and GHG emissions. As shown in the left part of Figure 24A, there is a big difference between GHG emissions for husk/shell/pit type of biomass and the other four categories of biomass. The huge GHG emissions for husk/shell/pit type of biomass mainly results from high feedstock production emission for palm kernel. Therefore, we present the GHG emissions results for the other four types of feedstock separately as follows. As shown in the right part of Figure 29A, higher ash content has the potential to decrease the total GHG emissions for the other four types of biomass while higher ash content has the potential to increase the total GHG emissions for husk/shell/pit type of biomass. The reason for different trends between the ash content and the GHG emissions is that there is an impact trade-off between product yields and the per MJ biofuel produced measurement basis. Biofuel yields decrease while biochar yields increase with higher ash content of biomass, which will decrease GHG accounted for bio-oil upgrading and increase GHG credits from biochar sequestration, further leading to a decreasing trend in the total GHG emissions. However, the total GHG emissions is calculated on 1 MJ fuel produced basis, and higher biofuel yields decrease the GHG emissions on a 1MJ fuel produced basis.

Figure 29(B & C) shows the impacts of O/C ratio of biomass on the GHG emissions. The impact of O/C ratio of biomass on the GHG emissions is not as consistent as the ash content impact. In Figure 24B, GHG emissions for husk/shell/pit type of biomass are relatively scattered, which might be due to the significant impact of biomass ash content. Higher O/C ratio of biomass has the potential to increase GHG emissions for woody biomass. The GHG emissions for straw, grass and organic residue types of biomass are more disperse. A wide range of selected ash content of biomass might be responsible for these scattered results. Figure 24C presents a more direct impact of biomass O/C ratio on the GHG emissions since feedstock are grouped by their ash content level. We can see that higher O/C ratio of biomass has the potential to increase GHG emissions for biomass with relatively lower ash content (ash 0-1% and 1-2%). However, for higher ash content
of biomass, the impacts of O/C ratio on GHG emissions are not obvious. The reasons for the unclear impact trend might be more GHG credits are generated due to a larger amount of biochar production for high ash content of biomass, which might counter-balance the impact of increasing biofuel yields with rising biomass O/C ratios. A few high ash content feedstock scenarios produce negative GHG emissions, it mainly results from a significant amount of GHG credits from extremely high biochar yields.

We randomly chose a set of GHG results for five types of feedstock to investigate how GHG emission distributes, as shown in Figure 30. Comparing the GHG emissions for petroleum fuels, which is presented as the red dash line as 93g/CO₂e/MJ fuel produced, GHG emissions reduction for four kinds of biomass could reach from 85% to 98%. GHG emission reductions for woody, straw, grass and organic residue type of biomass investigated in this study match the renewable fuel standard (RFS) GHG emission reduction requirement for advanced fuels, which is 50%. GHG emissions are mainly from five categories: feedstock production, natural gas for heat production, natural gas for H₂ production, fuel transportation and biochar sequestration. Feedstock production emissions vary with different types of feedstock. The total GHG emissions for

Figure 29: The impact of ash content and O/C ratio of biomass on GHG emissions (Biomass are categorized into five feedstock types in A & B and biomass are categorized into six ash content groups in C).
husk/shell/pit type biomass are extremely high due to high feedstock production emission for palm kernel. Natural gas for heat production is also one of the main sources of GHG emissions. Natural gas for H₂ production and transportation fuels play a less important role in contribution of the total GHG emission since only a small amount of natural gas and petroleum fuel are consumed in the whole process. GHG credits from biochar sequestration vary with biochar yields and could significantly reduce the total GHG emissions even close to zero, for example, as shown in the Figure 30, the final total GHG emission could be reduced to 1.1 CO₂e/MJ fuel produced for organic residue.

**Figure 30:** GHG distribution for five types of feedstocks (The representative feedstock of each category is randomly chosen by Mathematica).

