

# Biofuels from Pyrolysis in Perspective: Trade-offs between Energy Yields and Soil-Carbon Additions

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## S Supporting Information

**ABSTRACT:** Coproduction of biofuels with biochar (the carbon-rich solid formed during biomass pyrolysis) can provide carbon-negative bioenergy if the biochar is sequestered in soil, where it can improve fertility and thus simultaneously address issues of food security, soil degradation, energy production, and climate change. However, increasing biochar production entails a reduction in bioenergy obtainable per unit biomass feedstock. Quantification of this trade-off for specific biochar–biofuel pathways has been hampered by lack of an accurate-yet-simple model for predicting yields, product compositions, and energy balances from biomass slow pyrolysis. An empirical model of biomass slow pyrolysis was developed and applied to several pathways for biochar coproduction with gaseous and liquid biofuels. Here, we show that biochar production reduces liquid biofuel yield by at least 21 GJ Mg<sup>−1</sup> C (biofuel energy sacrificed per unit mass of biochar C), with methanol synthesis giving this lowest energy penalty. For gaseous-biofuel production, the minimum energy penalty for biochar production is 33 GJ Mg<sup>−1</sup> C. These substitution rates correspond to a wide range of Pareto-optimal system configurations, implying considerable latitude to choose pyrolysis conditions to optimize for desired biochar properties or to modulate energy versus biochar yields in response to fluctuating price differentials for the two commodities.



## INTRODUCTION

Extensive regions of the world are simultaneously challenged by food insecurity, soil degradation, and energy poverty.<sup>1</sup> With global CO<sub>2</sub> emissions on track to exceed 2 °C of warming this century,<sup>2</sup> it is becoming increasingly important that developments aiming to address these issues should be undertaken without increasing greenhouse gas (GHG) emissions. One technology that can address all of these issues, while also lowering net anthropogenic GHG emissions, is the use of bioenergy–biochar systems (BEBCS). BEBCS involves the pyrolysis of biomass, with the evolved volatile and gaseous compounds being utilized for biofuel or bioenergy production, while the carbon-rich solid residue (known variously as charcoal, char, or biochar) is used as a soil amendment. When applied to soils, biochar (as it is typically referred to in such applications) can provide several valuable environmental and economic benefits: (1) biochar benefits agriculture by improving soil fertility and crop production<sup>3,4</sup> and by reducing fertilizer<sup>5</sup> and irrigation<sup>6</sup> requirements; (2) the high stability of biochar relative to other forms of soil carbon<sup>7–10</sup> makes it an effective means to increase soil carbon stocks, thus sequestering carbon for centuries to millennia that would otherwise have contributed to atmospheric GHGs;<sup>11–15</sup> and (3) biochar can further lower GHG emissions by reducing nitrous oxide emissions from soil<sup>16</sup> and by enhancing net primary production.<sup>14</sup> Accounting for all these impacts, BEBCS can have a greater climate-change mitigation impact than production of bioenergy alone from the same quantity of

feedstock,<sup>14,17–22</sup> particularly when the biochar is applied to degraded or infertile soils that benefit most.<sup>14</sup> Conversely, when bioenergy can be used to offset emissions from carbon-intensive fuels, such as coal, increasing bioenergy yield at the expense of lowered biochar yield can lead to higher GHG abatement.<sup>14,23</sup> GHG abatement from BEBCS is higher if the bioenergy provides transport fuel rather than heat or electricity.<sup>20</sup>

Although BEBCS can provide both soil-improving carbon sequestration and bioenergy, it has been widely recognized that a trade-off exists, whereby increasing biochar production entails a corresponding reduction in the bioenergy that can be produced from a given amount of biomass.<sup>14,24</sup> The amount of biochar production that can be substituted for bioenergy (or vice versa) depends on several factors, including feedstock, pyrolysis conditions, and the thermochemical or biochemical pathways used for bioenergy production. Both pyrolysis temperature and heating rate are key parameters in determining the relative yields of bioenergy and biochar, with biochar yields falling with increasing temperature and heating rate. Pyrolysis technologies are often classified into slow pyrolysis (SP; heating rate <10 °C s<sup>−1</sup>), which has higher biochar yields, and fast pyrolysis (FP; heating rate >10 °C s<sup>−1</sup>), which increases the

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bio-oil yield. FP with its higher energy product yields has attracted greater research effort in recent years, particularly as a route to production of liquid transport fuels.<sup>20</sup> Simple empirical models for predicting product yields and composition from FP have been developed,<sup>25</sup> but these perform poorly when applied to SP (Supporting Information section 1.1). Reliable quantification of the trade-off between biochar and bioenergy has been hampered by lack of an adequate simple model for predicting the yields and composition of the solid, volatile, and gaseous products from SP, the technology of choice for significant biochar yields. Here, we address this gap by developing an empirical model to calculate mass and energy balances and product chemical compositions for SP of a wide range of biomass feedstocks at a wide range of temperatures. We then apply this model to quantify the trade-offs between energy and biochar yields in BEBCS for a range of possible biofuel pathways for the coproduction of biochar with liquid or gaseous biofuels. Target biofuels include both low-grade fuels suitable as heating fuels (such as unupgraded pyrolysis gas or bio-oil) and upgraded fuels suited to more demanding applications such as transport (e.g., alcohols, Fischer–Tropsch (FT) hydrocarbons, and synthetic natural gas (SNG)).

**A Note on Economies and Diseconomies of Scale.** We consider below conversion pathways applicable at both the small and large scale. Those which are likely to have large economies of scale include catalytic methanol synthesis and FT synthesis.<sup>26</sup> However, because biomass has a low energy density and is often geographically dispersed, transport costs can rise rapidly with size of biomass conversion facility.<sup>27</sup> When biochar transport is also considered, transport costs will rise more rapidly with scale for a BEBCS than they would for a pure bioenergy system (BES). Therefore, the most economic size may be smaller for a BEBCS than for a BES. It is uncertain, therefore, whether BEBCS could become economic at a scale that makes FT or methanol synthesis feasible under current economic conditions.<sup>28</sup> Nonetheless, we include such pathways in our analysis for four reasons. First, recent advances have made available catalysts that are better suited to small-scale conversion than has historically been the case, thus opening up potential for smaller scale biofuel facilities.<sup>29</sup> Second, where good infrastructure exists, or where large biomass waste streams are located (such as at sugar or rice mills), biomass transport costs can be minimized, allowing for larger scale biomass facilities to become more economic. Third, although biomass SP is, at present, typically undertaken as a small-scale activity using simple conversion technologies,<sup>30</sup> an analogous process (SP of coal for coke and town-gas production) has been widely applied as a large-scale industrial process,<sup>31</sup> suggesting that there are no fundamental barriers to the industrial scaling up of biomass SP technology. Fourth, if CO<sub>2</sub> mitigation becomes an urgent global concern,<sup>32,33</sup> technologies currently considered uneconomic may quickly become viable.

