

Energy Balance and Emissions Associated with Biochar Sequestration and Pyrolysis Bioenergy Production

JOHN L. GAUNT^{*,†,‡} AND
JOHANNES LEHMANN[†]

College of Agriculture and Life Sciences, Cornell University,
Ithaca, NY 14850, and GY Associates Ltd

Received June 7, 2007. Revised manuscript received
December 21, 2007. Accepted January 7, 2008.

The implications for greenhouse gas emissions of optimizing a slow pyrolysis-based bioenergy system for biochar and energy production rather than solely for energy production were assessed. Scenarios for feedstock production were examined using a life-cycle approach. We considered both purpose grown bioenergy crops (BEC) and the use of crop wastes (CW) as feedstocks. The BEC scenarios involved a change from growing winter wheat to purpose grown miscanthus, switchgrass, and corn as bioenergy crops. The CW scenarios consider both corn stover and winter wheat straw as feedstocks. Our findings show that the avoided emissions are between 2 and 5 times greater when biochar is applied to agricultural land ($2\text{--}19\text{ Mg CO}_2\text{ ha}^{-1}\text{ y}^{-1}$) than used solely for fossil energy offsets. 41–64% of these emission reductions are related to the retention of C in biochar, the rest to offsetting fossil fuel use for energy, fertilizer savings, and avoided soil emissions other than CO_2 . Despite a reduction in energy output of approximately 30% where the slow pyrolysis technology is optimized to produce biochar for land application, the energy produced per unit energy input at 2–7 MJ/MJ is greater than that of comparable technologies such as ethanol from corn. The C emissions per MWh of electricity production range from 91–360 $\text{kg CO}_2\text{ MWh}^{-1}$, before accounting for C offset due to the use of biochar are considerably below the lifecycle emissions associated with fossil fuel use for electricity generation (600–900 $\text{kg CO}_2\text{ MWh}^{-1}$). Low-temperature slow pyrolysis offers an energetically efficient strategy for bioenergy production, and the land application of biochar reduces greenhouse emissions to a greater extent than when the biochar is used to offset fossil fuel emissions.

Introduction

Fossil fuel sources are finite and contribute significantly to greenhouse gas emissions (1). Bioenergy produced from renewable biomass can replace fossil-fuel-based energy sources. Biomass can be converted into energy products through direct combustion and through a number of alternative routes which can be broadly divided into microbial fermentation, extraction of oils, pyrolysis, and gasification

(2). However, the value of bioenergy strategies for off-setting fossil fuel use and greenhouse gas emissions have been strongly criticized (3, 4). These authors question whether the energetics are favorable when all inputs and processes are taken into account (i.e., do we get more energy out than we put in). They also indicate that external environmental impacts associated with the production of bioenergy may counter the benefits of the greenhouse gas emissions offset achieved.

The focus of this paper is the use of pyrolysis as a technology for producing bioenergy. Pyrolysis is a thermochemical process where biomass is heated in the absence of oxygen (or partially combusted in the presence of a limited oxygen supply) (5). There are a wide range of process conditions that can be optimized, principally, feedstock quality, temperature, heating rate, and pressure to influence the nature of the products; bio-oil, (syngas) gas synthesis with differing energy values, and char recovered (6).

All pyrolysis systems produce some char as a product. In this paper we refer to this material as biochar (which is also sometimes called “agri-char” when used as a soil amendment as outlined below). Biochar is very stable compared to uncharred biomass (7) and has an inherent energy value which can be utilized to maximize the energy efficiency of the pyrolysis facility. However it has been established, both through field research (8, 9) and through observation of situations where historically biochar has been applied to soil (10), that application of biochar to soil enhances plant growth. When applied to soil, biochar improves the supply of nutrients to crops as well as soil physical and biological properties (11). This results in increased crop yields in low-input agriculture and increased crop yield per unit of fertilizer applied (fertilizer efficiency) in high-input agriculture as well as reductions in off-site effects such as runoff, erosion, and gaseous losses.

Preliminary research (12) suggests that nitrous oxide (N_2O) and methane (CH_4) emissions from soil may be significantly reduced by biochar application. Rondon et al. (12) found that CH_4 emissions were completely suppressed and N_2O emissions were reduced by 50% when biochar was applied to soil. Yanai et al. (13) also found suppression of N_2O when biochar was added to soil. The mechanisms by which N_2O and CH_4 emissions are reduced are not clear. However, the reduction in N_2O emissions observed by these authors is consistent with the more widespread observation that fertilizer is used more efficiently by crops in situations where biochar is applied to soil.

Thus we hypothesize that (i) in terms of the emission reductions biochar is more valuable as a soil amendment than as a fuel; and (ii) the energy balance is still above unity even if biochar is used as a soil amendment.

If these hypotheses are supported by the evidence presented, this will signal that combining pyrolysis for bioenergy with the application of biochar to soil offers a strategy to reduce greenhouse gas emissions and deliver environmental benefits.

