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Evaluation of ecological benefits and risks of biochar systems

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Gierig nimmt die **Kohle** aus Holz

Materie und Licht in sich auf

Großzügig stellt sie

Lebensraum und Wärme

Zur Verfügung

Doch das Wissen

Um ihr Wesen

Gibt sie

Nur widerstrebend preis

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Abbreviations and Symbols

ANOVA	analysis of variance
BAM	biochar application mass
C	carbon
CAM	compost application mass
C_{BC}	share of carbon in oven dry biomass contained in biochar
C_E	oxidized carbon fraction of dry biomass during biochar production process
CH_4	methane
Cl	chlorine
CO_2	carbon dioxide
CO_2-C	carbon content in carbon dioxide
CO_2e	carbon dioxide equivalent
DM	dry mass
eq	equation
$\tilde{f}_{Atm}$	monthly average of two-way atmospheric transmittance parameter
f_g	fraction of green vegetation at a certain point in time
$\tilde{f}_g$	average monthly fraction of green vegetation
$\tilde{f}_{sc}$	average monthly fraction of snow cover
FT	field trial
g	gram
GHG	greenhouse gas
GWP	Global Warming Potential
GWP_{albedo}	Global Warming Potential characterization factor for albedo changes
GWP_{bio}	Global Warming Potential characterization factor for biogenic CO_2 emissions
GWC	gravimetric water content

ISO	International Organization for Standardization
h	hour
ha	hectare
htc	hydrothermal carbonization
IEA	International Energy Agency
iRF	time-integrated radiative forcing
K	potassium
k_{CO2}	radiative efficiency of CO_2
kg	kilogram
k_T	monthly mean clearness index
kW_{el}	electrical kilowatt
kW_{th}	thermal kilowatt
kWh	kilowatt-hour
LCA	Life Cycle Analysis
M_{FS}	dry feedstock mass
Mg	Megagram
MJ	Megajoule
MODIS	moderate-resolution imaging spectroradiometer
MPa	Megapascal
MRT	mean residence time
MW_{el}	electrical Megawatt
MW_{th}	thermal Megawatt
N	nitrogen
N	surface reflectance averaged over near-infrared regions
N_s	surface reflectance of bare soil averaged over near-infrared regions
N_v	surface reflectance of dense vegetation averaged over near-infrared regions
N_2O	Nitrous oxide
NASA	National Aeronautics and Space Administration
min	minute

m²	square metre
n	amount of samples
odt	oven dry tonne
P	phosphorus
p	exceeding probability
PT	pot trial
ppmv	parts per million (volumetric)
R	surface reflectance averaged over visible regions
R_s	surface reflectance of bare soil averaged over visible regions
R_v	surface reflectance of dense vegetation averaged over visible regions
RF_α	radiative forcing cause by an albedo change
$\widetilde{RF}_\alpha$	monthly mean radiative forcing from a monthly mean surface albedo change
$\widetilde{R}_{TOA}$	monthly mean downward solar flux at the top of the atmosphere
RW	roundwood
s	second
SDVI	scaled difference vegetation index
t	(metric) tonne
T_a	fraction of shortwave irradiation reaching TOA after reflection at the surface
TH	time horizon
TOA	top of the atmosphere
UBA	Umweltbundesamt
US$_{2010}$	US-Dollar at the price level of the year 2010
W	Watt
wt	weight
yr	year
$\Delta\widetilde{\alpha}_s$	monthly mean surface albedo change
$\Delta\widetilde{\alpha}_{soil}$	albedo difference between different types of soil
λ	wavelength
µm	micrometer

1 Introduction

1.1 General background

According to the Goddard Institute for Space Studies of the National Aeronautics and Space Administration of the USA, the mean global temperature (combined land-surface air and sea-surface water temperature) has increased by 0.58 °C between the base period 1951-1980 and the year 2012 (Goddard Institute for Space Studies 2013). With the progression of climate change, mitigation and adaptation efforts are being intensified to prevent already perceived and expected negative impacts of changes in the biosphere. The latter include adverse effects on the global food security (Wheeler and von Braun 2013).

Independent from the expected impacts of climate change on the global food security, governmental and non-governmental organizations have already been struggling for a world without hunger since decades. While the number of the world´s undernourished people decreased from 980 million in the period 1990–92 to about 850 million in the period 2010–2012 (Wheeler and von Braun 2013), this implies that the right to food in article 25c of the Universal Declaration of Human Rights is still not guaranteed for a population substantially larger than that of the entire European Union. The first of the four dimensions of food security as defined by the United Nations' Food and Agricultural Organization is "the availability of sufficient quantities of food of appropriate quality" (Food and Agricultural Organization of the United Nations 2006). The long-term availability of soils with a sufficient fertility for food production is one of the main preconditions which have to be met to be able to warrant that sufficient quantities of food of appropriate quality are available.

