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Review of the pyrolysis platform for coproducing bio-oil and biochar†

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Abstract: Pyrolysis is a relatively simple, inexpensive, and robust thermochemical technology for transforming biomass into bio-oil, biochar, and syngas. The robust nature of the pyrolysis technology, which allows considerable flexibility in both the type and quality of the biomass feedstock, combined with a distributed network of small pyrolysis plants, would be compatible with existing agriculture and forestry infrastructure. Bio-oil can be used as a fuel in existing industrial boilers. Biochar can be used with existing infrastructure as a replacement for pulverized coal; however, use of biochar as a soil amendment results in significant environmental and agronomic benefits. Soil application of biochar is a means of sequestering large amounts of C and may have other greenhouse gas benefits. Preliminary reports of the impact of soil biochar applications on crop yields indicate that biochar quality is very important. Biochar is an effective adsorbent for both nutrients and organic contaminants, hence the presence of biochar in soils has been shown to improve water quality in column leaching and field lysimeters studies and it is anticipated to do the same for agricultural watersheds.

The pyrolysis platform for producing bio-oil and biochar from biomass appears to be a practical, effective, and environmentally sustainable means of producing large quantities of renewable bioenergy while simultaneously reducing emissions of greenhouse gases. At the present time, the pyrolysis platform is economically marginal because markets for bio-oil and biochar are highly competitive. However, if the USA adopts a program for controlling greenhouse gases, the pyrolysis platform would be highly competitive. Published in 2009 by John Wiley & Sons, Ltd.

Keywords: pyrolysis; bio-oil; biochar; biomass; carbon sequestration; soil quality; agriculture; Terra Preta

Introduction

The emerging bioenergy industry has been promoted as a means of simultaneously improving energy security, improving weak rural economies, and helping to mitigate the threat of global climate change. Concerns, however, have been raised that the bioenergy industry will exacerbate problems of global food security because of competition between bioenergy production and food production for land and other resources, and that by increasing both the

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extent and intensity of land use, bioenergy production will adversely impact soil and water quality and could actually have a negative impact on global climate change. Furthermore, the bioenergy industry faces numerous technological, economic and logistic challenges. Grain ethanol production – the most advanced bioenergy production technology platform in the USA – is approaching a ceiling imposed ultimately by the finite capacity of US agriculture to produce grain. Cellulosic ethanol production, the most widely promoted second-generation bioenergy technology platform, has yet to be demonstrated at an industrial scale and faces numerous logistic and technological challenges. Paramount among the challenges facing the cellulosic ethanol industry are doubts about the ability of agriculture to consistently supply large quantities of both high quality and homogeneous biomass to centralized biorefineries and the equally daunting challenge of safely transporting, storing, and handling large quantities of low-density biomass to and at a centralized facility. Pyrolysis, an alternative second-generation bioenergy production technology platform, has received little attention in the USA to date. This analysis considers both the strengths and weakness of the pyrolysis platform.

What is pyrolysis?

Pyrolysis is a thermochemical process that can be used to transform low-density biomass (~1.5 GJ m^{-3}) and other organic materials into a high-energy-density liquid known as bio-oil (~22 GJ m^{-3} or ~17 MJ kg^{-1})), a high-energy-density solid known as biochar (~18 MJ kg^{-1}), and a relatively low-energy-density gas known as syngas (~6 MJ kg^{-1}).[1,2] Fundamentally, pyrolysis involves the heating of organic materials to temperatures greater than 400°C in the absence of oxygen. At these temperatures, organic materials thermally decompose releasing a vapor phase and a residual solid phase (biochar). On cooling the pyrolysis vapor, polar and high-molecular-weight compounds condense out as liquid (bio-oil) while low-molecular-weight volatile compounds remain in the gas phase (syngas). The physics and chemistry occurring during a pyrolysis reaction are very complex and depend on both the nature of the biomass and the rector conditions.[3,4]

Pyrolysis technology

Pyrolysis has been used to produce biochar (a.k.a. charcoal) for thousands of years. Traditional earthen, brick, and steel kilns typically vent volatiles to the atmosphere during biochar production. These systems have a bad environmental reputation as they are associated with deforestation and air pollution.[5] Modern pyrolyzers are designed to capture the volatiles for the production of bio-oil and syngas.[6]

The thermochemical technologies for transforming biomass into renewable energy products can be classified into four general categories: slow pyrolysis, flash pyrolysis, gasification, and fast pyrolysis. Slow pyrolyzers are either batch systems known as 'charcoal kilns', or continuous systems that slowly heat the biomass to >400°C in the absence of oxygen. Moisture content and particle size are not critical for charcoal kilns while continuous systems do specify some size reduction and drying for optimal results. Product yields from slow pyrolysis are approximately 35% biochar, 30% bio-oil, and 35% syngas by mass.[7] Typically the bio-oil, in the form of vapors and aerosols, is not separated from the syngas. If exhausted to the atmosphere, as typically occurs in traditional kilns in the developing world, it represents a serious pollution emission. In developed countries, slow pyrolyzers are usually fitted with afterburners to control emissions of
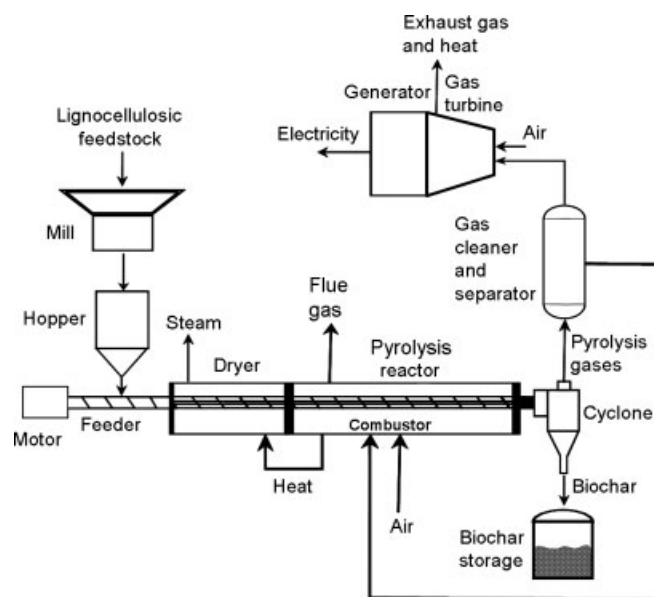

Figure 1. Schematic diagram showing processes and the flow of material in a continuous, auger-based, slow pyrolyzer. Biochar, electricity and heat are the primary products of this stream. The pyrolysis gases are consumed to generate heat for the pyrolyzer and to run a gas turbine for electricity generation. This is one of many possible designs for a slow pyrolyzer.

air pollutants, or the volatiles are used as fuel for the generation of heat or electricity (biopower) (Fig. 1). Flash pyrolysis, which is designed to maximize biochar production, involves the heating of batches of biomass under moderate to high pressure in a retort. Yields from flash pyrolysis are typically 60% biochar and 40% volatiles (bio-oil and syngas). Flash pyrolyzers are more likely to include heat-recovery equipment than traditional kilns. Gasification is designed to maximize production of syngas. A typical gasifier allows a small, carefully controlled amount of oxygen to enter the reaction chamber. The oxygen causes partial combustion of the biomass, which generates the heat needed to sustain the reaction. The reaction temperature is generally quite high (800–1200°C). Operated at sufficiently high temperatures, a gasifier produces very little char or bio-oil although many commercial gasifiers can produce 5–15% char and traces of bio-oil, which is referred to as 'tar'. Fast pyrolyzers are continuous-flow systems designed to maximize production of bio-oil. Fast pyrolysis product yields are typically 50–70% bio-oil, 10–30% biochar, and 15–20% syngas by mass. Biomass must first be dried and ground to <2 mm particle size before entering a fast pyrolyzer. Within the pyrolyzer, the biomass is heated rapidly in the absence of oxygen (typically to temperatures >400°C in less than 1 second) by one of several technologies, such as mixing biomass with pre-heated sand in a fluidized bed reactor (Fig. 2). The rapid heating causes the thermal decomposition of the biomass to vapors, aerosols, and light gases. To maximize bio-oil yield, the volatiles must be rapidly separated from the solids and cooled. These latter processes are typically accomplished using a series of cyclones followed by condensers or quenchers.