Materials and Methods

We consider two strategies for the integration of bioenergy and biochar management in an agricultural situation.

1. Switching from production of winter wheat to production of either miscanthus (*Miscanthus × giganteus*), switchgrass (*Panicum virgatum* L.), or forage corn (*Zea mays* L.) as bioenergy crops (BEC).

* Corresponding author phone: +1-607-330-097; fax: +1-607-330-097; e-mail: jlg84@cornell.edu.

[†] Cornell University.

[‡] GY Associates Ltd.

TABLE 1. Energy Inputs and Outputs for Each Feedstock Production Scenario, Comparing a Slow Pyrolysis System Optimized for Energy and Biochar Production

	switchgrass	miscanthus	forage corn	wheat straw	corn stover
	inputs (MJ ha⁻¹ y⁻¹)				
field production	5521	6505	20789	2024	2352
transportation and processing	3671	4430	11990	2410	2440
subtotal inputs	9192	10935	32779	4434	4792
	output (MJ ha⁻¹ y⁻¹)				
pyrolysis optimized for energy	64225	80050	99425	40056	43456
pyrolysis optimized for biochar	48811	60838	75563	30442	33027
	net output (MJ ha⁻¹ y⁻¹)				
pyrolysis optimized for energy	55033	69115	66646	35622	38665
pyrolysis optimized for biochar	39619	49903	42784	26008	28235
	energy yield MJ/MJ				
pyrolysis optimized for energy	7.0	7.3	3.0	9.0	9.1
pyrolysis optimized for biochar	5.3	5.6	2.3	6.9	6.9
	char yield (kg C ha⁻¹ y⁻¹)				
pyrolysis optimized for energy	0	0	0	0	0
pyrolysis optimized for biochar	867	1081	1338	534	599

TABLE 2. Carbon Dioxide Emissions (kg CO₂/MWh⁻¹) of Electricity Generation Using a Slow Pyrolysis System Optimized for Energy and Biochar Production, Respectively

	switchgrass	miscanthus	forage corn	wheat straw	corn stover
pyrolysis optimized for energy	119	113	274	92	91
pyrolysis optimized for biochar	156	149	360	121	120

2. Switching from the incorporation of wheat (*Triticum* spp.) straw or corn stover into soil to its use as a feedstock for bioenergy (CW).

For both BEC and CW we assume that after the change in management a mulch of 2 Mg ha⁻¹ y⁻¹ (at field moisture content) is retained to maintain soil quality.

For the BEC scenario we include energy inputs for field production, harvesting, transporting, and processing. For the CW scenario we only consider the additional energy inputs required to recover, process, and transport the feedstock. For both options we assume that the distribution of biochar back to land is integrated with existing fertilizer and input distribution networks and does not create additional emissions associated with transport or spreading.

Energy Inputs. Field Production. The field operations, agrochemical inputs, and levels of production described below are typical of the UK. Data used are summarized in Supporting Information Tables S-1, S-2, and S-3.

For agrochemical inputs, such as fertilizers and pesticides, the energy inputs are the sum of the energy used in the manufacture and distribution of the product (14). Activities that take place regularly but less frequently than annually are allocated a proportional value in the annual C budget. Similarly, agrochemicals that are applied together in one field operation are allocated a proportion of the energy used in their application. Data on energy used in the manufacture and distribution of the machinery, replacement parts, and the manufacture and distribution of agrochemicals is taken from West and Marland (14).

For all calculations we assume that 1 L of diesel fuel delivers 51.5 MJ and emits 1.13 kg C on combustion (14). This value also accounts for the fuel used in the distribution

of diesel. Where required we use a factor of 3.67 to convert from kg C to kg CO₂.

The crop establishment and agronomic practices for miscanthus and switchgrass described below are based on recommendations of the UK Department for Environment Food and Rural Affairs (Defra) (19) and the findings by Riche (16) in UK-based field trials. Miscanthus and switchgrass are rhizomatous perennial grasses and, once established, can grow in excess of 10 years. In this study we assume the crops are in place for 10 years. Miscanthus is propagated vegetatively using pieces of rhizome harvested from established plantations, whereas switchgrass is grown from seed. Because of the differences in establishment method, the establishment of miscanthus and switchgrass are considered separately below.

The current practice for establishment of Miscanthus is to plant rhizomes using a semiautomatic potato planter with one operator per row placing the rhizomes individually into the planting mechanism (14). In order for the planter to operate properly it is necessary to produce a fairly deep seedbed, but it is not necessary to produce a particularly fine tilth. Thus we assume that land preparation requires plowing and power harrowing and that once the crop is planted it is rolled to ensure good rhizome/soil contact and to level any ridges left by the planter.

Switchgrass is a small seeded grass. We assume a seed rate of 8 kg ha⁻¹ based on the experience of establishing switchgrass in UK field trials (16). The seedbed needs to be fine, similar to a seedbed produced for forage grasses. The seed is sown 5–10 mm deep into a firm seedbed, and it is good practice to consolidate the ground after sowing with a roller. Thus we assume that land preparation requires plowing, power harrowing, and that the soil is rolled twice.