**Objective 4:** Estimate carbon credits for indirect land use avoidance and compare system production costs.

**Introduction:** Given the application of biochar to cropland soils in the U.S. and globally, the expected yield increase should be attributed to the production of biofuels that produced biochar as a byproduct. That yield increase will result in GHG savings because less cropland will be required to produce the same amount of crop production. The CARD/FAPRI Model can assess the land-use change impacts and price effects from higher yields in the U.S. and globally. Together with the Greenhouse Gases from Agriculture Simulation Model (GreenAgSiM), carbon pool dynamics from land-use change and agricultural production can be assessed.
Results: The scenario that was executed with the CARD/FAPRI Model increases yields for corn, soybeans, and wheat by 1%. The effective increase by 2021 was 0.98%, 0.98%, and 0.77% for corn, soybeans, and wheat, respectively. The discrepancy comes from market adjustments that are internal, i.e., endogenous, to the economic model. The largest decrease in crop area (in thousand hectares) is seen in Brazil (183.49), Russia (77.94), Other Africa (65.66), and the United States (55.32). The global decrease in area from the 1% yield increase of the three U.S. crops is 467,095 hectares. Global crop area declines by 0.051% with above average percentage declines in the following countries:

- South Africa (-0.38%): The majority of the decline is driven by corn which decreases by 0.44%.
- Brazil (-0.30%)
- Paraguay (-0.18%): Soybeans decline by 0.18%.
- Russia (-0.17%): There is a significant decrease in area for oats (-0.11%) and wheat (-0.26%). Wheat constitutes over 58% of agricultural area modeled for Russia in the CARD/FAPRI Model.
- Mexico (-0.12%): Corn area declines by 0.19%.
- Morocco (-0.11%): Wheat declines by 0.11%.
- Other Africa (0.10%): Corn area declines by 0.35% whereas the area allocated to barley, peanuts, sorghum, and wheat increases by 0.13%, 0.02%, 0.01%, and 0.11%, respectively.
- United States (-0.06%): For a detailed break-down by crop, see Table I.
- Philippines (-0.06%): Corn area declines by 0.17%.

All other countries are below 0.05% decline on crop area. Global corn, soybeans, and wheat area decreases by 0.20%, 0.16, and 0.01% but some major crops such as barley, rapeseed, sorghum, sugar cane, and sunflower see small increases in crop area of 0.03%, 0.05%, 0.01%, 0.01%, and 0.02%, respectively. This increase is due to the fact that some countries see a yield decrease because the CARD/FAPRI Model incorporates price-induced yield changes. In those countries, there is no yield increase if higher U.S. yields due to biochar applications lead to lower commodity prices. Some countries see a decrease in yields in the scenario compared to the baseline due to lower prices. Results show a significant decrease of crop area in Brazil that is composed of carbon rich forests and pasture.

Table 8: Effects of yield increase on crop area in the United States (in 1,000 hectares)

<table>
<thead>
<tr>
<th>Crop</th>
<th>Baseline</th>
<th>Scenario</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barley</td>
<td>1,082.58</td>
<td>1,080.08</td>
<td>-0.232%</td>
</tr>
<tr>
<td>Corn</td>
<td>32,627.20</td>
<td>32,557.13</td>
<td>-0.215%</td>
</tr>
<tr>
<td>Oats</td>
<td>446.78</td>
<td>446.93</td>
<td>0.034%</td>
</tr>
<tr>
<td>Peanut</td>
<td>504.03</td>
<td>504.04</td>
<td>0.000%</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>494.59</td>
<td>494.22</td>
<td>-0.075%</td>
</tr>
<tr>
<td>Sorghum</td>
<td>1,868.52</td>
<td>1,866.99</td>
<td>-0.082%</td>
</tr>
<tr>
<td>Soybeans</td>
<td>31,054.71</td>
<td>31,041.10</td>
<td>-0.044%</td>
</tr>
<tr>
<td>Sugar Beet</td>
<td>510.74</td>
<td>511.01</td>
<td>0.054%</td>
</tr>
<tr>
<td>Sugar Cane</td>
<td>291.92</td>
<td>291.82</td>
<td>-0.033%</td>
</tr>
<tr>
<td>Sunflower</td>
<td>729.76</td>
<td>732.49</td>
<td>0.375%</td>
</tr>
<tr>
<td>Wheat</td>
<td>18,229.15</td>
<td>18,258.85</td>
<td>0.163%</td>
</tr>
<tr>
<td>Total</td>
<td>89,002.91</td>
<td>88,947.59</td>
<td>-0.062%</td>
</tr>
</tbody>
</table>
**Effect of yield increase on GHG emissions:** The decrease in CO₂-e emissions (in millions of metric tons) are 33.25 and 57.16 under medium and maximum carbon coefficients, respectively [60]. This equates to a global average of 71.18 and 122.37 t CO₂-e ha⁻¹. The results by major country/region are presented in Table 9.