Energy efficiency of pyrolysis

Plant engineers account for the amount of energy consumed within the boundaries of a pyrolysis plant. This energy cost is usually counted against the major product of the plant, although it can be apportioned among the various byproducts – usually according to mass fraction – if they have significant economic value. For example, a traditional charcoal kiln counts the charcoal as its only product with the result that the energy efficiency of charcoal production is relatively low, since much of the energy escapes in the form of waste heat and unburned vapors and gases. On the other hand, a modern, fast pyrolyzer counts bio-oil, which represents as much as 75 wt-% of products as the sole product of economic importance. On this basis, the energy
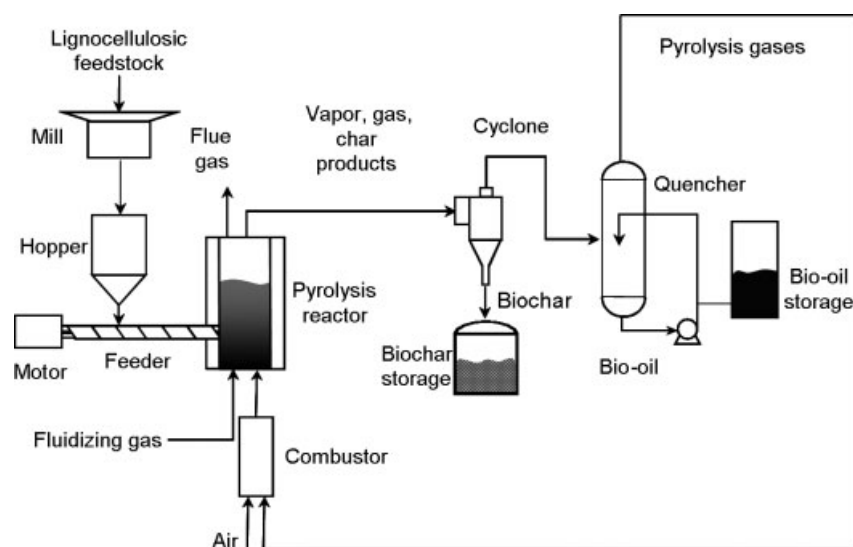
Figure 2. Schematic diagram showing processes and the flow of material in a fast pyrolyzer. The stream of incoming biomass is mixed with pre-heated sand in a fluidized bed rector where heat is rapidly transferred from the sand to the biomass (temperature increases to > 400°C in <1 s). This is one of many possible designs for a fast pyrolyzer. See Bridgwater et al.[1] for more information on fast pyrolyzers. This figure is adapted from Brown.[6]

efficiency is about 70%. However, if the energy content of the char is considered, the overall energy efficiency is more than 90%.[1,8] Of course, there is also energy associated with the production of pyrolysis products that occurs outside the confines of the plant. Energy is required to grow, harvest and transport biomass. Energy is also required to transport the bio-oil and biochar products to markets and to their ultimate site of utilization. A complete life-cycle accounting would include these energy costs as well as the energy required to fabricate the pyrolysis equipment and erect and maintain the plant.

Feedstock

Almost any form of organic material can be introduced into a pyrolyzer, including corn and wheat stover, forestry byproducts, urban yard wastes, industrial byproducts, animal manures, and sewage sludge. The high temperature of the pyrolysis process neutralizes any organic toxins (e.g., aflatoxin) and pathogens in the feedstock. The presence of ash and other inorganic compounds in the biomass can adversely affect bio-oil quality and yield.

Chemical properties of the feedstock have a significant influence on both product yields and product quality. Among cellulosic feedstocks, bio-oil yield decreases with increasing ash content and the average molecular weight of the bio-oil fraction increases with lignin content of the feedstock.[9] Pyrolysis of used tires produces high-value bio-oil and biochar; one of the bio-oil fractions can be used directly to boost the octane rating of gasoline.[10,11] Pyrolysis of cellulosic biomass feedstocks produces bio-oils that contain water and organic acids in addition to hydrocarbons. The acidic nature of such bio-oils renders them unsuitable for direct use as a fuel in diesel or gasoline engines. Although it is possible to pyrolyze municipal solid waste, this should only be done with caution and appropriate monitoring. Any heavy metals in municipal solid wastes will be concentrated in the biochar fraction after pyrolysis.

Annually, approximately 1.3 billion tons of biomass are potentially available in the USA for bioenergy production with the most abundant forms being corn, wheat, and forestry residues.[12] The Perlack et al.[12] study has been criticized because the decision on how much crop residue could be harvested and how much should be left on the field was

estimated using 't' values from the Revised Universal Soil Loss Equation. T values estimate the amount of residue that should to be left on the soil to protect it from erosion. Sustaining soil quality and preventing the loss of soil organic C requires greater annual inputs of crop residues than that needed to simply prevent wind and water erosion.[13]

Scalability

Pyrolyzers range in size from laboratory devices that process as little as a few milligrams of material per test to industrial equipment processing many tons per hour. The largest fast pyrolyzers in North America are capable of processing 250 and 200 dry tons of biomass per day. Slow pyrolyzers are less complicated and can be built at smaller scales than fast pyrolyzers. Several companies are currently marketing or soon will be marketing industrial-scale pyrolyzer systems. Pyrolyzers can be scaled from small to large to optimize the balance between economies of scale associated with processing biomass at a large centralized facility and reduced biomass transportation, storage and handling costs that accrue from processing biomass through a distributed network of small facilities located close to the biomass source.[14–16]

Potential uses of syngas

Syngas is primarily a mixture of H_2 and CO, but also typically contains CH_4, CO_2, H_2O, and several low-molecular-weight volatile organic compounds.[2] The heating value of syngas is relatively low ($\sim$6 MJ kg^{-1}) compared to that of natural gas ($\sim$54 MJ kg^{-1}). However, syngas can be burned to produce heat energy for various applications, such as drying and electricity generation. Before the widespread availability of natural gas, syngas produced via gasification of coal (a.k.a., producer gas or town gas) was widely used in the northeastern USA to provide energy for home heating, cooking, street lighting, etc. A likely use of syngas produced via pyrolysis of biomass for small- and medium-scale pyrolyzers will be to generate the heat and electricity needed to run the pyrolyzer itself (Figs 1 and 2).

Potential uses of bio-oil

Both the chemistry and the heating value of bio-oil vary substantially depending on the nature of the organic feedstock and the conditions under which the feedstock was

pyrolyzed. Bio-oil produced by fast pyrolysis of cellulosic biomass is an emulsion of water (~20% w/w) and a wide range of oxygenated organic compounds including organic acids, aldehydes, alcohols, phenols, carbohydrates, and lignin-derived oligomers.[7,17] The heating value of biomass bio-oil (about 17 MJ kg^{-1} wet weight basis or 22 MJ kg^{-1} dry weight basis) is typically about half that of No. 2 fuel oil.[1,2] Bio-oil produced from cellulosic biomass does not burn efficiently without pre-heating; it is acidic (pH ~2); and it tends to gel after sitting for prolonged periods of time, especially in cold climates. Because of these properties, bio-oil does not currently appear to be a good substitute for No. 2 fuel oil in home-heating applications, although research programs are underway to reduce its acidity and to improve its stability. However, bio-oil can be burned in industrial boilers. The use of bio-oil as an industrial fuel typically requires that the boiler be equipped with stainless steel or plastic-lined, fuel-injection components and storage tanks to resist corrosion, a system that heats and/or stirs the bio-oil during storage to prevent gelling, and a system that pre-heats the incoming bio-oil to the flash point (65°C) before nebulization to improve burning efficiency.

Although not suitable as transportation fuel, bio-oil can be upgraded into synthetic transportation fuels. One approach would gasify bio-oil and convert the syngas to synthetic gasoline and diesel through Fischer-Tropsch (F-T) catalytic synthesis. F-T synthesis is currently employed on an industrial scale in South Africa and Malaysia to convert coal and natural gas into transportation fuels, respectively. Relatively minor modifications would be required for these existing F-T refineries to use bio-oil as a feedstock. The European Union (EU) is considering the development of a distributed network of biomass pyrolyzers that would supply bio-oil to centralized F-T refineries.[18] The high initial investment required to build an F-T refinery is the biggest obstacle to the adoption of this approach in the USA. F-T refineries must be very large to achieve economies of scale. A second problem is the relatively low carbon-conversion efficiency of F-T refineries, which is only about 50%.[19] Another approach would hydrocrack bio-oil to transportation fuels in a manner similar to the refining of petroleum to gasoline.[20] As illustrated in Fig. 3, bio-oil vapors would be recovered as a carbohydrate-derived aqueous phase and a lignin fraction.
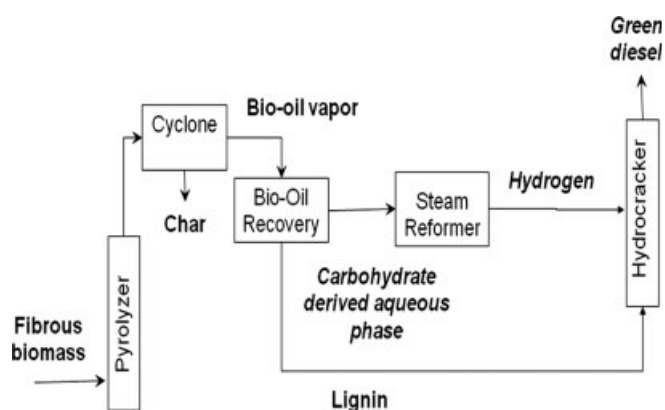

Figure 3. Schematic diagram of the production and hydrocracking of bio-oil into synthetic diesel.

