Life Cycle Assessment of Biochar Systems: Estimating the Energetic, Economic, and Climate Change Potential

KELLI G. ROBERTS, *, $^{+,+}$ BRENT A. GLOY, $^{+}$ STEPHEN JOSEPH, $^{\$}$ NORMAN R. SCOTT, $^{\perp}$ AND JOHANNES LEHMANN $^{+}$

College of Agriculture and Life Sciences, Cornell University, Ithaca, New York 14853, and School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2251, Australia

Received July 27, 2009. Revised manuscript received October 30, 2009. Accepted November 17, 2009.

Biomass pyrolysis with biochar returned to soil is a possible strategy for climate change mitigation and reducing fossil fuel consumption. Pyrolysis with biochar applied to soils results in four coproducts: long-term carbon (C) sequestration from stable C in the biochar, renewable energy generation, biochar as a soil amendment, and biomass waste management. Life cycle assessment was used to estimate the energy and climate change impacts and the economics of biochar systems. The feedstocks analyzed represent agricultural residues (corn stover), yard waste, and switchgrass energy crops. The net energy of the system is greatest with switchgrass (4899 MJ t⁻¹ dry feedstock). The net greenhouse gas (GHG) emissions for both stover and yard waste are negative, at -864 and -885 kg CO_2 equivalent (CO_2e) emissions reductions per tonne dry feedstock, respectively. Of these total reductions, 62-66% are realized from C sequestration in the biochar. The switchgrass biochar-pyrolysis system can be a net GHG emitter (+36 kg CO₂e t^{-1} dry feedstock), depending on the accounting method for indirect land-use change impacts. The economic viability of the pyrolysis-biochar system is largely dependent on the costs of feedstock production, pyrolysis, and the value of C offsets. Biomass sources that have a need for waste management such as yard waste have the highest potential for economic profitability (+\$69 t⁻¹ dry feedstock when CO₂e emission reductions are valued at \$80 t⁻¹ CO₂e). The transportation distance for feedstock creates a significant hurdle to the economic profitability of biochar-pyrolysis systems. Biochar may at present only deliver climate change mitigation benefits and be financially viable as a distributed system using waste biomass.

Introduction

There is an urgent need to develop strategies for mitigating global climate change. Promising approaches to reducing anthropogenic greenhouse gas (GHG) emissions often in-

10.1021/es902266r © 2010 American Chemical Society Published on Web 12/23/2009 clude energy generation from climate neutral renewable resources. However, pyrolysis of biomass with biochar applied to soil offers a direct method for sequestering C and generating bioenergy (1-3). Biochar is the stable, carbonrich charcoal that results from pyrolysis of biomass materials. Used as a soil amendment, biochar can improve soil health and fertility, soil structure, nutrient availability, and soil-water retention capacity (4-8), and is also a mechanism for longterm C storage in soils. Because carbonizing biomass stabilizes the C that has been taken up by plants, sustainably produced biochar applied to soils may proactively sequester C from the atmosphere, while also generating energy.

Pyrolysis is the thermal decomposition of organic material in the absence of oxygen, and is also an initial stage in both combustion and gasification processes (9, 10). Both slow and fast pyrolysis of biomass result in three coproducts: char, gas, and tarry oils, where the relative amounts and characteristics of each are controlled by the pyrolysis processing conditions such as temperature, residence time, pressure, and feedstock type. Slow pyrolysis is generally carried out at lower temperatures and longer residence times than fast pyrolysis, and the typical product yield is 35% char, 35% gas, and 30% liquid (9). Pyrolysis with biochar applied to soil offers potential solutions to the current climate and energy concerns. However, to avoid unintended consequences of a new technology or mitigation strategy, it is necessary to conduct analyses of potential life-cycle impacts of biocharpyrolysis systems, as it would be undesirable to have the system actually emit more GHG than sequestered or consume more energy than is generated. Because of its "cradle-tograve" approach and transparent methodology, life cycle assessment (LCA) is an appropriate tool for estimating the energy and climate change impacts of pyrolysis-biochar systems.

In this paper, we use LCA to estimate the full life-cycle energy, GHG emissions balance, and economic feasibility of biochar. The biomass feedstock sources compared are corn stover, yard waste, and a switchgrass energy crop. This range of feedstock provides insight into the use of biomass "waste" resources compared to bioenergy crops and the resulting energy and climate change impacts and economic costs of each scenario.

Methodology

Goal and Scope. The cumulative energy, climate change impacts, and economics of biochar production from corn stover, yard waste, and switchgrass feedstocks at a slowpyrolysis facility in the United States are estimated using process-based LCA in Microsoft Excel. The goal of the biochar energy, greenhouse gases, and economic (BEGGE) LCA is to quantify the energy, greenhouse gas, and economic flows associated with biochar production for a range of feedstocks. The biochar system for the LCA has four coproducts: biomass waste management, C sequestration, energy generation, and soil amendment. The functional unit of the biochar-pyrolysis system is the management of 1 tonne of dry biomass. The reference flows for this system are the mass and C in the biomass feedstock and the energy associated with biochar production.

System Boundaries. The industrial-scale biochar production system boundaries are illustrated in Figure 1a. The method of biomass production and collection is dependent on the feedstock (with more details provided in the individual process descriptions and in the online Supporting Information (SI)). Once the biomass is collected, it is transported to the pyrolysis facility where it is reduced in size and dried.