Climate change mitigation encompasses a wide range of options: among them are lifestyle chances, energy use efficiency increases, the deployment of renewable energy sources, and carbon sequestration methods. The concept of carbonizing biomass and using the obtained product for soil amelioration and carbon sequestration – the so called "biochar system" (Lehmann and Joseph 2009) - has gained much attention in the research community (Lehmann 2007) as well as in the media in the last four years. The attractiveness of this concept can be explained by its promise to contribute to climate change mitigation and to foster food security at the same time (Glaser et al. 2001; Kimetu et al. 2008; Molina et al. 2009). Role model for this concept is the existence of Terra Preta in the Amazonian region of

South America. Terra Preta (Portuguese for "black earth") is a very dark, fertile anthropogenic soil with an extraordinary high carbon content due to the presence of charred organic matter.

It seems to be no coincidence that the interest in biochar systems rose in parallel to the collapse of the popularity of biofuel production. A better understanding of the interactions between biofuel use, energy crop provision, direct and indirect land use change (Panichelli and Gnansounou 2008), food production and the resulting environmental impacts drastically changed the public opinion on biofuels as well the support policy for biofuels in the European Union in the recent years.

As both bioenergy and biochar systems are partly making use of the same resource basis and are thus subject to multiple interactions with the agricultural environment, it is foreseeable that an increase in biochar production will trigger critical questions on the realizable ecological benefits and the potential negative environmental effects of biochar systems. Answering these questions in an early stage of the market development might both help to avoid steering into ecological dead ends and to optimize potential future support schemes for biochar systems.

1.2   Objectives and structure of this thesis

The objective of this thesis is an evaluation of ecological benefits and risks of biochar systems. The scope of the thesis was focused on impacts of biochar systems on the climate system and on the potential impact of biochar systems on the polycyclic aromatic hydrocarbons (PAH) level in soils. As basis for this evaluation, the technical and economic development stage of different carbonization technologies was assessed.

Three studies, which build upon each other, were carried out to reach the objective of this thesis:

Due to the absence of public support schemes for biochar systems, the biochar market development in the recent years was solely driven by technological advancements of carbonization systems and the resulting competitiveness of biochar systems on unregulated markets. When this thesis was started in 2009, it was difficult to foresee the commercialization speed of different carbonization technologies and their future market

penetration. Both factors directly influence the type and extent of the environmental impacts triggered by biochar systems. Accordingly, this thesis started with a literature review dealing with the technical and economic development stage of four different carbonization technologies (pyrolysis, gasification, hydrothermal carbonization, flash carbonization) and their greenhouse gas balances:

• Meyer, Sebastian; Glaser, Bruno; Quicker, Peter (2011): Technical, Economical, and Climate-Related Aspects of Biochar Production Technologies: A Literature Review. In: ENVIRONMENTAL SCIENCE & TECHNOLOGY 45 (22), S. 9473–9483 (see chapter 2)

The article is online available at: http://pubs.acs.org/doi/abs/10.1021/es201792c

The article was cited 21 times in the ISI WEB of Knowledge and 39 times in Google Scholar until 20.01.2014. The Journal impact factor of ES&T for the year 2012 was 5.257.

The literature review revealed that the impact of biochar application on the surface albedo (the relation of reflected shortwave radiation to incoming shortwave radiation) had not yet been accounted for in climate assessment of biochar systems. Changes in surface albedo affect radiative forcing, thus large scale albedo changes directly influence the global climate. Thus, it could not be ruled out that a decrease in the surface albedo caused by biochar field application might overcompensate for the climate mitigation benefits of biochar systems. To quantify this risk, the second study was carried out:

• Meyer, Sebastian; Bright, Ryan M.; Fischer, Daniel; Schulz, Hardy; Glaser, Bruno (2012): Albedo Impact on the Suitability of Biochar Systems To Mitigate Global Warming. In: ENVIRONMENTAL SCIENCE & TECHNOLOGY 46 (22), S. 12726–12734 (see chapter 3)

The article is online available at: http://pubs.acs.org/doi/abs/10.1021/es302302g

The article was cited 3 times in the ISI WEB of Knowledge and 7 times in Google Scholar until 20.01.2014. The Journal impact factor of ES&T for the year 2013 is not available yet.

In this study, the results of the albedo research were complemented by an analysis of the temporal impacts of biogenic CO_2 emissions on the climate and by a complete greenhouse gas balance of a modeled biochar system to assess its overall climate impact.