**Table 9:** Changes in CO₂-e emissions (in million metric tons) from land-use change due to an increase in yields of corn, soybeans, and wheat in the United States.

<table>
<thead>
<tr>
<th>Mean Coefficients</th>
<th>Maximum Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argentina</td>
<td>(0.92)</td>
</tr>
<tr>
<td>Australia</td>
<td>1.14</td>
</tr>
<tr>
<td>Brazil</td>
<td>(19.56)</td>
</tr>
<tr>
<td>Canada</td>
<td>(0.16)</td>
</tr>
<tr>
<td>China</td>
<td>0.71</td>
</tr>
<tr>
<td>EU</td>
<td>(0.09)</td>
</tr>
<tr>
<td>India</td>
<td>(0.41)</td>
</tr>
<tr>
<td>Indonesia</td>
<td>(0.09)</td>
</tr>
<tr>
<td>Mexico</td>
<td>(2.20)</td>
</tr>
<tr>
<td>Other Africa</td>
<td>(3.64)</td>
</tr>
<tr>
<td>Other Asia</td>
<td>0.33</td>
</tr>
<tr>
<td>Other Europe</td>
<td>0.26</td>
</tr>
<tr>
<td>New Zealand</td>
<td>0.03</td>
</tr>
<tr>
<td>Russian Federation</td>
<td>(6.72)</td>
</tr>
<tr>
<td>United States of America</td>
<td>(1.92)</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>(33.25)</td>
</tr>
</tbody>
</table>

**Preliminary Results for Break-even Yield Requirements:** The purpose of simulating a 1% yield increase in the U.S. and its effect on global land-use change and GHG emissions is to calculate the indirect land-use change credit associated with biofuels. Kauffman et al. (2014) calculated the break-even yield necessary to achieve carbon neutrality from biochar-induced yield increase in the United States. The analysis is based on 2012 yield projections, a corn stover removal rate of 40% and 70% without and with biochar application, respectively. The functional unit to assess lifecycle emissions was 1 hectare and the application rate of biochar per acre was 10 tons.

**Table 10:** Break-even yield results

<table>
<thead>
<tr>
<th>ILUC</th>
<th>EPA 2022</th>
<th>EPA 2012</th>
<th>FAPRI 2017</th>
</tr>
</thead>
<tbody>
<tr>
<td>g CO₂-e/MJ</td>
<td>30.11</td>
<td>76.04</td>
<td>16.78</td>
</tr>
<tr>
<td>Break-even yield (10 tons/acre)</td>
<td>4.75%</td>
<td>5.90%</td>
<td>7.04%</td>
</tr>
<tr>
<td>Break-even yield (4 tons/acre)</td>
<td>1.60%</td>
<td>1.95%</td>
<td>2.23%</td>
</tr>
</tbody>
</table>
Table 10 summarizes the break-even effects under various assumptions. The value of 5.9% represents the result from Kauffman et al. (2014). We have also included a sensitivity analysis by reducing the application rate from 10 t/ac. to 4 t/ac., which would result in a quicker coverage of crop area with biochar. Reducing the application rate leads to a reduction in the break-even yield required because the yield increase is achieved quicker on more area. We have also included the lifecycle emissions based on yield projections for 2022 (“EPA 2022”) and by varying the indirect land-use change credit from biofuel based on the most recent CARD/FAPRI Model (“FAPRI 2017”). Note that a reduction in the indirect land-use change credit increases the break-even yield because the yield increase from biochar is most important when land-use change in the rest of the world are high.

To estimate the area that can be covered with biochar on a yearly basis, we have conducted a preliminary estimate of annual biochar production. The total 2016 harvested area (in million acres) for corn, soybeans, and wheat was 86.75, 82.74, and 43.89, respectively. Assuming a corn stover yield of 2 tons per acre for corn, we can collect 173.5 million tons of stover. Assuming a biochar yield of 17% and an application rate of 4 tons per acre, 7.37 million acres can be covered annually representing 4.35% of crop area for corn and soybeans.