We assume that that herbicide is applied at a rate of 5 L ha⁻¹ for switchgrass and 2 L ha⁻¹ for miscanthus during the first year to kill weeds present before planting and that in subsequent years, the vigorous crop growth and the lack of any cultivation suppresses weed activity. Currently there are no reports of fungal or pest problems (15, 16).

Given that the scenarios considered involve the crop being grown on agricultural soil, it is unlikely that any of the crops would show a response to P or K (14), so we assume that P and K are applied every five years to replace crop offtakes.

Land preparation for forage corn typically involves plowing using a moldboard plow, followed by two passes for discing, prior to drilling. For forage corn we assume fertilizer

TABLE 3. Avoided Emissions (kg CO₂ ha⁻¹ y⁻¹) for Bioenergy Crop (BEC) Scenarios, Comparing a Slow Pyrolysis System Optimized for Energy and Biochar Production

	energy			biochar		
	switchgrass	miscanthus	foragecorn	switchgrass	miscanthus	corn stover
feedstock: switch from winter wheat to bioenergy crop production						
emissions due to changes in crop production	1141	1107	338	1141	1107	338
application of biochar on cereal land						
avoided soil nitrous oxide emissions	0	0	0	1901	2369	2933
reduced fertilizer requirement	0	0	0	218	272	337
subtotal	0	0	0	2119	2641	3269
bioenergy production						
C stabilization	0	0	0	7065	8806	10 900
emissions for electricity generated using natural gas						
carbon dioxide	3087	3877	3739	2223	2800	2400
nitrous oxide	2	2	2	1	2	1
methane	4	5	5	3	4	3
subtotal	3093	3884	3746	2227	2805	2405
emissions for electricity generated using coal						
carbon dioxide	5228	6566	6331	3764	4741	4064
nitrous oxide	26	32	31	18	23	20
methane emissions	4	5	5	3	4	3
subtotal	5258	6603	6367	3785	4768	4087
total avoided emissions - offsets natural gas	4234	4992	4083	12 551	15 358	16 912
total avoided emissions - offsets coal	6399	7710	6705	14 109	17 321	18 595

rates of 120, 110, and 230 kg ha⁻¹ for N, P, and K, respectively (17). Herbicide at 2.96 kg ha⁻¹ active ingredient and pesticide at 0.24 kg ha⁻¹ reflect typical application rates.

Harvest Operations. Both miscanthus and switchgrass are unlikely to produce enough growth in the first year to justify harvesting (15, 16), thus we assume the crops are harvested from the second year. The 10 year average yields of miscanthus are assumed to be 12.3 Mg dry matter (DM) ha⁻¹ (15) and 10.2 Mg DM ha⁻¹ for switchgrass (16).

The crops are harvested using agricultural mowers, currently used in silage making, and then baled using Hesston-type machinery producing bales of approximately 500 kg each. These are stacked close to the field prior to transportation.

We assume that wheat straw removal is recovered through baling and carting of straw and that corn stover is collected using a forage harvester. To calculate the energy use we assume that the stover from swaths is raked prior to collection with a forage harvester and baled. We assume bales are stacked close to the field using a telescopic handler to stack bales at a rate of 10.5 Mg h⁻¹.

Postharvest Processing. We include emissions (10.5 Mg h⁻¹) associated with using a telescopic handler to load bales prior to transportation. We assume energy use of 110 MJ Mg⁻¹ straw or 8.001 kg CO₂ Mg⁻¹ biomass transported an average distance of 150 km using a large truck with a payload of 16 Mg of straw and an average fuel consumption of 32.8 L 100 km⁻¹ (18). We have assumed processing involves cutting the feedstock to approximately 12.7 mm at a processing rate of 25–30 Mg h⁻¹ using a 600 hp machine at 85% capacity (19).

Pyrolysis of Feedstocks. As described in the introduction, a range of pyrolysis and gasification technologies exist. We are interested in the application of pyrolysis in an agricultural setting using either bioenergy crops or crop waste materials as a feedstock. Thus we restricted our analysis to a slow pyrolysis system appropriate for bioenergy crops and crop wastes. The slow pyrolysis low-temperature system offers the distinct advantage that process conditions can be optimized for the recovery of biochar or syngas. In addition,

the process temperature parameters under slow pyrolysis are such that we avoid the formation of polyaromatic hydrocarbons in the biochar product (19).

We assume that the energy yield from the pyrolysis process is 50% of the energy contained in the feedstock if the system is optimized for syngas production and 38% where optimized for biochar production. This typical estimate is based on the operational experiences of Best Energies (19).