While we do not attempt to model transport costs or economies of scale in this study, it is important to give consideration both to (a) technologies that could feasibly be deployed at a small scale in a rural environment close to sources of feedstock and soils that can benefit from biochar and (b) also to larger scale technologies suited to deployment at point sources of biomass or in regions with intensive biomass production and good infrastructure. The most appropriate choice and scale of technology would be expected to vary geographically according to local socioeconomic drivers,

transport infrastructure, availability of different types of feedstock, and demands for different types of fuel.

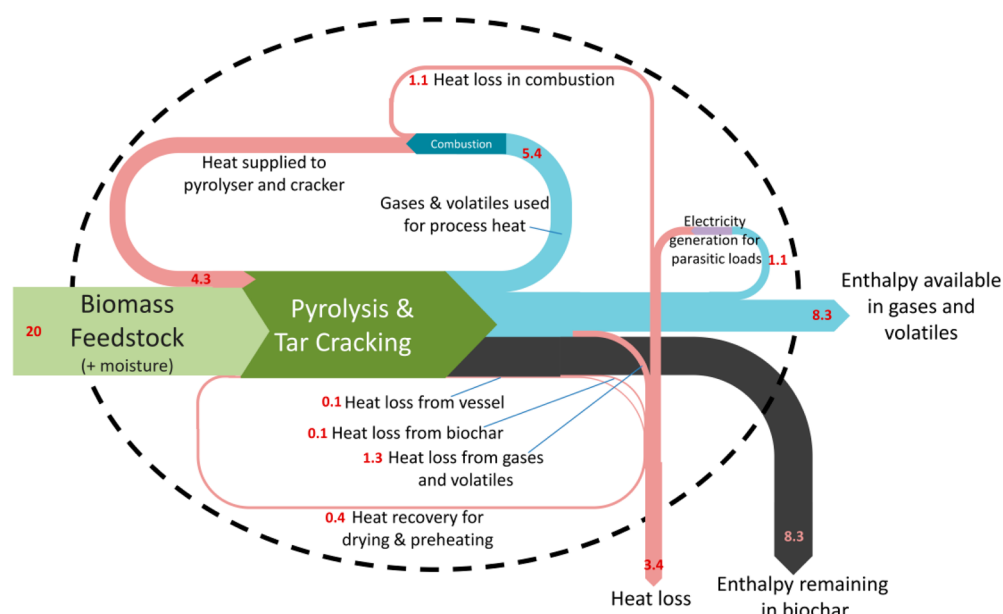
## ■ MODELING THE CONVERSION OF BIOMASS TO FUEL PLUS BIOCHAR

A detailed account of the model of biomass conversion to biofuels and biochar is given in the Supporting Information online, together with all the assumptions used. Here, we present an overview of the conversion pathways and modeling approach.

**Thermal Decomposition of Biomass.** All BEBCS pathways share a thermal decomposition stage in which limited or no oxidation takes place, yielding the biochar as a solid residue. Typically, this is achieved by heating biomass in an enclosed vessel with restricted aeration. When oxygen availability is near-zero, the thermal conversion is called pyrolysis. When a limited supply of oxygen and/or steam is introduced (typically at >700 °C), the process is referred to as gasification. Although gasification is a highly efficient (thermal efficiency of 75–80%) means to convert biomass to carbon monoxide- and hydrogen-rich syngas fuel, the biochar yield is typically low at around 5%.<sup>34,35</sup> Because the intention here is to investigate coproduction of biochar and bioenergy, the remainder of the discussion focuses mainly on pathways that utilize pyrolysis rather than gasification. In addition to heating rate and oxidant concentration, the other most important process parameter influencing the yield and chemistry of biochar is the maximum temperature during pyrolysis.<sup>25</sup> As well as reducing the yield of biochar, increasing temperature also enriches biochar in C, giving lower O:C and H:C ratios.<sup>25,36</sup> The O:C and H:C ratios are, in turn, indicators of the recalcitrance of the biochar in soils, with more C-rich chars produced at higher temperatures being more stable.<sup>10</sup> Other characteristics of the biochar, such as pH, nutrient content, and specific surface area, also vary with production conditions, and thus giving some latitude to tailor the quality of the biochar to suit different soils and environmental-management objectives.<sup>37</sup>

In addition to biochar, pyrolysis produces both non-condensable gases and volatiles. We refer to the non-condensable gases emitted in pyrolysis as “pyrolysis gas” and to the volatile organics as “tar” or “bio-oil”. The term “syngas” is used herein to denote a CO- and H<sub>2</sub>-rich gas derived either by gasification or by further processing of the pyrolysis gas and volatiles from pyrolysis.

**Tar-Cracking.** It can be desirable to convert organic volatiles and tars into gaseous compounds. The motive may be simply to increase the gas yield or to reduce adverse effects of tar on downstream processes (e.g., degradation of catalyst performance and blocking of filters, pipes, or heat exchangers). Cracking is the breaking down of larger organic molecules into smaller, simpler ones by the use of heat (thermal cracking) or in the presence of catalysts (catalytic cracking). The syngas produced by cracking is principally composed of CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, and H<sub>2</sub>O in proportions that depend on the reactant composition, temperature, pressure, and catalyst. H<sub>2</sub>O, CO<sub>2</sub>, and/or O<sub>2</sub> are sometimes added to the reactants to adjust the product composition to suit downstream processing. Thermal cracking usually requires the use of temperatures in excess of 1000 °C, which leads to high material costs, and may also produce soot, which can block filters and degrade downstream catalysts,<sup>38</sup> and polycyclic aromatic hydrocarbons (PAHs), which can be a health risk.<sup>39</sup> Therefore, catalytic cracking, which can operate at a lower temperature, is often considered



**Figure 1.** Sankey diagram of energy flows in pyrolysis and tar-cracking. The sizes of the energy flows (values shown in red are in GJ per Mg of dry, ash-free feedstock) are shown for an example system based on SP of pine chips at 450 °C followed by tar-cracking at 800 °C, with the energy for process heat and parasitic power-loads provided by a fraction of the syngas. Note that alternative system configurations could involve the use of other energy sources to provide heat and power including using a fraction of the biochar, using additional biomass, or using exogenous energy sources.

the preferred method. For the purposes of determining produce yields, we idealize catalytic cracking by assuming that the process occurs at 800 °C and brings products to equilibrium.