^{*} Corresponding author e-mail: kgr25@cornell.edu.

[†] Department of Crop and Soil Sciences, Cornell University.

[‡] Department of Applied Economics and Management, Cornell University.

[§] University of New South Wales.

 $^{^{\}perp}$ Department of Biological and Environmental Engineering, Cornell University.

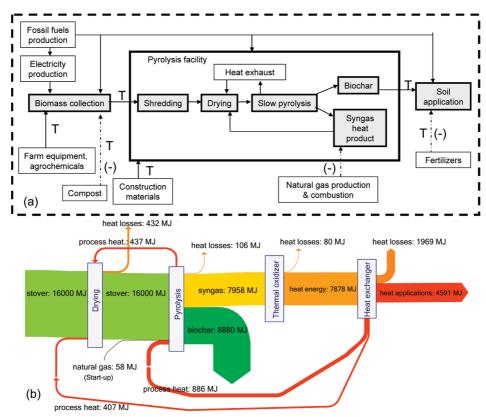


FIGURE 1. (a) System boundaries for the LCA of a biochar system with bioenergy production are denoted by the dashed box. Dashed arrows with (-) indicate avoided processes. The "T" represents transportation. The avoided compost process applies to the yard waste scenario only. (b) Energy flows (MJ t⁻¹ dry feedstock) of a pyrolysis system for biochar with bioenergy production using the late stover functional unit.

The biomass undergoes slow pyrolysis, which produces biochar, syngas, and tarry oils. The syngas and oils are combusted on-site for heat applications. The biochar is transported to a farm and applied to annual crop fields. The production of equipment specific to pyrolysis and feedstock processing (the pyrolysis facility, feedstock pretreatment equipment, farming equipment) is included, but the production of transportation vehicles is not included. The greenhouse gases, regulated emissions, and energy use in transportation (GREET) 1.8b (11) model for transportation fuel-cycles was used for compiling the upstream energy and air emissions for electricity generation, fossil fuel production and combustion, transportation, and agricultural inputs. The avoided processes incorporated into the analysis via system expansion are natural gas production and combustion, composting, and fertilizer production. Water consumption is not included in the LCA. The processes within the LCA are described in detail in the following section and the SI.

Crop Residues. Multiple studies have analyzed the energy and emissions related to ethanol production from corn stover (12-15). For this assessment, the energy and greenhouse gas emissions are from the LCA of corn stover collection conducted by Kim, Dale, and Jenkins (15) in Fulton County, IL (see the SI). Weather and field conditions can influence corn stover harvest times (16, 17), thus both late and early stover harvests are considered, with moisture contents (wet basis) of 15% and 30% mcwb, respectively (18).

Bioenergy Crops. Switchgrass as a pyrolysis feedstock is modeled in two ways (scenarios A and B) to compare the effects of land-use change on climate change impacts. While both switchgrass A and B use the energy and agricultural inputs associated with switchgrass establishment and collection from the lifecycle emissions model (LEM) (19) (Table S1 of the SI), the GHG emissions data are from two different models. The switchgrass A scenario uses LEM (19) for the land-use, fertilizer, and cultivation-related emissions of switchgrass production, with a net GHG of +406.8 kg CO₂e t⁻¹ dry switchgrass (see SI). The switchgrass B scenario uses the results from a comprehensive worldwide agricultural model for land-use change from Searchinger et al. (20). Both the LEM and Searchinger et al. models account for the effects of cropland diversion from annual crops to perennial grass energy crops (direct land-use change) and land conversion to cropland to replace the crops lost to bioenergy crops (indirect land-use change). However, differences between the models arise in the indirect land-use change accounting methods. The net GHG emissions of scenario B are +886.0 kg CO₂e t⁻¹ dry switchgrass (compared to +406.8 kg CO₂e t⁻¹ for switchgrass A). There is an obvious difference between these two approaches to modeling land-use change emissions, and we have used both as a means of capturing the range of outcomes.

Yard Waste Collection. The yard waste is assumed to be diverted from an industrial-scale composting facility, and no environmental burdens are assigned to the production of yard waste. The avoided compost process is included via the system expansion approach and is described in the SI.

Slow Pyrolysis: Biochar and Syngas Production. A very limited number of LCA studies have been conducted on pyrolysis facilities. Examples include a hazardous waste management plant in The Netherlands (*21*), fast pyrolysis for biofuel production (*22*), and a micropyrolysis-gas turbine system (*23*). However, detailed analyses of the energy and emissions associated with biochar production from slow pyrolysis have been performed where both biochar production from bioenergy crops and from crop residues result in net energy production and avoided GHG emissions (*3, 24*). The pyrolysis facility for this LCA is assumed to operate in a manner similar to industry prototypes under slow pyrolysis conditions as a continuous process with a biomass through-

put of 10 dry t hr⁻¹. A Sankey diagram of the energy flows of the biomass pyrolysis process is shown in Figure 1b. Pyrolysis is an exothermic process, and only a small amount of natural gas is used for the initial start-up of the pyrolysis kiln burner which is estimated at 58 MJ t^{-1} feedstock (21). The feedstock is pyrolyzed at 450 °C, and the pyrolysis gases flow into a thermal oxidizer which combusts the gases and oils at high temperature achieving clean combustion. A heat exchanger and air ducting system transfer the heat from the combustion gases to heating applications on-site. Exhaust heat from the facility is used for drying the incoming biomass. As a significant portion of the feedstock energy is in the biochar (\sim 50% assuming a lower heating value of 30 MJ kg⁻¹ for charcoal (25)), the overall efficiency from feedstock to available heat is 37%. More information on the pyrolysis process can be found in the SI.