Calculating Avoided Greenhouse Gas Emissions. In December 1997, the parties to the 1992 United Nations Framework Convention on Climate Change (UNFCCC) adopted the Kyoto Protocol (20) which established that emissions reductions or allowable C storage, realized as a result of a defined change in practice, could be monetized through trading mechanisms such as the Clean Development Mechanism (CDM) or Joint Implementation (JI) projects. We outline below the sources of avoided emissions associated with the BEC and CW scenarios.

Emissions Avoided Due to Changes in Field Operations. The impact of changes in crop management and inputs on emissions are considered for both BEC and CW scenarios by calculating the differences in energy use for crop production and harvesting before and after the change in practice. The principle that changes in emissions associated with changes in agricultural inputs is specifically recognized by the procedures put in place for small scale methodologies under CDM (21).

Fossil Fuel Substitution. To calculate the fossil fuel substitution and the CO₂ emissions we use the Intergovernmental Panel on Climate Change (IPCC) default emissions factors for stationary combustion in the energy industry 56 kg CO₂ GJ⁻¹, 0.001 kg CH₄ GJ⁻¹, and 0.0001 kg N₂O GJ⁻¹ for natural gas and 96 kg CO₂ GJ⁻¹, 0.001 kg CH₄ GJ⁻¹, and 0.0015 kg N₂O GJ⁻¹ for sub-bituminous coal (22). Values for CH₄ and N₂O were corrected to CO₂ equivalents accounting for their radiative forcing effects using values of 72 and 310, respectively (23).

Carbon Stabilization by Pyrolysis. In addition to fossil fuel substitution, slow pyrolysis stabilizes a portion of the C in

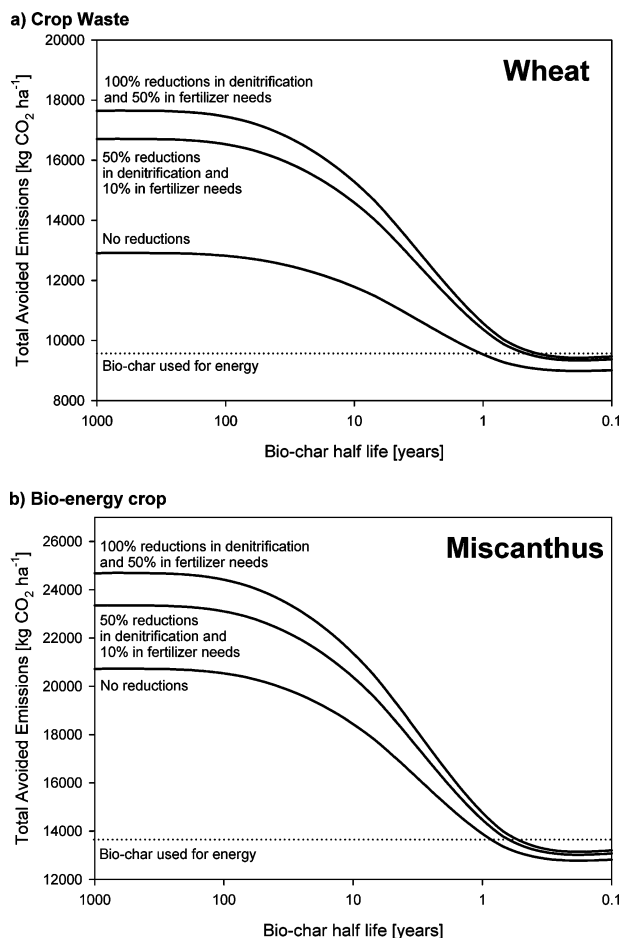


FIGURE 1. Sensitivity of avoided emissions to assumptions of biochar stability, and the interaction between (i) biochar and N₂O loss and (ii) fertilizer efficiency for wheat straw under the crop waste (CW) scenario and for miscanthus as a bioenergy crop (BEC).

the feedstock as biochar. The stability of the biochar will depend on the type of feedstock and production conditions (24). The UNFCCC methodology for small scale CDM projects AMS-III.L. considered biochar as biologically inert if the volatile-carbon/fixed-carbon ratio is equal to or lower than 1:1 (21). Therefore, we assume 100% stability over a 10 year period in our basic analysis and then use a sensitivity analysis to test the implications of this assumption as described below.

Effect of Biochar Application on Greenhouse Gas Emissions from Soil. We assume biochar produced is applied to land under cereal production at a rate of 5 Mg C ha⁻¹ as a single application. We assume that biochar is applied to land under continuous winter wheat production, under the input regime (typical of the UK) described above.

Based on empirical evidence that ammonium leaching was reduced by more than 60% in a greenhouse experiment over a 45 day period (8), observed significant reductions in N₂O emissions (12) and observations of improved crop performance (8, 9, 25) we assume that the fertilizer requirement can be reduced by 10% to account for the improved efficiency in use of fertilizer by crops.