Several types of tar-cracking catalysts have been developed, including calcined dolomite, alkali metal, nickel-based catalysts, and combinations of these. Biochar itself has also been shown to be an effective tar-cracking catalyst.<sup>40</sup> Ideally, tar-cracking catalysts should (1) be effective for tar removal; (2) be active for reforming methane if used for syngas production; (3) be resistant to degradation and easily regenerated; (4) be strong and inexpensive; and (5) not create an excessive environmental burden from disposal of spent catalyst.<sup>41</sup> Although many of these catalysts are promising in many respects, availability of a catalyst that exhibits all of the desired characteristics listed above is currently a bottleneck in the commercial viability of biomass gasification technologies.<sup>41</sup>

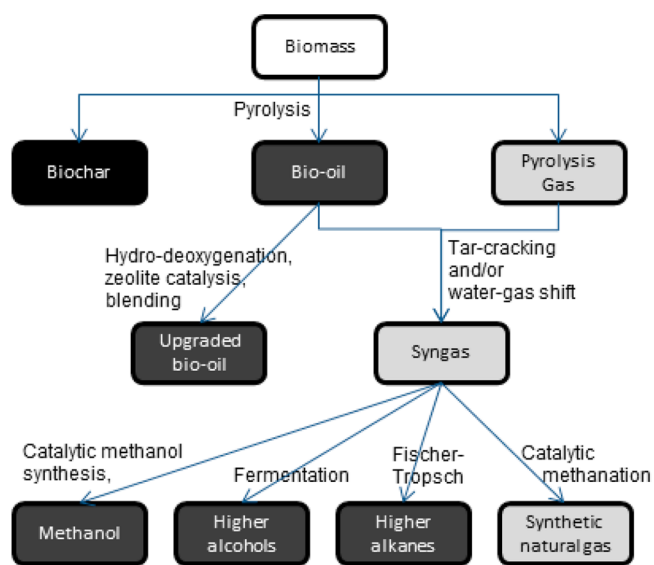
**Mass and Energy Balance.** During steady state, the net energy balance for the pyrolysis and tar-cracking system can be treated as a black box in which the total energy entering the system (biomass enthalpy) is equal to the energy leaving the system (i.e., the total enthalpy in the biochar, volatiles, and gases, plus heat losses) (Figure 1). Thus, when pyrolysis gases or volatile products provide the process heat and parasitic power requirements, the fraction of the initial energy content of the biomass that is available for use after pyrolysis and tar-cracking depends on two factors: (1) the energy remaining in the biochar and (2) the energy lost (either directly as heat from the thermal processing or as heat from parasitic power consumption).

A detailed account of how the mass and energy balances for pyrolysis were modeled can be found in the Supporting Information, section 1 (SP) and section 2.2.4 (FP). A comprehensive survey of published data was used to derive empirical equations for SP yields of biochar, bio-oil, H<sub>2</sub>O, CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub> (eqs S1–S5 and S12 in the Supporting Information) and chemical formulas of the biochar and bio-oil (eqs S6–S11 in the Supporting Information).

Calculation of the heat and energy balances is described in the Supporting Information section 1.4.

## ■ PATHWAYS TO BIOFUELS PLUS BIOCHAR

We have summarized a range of pathways to convert pyrolysis-derived bio-oil, pyrolysis gas, or syngas to various biofuels (Figure 2). Possible fuel products include liquid fuels, such as alcohols, alkanes, or bio-oil, and gaseous fuels, such as methane, other light hydrocarbons, or simply syngas itself. The lignin-rich residue from fermentation or anaerobic digestion (AD) of suitable biomass may also be pyrolyzed. The mass and energy balances of some of these possible pathways were modeled to



**Figure 2.** Summary of the potential pathways for coproduction of biofuels with biochar. Liquid fuels are shaded in dark gray and gaseous fuels in light gray.



compare how choice of conversion technology and process parameters would affect yields of biochar and biofuel attainable. The conversion pathways considered in this study are briefly summarized below, with a detailed description of each, together with the assumptions used to model them given in the Supporting Information, section 2. The nomenclature used to denote each pathway is summarized in Table 1.

**Table 1. Summary of Conversion Pathways Considered<sup>a</sup>**

symbol	thermochemical conversion	tar-cracking	postconversion	biofuel
SP+PG	SP	—	—	pyrolysis gas
SP+TC+SG	SP	yes	—	syngas
G+SG	G	—	—	syngas
SP+SNG	SP	—	separation	SNG
SP+M+SNG	SP	—	catalytic methanation	SNG
SP+TC+M+SNG	SP	yes	catalytic methanation	SNG
AD+SP+SNG	AD followed by SP	—	—	SNG
SP+TC+MeOH	SP	yes	catalytic methanol synthesis	methanol
SP+TC+EtOH	SP	yes	syngas fermentation	ethanol
SP+TC+FT	SP	yes	Fischer–Tropsch synthesis	liquid alkanes
FP-BC+BO	FP (no net biochar production)	—	—	biooil
FP+BC+BO	FP (With biochar production)	—	—	biooil

<sup>a</sup>SP = slow pyrolysis, FP = fast pyrolysis, G = gasification, TC = tar-cracking, AD = anaerobic digestion, SNG = synthetic natural gas.

For each of the conversion pathways it was assumed that all energy requirements for process heat and power would be provided entirely by onsite resources, using a fraction of gaseous and volatile products, biochar, and additional biomass, with results given for each of these possible process configurations.