Since the results of the literature review highlighted the economic and climate related advantages of using biogenic residues for biochar production, a critical evaluation of the opportunity of utilizing wood gasification residues in biochar systems was set in the focus of the third study. As wood gasification residues often contain large amounts of persistent and carcinogenic polycyclic aromatic hydrocarbons (Bruno Veyrand et al. 2013), the third study evaluated the efficiency of a thermal process designed to remove PAH from gasification residues. The analyzed process aims at the provision of biochars with a minimal soil pollution risk with regard to PAH:

• Meyer, Sebastian; Glaser, Bruno; Fischer, Daniel; Quicker, Peter; Noel, Yves; Kuffer, Georg (2014): Thermal Removal of PAH from Gasification Biochars. Dr. Maria C. Hernandez Soriano (Ed.), ISBN: 978-953-51-1235-8, InTech, DOI: 10.5772/57269 (see chapter 4)

This open access book chapter is online available without charge at:
http://www.intechopen.com/books/environmental-risk-assessment-of-soil-contamination/thermal-removal-of-polycyclic-aromatic-hydrocarbons-from-gasification-biochars

The mentioned three studies are presented in the following chapters. The main paper and the supporting information to the article "Albedo Impact on the Suitability of Biochar Systems to Mitigate Global Warming " have been integrated in chapter 3 to ensure a better readability. The discussion and the subsumption of the overall results of this thesis into the current state of scientific knowledge are presented in chapter 5. The conclusions of the entire thesis are presented in chapter 6. The results of the thesis are summarized in English in chapter 7 and in German in chapter 8.

2   Technical, economical and climate related aspects of biochar production technologies: A literature review

Sebastian Meyer, Bruno Glaser and Peter Quicker

2.1   Summary

For the development of commercial biochar projects, reliable data on biochar production technologies is needed. For this purpose, peer-reviewed scientific articles on carbonization technologies (pyrolysis, gasification, hydrothermal carbonization, and flash carbonization) have been analyzed. Valuable information is provided by papers on pyrolysis processes, less information is available on gasification processes, and few papers about hydrothermal and flash carbonization technologies were identified. A wide range of data on the costs of char production (between 51 US$ per tonne pyrolysis biochar from yard waste and 386 US$ per tonne retort charcoal) and on the GHG balance of biochar systems (between -1054 kg CO_2e and +123 kg CO2e per t dry biomass feedstock) have been published. More data from pilot projects are needed to improve the evaluation of biochar production technologies. Additional research on the influence of biochar application on surface albedo, atmospheric soot concentration, and yield responses is necessary to assess the entire climate impact of biochar systems. Above all, further field trials on the ability of different technologies to produce chars for agricultural soils and carbon sequestration are essential for future technology evaluation.

2.2   Introduction

In recent years, biochar application to soil has been put forward as a tool to mitigate global warming and improve soil properties (Glaser et al. 2001; Kimetu et al. 2008; Molina et al. 2009). In spite of considerable scientific work on the effects of biochar application to soil with respect to crop yields and stabilization of plant-derived carbon in agricultural soils, the commercial production of biochar for soil improvement and C sequestration is still very limited today. Parties interested in the development of commercial biochar need reliable and comprehensive data on the different technologies available for biochar production. For this reason, this paper summarizes the available peer-reviewed scientific literature (ISI Web of Knowledge) about the technological, economical, and climate-relevant aspects of carbonization technologies.

Biochar is defined as *"charred organic matter applied to soil in a deliberate manner, with the intent to improve soil properties"* in (Lehmann and Joseph 2009). Although biomass-derived char can be used as energy carrier, as adsorber, and for further applications, this paper focuses on the production of chars for the improvement of soil properties.

Carbonized organic matter can have fundamentally different physical and chemical properties depending on the technology (e.g., torrefaction (a pyrolysis process at low temperature), slow pyrolysis, intermediate pyrolysis, fast pyrolysis, gasification, hydrothermal carbonization (htc), or flash carbonization) used for its production. Research on torrefied material as soil amendment has started only recently (Trifonova et al. 2009). In contrast to considerable research which has already been carried out to assess the value of charcoal as soil amendment (Iswaran et al. 1980; Lehmann et al. 2003; Yamato et al. 2006; Steiner et al. 2007; Rajeev Jorapur and Anil K. Rajvanshi 1997), no publication was identified which examines the use of chars from modern gasifiers as soil amendment. Charcoal can be produced both in traditional earthen charcoal kilns where pyrolysis, gasification, and combustion processes are carried out in parallel below the earthen kiln layer and in modern charcoal retorts where pyrolysis and combustion processes are physically separated by a metal barrier. Two papers have been published on the suitability of htc-char for the stabilization of organic carbon (Steinbeiss et al. 2009; Libra et al. 2011), and another on the suitability of htc-char for the improvement of soil properties (Rillig et al. 2010). Only one publication is available today in the ISI Web of Knowledge on the suitability of the use of

carbonized material from flash carbonization as a soil amendment (Deenik et al. 2010). It is important to be aware that the results of the indicated publications with carbonized material from torrefaction, hydrothermal carbonization, and flash carbonization did not show an improvement of plant growth after the addition of carbonized material.