We assume that N₂O emission losses from fertilizer are reduced by 50%. This assumption is based on the findings that N₂O emissions were reduced by up to 50% when 20 g biochar kg⁻¹ soil was applied to soybean and by 80% in grass stands (12). Therefore, we modified the Kyoto assumption that 1.25% of N applied as fertilizer is lost as N₂O (26) and used a factor of 0.625. As described above we account for the greater radiative forcing effect of N₂O. We assume that all of

these effects of biochar remain for 10 years after initial application.

To test the sensitivity of our findings to assumptions of biochar stability and the effect of biochar on soil emissions we look at the relationship between biochar half-life and emissions. We calculated emission reductions for miscanthus (BEC) and wheat straw (CW) using three scenarios: biochar additions lead to a 100, 50, or 0% suppression in N₂O production together with a 50, 10, or 0% reduction in the amount of N fertilizer required to maintain current yields. The middle scenario corresponds with the data used throughout the study.

Results and Discussion

Net Energy Gain and Energy Yield. The annual net energy output (in the form of syngas) ranges from 35 622–69 115 MJ ha⁻¹ where char is used as a source of energy (Table 1) and 26 008–49 903 MJ ha⁻¹ where biochar is retained for soil amendment. This corresponds to an energy yield as syngas of 2–7 MJ MJ⁻¹ where biochar is retained for soil amendment and 3–9 MJ MJ⁻¹ when char is used as an energy source. These figures suggest that the production of bioenergy through slow pyrolysis compares favorably with the production of ethanol from corn which currently yields 0.7–2.2 MJ MJ⁻¹ (27, 28) and is likely to remain competitive with future cellulosic ethanol technologies that are projected to return ~4–6 MJ MJ⁻¹ (29).

Assuming that the energy in syngas is converted to electricity with an efficiency of 35%, the recovery in the life cycle energy balance ranges from 92 to 274 kg CO₂ MW⁻¹ of electricity generated where the pyrolysis process is optimized for energy and 120 to 360 kg CO₂ MW⁻¹ where biochar is applied to land (Table 2). This compares to emissions of 600–900 kg CO₂ MW⁻¹ for fossil-fuel-based technologies (30).

Our results also show that the energy yields remain positive and competitive with alternative technologies even when biochar is retained for soil amendment. This offers the realistic prospect of combining a bioenergy system with a strategy for the return of biochar to soil. It should also be noted that under operational conditions significant heat is produced that could be used to further offset fossil fuel use. This additional benefit is not considered in the present analysis.

Avoided Greenhouse Gas Emissions. Considering the inputs required for the field production of bioenergy crops it can be seen that the energy inputs for switchgrass and miscanthus are similar at 5521 and 6505 MJ ha⁻¹ y⁻¹, respectively, whereas the forage corn crop requires 20 789 MJ ha⁻¹ y⁻¹ (Table 1). The greater energy inputs for the forage corn are due to the fact that corn is an annual crop grown with higher levels of fertilizer inputs than the perennial miscanthus and switchgrass crops. The breakdown of inputs used can be found in the Supporting Information Tables provided with this paper.

Under the BEC the total avoided emissions range from 12 551–18 595 kg CO₂ ha⁻¹ y⁻¹ (Table 3) and from 9575–11 833 kg CO₂ ha⁻¹ y⁻¹ for the CW scenario (Table 4). In both cases the lower estimate is where the bioenergy produced displaces natural gas and the upper estimate is where coal is displaced.

Optimizing the pyrolysis process for energy production reduces the net emissions by 60–67% to 4083–7710 kg CO₂ ha⁻¹ y⁻¹ for the BEC scenario (Table 3) and by 68–79% to 2002–3736 kg CO₂ ha⁻¹ y⁻¹ for the CW scenario (Table 4).

Carbon stabilization as biochar ranges from 7065–10 900 kg CO₂ ha⁻¹ y⁻¹ for the BEC scenarios and 4348–4878 kg CO₂ ha⁻¹ y⁻¹ for the CW scenarios. The greater stabilization for the BEC scenarios reflects the larger amounts of feedstock produced per area of land where purpose grown bioenergy crops are utilized as feedstock.

Biochar Stability, Fertilizer Savings and N₂O Emissions. Figure 1a and b shows the effect of biochar stability and

TABLE 4. Avoided Emissions (kg CO₂ ha⁻¹ y⁻¹) for Crop Waste Scenarios, Comparing a Slow Pyrolysis System Optimized for Energy and Biochar Production

	energy		biochar	
	winter wheat	corn stover	winter wheat	corn stover
use of biochar on crop land				
avoided soil nitrous oxide emissions	0	0	3678	4126
reduced fertilizer requirement	0	0	89	100
subtotal	0	0	3768	4227
fossil fuel substitution				
C stabilization	0	0	4348	4878
emissions for electricity generated using natural gas				
carbon dioxide	1998	2169	1459	1584
nitrous oxide	1	1	1	1
methane	3	3	2	2
subtotal	2002	2173	1462	1587
emissions for electricity generated using coal				
carbon dioxide	3423	3716	2499	2713
nitrous oxide	17	18	12	13
methane	3	3	2	2
subtotal	3442	3736	2513	2729
total avoided emissions - offsets natural gas	2002	2173	9575	10688
total avoided emissions - (straw incorporated, offsets coal)	3442	3736	10629	11833