The aqueous phase would be steam reformed to hydrogen. The lignin fraction would be hydrocracked to hydrocarbons. The large volume of hydrogen required for this process would come from the steam reformer. The process is economically attractive and could employ the infrastructure at existing petroleum refineries to support bio-oil hydrocracking.

Potential uses of biochar

Biochar is a combustible solid (~18 MJ kg^{-1}) that can be burned to generate heat energy in most systems that are currently burning pulverized coal. The sulfur content of biochar is low and hence industrial combustion of biochar generally does not require technology for removing SOx from emissions to meet EPA emission limits. Emissions of NOx from combustion of biochar are comparable to that coming from coal combustion and require similar abatement technology. The ash content of biochar depends substantially on the feedstock. Some sources of biomass, such as corn stover, rice husks and *Miscanthus giganteus* contain relatively high levels of Si, and after pyrolysis the Si is concentrated in the biochar. Combustion of high Si biochars will cause scaling on the walls of combustion chambers and decrease the usable life of those chambers. Low-ash biochars are also use in metallurgy and as a feedstock for production of activated carbon, which has many uses, such as an adsorbent to remove odorants from air streams and both organic and inorganic contaminants from waste-water streams.

An emerging new use of biochar is as a soil amendment, which is discussed in detail below.[21–24]

The impact of biomass harvesting on soil quality

The harvesting of crop residues for the production of bioenergy could have adverse impacts on soil and environmental quality.[25–27] The harvesting of residue removes substantial amounts of plant nutrients from soil agro-ecosystems. Unless these nutrients are replaced by the addition of synthetic fertilizers, manure, or other soil amendments, the productivity of the soil will decline. Even if synthetic fertilizers are added to maintain soil fertility, the sustained removal of crop residues without compensating organic amendments will cause a decline in levels of soil organic matter, a decline in the cation exchange capacity, a decline in water-holding capacity, and accelerated acidification of soils. The sustained removal of residues will also cause degradation of soil structure and thereby restrict the movement of air and water through soils and the growth of plant roots. Declining levels of organic matter will increase the surface crusting of soils, which will restrict infiltration of water and increase surface runoff and erosion. The increased loss of nutrients to leaching will mean increased nutrient contamination of surface and ground-water reservoirs. Furthermore, any carbon credit claimed for bioenergy displacing fossil fuel will be severely discounted due to the loss of soil organic matter and the increased energy used for fertilizer production and tillage.

Recognition of the above sustainability issues has motivated numerous scientists to investigate potentially more sustainable biomass production systems.[28,29] Examples include the use of 'no tillage' to minimize adverse soil impacts; the use of fall and perennial cover crops to protect the soil from erosion and to return additional organic C to the soil; crop rotations that include deep-rooted species such as alfalfa that build soil organic matter; dedicated perennial biomass crops; and both long-season crops and double-cropping systems that maximize the use of available growing degree-days during the cropping season. The return of the biochar coproduct of pyrolysis to the soils from which the biomass was harvested has also been proposed as a means of enhancing soil quality and thereby the sustainability of bioenergy production systems.[23] Furthermore, many of the nutrients in biomass are recovered with the char product, offering opportunities for nutrient recycling.[28]

The history of Terra Preta soils and anecdotal evidence of the impact of biochar on soil productivity

Francisco de Orellana was the first European to explore the central Amazon in the year 1542. He reported back to the Spanish court that a large agricultural civilization existed along the banks of the Amazon and its tributaries. Sixty years later, when the next Europeans ventured into the central Amazon, the civilization had vanished. For centuries, most people assumed that de Orellana had invented the stories of a civilization in Amazonia. During the twentieth century, however, anthropologists found evidence of extensive regions of Terra Preta soils (Portuguese for 'dark earth') along the Amazon (Fig. 4).[30,31] Pot shards and other human artifacts associated with the Terra Preta soils indicated that these soils were anthropogenic. During the 1990s, soil scientists discovered that the Terra Preta soils contained large amounts of biochar.[32] Apparently, the ancient Amazonian farmers practiced a form of *slash and char* agriculture, which allowed them to incorporate large amounts of biochar along with other organic materials, such as manure and fish bones, into the otherwise infertile Oxisols of the Amazon region.[32] Today, over 500 years after the practices ceased that led to their genesis, the Terra Preta soils are the prize horticultural and agricultural soils of Amazonia. Terra Preta soils contain substantially higher levels of organic C and plant
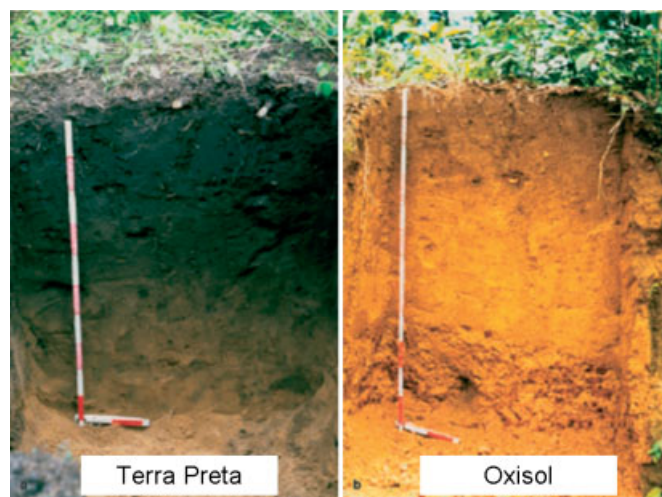

Figure 4. Representative Terra Preta and Oxisol soil profiles (Images from Glaser *et al.*[32] and reprinted with permission from *Naturwissenschaften*).

nutrients and have lower leaching rates for plant nutrients than the Oxisols from which they were made.[33]

Other anecdotal evidence suggesting that biochar additions improve soil quality include the use of biochar as a soil amendment in traditional Japanese horticultural practices, and several reports from Africa and South America documenting substantially higher yields for crops grown on charcoal kiln sites than on adjacent soils.[34,35] The prairie soils of the Midwest USA are notorious for their high fertility and their ability to sustain productivity. Recent evidence indicates that ~10% of the carbon in prairie soils is biochar, a legacy of >10 000 years of prairie fires.[36,37]

Impact of biochar amendments on soil and water quality

Most of the published research to date has focused on documenting differences between the Terra Preta soils and adjacent Oxisols or between soils on charcoal kiln sites with adjacent sites.[21,33] Terra Preta soils typically have higher levels of organic matter, higher moisture-holding capacity, higher pH values, greater nutrient-holding capacity, and higher levels of bioavailable N, P, Ca and K than the Oxisols from which they were derived.[32,38] Oxidation of biochar surfaces and the retention of oxygen-rich organic compounds on surfaces of biochar add substantial cation exchange capacity to the Terra Preta soils of Brazil.[39] Biochar enhances microbial – especially mycorrhizal – activity, and is known to accelerate nitrification in forest ecosystems probably by adsorbing compounds (phenolics) that inhibit nitrification in the absence of biochar.[40,41] A recently completed 500-day soil column leaching/incubation study (Table 1) found that biochar additions decreased NO_3^- leaching by 10% and P leaching by 40 to 70%.[42,43] Leaching of K^+ increased with biochar additions due to the K^+ added

with the biochar, however, the presence of biochar decreased leaching of K^+ that was subsequently added with manure. Similar results were observed for Ca^{2+} and Mg^{2+}. The cation exchange capacity was 5–20% higher and the pH was up to 1 pH unit higher for the biochar amended soils relative to the controls 500 days after the biochar was added. Soil organic C, total N and microbial respiration all increased systematically with the amount of biochar added. Soil bulk density measured six times during the study was significantly lower for the biochar-amended soils than the control soils. In summary, biochar additions and the presences of even >500-year-old biochar in soils has been found to improve most measures of soil quality.