**Progress**

Given the current political environment in the U.S., it is unlikely that carbon credits or other programs to address climate change will be enacted by congress in the near future. Hence, the vanguard PBBP industry is obliged to compete directly with the petroleum industry in the production of liquid transportation fuels and other co-products. Our technoeconomic analysis (Objective 3; Figure 26) indicates typical operating costs of $2.99 to $3.76 per gallon of diesel/gasoline for the industrial scale PBBP. This price is currently not competitive with oil. The value of the biochar co-product for this TEA, however, was discounted to just $20 MT; a value based on the higher heating value of biochar, which assumes that the biochar would be burned as a solid fuel rather than used as a soil amendment. If the value of the biochar co-product could be reliably increased to $150-$300/MT based on its’ value as a soil amendment, the economic viability of the PBBP would be substantially improved. Hence, research conducted under Objectives 1, 2, and 4 is focused on developing and assessing the value proposition for biochar.

We successfully developed (Figure 1) and published [25] the APSIM Biochar Model and are currently developing a stochastic biochar model (Figure 13). These models will allow farmers and land managers to assess the probability of agronomic and environmental benefits from the application of a specific type of biochar, on a specific soil type, under specific climate conditions, and assuming a specific management scenario. Given the diversity of biochar types and the complexity of biochar-soil-crop-climate-management interactions, this achievement is major step forward in biochar science and provides for the first time a means of assessing the value proposition for biochar applications from the farmer or land managers perspective.
While the APSIM Biochar Model is up and running much more work is still needed to refine, calibrate, and validate the model so that the model output consistently predicts crop yield and soil and environmental quality responses to biochar applications. Our ongoing research under Objective 1 is addressing this need by quantifying the capacity of diverse biochars to retain NO₃ and NH₄ (Figures 4 & 5), the influence of biochar amendments on N cycling and N availability under laboratory conditions (Figure 8) and in agricultural fields (Figures 11 & 12), by developing methods to rapidly quantify the biologically labile and recalcitrant biochar fractions (Figures 9 & 10), and by validating the model output against measured data from diverse (Table 3) field and laboratory studies (Figures 13-17). Furthermore, we are exploring means of adding value to biochar through the development of biochar-zero valent iron complexes, which have the ability to reductively dechlorinate organic compounds [61], and by identifying the feedstock and production conditions necessary to produce biochars with high anion exchange capacity [62 & 63]. Biochars produce with these properties are expected to have high value.

Now that the APSIM biochar model is fully functional, work under Objective 2 has focused on assembling a database using APSIM Biochar Model simulations for major crops grown on representative soils and under both historic and projected climates for the Upper Mississippi River Basin, California, and U.S. Southeast (Figures 18-21). Assessing the impacts of biochar and the value proposition for the PBBP in these three regions is moving forward through an iterative calibration and validation process integrating TEA and APSIM Biochar Model output. A key hypothesis being tested is that spatially targeted applications of biochar on marginal land with low-quality soils would have substantial benefits in terms of carbon sequestration and yield enhancement.

Under Objective 3, the TEA results indicate that high ash content and O/C ratios in the biomass feedstock have adverse impacts on the economic and environmental performance of the PBBP. Therefore, there is a trade-off between economic and environmental benefits when choosing a specific feedstock to use. We also conclude that PBBP is very promising for producing carbon negative energy even when indirect land use (Objective 4) and synergistic agronomic and environmental effects (Objective 1) are discounted. If we could produce heat and H₂ more efficiently, or decrease the natural gas consumption, such as reducing heat requirement by replacing conventional pyrolysis with autothermal fast pyrolysis, we could reduce the GHG emissions and thereby produce carbon-negative energy. More efficient feedstock plantation and collection would also move this platform to carbon negative. Finally, factoring in the agronomic and environmental value of using biochar as a soil amendment into the TEA will further improve the performance of the PBBP.

The following tasks were listed in the 2016 annual report to be completed under Objective 4:

1. Add the fertilizer supply functions and endogenize the fertilizer price;
2. Set up world price solvers for all the commodities;
3. Update and calibrate the new model with the most recent historical data;
4. Add biofuel policies for all modeled countries;
5. Run/test the model and make the necessary modifications/corrections;
6. Use the new model to establish a baseline;
7. Develop scenarios on major policy initiatives to be analyzed using the land allocation models including biochar, biofuel and trade policy scenarios;
8. Implement the policy scenarios and run the models;
9. Assess results from the model runs and rerun of models if results warrant modifications;

With the calibration of the CARD/FAPRI Model with the most recent data as well as executing the baseline and the 1% yield increase scenario, tasks 2 through 9 have been successfully accomplished. The current GreenAgSiM version includes static fertilizer application rates by country but this will be endogenized in the next year.