**Gaseous Fuels.** Although combustible gases are produced directly from SP (SP+PG), they are of low grade, with a low heating value. For applications that demand higher grade fuels (e.g., transport), it may be desirable to upgrade the pyrolysis gas to a CH<sub>4</sub>-rich synthetic natural gas (SNG). There are currently around 15 million natural gas (CH<sub>4</sub>) powered vehicles (NGVs) worldwide. Although this represents just 1% of all vehicles, growth has been exponential over the last two decades at a rate of 23% per annum. There is also considerable regional variation in the market penetration, with NGVs providing 77% (Armenia), 64% (Pakistan), and 15–25% (Argentina, Bangladesh, Bolivia, and Iran) of the vehicle fleet in some countries.<sup>42</sup>

Three pathways for the production of SNG were considered (see also Supporting Information, section 2.1.2): (1) methane and light hydrocarbons are evolved during SP, the simplest means of production therefore being to separate them from the pyrolysis gas (SP+SNG); (2) CO and H<sub>2</sub> in the pyrolysis gas (SP+M+SNG) or in syngas (SP+TC+M+SNG) can react to form CH<sub>4</sub> using catalytic methanation (Supporting Information Table S3); (3) AD can be used to produce CH<sub>4</sub> from suitable

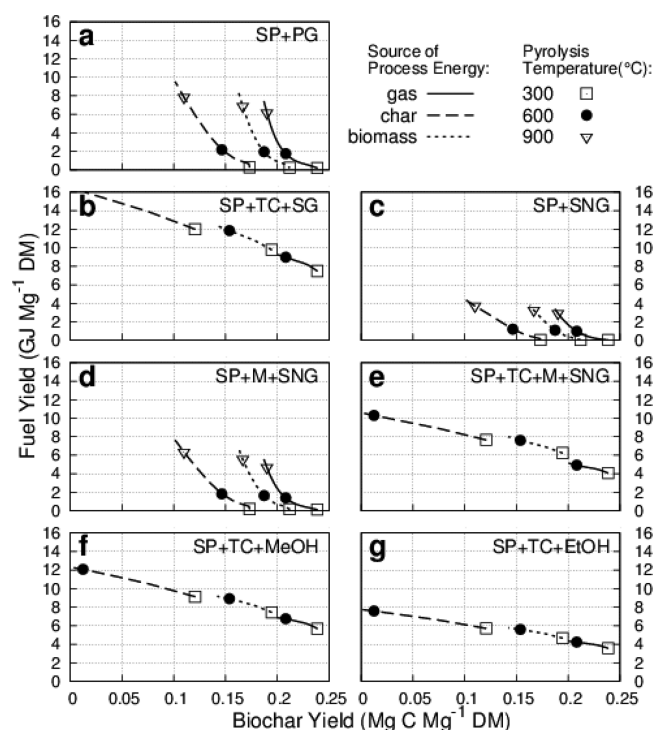
feedstocks (e.g., municipal organic waste, sewage sludge, or manure), with the undigested solid residue then being pyrolyzed to produce biochar (AD+SP+SNG).

**Liquid Fuels.** Four liquid fuel and biochar coproduction pathways were considered in this study. The first three pathways involve SP followed by tar-cracking to produce a CO- and H<sub>2</sub>-rich syngas. For processes involving chemical catalysts, the CO/H<sub>2</sub> ratio was then adjusted to the stoichiometrically optimal by the water gas-shift reaction (Supporting Information Table S3). This stage is unnecessary for syngas fermentation. CO and H<sub>2</sub> can then be converted to either (1) methanol by catalytic methanol synthesis (SP+TC+MeOH; see Supporting Information, section 2.2.1); (2) ethanol by microbial fermentation, using the Ljungdahl–Wood pathway (SP+TC+EtOH; see Supporting Information, section 2.2.2); or (3) a combination of biogasoline, biodiesel, and bio-LPG (liquefied petroleum gas) by Fischer–Tropsch (FT) synthesis (SP+TC+FT; see Supporting Information, section 2.2.3). In conventional FT systems, yield of gas is typically minimized (because liquid fuel is the desired product), which causes a substantial fraction of the hydrocarbon products to be long-chain waxes that require further hydrocracking and refining to produce fuels. However, when pyrolysis is used for the primary conversion to syngas, an alternative system configuration is feasible that would preclude the need for a centralized refinery. In a SP+TC+FT system, the FT gas products could be recycled to provide heat for pyrolysis and tar-cracking, thus allowing the FT stage to be optimized to produce precisely enough gas to supply process energy requirements while minimizing wax production, and thus removing the requirement for further downstream hydrocracking (see Supporting Information, section 2.2.3). Reducing wax yields while increasing the gas yields in FT typically involves the use of higher temperatures and shorter residence times than conventional FT and is the FT process assumed here. It should be noted, however, that such an approach to SP+TC+FT is not yet established technology, but should be considered, rather, as a technology option at the “strong potential” stage.

A fourth liquid-fuel pathway considered is the use of FP to produce bio-oil together with biochar (FP+BC+BO; see Supporting Information, section 2.2.4). It is becoming standard practice in industrial fast-pyrolysis systems to combust the char product to supply process energy, leaving no overall net production of BC (FP–BC+BO). If the biochar were instead to be used as a soil amendment, an alternative source of process energy would be required, which was assumed here to be an amount of bio-oil with energy content equivalent to the biochar (to be consistent with the assumptions made for the SP pathways that all process energy requirements would be supplied from onsite resources).

## RESULTS

**Biofuel and Biochar Yields.** The energy content of the pyrolysis gas increases with pyrolysis temperature (Figure 3a), due to a combination of increasing gas yields (Figure S1 in the Supporting Information) and, also, increasing higher heating value (HHV) of the gas mixture (Figure S5 in the Supporting Information). It is possible to substitute between energy and biochar yields by changing the fuel used to provide process energy. In other words, system configurations utilizing different fuels for process energy have different net yields of biochar and biofuel, relative to other configurations. The highest biochar and lowest fuel yields occur when pyrolysis gases (including



**Figure 3.** Yields of biofuels and biochar as pyrolysis temperature varied from 300–1000 °C without tar-cracking or from 300–700 °C followed by catalytic tar-cracking at 800 °C. In each panel, three lines represent case when process energy is supplied by (i) gases (including volatiles), (ii) additional biomass, or (iii) biochar. Pyrolysis temperatures along each of these yield curves is indicated by markers at 300, 600, and 900 °C. The biofuel products shown are (a) pyrolysis gas directly from pyrolysis (SP+PG); (b) syngas from pyrolysis with tar-cracking (SP+TC+SG); (c) SNG directly from pyrolysis (SP+SNG); (d) SNG from pyrolysis followed by catalytic methanation (SP+M+SNG); (e) SNG from pyrolysis, followed by tar-cracking and then catalytic methanation (SP+TC+M+SNG); (f) catalytic methanol synthesis (SP+TC+MeOH); and (g) fermentation of syngas to ethanol (SP+TC+EtOH).

volatiles) are used as the energy source for process heat and power (Figure 3, solid lines). A higher yield of biofuel is obtained if additional biomass is instead used for process energy, but at a reduced yield of biochar per unit biomass consumed (Figure 3, dotted lines). An even greater yield of biofuel can be achieved if some of the biochar is combusted to provide the process energy, but at the cost of an even lower yield of remaining biochar (Figure 3, dashed lines).