As reported in ref 25, the yields of biochar from slow pyrolysis at 0.1 MPa (atmospheric pressure) have been found to range from 28.8 (birch wood) to 33.0 wt.% (spruce wood). The biochar yields, ash content of the biochar, and syngas energy yields are listed in Table S2. All of the ash (mineral elements except N and S) in the feedstock is assumed to remain in the biochar, and the mass of the biochar product includes the mass of the stable carbon, ash, and volatile matter.

Stable Carbon in Biochar. Of the C in the biochar, the majority is in a highly stable state and has a mean residence time of 1000 years or longer at 10 °C mean annual temperature (1, 26-31). However, the stability of the biochar does vary with feedstock, processing, and environmental conditions. For this assessment we assume that the slow-pyrolysis process has been optimized for high yields of stable C. With this in mind, we use a conservative estimate of 80% of the C in the biochar as stable (*28, 32*). The remaining 20% of the C is labile and released into the atmosphere as biogenic CO₂ within the first few years of applying it to the soil.

Improved Fertilizer Use Efficiency. As part of the application to the soil, the biochar not only sequesters *C*, but also improves crop performance. Although increased crop yields with biochar additions are reported in many cases, the greatest and most consistent yields are found on highly degraded soils (4–7). In the present analysis, the biochar is applied to comparatively productive soils in the U.S. Corn Belt, and therefore we do not consider crop yield increases with biochar. However, we do include improved fertilizer use efficiency (33) which enhances crop performance and thus reduces the amount of commercial chemical fertilizers applied. The difference of 7.2% between total N recovery in soils fertilized with biochar and the control (33) is used as the baseline scenario for improved N, P, and K fertilizer use efficiency.

Soil $\dot{N_2O}$ **Emissions.** In addition to the reduced need for chemical fertilizers, biochar reportedly reduces N₂O soil emissions that result from N fertilizer application (34–37). For this analysis, the baseline scenario assumes that the biochar processing is done under conditions such that soil N₂O emissions from N fertilizer applications are reduced by 50%.

Impact Assessment. The net energy of the functional unit incorporates all energy inputs to the system and energy produced by the system. Energy produced by the system includes syngas energy and energy from avoided processes such as fossil fuel production, fertilizer production, and composting. The 100 year global warming potential of CO_2 , CH_4 , and N_2O (1, 25, and 298 CO_2e , respectively) from the IPCC for 2007 (*38*) were used to calculate the climate change impacts of each process. The net climate change impact is the sum of the "net GHG reductions" and the net GHG emissions. To be consistent with terminology, the "net GHG reductions" are the sum of the "CO₂e sequestered" and the "avoided CO_2e emissions". The C sequestration is a direct result of the stable C in the biochar, while the avoided emissions are from the avoided processes such as fossil fuel production and composting. The biogenic CO_2 emissions are accounted for in the C balance of each biomass-to-biochar system (illustrated in Figure S1 for late stover). It is important to also note that improvements to the soil structure and fertility upon biochar application are not included in this analysis. These soil improvements could further reduce GHG emissions and energy consumption, while potentially adding value to the biochar product because of enhanced crop productivity.

Economic Assessment. The primary costs of biochar production are the feedstock collection and pyrolysis, while the feedstock transport, biochar transport, and biochar application have small contributions to the total (see Table S5 for a summary of the costs and revenues for each feedstock). The revenues come from the biochar value, the energy produced, and the tipping fee (in the case of the yard waste). The value assigned to the biochar is based on three components: (i) the P and K content of the biochar, (ii) the improved fertilizer use efficiency, and (iii) the GHG emission reduction. For valuing the GHG offsets, there are two approaches one can use: either to value only the stable C in the biochar, or to value the total life-cycle GHG emission reduction in the entire biochar system. For this analysis, we use the life-cycle C emission reduction to calculate the GHG offset, adding more value to the biochar because it incorporates the emission offsets from avoided fossil fuels, fertilizers, reduced soil N2O emissions, etc. The SI provides results on valuing the stable C in the biochar only. The other variable in the GHG offsets is in the value assigned per t of CO₂e emission reduction. Low and high revenue scenarios are considered, where values of \$20 and \$80 t^{-1} CO₂e are used, based on the IPCC recommendations (39). The syngas value per MJ is assumed equivalent to natural gas. All costs and revenues are described in more detail in the SI.

Results and Discussion

Energy. For each feedstock assessed, the net energy of the system is positive, i.e., more energy is generated than consumed (Figure 2a). The net energy of 1 dry tonne of late stover, early stover, switchgrass, and yard waste is +4116, +3044, +4899, and +4043 MJ, respectively. The excess syngas heat energy produced per tonne of feedstock is +4859, +4002, +5787, and +3507 MJ for the late stover, early stover, switchgrass, and yard waste, respectively. Early stover consumes the most fossil fuels (-1007 MJ), while yard waste actually yields a net +424 MJ of fossil fuels due to the avoided composting process. The late stover functional unit consumes the least amount of energy of all feedstocks. Drying, agrochemicals, and field operations are the highest energy consuming processes for stover and switchgrass. The role of the feedstock moisture content on the energy consumed in drying is evident, as the early stover clearly consumes more energy in drying than the late stover, and yard waste (45% mcwb) consumes the most energy for drying. The energy associated with the feedstock production and collection is highest for switchgrass, as shown by the agrochemicals (44% of the total) and field operations (27%). For energy generation, the heat energy produced has the highest contribution for all feedstocks, at 90-94% of the total energy generated. Avoided fossil fuel production is only a small fraction of the total, from 4-6% of the total energy generated. The contribution analysis also highlights the relatively small impact that the biomass transport (2-3%) and the plant construction (2-4%) each have on the energy consumption. The "other processes" category, aggregated in Figure 2a for clarity, includes the processes that contribute only a minor amount