Impact of biochar amendments on soil carbon sequestration and greenhouse gas emissions from soils

Biochar is very stable in soil environments[21] and is commonly the oldest form of organic C in soils[44] with radiocarbon dates often measured in 1000s y.b.p.[45–47] In forest ecosystems, radiocarbon dates for biochar greater than 10 000 y.b.p. have been reported.[48] Mass balance analysis did not detect any loss of biochar C, whereas less than 20% of manure C remained in the soils after a 500-day incubation (Table 1).[42,43] Thus applications of biogenic organic residues (plant and animal residues) to soils provide only temporary C storage (half-lives measured in weeks or months), whereas applications of biochar to soils removes C from the atmosphere for millennia (Fig. 5). On the other hand, a few reports have found substantial losses of biochar C in soils after only a few years.[49,50] Differences in biochar quality are a likely explanation for the discrepancy. Some of the C in biochars produced by low-temperature pyrolysis is bioavailable, while C in high-temperature biochars is either

Table 1: Impact of biochar additions on soil quality (Laird *et al.*[42]; Rogovska *et al.*[43]). Soil properties were measured 500 days after biochar applications in a soil column leaching and incubation study (48 columns = 8 treatments x 6 replications). Bulk density (BD) was measured on day 483. Values followed by a different letter are significantly different (P < 0.05).

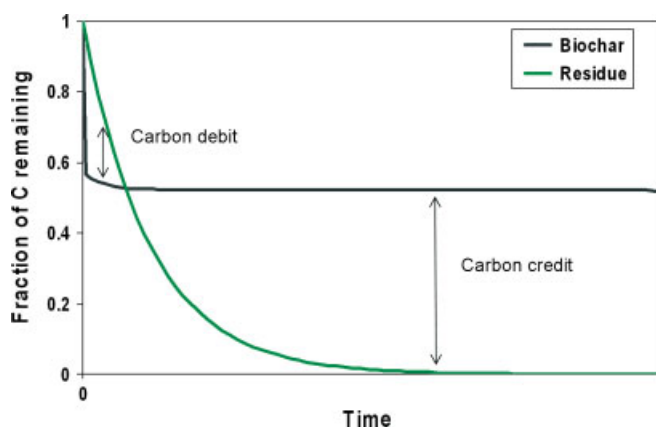| Biochar (g/kg)	C (g/kg)	N (g/kg)	CEC (cmol/kg)	BD (g/cm^3)	pH
0	20.5 A	1.73 A	18.1 A	1.34 A	6.33 A
5	24.1 B	1.74 A	20.8 B	1.24 B	6.55 A
10	28.2 C	1.81 B	21.6 B	1.24 B	6.88 B
20	34.6 D	1.85 B	21.7 B	1.24 B	7.23 C

Figure 5. Impact of biomass pyrolysis with soil application of **Biochar** on the amount of original biomass C remaining in the soil relative to the amount of C remaining in the soil if the same biomass is returned to the soil as a biological **Residue**. For the Biochar example, about 40% of the C is lost at time 0 when the biomass is pyrolyzed, 10% of the total C is lost to mineralization over a few months, and the remaining 50% of the total C is stable for millennia. For the Residue example, the half-life of the residue C is assumed to be 6 months and 99% of the C is lost to mineralization after 4 years. The biochar scenario results in a C debit for the first 6 months and a C credit thereafter relative to the residue scenario. See Lehmann *et al.*[49,58] for more information on the relative stability of biochar and residue C.

nondegradable by micro-organisms or the rate of microbial degradation is exceedingly slow. All biochars are subject to slow abiotic oxidation in soil environments and will eventually be degraded.[51]

The presence of biochar in soil environments enhances microbial activity and may accelerate the degradation of organic residues and biogenic humic substances.[52] Recent work by *Kuzyakov et al.*[53] using ^{14}C-labeled feedstocks and typical agricultural soils suggests that this effect is minor, if it occurs at all in agronomic situations. The cause of this increase in soil microbial activity is not clear; however, several factors – such as lower bulk densities, improved aeration, higher pHs, increased sorption of phenolic compounds that may inhibit microbial activity, and the porosity in biochar providing a favorable habitat for soil micro-organisms – all may enhance soil microbial activity. The accelerated degradation of soil humic substances will result in increased net emissions of CO_2 from fallow soils amended with biochar. When plants are growing, the

increased microbial activity will increase nutrient cycling, which should promote plant growth and hence increase the input of new C to the soil through photosynthesis. Biochar strongly adsorbs dissolved organic compounds (DOC) from the soil solution, and adsorbed DOC is less bioavailable than DOC that remains in the soil solution. Adsorption of DOC and biochar surface catalyzed hetero-polymerization reactions are hypothesized to increase the rate and efficiency by which organic materials are transformed into new humic substances. It is not known whether the affects of biochar on humic substance formation and the accelerated input of new C to soils through photosynthesis will balance the accelerated biodegradation of existing soil humic materials. Anecdotally, the presence of high levels of both biochar and biogenic humic materials in the Terra Preta soils of Brazil suggests that the net effect of biochar is to promote the accumulation of humic materials; otherwise the Terra Preta soils would be expected to contain little biogenic humic material after more than 500 years.

The radiative forcing of N_2O is 296 times that of CO_2, and emissions of N_2O from agricultural soils may have a larger impact on global climate change than emissions of CO_2 from agricultural soils. Several recent reports indicate that biochar additions may reduce emissions of N_2O from soils.[43,54] For example, a 70% reduction in N_2O emissions for soils receiving biochar relative to controls was observed approximately one year after the biochar application during the 500-day incubation/leaching study.[43] The N_2O results are consistent with the observed reduction in bulk density (Table 1) for the biochar-amended soils, which would increase soil aeration and hence decrease denitrification. Much research is needed to quantify the interactions between biochar, soil properties, soil moisture content, management practices and N_2O emissions.

Ancillary impacts of soil biochar amendments on net greenhouse gas Emissions

In a recent article, Searchinger *et al.*[55] argued in effect that *the conversion of an acre of Iowa farmland from food production to biofuel production provides an economic incentive for a Brazilian farmer to cut down an acre of native rainforest and plant food crops; and that the large amount of C lost to the atmosphere as CO_2 when the acre of native rainforest is converted to cropland is much larger than any C credit*

claimed by the Iowa farmer for producing biofuels. The pyrolysis platform partly addresses these concerns as soil biochar amendments in temperate and tropical regions are expected to increase soil productivity and hence both crop and biomass yields per unit area of land. Increasing agricultural intensity will decrease the incentive for converting land in native vegetation to new cropland. Use of corn and wheat stover, urban yard wastes, or forestry residues as feedstock for pyrolysis will not compete with food crop production. However, dedicated biomass crops grown on prime agricultural land for pyrolysis would compete with food crop production for land resources. The net effect of a pyrolysis industry on global land use over the next few decades will depend on the balance between the rate and extent of agricultural intensification and the rate of growth in demand for food and biomass crops.

Soil biochar applications will merit additional carbon credits if they displace agricultural lime and fertilizer and increase fertilizer use efficiency. Agricultural lime is a major source of greenhouse gas emissions, as a substantial amount of energy is required to mine and crush limestone in the production of agricultural lime, and when agricultural lime is spread on soils, the $CaCO_3$ reacts with $2H^+$

to produce H_2O and CO_2.[56] During pyrolysis of biomass, acids are partitioned into the bio-oil fraction while bases – primarily K_2O, CaO, and MgO – are partitioned into the biochar fraction. The reaction of oxide bases in soil environments does not release CO_2. Based on stoichiometry and assuming typical N fertilizer application rates for corn production and that anhydrous ammonia is used as the source of N fertilizer, the lime credit for the biochar produced from stover harvested from one acre of land would only neutralize about 20% of the acid generated during nitrification of the anhydrous ammonia applied per acre of land. Thus it does not appear that biochar applications will ever fully replace agricultural lime applications. Increased fertilizer use efficiency resulting from biochar applications would potentially decrease fertilizer application rates.