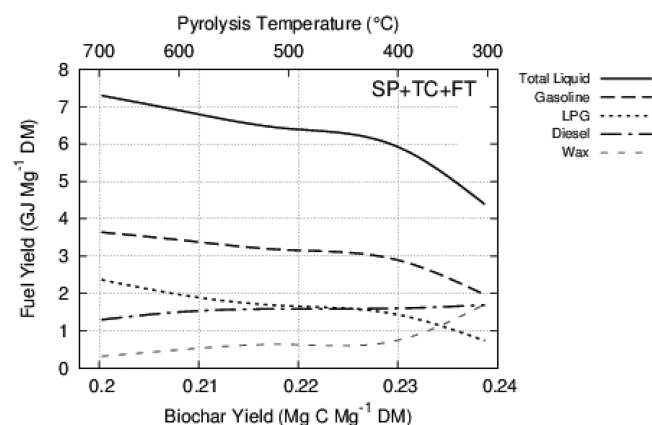
Although the highest yields of gaseous fuel energy occurs at the higher (1000 °C) end of this temperatures range (Figure 3a), it should be borne in mind that most biomass SP is currently conducted at <600 °C and that operating at higher temperatures would entail the use of more expensive construction materials.<sup>30</sup> For SP+PG below 600 °C, the recoverable energy content in the permanent gases is <10% of the heating value of the original feedstock (Figure 3a).

One means to increase the production of gaseous fuels while keeping the pyrolysis temperature low is to use tar-cracking (SP+TC+SG), whereby only gases and vapors from pyrolysis are heated to above 800 °C. Equilibrium calculations (Supporting Information, section 1.2) predict that pyrolysis at >700 °C leads to significant soot formation in the tar-cracker; therefore, all pathways that utilize tar-cracking were restricted to pyrolysis temperatures of below 700 °C. We found that catalytic tar-

cracking at 800 °C would give a 36-fold increase in the net combustion energy available from noncondensable gases for pyrolysis at 300 °C (compare Figure 3a and 3b). This gain in gaseous-fuel energy resulting from tar-cracking diminishes with increasing pyrolysis temperature (due to the combination of higher gas yields and lower tar production in high-temperature pyrolysis), falling to a 35% gain for pyrolysis at 1000 °C. A tar-cracking and reforming unit is an essential component of many of the other pathways considered here because it allows the production of a CO- and H<sub>2</sub>-rich syngas as required for further chemical conversion, while keeping the pyrolysis temperature low enough to permit the use of lower cost materials in the pyrolyser.

Upgrading the pyrolysis gas by extracting its methane and light hydrocarbon content (SP+SNG) would approximately halve its energy content (compare Figure 3a and 3c). However, upgrading the pyrolysis gas to SNG by catalytic methanation (SP+M+SNG) would reduce the yield of gaseous-fuel energy by only 20% (compare Figure 3a and 3d). Catalytic methanation of CO- and H<sub>2</sub>-rich syngas (SP+TC+M+SNG) could provide a means to increase gaseous biofuel yield while also yielding an upgraded fuel with higher energy density than the unmodified pyrolysis gas (compare Figure 3a and 3e).

The greater energy density and economic value of liquid fuels relative to gaseous fuels make them the preferred choice in many circumstances. Although achievable yields of liquid fuels (Figures 3f, 3g, and 4) are lower than for syngas (Figure 3b),



**Figure 4.** Yields of bio-LPG, biogasoline, biodiesel, wax, and biochar from SP at 300–700 °C with catalytic tar-cracking at 800 °C, followed by conversion of the resultant syngas by Fischer–Tropsch synthesis (SP+TC+FT). A high temperature Fischer–Tropsch process is assumed, in which the chain-growth probability,  $\alpha$ , is set to be such that the yield of methane together with unreacted syngas after a single pass is just sufficient to supply the energy required for process heat and power.

they are nonetheless comparable to, or greater than, yields of upgraded SNG (Figures 3c–e). The potential yields of methanol from SP+TC+MeOH (Figure 3f) and Fischer–Tropsch alkanes from SP+TC+FT (Figure 4) are both between 5 and 7 GJ Mg<sup>-1</sup> DM when syngas is used to provide process energy. Yields of ethanol from SP+TC+EtOH are, however, lower (3.6–4.2 GJ Mg<sup>-1</sup> DM) when syngas is used as the energy source; Figure 3g). The principal reason for the lower energy yield of SP+TC+EtOH is the high energy cost of distilling a ternary mixture that includes some acetate product with the ethanol and water (0.64 GJ heating fuel required per GJ ethanol produced, of which at most 28% could be supplied

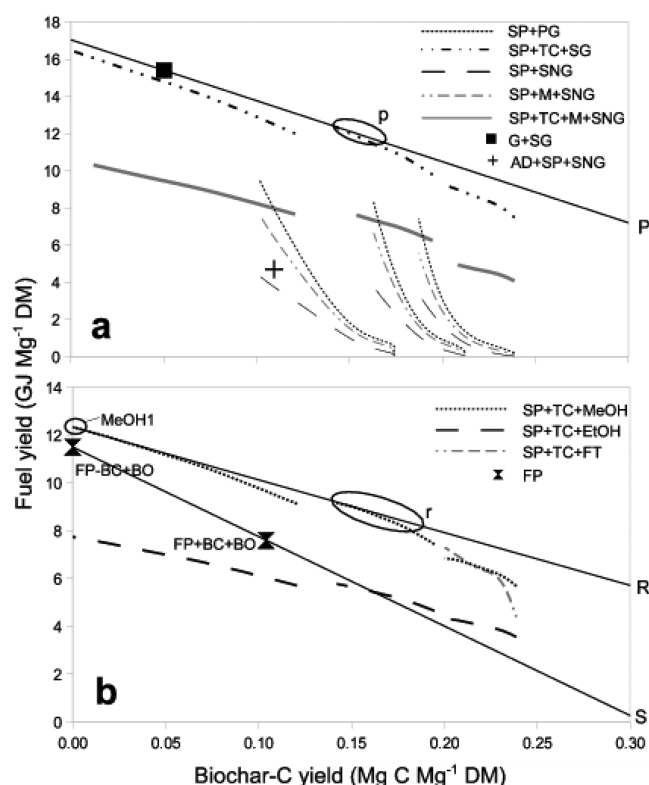
by heat recovery from the syngas; see Supporting Information, section 2.2.2).