TABLE 5. Cost of Avoided CO₂ Emissions Created by Switching from a System Optimized for Energy Production to One That Also Delivers Biochar for Land Application to Maximize Avoided Emissions

	bioenergy crop			crop waste	
	switchgrass	miscanthus	corn	wheat straw	corn stover
electricity production^a (MW y⁻¹)					
annual production - optimized for energy	11667	11667	11706	11822	11433
annual production - optimized for biochar	8867	8867	8896	8985	8689
reduction in energy under biochar scenario	2800	2800	2809	2837	2744
value of energy diverted into biochar^b (U.S. \$ y⁻¹)					
	224,002	224,002	224,748	226,988	219,522
avoided emissions CO₂ equivalents (Mg CO₂ y⁻¹)					
offsets natural gas					
optimized for energy	7911	7483	4945	6078	5881
optimized for biochar production	23 451	23 023	20 480	29 067	28 925
additional avoided emissions under biochar scenario	15 540	15 540	15 535	22 990	23 044
offsets coal					
optimized for energy	12 068	11 672	8208	6432	6981
optimized for biochar production	26 444	26 048	22 574	32 268	32 022
additional avoided emissions under biochar scenario	14 376	14 376	14 366	25 836	25 041
cost of CO₂ (U.S. \$ Mg⁻¹)					
offsets natural gas	14	14	14	10	10
offsets coal	16	16	16	9	9
cost of biochar (U.S. \$ Mg⁻¹)					
	47	47	47	47	46

^a Assumes plant operates on 16 000 Mg DM of feedstock per year. ^b Assumes price of Electricity of U.S. \$80 per MW.

assumptions of the effect of biochar on denitrification and fertilizer needs. These findings show that at half-lives above 100 years the effect of biochar decomposition on our assumptions are negligible and that the benefits of application of biochar are realized at biochar half-lives of approximately 1 year. The half-lives of biochar produced as a byproduct of bioenergy using the pyrolysis pathway have not been established (31). As discussed above, existing CDM methodologies treat biochar as biologically inert if the volatile-carbon/fixed-carbon ratio is equal to or lower than 50%, and we can safely assume that they lie in centennial rather than

decadal or annual time scales given the much slower decomposition of woody biomass after charring at up to 350 °C (7).

It can be seen that for all the assumptions of impact of biochar on N₂O production and fertilizer efficiency the benefits of the biochar application to soil outweigh the use of biochar for energy. These findings indicate strongly that in terms of mitigation of climate change a strategy that combines pyrolysis for bioenergy production with application of biochar to soil is more effective than producing solely bioenergy.

Opportunities for C Emissions Trading. We have outlined and quantified avoided greenhouse gas emissions derived from the following sources:

1. Changes in the emissions associated with the production of feedstocks.
2. Avoided emissions associated with the substitution of fossil fuel with bioenergy.
3. Stabilization and storage of carbon in biochar.
4. The reduction in agricultural emissions of N_2O and savings in fertilizer associated with use of biochar on agricultural land.

Our interpretation of the UNFCCC guidelines is that these avoided emissions could be monetized under the existing regulations for CDM or JI projects. The use of controlled pyrolysis as a strategy to avoid emissions from crop residues and stabilize C and the principle that avoided emissions associated with changes in agricultural practice can be monetized is established under the small scale CDM methodology AMS-III.L (21).

As described above CDM methodology AMS-III.L recognizes that biochar represents a stabilized form of carbon. Given that biochar has distinct chemical characteristics which enable both the presence of biochar in a specific area of land and its source to be verified, we see no reason why biochar used as a soil conditioner cannot be accounted for as part of a C trading project.

Thus our understanding is that a project utilizing biochar and pyrolysis will deliver "Kyoto compliant" net-negative emissions. However, there are currently no projects that have used this approach. An important next step is to propose a methodology to the UNFCCC for approval.

The Costs of Avoided Emissions. An important final question relates to the likely financial and economic case for producing biochar for application to soil. The overall financial justification for investment in a pyrolysis plant will be location specific and depends on the following: revenues for the biochar and energy products (heat and electricity), market value of avoided CO_2 emissions, costs of feedstocks, as well as the costs for installation and operation.

Such an analysis is beyond the scope of this paper; however, it is possible to answer the question: "Why would you produce biochar to apply to soil rather than use it to produce energy?" We have already answered this question in terms of the enhanced potential to avoid greenhouse gas emissions while delivering environmental benefits and we now examine the financial case in a simple way.