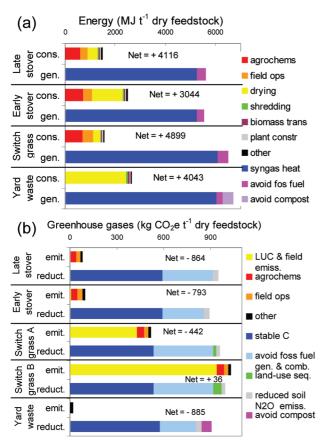


FIGURE 2. (a) Contribution analysis for the net energy per dry tonne of late stover, early stover, switchgrass, and yard waste in biochar systems with bioenergy production. Each pair of bars is associated with a feedstock, where the top bar represents the energy consumption, the bottom bar is energy generated, and the difference represents the net energy of the system. Switchgrass A and B have the same energy contribution profile, and only scenario A is shown. (b) Contribution analysis for the net climate change impact per dry tonne of late stover, early stover, switchgrass, and yard waste in biochar systems with bioenergy production. Each pair of bars is associated with a feedstock, where the top bar represents the GHG emissions, the bottom bar is GHG emission reduction, and the difference represents the net GHG emission balance of the system. (LUC = land-use change.)

to the energy consumption or production: biochar transport, plant dismantling, farm equipment, biochar application and avoided fertilizer production.

Climate Change–**Emission Balance.** For climate change impacts, net negative GHG emissions imply more CO_2e reductions than emissions. The net GHG emissions for late stover, early stover, and yard waste are -864, -793, and -885kg CO_2e t⁻¹ dry biomass (Figure 2b). Of all of the biomass sources, the yard waste system results in the most GHG emissions reductions per functional unit, primarily because there are no emissions associated with the yard waste production or collection but only for transport.

The switchgrass results demonstrate the critical role that land-use change plays in the life-cycle climate change impacts of bioenergy crops. For the switchgrass A scenario, the net GHG emissions are negative $(-442 \text{ kg CO}_2 \text{ t}^{-1})$, while for the switchgrass B scenario the net GHG emissions are positive $(+36 \text{ kg CO}_2 \text{ t}^{-1})$. By estimating the GHG emissions from a global approach which accounts for land conversion as discussed in the Methodology and SI, the impact assessment reveals the potential consequences of using U.S. croplands for biofuels. Even for a strategy as promising as biochar for

C sequestration, the net GHG emissions of the global system do not favor the switchgrass scenario when these energy crops are grown predominantly on existing cropland. Carbon sequestration in one place may be replaced by land-use change emissions in another location. Although the switchgrass A scenario could reduce GHG emissions by 442 kg CO₂e t⁻¹ switchgrass, this would only be applicable for land conversion that is predominantly temperate grasses and existing croplands, rather than temperate, tropical, or boreal forests (see SI). In an attempt to globally sequester C, it would be undesirable to generate GHG elsewhere as an unintended consequence of domestic industrial activities (40). Although a recent report by Kim et al. (41) indicates that it is inappropriate to assign the entirety of indirect land-use change emissions to biofuels, it is a potential consequence that must be considered. Despite the fact that land-use change decisions in other countries are complex and have multiple influences, the pressures of large biofuel industries and agricultural markets have significant influences on landuse change in developing countries (40).

Contribution Analysis. The contribution analysis for climate change impacts (Figure 2b) illustrates that land-use change and field emissions associated with feedstock production are the dominant processes for both the A and B switchgrass scenarios, contributing 83% and 91% of the GHG emissions, respectively. For both stover and switchgrass, agrochemical production and field operations are responsible for a large proportion of GHG emissions. The "other processes" category is an aggregation of those processes contributing a minor amount of GHG emissions or reductions, including biomass transport, biochar transport, chipping, plant construction and dismantling, farm equipment, biochar application, and avoided fertilizer production. For the late stover scenario, biomass transport 15 km to the facility contributes <4% of the total GHG emissions, while biochar transport 15 km to the field contributes $\sim 1\%$.

For the net GHG emissions reductions, the stable C sequestered in the biochar contributes the largest percentage for all feedstocks: 66% and 62% for early and late stover, 56% and 54% for switchgrass A and B, and 63% for yard waste. However, the avoided fossil fuel production and combustion also accounts for a significant portion, between 26 and 40% depending on the feedstock. Land-use change for the switchgrass A and B scenarios contributes another 2% and 5%, respectively, of the reduced GHG emissions due to CO_2 sequestration in biomass and soils. Reduced N_2O emissions from the soil upon biochar application to the soil contribute only 2–4% of the total emission reduction.