The net impact of biomass pyrolysis with soil applications of the biochar on greenhouse gas emissions will include all of the direct and ancillary effects discussed earlier (Fig. 6). A complete life-cycle analysis to quantify the net impact of the pyrolysis platform on greenhouse gas emissions is not possible without additional research on many of these factors and processes.
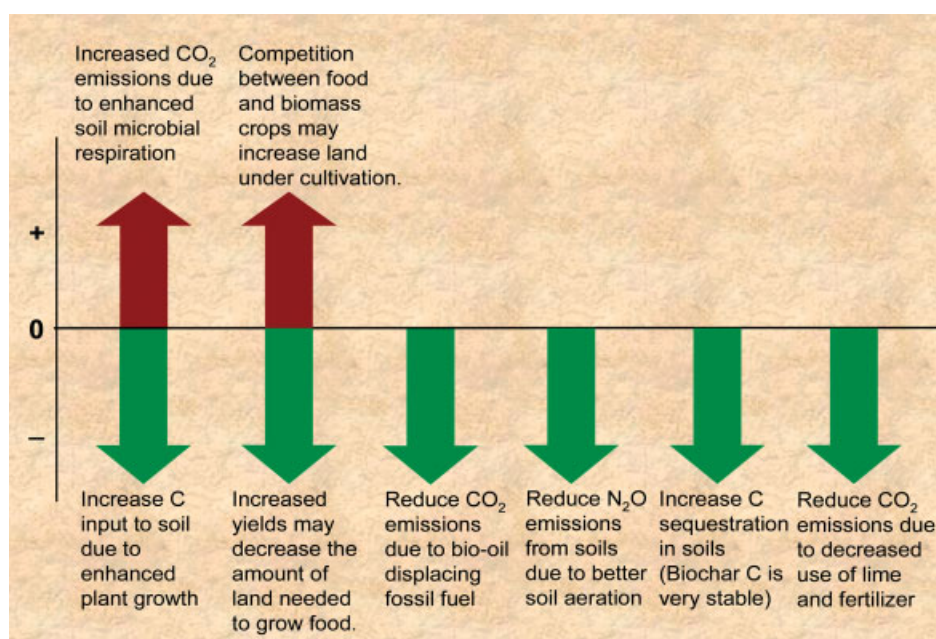

Figure 6. Factors that will influence the net impact of a pyrolysis industry with soil biochar applications on greenhouse gas emissions. Adapted with significant changes from a figure presented by Rogovska *et al.*[43].

Potential impact of a pyrolysis industry on the global carbon cycle

Photosynthesis and the biological decay of organic residues are the dominant sinks and sources of atmospheric CO_2 in the global C cycle. Currently the production of biochar through incomplete combustion of biomass is a trivial C sink, responsible for sequestering ~0.1-0.3 Gt of C per year.[57] Global implementation of a pyrolysis platform for transforming biomass into bio-oil and biochar with the use of biochar as a soil amendment has the potential for a large impact on the global C cycle.[23,24,54,58–60]

Accurate estimation of the impact of a pyrolysis industry on the global C cycle is not possible without considering the details discussed earlier. However, with numerous simplifying assumptions and global estimates of biomass utilization,[61] it is possible to obtain first-order estimates of the impact under nominally sustainable conditions. We define these conditions as involving no further increase in the human appropriation of the annual biomass C fixed by photosynthesis, which currently stands at about 12% of total biomass fixed and 20% of that located above ground.[62] The current global C cycle (Fig. 7A) is out of balance by 4.9 Gt C year. Development of a sustainable pyrolysis industry, in which 50% of global crop residues and 67% of global forestry residues (felling losses) serve as the only feedstocks and biomass plantations are not expanded beyond their current extent, could decrease the global imbalance by about 0.9 Gt C each year (Fig. 7B). If forestry residues were expanded to include 67% of below-ground biomass from harvested forests (stumpage), and steps were taken to thin disease-ridden forests and otherwise apply pyrolysis to avoid 50% of human-induced burning of biomass, an additional 0.9 Gt C could be sequestered annually (Fig. 7C). Carbon released by human-induced fires represents about one-third of the total C released by fire, and perhaps even further sustainable biomass harvesting can be done in the world's forests to divert biomass C from the open combustion pool and into the pyrolysis pool to yield sequestration and bioenergy benefits while at the same time preserving biodiversity. Estimates of the land available to receive the C converted to biochar suggest that between 80 and 270 Gt C could be sequestered in this fashion (depending on the depth of incorporation), a range that brackets the current atmospheric imbalance of about 220 Gt C.[60]

Humanity has limited options for bringing balance to the global C cycle. Either we can decrease CO_2 emissions from the burning of fossil fuels or from the biological mineralization of biomass C. As shown in Fig. 7, the pyrolysis platform simultaneously does both and thus can be a powerful tool for climate change mitigation.

Biochar quality

Biochar is a diverse group of materials with a continuum of properties that depend on properties of the feedstock, the conditions under which it was pyrolyzed, and any post-pyrolysis changes caused by aging or treatments. The relevant properties of biochar include the chemical forms and concentrations of C, N, and bases present in the biochar, total porosity, pore-size distribution, and the density and types of polar surface functional groups. Concentrations of bases in biochar depend primarily on the mineral content of the biomass feedstock and will determine both the agricultural lime credit and credits for nutrients such as P, K^+, Ca^{2+}, and Mg^{2+} that may be given for agricultural applications of biochar. Softwood biochars tend to have low ash content; hardwood biochars have intermediate ash content; and biochars derived from corn or wheat stover typically have higher ash content. About half of the N in biomass is partitioned into bio-oil and half into biochar. However, much of the N in biochar is heterocyclic N,[63] which is highly stable in soil environments and will be released very slowly from the biochar to the soil solution. Freshly made biochar is hydrophobic and contains few polar surface functional groups; however, on exposure to water and oxygen in soil environments, the surfaces of biochar oxidize, forming carboxyl and other oxygen-containing functional groups, which adds cation exchange capacity and transforms the biochar from hydrophobic to hydrophilic material.[51] High temperature biochars tend to have greater concentrations of condensed aromatic C, while biochar produced by lower-temperature pyrolysis may contain remnants of biopolymers. Application to soils of low-temperature biochars that contain substantial amounts of bioavailable C may result in nutrient immobilization as the bioavailable C is mineralized.

During pyrolysis, the C in biopolymers is condensed into complex aromatic structures that range in size from single ring to large graphene sheets. Lighter aromatic molecules,
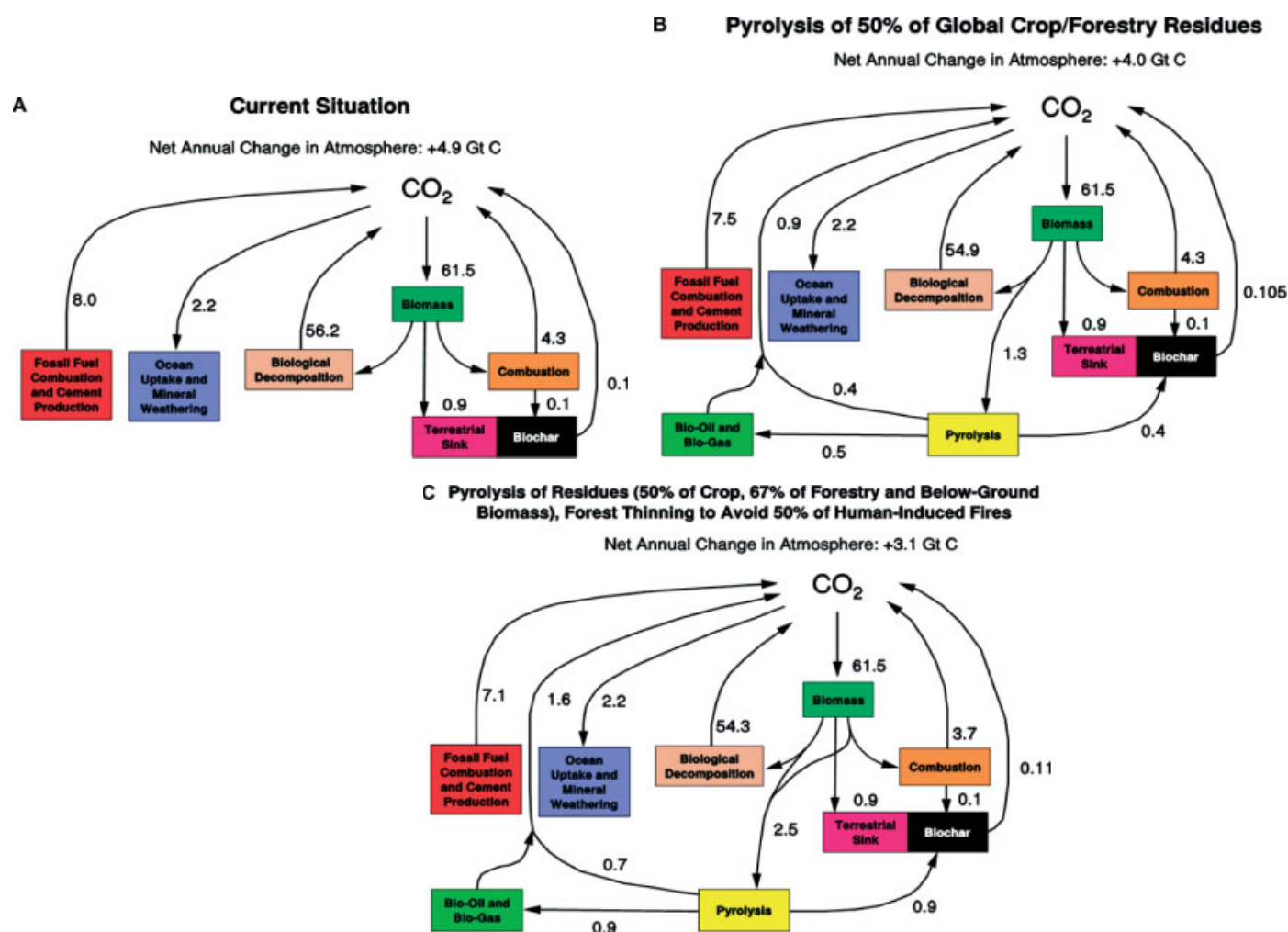
Figure 7. Assuming no other changes or ancillary effects and a 1:1 energy equivalence for bio-oil C and fossil-fuel C, the 4.9 Gt C imbalance in the current global C cycle (A) could be improved by about 0.9 Gt C by annually diverting 50% of global crop residues and 67% of global forestry felling losses to a pyrolysis industry without further expansion of biomass plantations (B). An additional 0.9 Gt C could be sequestered by pyrolysis of currently unused below-ground biomass residues (primarily forestry related), and from the avoidance of 50% of human-induced fires through diversion of thinning products and other biomass that currently is combusted in the open (C). The figure was adapted with significant changes from figures previously presented by Lehmann et al.[58] and Amonette et al.[59,60].