To put a value on the reduction in electricity produced under the biochar to land scenarios we assume the wholesale price for electricity of U.S. \$80/MW. This is a realistic wholesale price for renewable electricity sources in the UK that includes the value of any associated Renewable Obligation Certificates. We assume that the pyrolysis facility has a capacity to process a feedstock throughput of 16 000 Mg DM annually producing 4800 Mg of biochar.

For all scenarios the lost electricity by using biochar as a soil amendment is close to 2800 MWh y^{-1} (Table 5). The small variations are due to variation in the energy content of the feedstock. The cost in terms of lost electricity production is approximately \$220,000 per year.

Knowing the amount of biochar that will be produced when the system is optimized to produce char we calculate the cost of producing biochar in terms of lost electricity revenue. Using this calculation the value of the biochar is \$47 Mg^{-1} . This is significantly lower than values estimated by others. For example a value of \$120 Mg^{-1} biochar was calculated assuming the cost of producing biochar at around \$4 GJ^{-1} and a heating value of 30 GJ Mg^{-1} biochar (32, 33).

The cost of U.S. \$9–16 Mg^{-1} CO_2 is competitive when compared to current C market prices for CO_2 . Market prices for one Mg of CO_2 have been in the range of \$4 at the Chicago

Climate Exchange, up to \$20 for Futures at the European Union Emission Trading Scheme, and should lie around \$25–85 if the social costs of climate change are used as the basis for calculating prices (34).

From this preliminary analysis it can be appreciated that if a pyrolysis facility is financially viable, then the potential revenue from C emissions trading alone can justify optimizing the plant to produce biochar for application to land.

The analysis presented demonstrates the potential contribution that pyrolysis and biochar application to land can make to the reduction of greenhouse gas emissions. Although we take a comprehensive approach, the study is bounded essentially at the scale of a single facility. To understand the likely impact of widespread adoption of the approach, a more comprehensive evaluation of the potential impact would be required. As with other strategies for bioenergy production, it will be important to account for the dynamic economic interactions that will inevitably arise with widespread adoption. Recent experiences on the impact of the U.S. Government policy to subsidize ethanol production, on price paid for corn and the areas planted to this crop, have had a widespread effect on both prices for other cereals and corn-based food products. As the markets for bioenergy grow, such impacts may become more marked with implications for the use of land and other resources.

Acknowledgments

We acknowledge financial support from McIntire Stennis Fund for this study. John Gaunt is a director of GY Associates Ltd (WWW.GYA.CO.UK) and gratefully acknowledges the support provided by GYA that allowed him to undertake this collaborative research with Cornell University as an Adjunct Professor. We thank Adriana Downie and colleagues at Best Energies (<http://www.bestenergies.com>) for data on slow-pyrolysis and their valuable comments and suggestions on an early draft of this paper and Andrew Riche and Ian Shield of Rothamsted Research, UK for valuable information on the agronomy of the bioenergy crops considered here.

Supporting Information Available

A full breakdown of the values used to obtain the energy balances are provide in Tables S1–S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) IPCC. Climate Change 2001. *The Scientific Basis, Technical Summary by Workgroup I of the Intergovernmental Panel on Climatic Change*; Cambridge Press: Cambridge, UK, 2001.
- (2) McKendry, P. Energy production from biomass (part 2): Conversion technologies. *Bioresour. Technol.* **2002**, *83* (1), 47–54.
- (3) Koonin, S. E. Getting serious about bio-fuels. *Science* **2006**, *311*, 435.
- (4) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. The path forward for biofuels and biomaterials. *Science* **2006**, *311*, 484–489.
- (5) Bridgwater, A. Renewable fuels and chemicals by thermal processing of biomass. *Chem. Eng. J.* **2003**, *91*, 87–102.
- (6) Yaman, S. Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Convers. Manage.* **2004**, *45*, 651–671.
- (7) Baldock, J.; Smernik, R. Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. *Org. Geochem.* **2002**, *33*, 1093–1109.
- (8) Lehmann, J.; da Silva, J., Jr.; Steiner, C.; Nehls, T.; Zech, W.; Glaser, B. Nutrient availability and leaching in an archaeological Anthroisol and a Ferralsol of the Central Amazon basin: Fertilizer manure and charcoal amendments. *Plant Soil* **2003**, *249*, 343–357.
- (9) Rondon, M.; Lehmann, J.; Ramírez, J.; Hurtado, M. Biological nitrogen fixation by common beans (*Phaseolus vulgaris* L.) increases with biochar additions. *Biol. Fertil. Soils* **2007**, *43*, 699–708.