A biochar greenhouse gas accounting analysis by Gaunt and Cowie (24) has calculated the total emissions abatement of biomass pyrolysis with biochar applied to soil to be between 2.6 and 16 t CO_2e t⁻¹ biochar, depending on the feedstock, its conventional management practice, fossil fuel substitution, and cropland to which biochar is applied. For wheat straw residue and natural gas substitution, the result is 2.6-7.6 t CO₂e t⁻¹ biochar, while yard waste (diverted from composting) ranges from 7.4 to 12.5 t $CO_2e t^{-1}$ biochar. Converting our results for the late stover and vard waste to similar units, we find 2.9 and 3.0 t CO_2e t⁻¹ biochar, respectively, which fall on the lower end of the range found in their accounting. Another detailed analysis from Gaunt and Lehmann (3) calculated the avoided GHG emissions for biochar production and found 10.7 t CO₂e ha⁻¹ yr⁻¹ for corn stover and 12.6 t CO₂e ha⁻¹ yr⁻¹ for switchgrass. Converting our results to these units, we find 7.0 and 5.3 t CO_2e ha⁻¹ yr⁻¹ for stover and switchgrass (scenario A), respectively. Differences in our LCA results and the calculations from both Gaunt and Cowie (24) and Gaunt and Lehmann (3) arise primarily due to their higher estimates for avoided CH₄ and N₂O emissions in composting; avoided emissions when

biochar is used as a soil amendment; as well as their not accounting for emissions associated with other processes (harvesting the wheat straw, land-use change effects, or nutrient losses in residue removal). (See the SI for further discussion comparing energy yields.)

Alternative Biomass Uses. We can also compare the scenario of *biochar-to-soil* to that of *biochar-as-fuel*, assuming the biochar is replacing coal combusted in an integrated gasification combined cycle (IGCC) plant. For the late stover scenario, the avoided emissions for biochar production followed by biochar combustion (assuming an energy content of ~30 MJ kg⁻¹ biochar, i.e., 8880 MJ per functional unit) in replacement of coal are -617 kg CO₂e t⁻¹ dry stover. This comparison illustrates that 29% more GHG emissions reductions are made when the biochar is applied to soil (-864 kg CO₂e t⁻¹ dry stover) rather than used as a fuel.

If we compare biomass direct combustion to biomass-tobiochar-to-soil (where the avoided fossil fuels impacts are not included for either scenario), the resulting net GHG for *biomass direct combustion* is $+74 \text{ kg CO}_2 \text{e t}^{-1}$ stover and for biomass-to-biochar-to-soil is -542 kg CO₂e. This indicates that emission reductions are greater for a biochar system than for direct combustion. If natural gas is used as the avoided fossil fuel in both scenarios, the net GHG are -987 and $-864 \text{ kg CO}_2 \text{e t}^{-1}$ dry stover for the *biomass combustion* and biomass-to-biochar-to-soil, respectively. When viewed in this light the net GHG look comparable. However, in the biomass-to-biochar-to-soil, 589 kg of CO2 are actually removed from the atmosphere and sequestered in soil, whereas the biomass combustion benefits from the avoidance of future fossil fuel emissions only. This example highlights the need for transparent system boundaries when comparing between biomass management alternatives.

Large-Scale Emission Reductions. As a first approximation to potential GHG reductions on a larger scale, we use the late stover baseline model for biomass residues. On a global scale, using 50% of the 1.5 billion tonnes of currently unused crop residues annually (42), the net GHG reductions are 0.65 Gt CO₂e per year. (The amount of global unused residues is calculated as the difference between the available residues and the used portion, which are dependent on the crop, region, harvest factor, and recovery rate.) With a goal of reducing global fossil fuel GHG emissions from the 2007 level (31 Gt CO₂e (43)) by 50% in 2050 (according to IPCC recommendation to stabilize warming at 2.0-2.4 °C (39)), biochar would provide $\sim 4\%$ of these emissions reductions with 50% of crop residues alone. Or, for the U.S., assuming 141.1 million tonnes of currently unused crop residues and 124.7 million tonnes of currently unexploited forest residues annually (44), the net GHG reductions are 230 Mt CO₂e per year. (The amount of unused crop residues in the U.S. is calculated as 80% of the currently available residues (20% are currently used), and a 40% residue recovery potential.) If the U.S. were to adopt policies aiming to reduce fossil fuel GHG emissions by 50% of the 2007 level (5820 Mt CO₂e (43)) by 2050, 222.6 Mt CO2e from sustainable biochar production could contribute ~8% of these annual emissions reductions. These estimates demonstrate that sustainable biochar production from unused biomass waste resources may play a significant role in mitigating climate change on a global level. Future studies will seek to evaluate these larger scale scenarios

Economic Analysis. The economic analysis indicates that the uncertainty in the value of sequestered CO₂e creates a large variability in the net profitability. Each feedstock shown in Figure 3a has a high and low revenue scenario, according to an \$80 t⁻¹ CO₂e versus a \$20 t⁻¹ CO₂e GHG offset value. The high revenue of late stover (+\$35 t⁻¹ stover) indicates a moderate potential for economic viability. Neither the switchgrass A nor B scenarios are profitable in the low revenue