**Future Plans**

During the third and final year of the project the primary focus under Objective 1 will be on completing numerous ongoing studies, updating and validating the APSIM Biochar Model, and preparing manuscripts for publication. On-going studies that will be completed include:

1) Complete the long-term incubation study which is comparing the thermally and chemically labile and recalcitrant biochar fractions with biologically labile and recalcitrant biochar fractions. The study is designed to develop a rapid means of determining the size and the quality of biochar labile and recalcitrant fractions and to provide readily measurable biochar quality data that can be used as input parameters for the APSIM biochar model. One manuscript assessing chemical and thermal method is in preparation and a second manuscript documenting the outcomes of the biological incubations is anticipated.

2) Complete the soil nitrification study. At this time we are waiting on results for nitrogen isotope analysis. Once we have this data we will complete the data analysis and prepare a manuscript for publication. Depending on the results, we may need to modify the current nitrogen dynamics algorithms within the APSIM biochar model.

3) The APSIM model uses pedotransfer functions developed by Saxton and Rawls (2006) to populate missing data [64]. For example, the field capacity of a soil is estimated as a function of the soil's organic matter content and texture, two parameters readily available in the SSURGO soils database. We are currently evaluating the viability of using the Saxton and Rawls (2006) pedotransfer functions for biochar amended soils using experimental field data. Specifically we are determining if biochar C has the same influence on soil water parameters as biogenic C in soil organic matter. Results of this study will be reported as part of Debbie Aller’s PhD dissertation and in a related refereed publication.

4) Evaluate the ability of APSIM biochar model to predict crop yields and soil quality responses to biochar amendments using experimental soil, crop yield, and
management data from published literature and our own the long-term bioenergy cropping systems field experiments.

5) Refine the stochastic model for predicting the probability of a crop yield responses to biochar applications. When the new database is built, the biochar model will be recalibrated and run over the whole United States. Once validated the model will be shared broadly via an interactive web tool application. This tool will allow researchers, farmers, and land managers to interact with the model and make simple predictions/decision based on specific soil type and management conditions. Figure 31 shows example output from the web-based application.

**Figure 31:** Example output from the web-based application showing probability of achieving a positive crop yield response from biochar application on a specific farm field. Red regions have a high probability while dark blue regions have a low probability of a positive crop yield response.
Under Objective 2 we will develop the characterization of a regional model with demand and supply for biochar that will develop formulas and then apply them to determine what type of organization will be engaged in producing biochar (and to what extent they will rely on vertical integration or contracting). This will allow us to determine the supply of biochar, and by knowing its demand, derived from micro-level studies on contribution of biochar to productivity and greenhouse gas emissions, we will be able to calculate the price of biochar. Most importantly, our analysis will determine the characteristics of demand and supply that will lead to emergence of the biochar sector. We need to further interact with scientists to understand conversion methods and rates for various types of feedstock to biochar, and their associated costs, to develop alternative specifications of biochar supply. This will allow us to derive the pricing of biochar and the industrial organization of a biochar sector under various conditions.

The future plans for Objective 3 are to develop TEA and LCA models considering regional factors. We will compare economic and environmental performance for three different regions, including UMRB, California, and U.S. Southeast. Parameters including feedstock cost, feedstock type, product yields, capital cost, operating cost, market demands for different products, feedstock production emissions may vary with regions, which will lead to various TEA and LCA results. We will combine the results gathered from Objectives 1 and 2 with our current TEA and LCA models, and develop a location sensitive TEA & LCA model for the pyrolysis-bioenergy-biochar platform.

The next steps under Objective 4 are to obtain more realistic yield impact by soil type and crop estimates from APSIM, complete a U.S. life cycle analysis not only based on the functional unit of 1 ha of land but specific to the entire U.S., and incorporate the 4.35% of land that can be treated/improved with biochar annually into the CARD FAPRI and GreenAgSiM analyses.

**Publications and Presentations**

*Publications during year 2*


Publications in Press

Publications submitted and in preparation
22. Zilberman, David, Liang Lu and Thomas Reardon. “Innovation-induced food supply chain design.” Food Policy. (Forthcoming).
23. Aller, D., Rathke, S., Laird, D., Hatfield, J., Cruse, R. Quantifying the impacts of aged biochar on plant available water and water use efficiency. (In prep. for submission to Geoderma).


Presentations during year 2

References


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