- (10) Lehmann, J.; Kern, D.; German, L.; McCann, J.; Martins, G.; Moreira, A. Soil fertility and production potential. In *Amazonian Dark Earths: Origin, Properties, Management*; Lehmann, J., Kern, D. C., Glaser, B., Woods, W. I., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2003; pp 105–124.
- (11) Glaser, B.; Lehmann, J.; Zech, W. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal—A review. *Biol. Fertil. Soils* **2002**, *35*, 219–230.
- (12) Rondon, M.; Ramirez, J.; Lehmann, J. Charcoal additions reduce net emissions of greenhouse gases to the atmosphere. In *Proceedings of the 3rd USDA Symposium on Greenhouse Gases and Carbon Sequestration*; March 21–24, Baltimore, MD, 2005; p 208.
- (13) Yanai, Y.; Toyota, K.; Okazaki, M. Effects of charcoal addition on N₂O emissions from soil resulting from rewetting air-dried soil in short-term incubation experiments. *Soil Sci. Plant Nutr.* **2007**, *53*, 181–188.
- (14) West, T. O.; Marland, G. A synthesis of carbon sequestration carbon emissions, and net carbon flux in agriculture: Comparing tillage practices in the United States. *Agric. Ecosyst. Environ.* **2002**, *91*, 217–232.
- (15) DEFRA. *Planting and Growing Miscanthus*; DEFRA Publications PB No. 5424: London, UK, 2001.
- (16) Riche, A. *A Trial of the Suitability of Switchgrass and Reed Canary Grass As Biofuel Crops under UK Conditions*, DTI project summary No PS254; DTI: London, UK, 2006; www.dti.gov.uk/files/file34815.pdf.
- (17) DEFRA. *Fertiliser Recommendations for Agricultural and Horticultural Crops (RB209)*, 7th ed.; DEFRA: London, UK, 2000; <http://www.defra.gov.uk/farm/environment/land-manage/nutrient/fert/rb209/index.htm>.
- (18) Lewis, C. *Fuel and Energy Production Emission Factors, MEET Project: Methodologies for Estimating Air Pollutant Emissions from Transport*, task no. 3.4. Deliverable no. 20. contract no. ST-96-SC.204; EU COST Programme: Brussels, Belgium, 1997; <http://www.inrets.fr/infos/cost319/MEETdeliverable20.pdf>.
- (19) Downie, A. Personal communication, 2007.
- (20) United Nations. *Kyoto Protocol to the United Nations Framework Convention on Climate Change*; UN: New York, 1998; http://unfccc.int/kyoto_protocol/items/2830.php.
- (21) United Nations. *Report of the Conference of the Parties Serving As the Meeting of the Parties to the Kyoto Protocol on Its First Session, Held at Montreal from 28 November to 10 December 2005. Part Two: Action Taken by the Conference of the Parties Serving As the Meeting of the Parties to the Kyoto Protocol at Its First Session*; UN: New York, 2006. <http://cdm.unfccc.int/methodologies/SSCmethodologies/approved.html>.
- (22) IPCC. 2006 IPCC Guidelines for National Greenhouse Gas Inventories. Volume 2 energy; 2006; <http://www.ipcc-nggip.iges.or.jp/public/2006gl/vol2.htm>.
- (23) IPCC. *Climate change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment report of the Intergovernmental Panel on Climate Change*; Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., Miller, H. L., Eds.; Cambridge University Press: New York, 2007.
- (24) Lehmann, J.; Gaunt, J.; Rondon, M. Biochar sequestration in terrestrial ecosystems—A review. *Mit. Adapt. Stratos. Global Change* **2006**, *11*, 403–427.
- (25) Steiner, C.; Teixeira, W.; Lehmann, J.; Nehls, T.; Macedo, J.; Blum, W.; Zech, W. Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. *Plant Soil* **2007**, *291*, 275–290.
- (26) IPCC. *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories*; In Greenhouse Gas Inventory Reference Manual Volume 3, Houghton, J., Meira Filho, L., Lim, B., Treanton, K., Mamat, I., Bonduki, Y., Griggs, D., Callender, B., Eds.; IPCC/OECD/IEA Meteorological Office: Bracknell, UK, 1996.
- (27) Patzek, T.; Pimentel, D. Thermodynamics of energy production from biomass. *Crit. Rev. Plant Sci.* **2005**, *24*, 327–364.
- (28) Metzger, J. Production of liquid hydrocarbons from biomass. *Angew. Chem. Int. Ed.* **2006**, *45*, 696–698.
- (29) Hammerschlag, R. Ethanol's energy return on investment: A survey of the literature 1990–Present. *Environ. Sci. Technol.* **2006**, *40*, 1744–1750.
- (30) *Carbon Dioxide Emissions from the Generation of Electric Power in the United States, July 2000*; Department of Energy; Environmental Protection Agency: Washington, DC, 2000.
- (31) Lehmann, J. Bio-energy in the black. *Front. Ecol. Environ.* **2007**, *5*, 381–387.
- (32) Lehmann, J. A handful of carbon. *Nature* **2007**, *447*, 143–144.
- (33) Polagye, B. L.; Hodgson, K. T.; Malte, P. C. A economic analysis of bio-energy options using thinnings from overstocked forests. *Biomass Bioenergy* **2007**, *31*, 105–125.
- (34) Stern, N. *The Economics of Climate Change: The Stern Review*; Cambridge University Press: Cambridge, 2007.

ES071361I