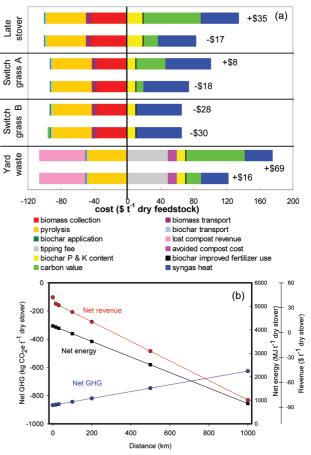


FIGURE 3. (a) Contribution analysis for the economic costs per tonne dry feedstock for the late stover, switchgrass A and B, and yard waste in biochar systems with bioenergy production. Each pair of bars is associated with a feedstock, where the top bar represents the high revenue scenario, and the bottom bar is the low revenue scenario. The net revenue (+) or cost (-) is indicated adjacent to each. (b) Effect of transportation distance in biochar systems with bioenergy production using the example of late stover feedstock (high revenue scenario) on net GHG (blue circles), net energy (black squares), and net revenue (red circles).

scenario due to the lower C revenues for A and the C costs for B, while switchgrass A has marginal potential for profitability (+\$8 t⁻¹) in the high revenue scenario. Despite the revenues from the biochar and energy products for all feedstocks, the overall profitability is hindered by the cost of feedstock collection and pyrolysis, even when C is valued at \$80 t⁻¹ CO₂e. A breakeven analysis reveals that the minimum CO₂e price would need to be \$40 t⁻¹ CO₂e for late stover, \$62 t⁻¹ CO₂e for switchgrass A, and only \$2 t⁻¹ CO₂e for yard waste. Due to the net GHG emissions for switchgrass B there is no price for GHG offsets that would make it profitable.

The overall economic results highlight the potential revenue for waste stream feedstocks such as yard waste (net +\$69 and +\$16 for the high and low scenarios) when there is a tipping fee or cost associated with managing the waste under current practices. Other biomass waste resources that may be promising for biochar production are livestock manures such as poultry, horse, and cattle. However, challenges arise if the feedstock has a high moisture content, such as in dairy manure.

Sensitivity Analysis. The sensitivity to variations or uncertainties is significantly different for various process parameters. The GHG balance is relatively insensitive to rather large changes in biochar properties such as between 80 and 90% of stable C (9% change) and between 80 and 0% decrease in N₂O emissions from soil (Table S8). The GHG balance is more sensitive to feedstock collection (change from -12% to +2% depending on assumptions), in contrast to the energy balance (<3% change). The net energy is very sensitive to the syngas energy yield; however, even a conservative estimate of 50% of the baseline results in a net positive energy balance, even though it is 63% less than the baseline. The GHG balance is also sensitive to the avoided fossil fuel process (10 and 24% increased for diesel and coal, respectively), while the net energy changes only ± 6 %. More details on the sensitivity analysis can be found in the SI.

Transportation distance has significant effects on costs, whereas ramifications for GHG emissions are low (Figure 3b). Even transporting the feedstock and biochar each 200 km, the net CO_2 emission reductions decrease by only 5% of the baseline (15 km). At 1000 km, the net GHG emission reductions decrease by 28% to -626 kg CO_2e . The net energy is more sensitive than the GHG emissions to the transport distance. At 200 km the net energy decreases by 15%, and at 1000 km, the net energy decreases by 79% to 863 MJ. Costs are the most sensitive to transportation distance, where costs increase by \$0.80 t⁻¹ for every 10 km. Therefore, biochar systems are most economically viable as distributed systems with low transportation requirements.

In summary, several biomass pyrolysis systems with biochar returned to soil have potential for C sequestration, GHG emission reductions, renewable energy generation, and economic viability. Careful feedstock selection is required to avoid unintended consequences such as net GHG emissions or consuming more energy than is generated, and also to ensure economic and environmental sustainability throughout the process life cycle. Waste biomass streams such as vard waste have the greatest potential to be economically viable while still being net energy positive and reducing GHG emissions. Agricultural residues such as corn stover have high yields of energy generation and GHG reductions, and have moderate potential to be profitable, depending on the value of C offsets and feedstock collection costs. If energy crops such as switchgrass are grown on land diverted from annual crops, indirect land-use change impacts could mean that more GHG are actually emitted than sequestered. Even if switchgrass is grown on marginal lands, the economics for switchgrass biochar are unfavorable. The primary barriers to the economic viability of pyrolysis-biochar systems are the pyrolysis process and the feedstock production costs. A diversified farm system with mixed feedstocks for biochar production may bring sustainability benefits that exceed those of a single feedstock alone which should be evaluated in future analyses. Valuing greenhouse gas offsets at a minimum of \$40 t⁻¹ CO₂e (as calculated for the stover scenario) and further development of pyrolysis-biochar systems will encourage sustainable strategies for renewable energy generation and climate change mitigation.

Acknowledgments

We acknowledge financial support for this work from the Cornell Center for a Sustainable Future, NYSERDA, and USDA Hatch grant. We also thank John Gaunt (GY Associates), Jim Fournier (Biochar Engineering Corporation), and Mike McGolden (Coaltec) for their valuable feedback on the pyrolysis process. We are grateful to three anonymous referees for their constructive suggestions to the manuscript.

Supporting Information Available

Detailed process data and descriptions used in the LCA and the results of the sensitivity analysis. The inventory analysis is also available in spreadsheet format providing all of the inputs and outputs as matrices along with the result vector for each feedstock system. This information is available free of charge via the Internet at http://pubs.acs.org/.