including most single ring and smaller polycyclic aromatic hydrocarbons (PAHs) are distilled into the bio-oil fraction during pyrolysis; however, some residual aromatic molecules may remain in the biochar. Any residual PAHs will be very strongly adsorbed to the biochar and are unlikely to leach in soil environments. For example, biochar additions to soil have been shown to decrease both leaching and bioavailability of ^{14}C-phenanthrene.[64] Oxidation of residual aromatic molecules may lead to the production of phytotoxic phenolic compounds. However, phenolic compounds are also strongly

adsorbed by biochar and are unlikely to leach or be bioavailable.[65] In germination studies, Garnett et al.[66] observed that biochar adsorbed phenolic compounds in leaf-litter extracts and enhanced seedling growth relative to controls exposed to the leaf-litter extracts without the biochar. Pyrolysis condition, however, will have a large influence on the loading of residual aromatic molecules in biochar. Biochars cooled in the presence of pyrolysis volatiles or exposed to bio-oil after cooling will adsorb PAHs and other aromatic molecules; and biochars with high loadings of aromatic

molecules could become sources rather than sinks for these molecules in soil environments.

Safety and handling of biochar

Biochar produced by fast pyrolyzers is a fine powder. Surface applications of biochar powders to agricultural soils will result in substantial particulate emissions. Such particulate emissions may adversely affect the quality of life and pose an unacceptable health risk for anyone exposed to the dust. Biochar is a flammable solid and biochar powders may spontaneously combust if exposed to moisture and oxygen during storage. Large concentrations of biochar dust in an enclosed area are potentially explosive. Engineering solutions to resolve these problems include pelletizing biochar or preparing biochar as a slurry with water or liquid wastes such as swine or dairy manure. However, both of these options may increase the cost of handling and applying biochar to agricultural soils. Biochar will need to be incorporated into agricultural soils either during waste application (slurry injection) or immediately after a surface application. Tillage operations to incorporate biochar may not be compatible with no-tillage management systems, although in many systems a one-time application of biochar may be all that is envisioned.

Harvesting, storage and transport of biomass and soil applications of biochar will place additional labor demands on farmers and land managers. Harvest is often a period of critical labor shortage in modern production agriculture. For the pyrolysis industry, crop residues can be harvested after grain has been harvested thereby spreading out the peak demand for labor. On many farms, corn and wheat stover could be harvested with existing, large, round or square balers, which will minimize the need for farmers to purchase expensive new equipment. Biomass for pyrolysis can be stored on-farm with just-in-time delivery to the local pyrolyzer, thus avoiding problems associated with the storage of large concentrations of biomass in one location.

Crop yield response to biochar applications

Several studies have reported substantial crop-yield increases in response to soil biochar applications.[21,67–71] Most of these studies, however, were conducted in the Tropics using biochar produced in local earthen or steel kilns and applied to soils with low organic-matter content. Based on greenhouse pot studies, Deenik *et al.*[72] recently reported reduced plant growth for soils amended with biochars having high levels of volatile matter. Volatile matter is typically high for low-temperature biochars and the amount of volatile matter may be correlated with levels of bioavailable C (hence the potential for nutrient immobilization). At the small plot scale, Gaskin *et al.*[73] observed no yield or biomass response to 11.2 Mg ha^{-1} and 22.4 Mg ha^{-1} pine chip and peanut hull biochar + fertilizer applications on a Tifton loamy sand (fine loamy, koalinitic, thermic, plinthic Kandiudults) in the southeastern United States; without fertilizer a small stover but no grain yield response was observed for the peanut hull biochar applications. The biochars used in this study were produced by relatively low-temperature (400°C) slow pyrolysis with steam. Field trials are currently underway at several locations across the USA using various sources of biochar. However, much more research is needed to understand the interactions between various biochars, soils, climates, and crops.

Economics

The production cost of bio-oil could be as low as $26 per barrel in 550-ton-per-day plants, although smaller plants would likely have higher production costs.[74,75] Existing pyrolyzers are primarily exploiting niche markets for high-value coproducts of pyrolysis. The current bulk commodity market for bio-oil is as a replacement for No. 2 fuel oil in industrial boilers. Bio-oil could also be used by utilities as a replacement for coal, but at current prices bio-oil is not economically competitive with coal. Industrial-scale technology for transforming bio-oil into higher-value transportation fuels is an attractive possibility but is not ready for commercialization.

The primary market for biochar at this time is as a replacement for bulk coal. These existing markets are highly competitive and offer very thin margins for the emerging pyrolysis industry. The key advantage for the pyrolysis platform is that bio-oil and biochar are intrinsically greenhouse-gas-neutral energy products, and any bio-oil cogenerated with biochar that is used as a soil amendment is a greenhouse-gas-negative energy product. Carbon credits assigned for soil biochar applications are potentially high-value as the

weight of each truckload of biochar leaving the pyrolyzer would be known and the half-life of the biochar C is in excess of 100 years. No direct mechanism currently exists for evaluating the ancillary agronomic and environmental benefits from soil biochar applications. Indirectly, soil biochar applications will accrue value through increased crop yields, reduced fertilizer costs, and/or increased land values. But these indirect benefits are probably not enough to promote widespread use of biochar as a soil amendment. Ultimately the development of a pyrolysis industry will depend heavily on government policy. If a *cap-and-trade* or similar policy is codified and adds significant value for systems that reduce net greenhouse gas emissions, then the pyrolysis platform will be highly competitive.

References

1. Bridgwater AV, Meier D and Radlein D, An overview of fast pyrolysis of biomass. *Organic Geochem* **30**:1479–1493 (1999).

2. Ioannidou O, Zabaniotou A, Antonakou EV, Papazisi KM, Lappas AA and Athanassiou C, Investigating the potential for energy, fuel, materials and chemicals production from corn residues (cobs and stalks) by non-catalytic and catalytic pyrolysis in two reactor configurations. *Renew Sustain Energy Rev* **13**:750–762 (2009).

3. Di Blasi C, Modeling chemical and physical processes of wood and biomass pyrolysis. *Prog Energ Combust Sci* **34**:47–90 (2008).

4. Babu BV, Biomass pyrolysis: a state-of-the-art review. *Biofuels, Bioprod Bioref* **2**:393–414 (2008).

5. Namaalwa J, Sankhayan PL and Hofstad O, A dynamic bio-economic model for analyzing deforestation and degradation: An application to woodlands in Uganda. *Forest Policy Econ* **9**:479–495 (2007).

6. Brown R, Biochar production technology, in *Biochar for Environmental Management*, ed by Lehmann J and Joseph S. Earthscan, London, pp 127–146 (2009).

7. Goyal HB, Seal D and Saxena RC, Bio-fuels from thermochemical conversion of renewable resources: A review. *Renew Sustain Energy Rev* **12**:504–517 (2008).