The partitioning of SP+TC+FT biofuel products between LPG, gasoline, diesel, and wax varies with pyrolysis temperature (and thus, also, with biochar yield; Figure 4), because the chain-growth probability which determines the relative yields of short-, medium-, and long-chain hydrocarbons (see Supporting Information, section 2.2.3) was assumed to be determined such that the quantity of gas after FT synthesis would be equal to the quantity required to provide process energy (an energy demand that varies with pyrolysis temperature). As pyrolysis temperature is increased from 300 to 700 °C, the increasing demand for fuel gas to provide process energy means that an increasing fraction of the FT products would optimally be methane. Thus, higher pyrolysis temperatures give a correspondingly lower yield of wax (defined as  $\geq C_{16}$  alkanes) (Figure 4). The yield of FT fuels (excluding gases, which are entirely used to provide process energy) increases from 6.1 GJ Mg<sup>-1</sup> DM at 300 °C to 7.6 GJ Mg<sup>-1</sup> DM at 700 °C. The percentage of this fuel production accounted for by wax falls from 28% to 4% (on an HHV basis) over the same pyrolysis temperature range. When wax fraction is lowest, at a pyrolysis temperature of 700 °C, gasoline (defined here as  $C_5$ – $C_9$  alkanes) accounts for 50% of the liquid-fuel produced, LPG ( $C_3$ – $C_4$ ) for 32%, and diesel ( $C_{10}$ – $C_{15}$ ) for 18%.

#### Trade-off between Energy and Biochar Production.

We begin this section by defining some terminology. First, we define “Pareto-optimal” system configurations (with respect to product yields) as those for which it is not possible to increase bioenergy yield without sacrificing biochar yield (or vice versa). The “Pareto frontier” is then defined as the set of Pareto-optimal systems. Second, we define a “bioenergy penalty” when comparing one BEBCS configuration to another as the amount of bioenergy that is sacrificed per unit increase in biochar yield (in units of GJ Mg<sup>-1</sup> C). The pathway that optimizes gaseous-fuel yield is G+SG, with other options allowing higher biochar yields in exchange for less fuel (Figure 5a). The minimum bioenergy penalty at which biochar can be substituted for bioenergy (relative to the energy-maximizing G+SG) is given by the straight line with the least negative slope that passes through G+SG and also through another point on the Pareto frontier, representing a pathway with higher biochar yield (Figure 5a, solid line P). Note that any line through G+SG having a slope less than P will not pass through the Pareto boundary, indicating that no system configurations exist that would allow a bioenergy sacrifice rate lower than P. This minimum bioenergy penalty corresponds to a line passing through SP+TC+SG at a pyrolysis temperature of 700 °C and using additional biomass for process energy (Figure 5a, ellipse labeled “p”), which entails a reduction of 32.9 GJ fuel per Mg increase in biochar C relative to gasification (slope of line P).

Maximum production of liquid fuels can be achieved by SP+TC+MeOH, with pyrolysis at 650 °C, and all the biochar being used to provide all process heat and power (Figure 5b point MeOH1). This energy-maximizing system configuration yields comparable, but slightly higher, biofuel yields to FP–BC+BO (Figure 5b). The maximum rate at which biochar can be substituted for liquid fuels relative to this energy-maximizing point, MeOH1, is a penalty of 21.0 GJ Mg<sup>-1</sup> C (Figure 5b, line R), when SP+TC+MeOH is used, with process energy supplied by combusting additional biomass (Figure 5b, ellipse r). This represents a significantly smaller energy penalty for biochar production than would be incurred if FP biochar were used for



**Figure 5.** Comparison of fuel and biochar yields for all pathways shown in Figure 4 for (a) gaseous fuels and (b) liquid fuels. The solid line labeled P represents the maximum rate at which biochar yield can be substituted for gaseous fuel yield, relative to the energy-maximizing point for gasification. The solid line labeled R represents the maximum rate at which biochar yield can be substituted for liquid fuel yield (relative to the energy-maximizing point, FP–BC+BO). Line S shows the rate at which biochar yield would be substituted for energy yield if FP with biochar production (FP+BC+BO) were substituted for FP with the biochar consumed for process energy (FP–BC+BO).

C sequestration (Figure 5b, point FP+BC+BO) rather than for process energy (Figure 5b, point FP1) in which case a reduction in fuel production of 37.5 GJ Mg<sup>-1</sup> C would be incurred.

## DISCUSSION

We have shown liquid fuel production from SP-based systems could be maximized by use of methanol synthesis configured such that all the biochar is utilized for process energy. Such a system could produce comparable biofuel yields to FP with no net biochar production. We have also shown that to coproduce biochar with liquid fuels entails a reduction in liquid fuel yield of at least 21 GJ Mg<sup>-1</sup> C (biofuel energy sacrificed per unit mass of biochar C), with the pathway that gives this minimal energy penalty being SP+TC+MeOH, utilizing additional biomass for process energy. SP+TC+FT would entail a slightly higher energy penalty than SP+TC+MeOH of 24.4 GJ Mg<sup>-1</sup> C. For gaseous-biofuel production, the minimum energy penalty for biochar production is 33 GJ Mg<sup>-1</sup> C, when G+SG is substituted with SP+TC+SG.