Literature Cited

- Lehmann, J. Bio-energy in the black. *Front. Ecol. Environ.* 2007, 5 (7), 381–387.
- (2) Lehmann, J. A handful of carbon. *Nature* **2007**, *447* (7141), 143–144.
- (3) Gaunt, J. L.; Lehmann, J. Energy balance and emissions associated with biochar sequestration and pyrolysis bioenergy production. *Environ. Sci. Technol.* 2008, 42 (11), 4152–4158.
- (4) Rondon, M.; Lehmann, J.; Ramirez, J.; Hurtado, M. Biological nitrogen fixation by common beans (*Phaseolus vulgaris* L.) increases with bio-char additions. *Biol. Fertil. Soils* 2007, 43, 699–708.
- (5) Kimetu, J.; Lehmann, J.; Ngoze, S.; Mugendi, D.; Kinyangi, J.; Riha, S.; Verchot, L.; Recha, J.; Pell, A. Reversibility of soil productivity decline with organic matter of differing quality along a degradation gradient. *Ecosystems* **2008**, *11* (5), 726–739.
- (6) Lehmann, J.; Pereira da Silva, J.; Steiner, C.; Nehls, T.; Zech, W.; 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* 2003, 249 (2), 343–357.
- (7) Steiner, C.; Teixeira, W.; Lehmann, J.; Nehls, T.; de Macêdo, 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 (1), 275–290.
- (8) Ayodele, A.; Oguntunde, P.; Joseph, A.; Dias, M. d. S. Numerical analysis of the impact of charcoal production on soil hydrological behavior, runoff response and erosion susceptibility. *R. Bras. Ci. Solo* **2009**, *33*, 137–145.
- (9) Bridgwater, A. V.; Czernik, S.; Piskorz, J., The status of biomass fast pyrolysis. In *Fast Pyrolysis of Biomass: A Handbook*; Bridgwater, A. V., Ed.; CPL Press Liberty House: Newbury, UK, 2008; Vol. 2, pp 1–22.
- (10) Reed, T. B.; Jantzen, D., Introduction. In *Encyclopedia of Biomass Thermal Conversion: The Principles and Technology of Pyrolysis, Gasification and Combustion*, 3rd ed.; Reed, T. B., Ed.; The Biomass Energy Foundation Press, 2002.
- (11) Wang, M. Greenhouse gases, regulated emissions, and energy use in transportation (GREET) model, 1.8b; UChicago Argonne, LLC: Chicago, IL, 2008.
- (12) Sheehan, J.; Aden, A.; Paustian, K.; Killian, K.; Brenner, J.; Walsh, M.; Nelson, R. Energy and environmental aspects of using corn stover for fuel ethanol. *J. Ind. Ecol.* **2003**, 7 (3–4), 117–146.
- (13) Spatari, S.; Zhang, Y.; MacLean, H. L. Life cycle assessment of switchgrass- and corn stover-derived ethanol-fueled automobiles. *Environ. Sci. Technol.* **2005**, 39 (24), 9750–9758.
- (14) Wu, M.; Wang, M.; Huo, H. Fuel-cycle assessment of selected bioethanol production pathways in the United States; Center for Transportation Research, Energy Systems Division, Argonne National Laboratory: Chicago, IL, 2006.
- (15) Kim, S.; Dale, B.; Jenkins, R. Life cycle assessment of corn grain and corn stover in the United States. *Int. J. Life Cycle Assess.* 2009, *14* (2), 160–174.
- (16) Agriculture and Agri-Food Canada. Corn Stover: Harvesting Techniques, http://www.agr.gc.ca (January 20, 2009).
- (17) Corn Stover for Bioethanol--Your New Cash Crop? DOE/GO-102001-1273; National Renewable Energy Laboratory: Golden, CO, 2001.
- (18) Womac, A. R.; Igathinathane, C.; Sokhansanj, S.; Pordesimo, L. O. Field corn stover moisture relations determined by insitu weight and grab sample techniques; ASAE/CSAE Annual International Meeting, Ottawa, Ontario, Canada, 2004.
- (19) Deluchi, M. A Lifecycle Emissions Model (LEM): Lifecycle Emissions from Transportation Fuels, Motor Vehicles, Transportation Modes, Electricity Use, Heating and Cooking Fuels, and Materials; UCD-ITS-RR-03-17; University of California Davis: Davis, CA, 2003.
- (20) Searchinger, T.; Heimlich, R.; Houghton, R. A.; Dong, F.; Elobeid, A.; Fabiosa, J.; Tokgoz, S.; Hayes, D.; Yu, T.-H. Use of U.S. croplands for biofuels increases greenhouse gases through emissions from land-use change. *Science* **2008**, *319* (5867), 1238– 1240.
- (21) Saft, R. J. Life cycle assessment of a pyrolysis/gasification plant for hazardous paint waste. *Int. J. Life Cycle Assess.* 2007, *12* (4), 230–238.
- (22) Manyele, S. V. Lifecycle assessment of biofuel production from wood pyrolysis technology. *Educ. Res. Rev.* 2007, 2 (6), 141–150.