8. Boateng AA, Hicks KB and Vogel KP, Pyrolysis of switchgrass (*Panicum virgatum*) harvested at several stages of maturity. *J Anal Appl Pyrolysis* **75**:55–64 (2006).

9. Fahmi R, Bridgwater AV, Donnison I, Yates N, Jones JM, The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. *Fuel* **87**:1230–1240 (2008).

10. Roy C, Darmstadt H, Benallal B, Chaala A and Schwerdtfeger AE, Vacuum pyrolysis of used tires. http://www.p2pays.org/ref/11/10504/html/biblio/html4/pyh3.htm. (1995) [July 21, 2009].

11. Benallal B, Roy C, Pakdel H, Chabot S and Poirier MA, Characterization of pyrolytic light naphtha from vacuum pyrolysis of used tires – Comparison with petroleum naphtha. *Fuel* **74**:1589–1594 (1995).

12. Perlack RD, Wright LL, Turhollow AF, Graham RL, Stokes BJ and Erbach DC, Biomass as feedstock for a bioenergy and bioproducts industry: The technical feasibility of a billion-ton annual supply. DOE/USDA Tech. Rep. DOE/GO-102005–2135 ORNL/TM-2005/66. USDOE, Office of Scientific & Technical Information, Oak Ridge, TN (2005). www.ornl.gov/~webworks/cppr/y2001/rpt/123021.pdf

13. Wilhelm WW, Johnson JMF, Karlen DL and Lightle DT, Corn stover to sustain soil organic carbon further constrains biomass supply. *Agron J* **99**:1665–1667 (2007).

14. Badger PC and Fransham P, Use of mobile fast pyrolysis plants to densify biomass and reduce biomass handling costs—A preliminary assessment. *Biomass Bioenerg* **30**:321–325 (2006).

15. Czernik S, Evans R and French R, Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil. *Catalysis Today* **129**:265–268 (2007).

16. Wright MM, Brown RC and Boateng AA, Distributed processing of biomass to bio-oil for subsequent production of Fischer-Tropsch liquids. *Biofuels, Bioprod Bioref* **2**:229–238 (2008).

17. Tsai WT, Lee MK and Chang YM, Fast pyrolysis of rice husk: Product yields and compositions. *Biores Technol* **98**:22–28. (2007).

18. Leibold H, Hornunga A and Seiferta H, HTHP syngas cleaning concept of two stage biomass gasification for FT synthesis. *Powder Technology* **180**:265–270 (2008).

19. Lu YJ and Lee T, Influence of the feed gas composition on the Fischer-Tropsch synthesis in commercial operations. *J Natural Gas Chem* **16**:329–341 (2007).

20. Donnis B, Egeberg RG, Blom P and Knudsen KG, Hydroprocessing of bio-oils and oxygenates to oydrocarbons. Understanding the reaction routes. *Topics Catalysis* **52**:229–240 (2009).

21. Glaser B, Lehmann J and Zech W, Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal – a review. *Biol Fertil Soils* **35**:219–230 (2002).

22. Lehmann J, Bio-energy in the black. *Frontiers Ecol Envir* **5**:381–387 (2007).

23. Laird DA, The Charcoal Vision: A win-win-win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. *Agron J* 100:178–181 (2008).

24. Laird DA, Use of charcoal to enhance soil quality in a future powered by bioenergy. in *Growing the Bioeconomy: Biobased Industry Outlook Conference*. August 30, 2005. (2005) Available at www.valuechains.org/bewg/Conf2005/Presentations/David_Laird.pdf [July 21, 2009].

25. Lal R, Is crop residue a waste? *J Soil Water Conser* **59**:136–139 (2004).

26. Wilhelm WW, Johnson JF, Hatfield JL, Voorhees WB and Linden DR, Crop and soil productivity response to corn residue removal: A Literature Review. *Agron J* **96**:1–17 (2004).

27. Lal R and Pimentel D, Biofuels from crop residues. *Soil Tillage Res* **93**:237–238 (2007).

28. Anex RP, Lynd LR, Laser MS, Heggenstaller AH and Liebman M, Potential for enhanced nutrient cycling through coupling of agricultural and bioenergy systems. *Crop Sci* **47**:1327–1335 (2007).

29. Heggenstaller AH, Anex RP, Liebman M, Sundberg DN and Gibson LR, Productivity and nutrient dynamics in bioenergy double-cropping systems. *Agron J* **100**:1740–1748 (2008).

30. Sombroek W, *Amazon soils – a reconnaissance of soils of the Brazilian Amazon region*. Centre for Agricultural Publications and Documentation, Wageningen, the Netherlands, pp 292 (1966).

31. Smith NJH, Anthrosols and human carrying capacity in Amazonia. *Ann Assoc Am Geog* **70**:553–566 (1980).

32. Glaser B, Haumaier L, Guggenberger G and Zech W, The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics. *Naturwissenschaften* **88**:37–41 (2001).

33. Lehmann J, da Silva Jr JP, Steiner C, Nehls T, Zech W and Glaser B, Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: fertilizer, manure and charcoal amendments. *Plant Soil* **249**:343–357 (2003).

34. Ishii T and Kadoya K, Effects of charcoal as a soil conditioner on citrus growth and vesicular–arbuscular mycorrhizal development. *J Jap Soc Hortic Sci* **63**:529–535 (1994).

35. Oguntunde PG, Fosu M, Ajayi AE and van de Giesen ND, Effects of charcoal production on maize yield, chemical properties and texture of soil. *Biol Fert Soils* **39**:295–299 (2004).

36. Skjemstad JO, Reicosky DC, Wilts AR and McGowan JA, Charcoal carbon in U.S. agricultural soils. *Soil Sci Soc Am J* **66**:1249–1255 (2002).

37. Laird DA, Chappell MA, Martens DA, Wershaw RL and Thompson ML, Distinguishing black carbon from biogenic humic substances in soil clay fractions. *Geoderma* **143**:115–122 (2008).

38. Zech W, Haumaier L, Hempfling R, Ecological aspects of soil organic matter in tropical land use, in *Humic substances in soil and crop sciences: Selected readings*, ed by McCarthy P, Clapp CE, Malcolm RL and Bloom PR. Soil Science Society of America, Madison Wisconsin, pp 187–202 (1990).

39. Liang B, Lehmann J, Solomon D, Kinyangi J, Grossman J, O'Neill B, Skjemstad JO, Thies J, Luiza FJ, Petersen J and Neves EG, Black carbon increases cation exchange capacity in soils. *Soil Sci Soc Am J* **70**:1719–1730 (2006).

40. Warnock DD, Lehmann J, Kuyper TW and Rillig MC, Mycorrhizal responses to biochar in soil – concepts and mechanisms. *Plant Soil* **300**:9–20 (2007).

41. DeLuca TH, MacKenzie MD, Gundale MJ and Holben WE, Wildfire-produced charcoal directly influences nitrogen cycling in ponderosa pine forests. *Soil Sci Soc Am J* **70**:448–453 (2006).

42. Laird DA, Fleming P, Wang B, Horton R and Karlen D, Impact of soil biochar applications on nutrient leaching. *Abstracts of 2008 International Annual Meetings ASA CSSA SSSA*. No. 665–8 (2008).

43. Rogovska N, Fleming P, Cruse R and Laird D, Greenhouse gas emissions from soils as affected by addition of biochar. *Abstracts of 2008 International Annual Meetings ASA CSSA SSSA*. No. 666–5 (2008).

44. Schmidt MWI, Skjemstad JO, Gehrt E and Kögel-Knabner I, Charred organic carbon in German chernozemic soils. *Euro J Soil Sci* **50**:351–365 (1999).

45. Skjemstad JO, Janik LJ and Taylor JA, Non-living soil organic matter: What do we know about it? *Aust J Exp Agr* **38**:667–680 (1998).

46. Swift RS, Sequestration of carbon by soil. *Soil Sci* **166**:858–871 (2001).

47. Pessenda LCR, Gouveia SEM and Aravena R, Radiocarbon dating of total soil organic matter and humin fraction and its comparison with 14C ages of fossil charcoal. *Radiocarbon* **43**:595–601 (2001).

48. Preston CM and Schmidt MWI, Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions. *Biogeosciences* **3**:397–420 (2006).

49. Lehmann J, Czimczik C, Laird D and Sohi S, Stability of biochar in soil, in *Biochar for Environmental Management*, ed by Lehmann J and Stephen J. Earthscan, London, pp183–206 (2009).

50. Tagoe SO, Horiuchi T and Matsui T, Effects of carbonized and dried chicken manures on the growth, yield, and N content of soybeans. *Plant Soil* **306**:211–220 (2008).