One useful application of these calculations of energy penalties is to quantify the biochar-to-biofuel production ratio that would maximize total revenue from sale of these two streams.<sup>43</sup> Thus, we can see that when biochar prices (per Mg C) are less than 33 times the price (per GJ) of gaseous fuels or



21 times the price of liquid pyrolysis fuels, coproduction of biochar with biofuels will reduce revenues compared to biofuel-only production. At current U.S. average fuel prices (\$4.06 GJ<sup>-1</sup> for natural gas and \$15.4 GJ<sup>-1</sup> for crude oil; [www.eia.gov](http://www.eia.gov)), this would imply a minimum biochar price of at least \$134 Mg<sup>-1</sup> C or \$320 Mg<sup>-1</sup> C before revenues from increased biochar production could offset lost revenues from foregone gaseous or liquid fuels, respectively. This finding is in accord with McCarl et al.<sup>44</sup> who also found that high biochar prices and low energy prices would favor slow-pyrolysis biochar production, with SP becoming profitable at biochar prices greater than \$246 Mg<sup>-1</sup>.

It is interesting to note (as seen in Figures 3 and 4) that conversion pathways with a tar-cracking stage tend to produce Pareto-optimal results independent of pyrolysis temperature and that the exact fuel–char ratio can be widely adjusted by changing the ratios of process fuels used. This implies considerable latitude to choose pyrolysis conditions to optimize for desired biochar properties to suit local soil conditions and carbon sequestration objectives or to modulate energy versus biochar yields in response to fluctuating price differentials for the two commodities.

In practice, selection of the most appropriate technology for a specific situation will depend not only on biochar-biofuel yields but also on several other factors, including capital cost; interactions between economies of scale and biomass transport; reliability and maintenance costs; and environmental burdens of waste streams. A full techno-economic comparison of different technological options would require that these other factors be accounted for as well.<sup>45</sup> Because of the wide range of pathways, scales, and operating conditions considered here, such a full techno-economic comparison is not feasible in the scope of the current study.

Where and when biochar production would be economically attractive is not yet known and will require further research. In the near term, biochar production will be most favored in regions with poor soils and lower energy demand, where its value relative to energy will be highest. Conversely, it is unlikely to be economic at current energy and carbon prices in regions where the value of biochar's agricultural impacts is low.<sup>21</sup> In the longer term, biological carbon capture and storage may be critical to climate stabilization at <2 °C,<sup>46</sup> and the increasing value of carbon sequestration as a means to meet climate-change mitigation targets<sup>47</sup> can, thus, be expected to increase the range of situations in which biochar production would be favorable.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Detailed description of the modeling methods, parametrization, and assumptions. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Lal, R. Managing soils for a warming earth in a food-insecure and energy-starved world. *J. Plant Nutr. Soil Sci.* **2010**, *173*, 4–15.
- (2) Meinshausen, M.; Meinshausen, N.; Hare, W.; Raper, S. C. B.; Frieler, K.; Knutti, R.; Frame, D. J.; Allen, M. R. Greenhouse-gas emission targets for limiting global warming to 2 °C. *Nature* **2009**, *458*, 1158–1162.
- (3) Jeffery, S.; Verheijen, F. G. A.; van der Velde, M.; Bastos, A. C. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. *Agric., Ecosyst. Environ.* **2011**, *144*, 175–187.
- (4) 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*, 726–739.
- (5) 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*, 343–357.
- (6) Laird, D. A.; Fleming, P.; Davis, D. D.; Horton, R.; Wang, B.; Karlen, D. L. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. *Geoderma* **2010**, *158*, 443–449.
- (7) Schmidt, M. W. I.; Noack, A. G. Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges. *Global Biogeochem. Cycles* **2000**, *14*, 777–793.
- (8) Kuzyakov, Y.; Subbotina, I.; Chen, H.; Bogomolova, I.; Xu, X. Black carbon decomposition and incorporation into soil microbial biomass estimated by <sup>14</sup>C labeling. *Soil Biol. Biochem.* **2009**, *41*, 210–219.
- (9) 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 DOI: 10.1029/2007JG000642.
- (10) Spokas, K. Review of the stability of biochar in soils: Predictability of O:C molar ratios. *Carbon Manage.* **2010**, *1*, 289–303.
- (11) Sombroek, W. G.; Nachtergaele, F. O.; Hebel, A. Amounts, dynamics, and sequestering of carbon in tropical and subtropical soils. *Ambio* **1993**, *22*, 417–426.
- (12) Glaser, B. Prehistorically modified soils of central Amazonia: A model for sustainable agriculture in the twenty-first century. *Philos. Trans. R. Soc., B* **2007**, *362*, 187–196.
- (13) Lehmann, J.; Gaunt, J.; Rondon, M. Bio-char sequestration in terrestrial ecosystems—A review. *Mitigat. Adapt. Strat. Global Change* **2006**, *11*, 395–419.
- (14) Woolf, D.; Amonette, J. E.; Street-Perrott, F. A.; Lehmann, J.; Joseph, S. Sustainable biochar to mitigate global climate change. *Nat. Commun.* **2010**, *1*, 1–9.
- (15) Gurwick, N. P.; Moore, L. A.; Kelly, C.; Elias, P. A systematic review of biochar research, with a focus on its stability in situ and its promise as a climate mitigation strategy. *PLoS One* **2013**, *8*, e75932.
- (16) Cayuela, M. L.; Sánchez-Monedero, M. A.; Roig, A.; Hanley, K.; Enders, A.; Lehmann, J. Biochar and denitrification in soils: when, how much, and why does biochar reduce N<sub>2</sub>O emissions? *Sci. Rep.* **2013**, *3*.
- (17) Fowles, M. Black carbon sequestration as an alternative to bioenergy. *Biomass Bioenergy* **2007**, *31*, 426–432.
- (18) Gaunt, J. L.; Lehmann, J. Energy balance and emissions associated with biochar sequestration and pyrolysis bioenergy production. *Environ. Sci. Technol.* **2008**, *42*, 4152–4158.
- (19) Roberts, K. G.; Gloy, B. A.; Joseph, S.; Scott, N. R.; Lehmann, J. Life cycle assessment of biochar systems: Estimating the energetic, economic, and climate change potential. *Environ. Sci. Technol.* **2010**, *44*, 827–833.
- (20) Wang, Z.; Dunn, J. B.; Han, J.; Wang, M. Q. Effects of co-produced biochar on life cycle greenhouse gas emissions of pyrolysis-derived renewable fuels. *Biofuels, Bioprod. Biorefin.* **2014**, *8*, 189–204.
- (21) Field, J. L.; Keske, C. M. H.; Birch, G. L.; DeFoort, M. W.; Cotrufo, M. F. Distributed biochar and bioenergy coproduction: A

regionally specific case study of environmental benefits and economic impacts. *GCB Bioenergy* **2013**, *5*, 177–191.