- (23) Maria, F. D.; Fantozzi, F. Life cycle assessment of waste to energy micro-pyrolysis system: Case study for an Italian town. *Int. J. Energy Res.* 2004, 28, 449–461.
- (24) Gaunt, J.; Cowie, A., Biochar, greenhouse gas accounting and emissions trading. In *Biochar for Environmental Management: Science and Technology*, Lehmann, J., Joseph, S., Eds.; Earthscan: London, UK, 2009; pp 317–340.
- (25) Antal, M. J.; Grønli, M. The art, science, and technology of charcoal production. *Ind. Eng. Chem. Res.* 2003, 42 (8), 1619– 1640.
- (26) Cheng, C.-H.; Lehmann, J.; Thies, J. E.; Burton, S. D. Stability of black carbon in soils across a climatic gradient. *J. Geophys. Res.* 2008, 113, G02027.
- (27) Sombroek, W.; Ruivo, M. L.; Fearnside, P. M., Amazonian Dark Earths as carbon stores and sinks. In *Amazonian Dark Earths: Origin, Properties, Management*; Lehmann, J., Kern, D. C., Glaser, B., Woods, W. I., Eds.; Kluwer Academic Publishers: Dordrecht, Netherlands, 2003.
- (28) Lehmann, J.; Czimczik, C.; Laird, D.; Sohi, S., Stability of biochar in soil. In *Biochar for Environmental Management: Science and Technology*, Lehmann, J., Joseph, S., Eds.; Earthscan: London, UK, 2009; pp 183–206.
- (29) Lehmann, J.; Skjemstad, J.; Sohi, S.; Carter, J.; Barson, M.; Falloon, P.; Coleman, K.; Woodbury, P.; Krull, E. Australian climatecarbon cycle feedback reduced by soil black carbon. *Nat. Geosci.* **2008**, *1* (12), 832–835.
- (30) Kuzyakov, Y.; Subbotina, I.; Chen, H.; Bogomolova, I.; Xu, X. Black carbon decomposition and incorporation into soil microbial biomass estimated by ¹⁴C labeling. *Soil Biol. Biochem.* **2009**, *41* (2), 210–219.
- (31) Liang, B.; Lehmann, J.; Solomon, D.; Sohi, S.; Thies, J. E.; Skjemstad, J. O.; Luizão, F. J.; Engelhard, M. H.; Neves, E. G.; Wirick, S. Stability of biomass-derived black carbon in soils. *Geochim. Cosmochim. Acta* **2008**, *72* (24), 6069–6078.
- (32) Baldock, J. A.; Smernik, R. J. Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. *Org. Geochem.* 2002, *33* (9), 1093–1109.
- (33) Steiner, C.; Glaser, B.; Teixeira, W. G.; Lehmann, J.; Blum, W. E. H.; Zech, W. Nitrogen retention and plant uptake on a highly weathered central Amazonian Ferralsol amended with compost and charcoal. *J. Plant Nutr. Soil Sci.* 2008, 171 (6), 893–899.
- (34) Rondon, M. A.; Molina, D.; Hurtado, M.; Ramirez, J.; Lehmann, J.; Major, J.; Amezquita, E. Enhancing the productivity of crops and grasses while reducing greenhouse gas emissions through bio-char amendments to unfertile tropical soils. 18th World Congress of Soil Science, 9–15 July 2006, Philadelphia, PA, 2006.

- (35) Yanai, Y.; Toyota, K.; Okazaki, M. Effects of charcoal addition on N₂O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments. *Soil Sci. Plant Nutr.* 2007, 53, 181–188.
- (36) Spokas, K. A.; Koskinen, W. C.; Baker, J. M.; Reicosky, D. C. Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. *Chemosphere* **2009**, 77 (4), 574–581.
- (37) Singh, B. P.; Hatton, B.; Singh, B.; Cowie, A. L.; Kathuria, A. Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. *J. Environ. Qual.* **2010**, *39.*
- (38) Forster, P.; Ramaswamy, V.; Artaxo, P.; Berntsen, T.; Betts, R.; Fahey, D. W.; Haywood, J.; Lean, J.; Lowe, D. C.; Myhre, G.; Nganga, J.; Prinn; R. Raga, G.; Schulz, M.; Dorland, R. V. 2007: Changes in atmospheric constituents and in radiative forcing. In *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: Cambridge, United Kingdom and New York, 2007.
- (39) IPCC. Climate Change2007: Synthesis Report; Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Pachauri, R. K., Reisinger, A., Eds.; IPCC: Geneva, Switzerland, 2007; p 104.
- (40) Melillo, J. M.; Gurgel, A. C.; Kicklighter, D. W.; Reilly, J. M.; Cronin, T. W.; Felzer, B. S.; Paltsev, S.; Schlosser, C. A.; Sokolov, A. P.; Wang, X. Unintended environmental consequences of a global biofuels program; 168; MIT Joint Program on the Science and Policy of Global Change, 2009.
- (41) Kim, H.; Kim, S.; Dale, B. E. Biofuels, land use change, and greenhouse gas emissions: Some unexplored variables. *Environ. Sci. Technol.* 2009, *43* (3), 961–967.
- (42) Krausmann, F.; Erb, K.-H.; Gingrich, S.; Lauk, C.; Haberl, H. Global patterns of socioeconomic biomass flows in the year 2000: A comprehensive assessment of supply, consumption and constraints. *Ecol. Econ.* **2008**, 65 (3), 471–487.
- (43) Fossil-Fuel CO₂ Emissions; Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory: Oak Ridge, TN, 2009; http://cdiac.ornl.gov/trends/emis/meth_reg.html.
- (44) Perlack, R. D.; Wright, L. L.; Turhollow, A. F.; Graham, R. L.; Stokes, B. J.; Erback, D. C. Biomass as feedstock for a bioenergy and bioproducts industry: The technical feasibility of a billionton annual supply, U.S. Department of Energy and U.S. Department of Agriculture: Oak Ridge, TN, 2005.

ES902266R