51. Cheng CH, Lehmann J and Engelhard MH, Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence. *Geochim Cosmochim Acta* **72**:1598–1610 (2008).

52. Wardle DA, Nilsson MC and Zackrisson O, Fire-derived charcoal causes loss of forest humus. *Science* **320**:629 (2008).

53. Kuzyakov Y, Subbotina I, Chen HQ, Bogomolova I and Xu XL, Black carbon decomposition and incorporation into soil microbial biomass estimated by 14C labeling. *Soil Biol Biochem* **41**:210–219 (2009).

54. Fowles M, Black carbon sequestration as an alternative to bioenergy. *Biomass Bioenerg* **31**:426–432 (2007).

55. Searchinger T, Heimlich R, Houghton RA, Dong F, Elobeid A, Fabiosa J, Tokgoz S, Hayes D and Yu TH, Use of U.S. croplands for biofuels increases greenhouse gases through emissions from land use change. *Science* **319**:1238–1240 (2008).

56. Suarez DL, Impact of agriculture on CO_2 as affected by changes in inorganic carbon, in *Global Climate Change and Pedogenic Carbonates*, ed by Lal R, Kimble JM, Eswaran H and Stewart BA, Lewis Publishers (CRC Press), Boca Raton, FL (2000).

57. Kuhlbusch TAJ and Crutzen PJ, Toward a global estimate of black carbon in residues of vegetation fires representing a sink of atmospheric CO_2 and a source of O_2. *Global Biogeochemical Cycles* **9**:491–501 (1995).

58. Lehmann J, Gaunt J and Rondon M, Bio-char sequestration in terrestrial ecosystems – A review. *Mitigation and Adaptation Strategies for Global Change* **11**:403–427 (2006).

59. Amonette JE, Lehmann J and Joseph S, Terrestrial carbon sequestration with biochar: A preliminary assessment of its global potential. Presentation December 13, 2007 at Fall Meeting of the *American Geophysical Union, Eos Trans AGU* **88**(52), Fall Meet. Suppl. Abstract U42A-06 (2007).

60. Amonette JE, Lehmann J and Joseph S, Biomass carbonization: The dark side of terrestrial carbon sequestration. Poster Presentation January 15, 2008 at *8th Annual Conference National Council on Science and the Environment*, Washington, DC (2008).http://ncseonline.org/2008conference/cms.cfm?id=2163 [February 16, 2009].

61. Krausmann F, Erb KH, Gingrich S, Lauk C and Haberl H, Global patterns of socioeconomic biomass flows in the year 2000: A comprehensive assessment of supply, consumption and constraints. *Ecol Econ* **65**:471–487 (2008).

62. Haberl H, Erb KH, Krausmann F, Gaube V, Bondeau A, Plutzer C, Gingrich S, Lucht W and Fischer-Kowalski M, Quantifying and mapping the human appropriation of net primary production in earth's terrestrial ecosystems. *Proc Natl Acad Sci* **104**:12942–12947 (2007).

63. Koutcheiko S, Monreal CM, Kodama H, McCracken T and Kotlyar L, Preparation and characterization of activated carbon derived from the thermo-chemical conversion of chicken manure. *Biores Technol* **98**:2459–2464 (2007).

64. Rhodes AH, Carlin A and Semple KT, Impact of black carbon in the extraction and mineralization of phenanthrene in soil more options. *Env Sci Tech* **42**:740–745 (2008).

65. Keech O, Carcaillet C and Nilsson MC, Adsorption of allelopathic compounds by wood-derived charcoal: the role of wood porosity. *Plant Soil* **272**:291–300 (2005).

66. Garnett E, Jonsson LM, Dighton J and Murnen K, Control of pitch pine seed germination and initial growth exerted by leaf litters and polyphenolic compounds. *Biology Fertility Soils* **40**:421–426 (2004).

67. Iswaran V, Jauhri KS and Sen A, Effect of charcoal, coal and peat on the yield of moong, soybean and pea. *Soil Biol Biochem* **12**:191–192 (1980).

68. Marjenah MS, Effect of charcoaled rice husks on the growth of Dipterocarpaceae seedlings in East Kalimantan with special reference to ectomycorrhiza formation. *J Jap Forestry Soc* **76**:462–464 (1994).

69. Mbagwu JSC and Piccolo A, Effects of humic substances from oxidized coal on soil chemical properties and maize yield, in *The role of humic substances in the ecosystems and in environmental protection*, ed by Drozd J, Gonet SS, Senesi N and Weber J. IHSS, Polish Society of Humic Substances, Wroclaw Poland, pp 921–925 (1997).

70. Kishimoto S and Sugiura G, Charcoal as a soil conditioner. *Int Achieve Future* **5**:12–23 (1985).

71. Yamato M, Okimori Y, Wibowo IF, Anshiori S and Ogawa M, Effects of the application of charred bark of Acacia mangium on the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia. *Soil Sci Plant Nutr* **52**:489–495 (2006).

72. Deenik JL, Uehara G, Sumiyoshi Y, Sidibe A, McClellan A and Antal M, Charcoal Volatile Matter content and its effects on plant growth and biological properties of an infertile tropical soil. *Program and Abstracts, 2008 Joint Annual Meeting of GSA, ASA-CSSA-SSSA and GCAGS*. Abstract # 665-5 (2008).

73. Gaskin J, Speir RA, Harris KR, Lee RD, Morris L and Das KC, Effect of two types of pyrolysis chars on corn yield, soil nutrient status, and soil C in loamy sand soil of the Southeastern United States. *Program and Abstracts for 2007 Annual Meetings ASA-CSSA-SSSA*, Abstract # 243-8 (2007).

74. Ringer M, Putsche V and Scahill J, Large-scale pyrolysis oil production: a technology assessment and economic analysis, NREL Report NREL/TP-510-37779 November (2006).

75. Wright M and Brown RC, Establishing the optimal sizes of different kinds of biorefineries, *Biofuels Bioproces Bioref* **1**:191–200 (2007).

Appendix

Biochar agricultural and forestry research priorities:

1) Research is needed to quantify the relationships between properties of biochar and its impact on soil quality and agricultural/forest productivity.

2) Research is needed to develop sustainable agricultural systems that integrate soil biochar amendments with cropping/agroforestry systems to more effectively utilize soil, water, and energy resources and to maximize food and biomass productivity.

3) Research is needed to develop strategies for optimum placement of biochar within fields and across landscapes to maximize agricultural/forestry productivity response to biochar applications.

4) Research in genetics and plant breeding is needed to develop new, high-yielding hybrids of cereal crops and dedicated biomass crops that optimize the quality and maximize the quantity of biomass for a pyrolysis industry.

5) Research is needed to develop approaches for the strategic placement of biochar within watersheds to intercept nutrient or contaminant plumes before they enter surface or ground-water reservoirs.

6) Research is needed to understand and quantify the stability of biochar C and the influence of soil biochar C additions on the cycling of C and plant nutrients through biomass, residues and soil organic matter.

7) Research is needed to understand and quantify interactions between biochar, the N cycle and emissions of N_2O.

Biochar engineering research priorities:

1) Research is needed to correlate biochar agronomic and carbon sequestration performance with the physical and chemical properties of biochar.

2) Research is needed to understand how pyrolysis conditions influence the development of desirable biochar properties.

3) Research is needed to understand the fate and role of inorganic nutrients during pyrolysis of biomass.

4) New pyrolyzers need to be developed that simultaneous produce high-quality energy products and high-quality biochar with low energy inputs and low air pollution emissions.

5) Fast and slow pyrolyzers ranging in scale from 1 ton per day to 200 tons per day need to be constructed to produce large quantities of well-characterized biochar for field trials.

6) Processes need to be developed that upgrade bio-oil into transportation fuels or other value-added products.

7) Engineering solutions are needed to prevent the dust and fire hazards associated with the storage and

handling of biochar and to develop effective means of incorporating biochar into agricultural soils.

Economics and policy research priorities:

1) Research is needed to evaluate the impact of various government policy scenarios on the economic viability of a pyrolysis industry and soil biochar applications.

2) Economic analysis is needed to identify the optimum scale and processing technology for pyrolysis plants considering labor, capital, infrastructure, the distribution and nature of biomass feedstocks, and social and environmental impacts.

3) Complete life-cycle assessments are needed to quantify the net energy efficiency and greenhouse gas impacts of a pyrolysis industry with soil applications of biochar.

4) The impact of a pyrolysis industry on energy security, food security, global climate change, soil and water quality, and rural economies needs to be quantified.

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