(22) Hammond, J.; Shackley, S.; Sohi, S.; Brownsort, P. Prospective life cycle carbon abatement for pyrolysis biochar systems in the U.K. *Energy Policy* **2011**, *39*, 2646–2655.

(23) Hanandeh, A. E. Carbon abatement via treating the solid waste from the Australian olive industry in mobile pyrolysis units: LCA with uncertainty analysis. *Waste Manage. Res.* **2013**, *31*, 341–352.

(24) Jeffery, S.; Bezemer, T. M.; Cornelissen, G.; Kuiper, T. W.; Lehmann, J.; Mommer, L.; Sohi, S. P.; van de Voorde, T. F. J.; Wardle, D. A.; Van Groenigen, J. W. The way forward in biochar research: Targeting trade-offs between the potential wins. *GCB Bioenergy* **2013**, DOI: 10.1111/gcbb.12132.

(25) Neves, D.; Thunman, H.; Matos, A.; Tarelho, L.; Gómez-Barea, A. Characterization and prediction of biomass pyrolysis products. *Prog. Energy Combust. Sci.* **2011**, *37*, 611–630.

(26) Wilhelm, D.; Simbeck, D.; Karp, A.; Dickenson, R. Syngas production for gas-to-liquids applications: Technologies, issues and outlook. *Fuel Process. Technol.* **2001**, *71*, 139–148.

(27) Shackley, S.; Hammond, J.; Gaunt, J.; Ibarrola, R. The feasibility and costs of biochar deployment in the U.K. *Carbon* **2011**, *2*, 335–356.

(28) Shabangu, S.; Woolf, D.; Fisher, E. M.; Angenent, L. T.; Lehmann, J. Techno-economic assessment of biomass slow pyrolysis into different biochar and methanol concepts. *Fuel* **2014**, *117* (Part A), 742–748.

(29) Deshmukh, S. R.; Tonkovich, A. L. Y.; Jarosch, K. T.; Schrader, L.; Fitzgerald, S. P.; Kilanowski, D. R.; Lerou, J. J.; Mazanec, T. J. Scale-up of microchannel reactors for Fischer–Tropsch synthesis. *Ind. Eng. Chem. Res.* **2010**, *49*, 10883–10888.

(30) Laird, D. A.; Brown, R. C.; Amonette, J. E.; Lehmann, J. Review of the pyrolysis platform for coproducing bio-oil and biochar. *Biofuels, Bioprod. Biorefin.* **2009**, *3*, 547–562.

(31) Crelling, J. C.; Hagemann, H. W.; Sauter, D. H.; Ramani, R. V.; Vogt, W.; Leininger, D.; Krzack, S.; Meyer, B.; Orywal, F.; Reimert, R.; et al. Coal. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Berlin, Germany, 2000.

(32) Barrett, S.; Dannenberg, A. Sensitivity of collective action to uncertainty about climate tipping points. *Nat. Clim. Change* **2014**, *4*, 36–39.

(33) Lenton, T. M. Game theory: Tipping climate cooperation. *Nat. Clim. Change* **2014**, *4*, 14–15.

(34) Mathieu, P.; Dubuisson, R. Performance analysis of a biomass gasifier. *Energy Convers. Manage.* **2002**, *43*, 1291–1299.

(35) Prins, M. J.; Ptasinski, K. J.; Janssen, F. J. J. G. From coal to biomass gasification: Comparison of thermodynamic efficiency. *Energy* **2007**, *32*, 1248–1259.

(36) Antal, M.; Grønli, M. The art, science, and technology of charcoal production. *Ind. Eng. Chem. Res.* **2003**, *42*, 1619–1640.

(37) Enders, A.; Hanley, K.; Whitman, T.; Joseph, S.; Lehmann, J. Characterization of biochars to evaluate recalcitrance and agronomic performance. *Bioresour. Technol.* **2012**, *114*, 644–653.

(38) Huber, G. W.; Iborra, S.; Corma, A. Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. *Chem. Rev.* **2006**, *106*, 4044–4098.

(39) Morf, P.; Hasler, P.; Nussbaumer, T. Mechanisms and kinetics of homogeneous secondary reactions of tar from continuous pyrolysis of wood chips. *Fuel* **2002**, *81*, 843–853.

(40) Dayton, D. *A Review of the Literature on Catalytic Biomass Tar Destruction*; NREL: Golden, CO, 2002.

(41) Sutton, D.; Kelleher, B.; Ross, J. R. H. Review of literature on catalysts for biomass gasification. *Fuel Proc. Technol.* **2001**, *73*, 155–173.

(42) NGV Global. *Current Natural Gas Vehicle Statistics*, NGV Global Knowledgebase; <http://www.iangv.org/current-ngv-stats/>, 2012.

(43) Yoder, J.; Galinato, S.; Granatstein, D.; Garcia-Pérez, M. Economic tradeoff between biochar and bio-oil production via pyrolysis. *Biomass Bioenergy* **2011**, *35*, 1851–1862.

(44) McCarl, B.; Peacocke, C.; Chrisman, R.; Chih-Chun, K.; Sands, R. Chapter 19: Economics of biochar production, utilisation and emissions. In *Biochar for environmental management: Science and technology*; Lehmann, J., Joseph, S., Eds.; Earthscan: Oxford, U.K., 2009.

(45) Brown, T. R.; Wright, M. M.; Brown, R. C. Estimating profitability of two biochar production scenarios: Slow pyrolysis vs fast pyrolysis. *Biofuels, Bioprod. Biorefin.* **2011**, *5*, 54–68.

(46) Smith, P.; Bustamente, M. Ch.11, Agriculture, Forestry and Other Land Use. In *Climate Change 2014: Mitigation of Climate Change, Working Group III Contribution to the IPCC 5th Assessment Report*; IPCC: Geneva, Switzerland.

(47) Moss, R. H.; Edmonds, J. A.; Hibbard, K. A.; Manning, M. R.; Rose, S. K.; Vuuren, D. P. van; Carter, T. R.; Emori, S.; Kainuma, M.; Kram, T.; et al. The next generation of scenarios for climate change research and assessment. *Nature* **2010**, *463*, 747–756.