As phytotoxic components have been found in torrefied material (Trifonova et al. 2009) and torrefied material has hydrophobic properties, this technology is treated in less detail in this review. Apart from that, all main technology routes already mentioned have been fully included in this literature review as today's knowledge on the suitability of carbonized material from modern gasification, hydrothermal carbonization, and flash carbonization for the improvement of soil properties is still very limited. However, it is indispensable to further assess the ability of the different technologies to produce carbonized material suitable to increase the fertility of agricultural soils and to store carbon over a long period of time. In this context, special care has to be taken to avoid the use of chars contaminated with polycyclic aromatic compounds or dioxins for agricultural purposes. A detailed discussion of dioxin formation is presented by (McKay 2002) and limits for dioxin and polycyclic aromatic hydrocarbon levels in compost and sewage sludge in European countries can be found in (Libra et al. 2011).

It should be noted that in field trials, often mixtures of char and compost are used with the aim to produce a soil amendment similar to the fertile Terra Preta soils in the Amazon region (Glaser et al. 2001). Though char makes up a minor weight component of this soil amendment, it is an essential part of the final product.

2.3 Methodology

To identify the relevant literature for this review, the ISI Web of Knowledge was explored with the following method: By searching for articles containing the keywords "pyrolysis", "gasification", "hydrothermal carbonization", and "flash carbonization" in connection with the keywords "reliability", "availability", "durability", "development + hours", and "scale up", the *technological maturity* of carbonization technologies was assessed. To retrieve publications that analyze the *economical profitability* of carbonization technologies, the keywords "profitability", "economics", "production costs + char", and "return + char" were

used. Regarding *the climate impact* of carbonization technologies, the keywords "GHG balance", "LCA", "albedo", and "atmospheric soot" were selected.

The available peer-reviewed scientific literature about the technological, economical, and climate-relevant aspects of the different technologies varies considerably.

Table 1: Publications identified and reviewed per category

technology type	technological maturity	profitability analyses	climate impacts
Pyrolysis	2	7	6
Gasification	7	2	1
hydrothermal carbonization	2	0	0
flash carbonization	1	1	0

This can be seen in the overview on the number of publications identified and reviewed per technology and assessment aspect (Table 1). In addition to that, information on carbonization technologies is often focused on the production of energy carriers only. This will be reflected in the following chapters. As this paper concentrates on publications in the ISI, it cannot be excluded that additional publications are available in other scientific databases.

2.4   Overview on carbonization technologies

To produce carbonized organic matter, pyrolysis, gasification, hydrothermal carbonization, and flash carbonization technologies can be used. Pyrolysis can be differentiated from gasification by the (nearly) complete absence of oxygen in the conversion process (Bridgwater 2007).

Pyrolysis technologies can be further differentiated by the reaction time of the pyrolysis material (e.g., slow and fast pyrolysis processes) and the heating method (e.g., pyrolysis processes started by the burning of fuels, by electrical heating, or by microwaves). (Bridgwater 2007) and (IEA Bioenergy o.J.) differentiate pyrolysis technologies according to the temperature and the residence time of the pyrolysis process (see Table 2).

In gasification processes, the biomass is partially oxidized in the gasification chamber (Bridgwater et al. 2002) at a temperature of about 800 °C (Bridgwater 2007) at atmospheric

or elevated pressure. As already indicated by its name, the main product of this process is gas, only small amounts of char and liquids are formed.

Table 2: Solid product yields, solid product carbon content and carbon yield of different technologies

process type	typical process temperature	typical residence time	typical solid product yield on a dry wood feed-stock basis [in mass %]	typical carbon content of the solid product [in mass %]	typical carbon yield: (mass $_{carbon, product}$ /mass $_{carbon, feedstock}$)	reference
torrefaction	~ 290 °C	10 – 60 min	61 - 84 %	51 - 55 %	0.67 – 0.85	(Bridgwater 2007; Yan et al. 2009)
slow pyrolysis	~ 400 °C	min to days	≈ 30 %	95 %	≈ 0.58	(Bridgwater 2007; Antal and Gronli 2003)
fast pyrolysis	~ 500 °C	~ 1 s	12 - 26 %	74 %	0.2 – 0.26	(Bridgwater 2007; IEA Bioenergy o.J.; DeSisto et al. 2010; Repo et al. 2011)
gasification	~ 800 °C	~ 10 to 20 s	≈ 10 %	-	-	(Bridgwater 2007)
htc	~ 180-250 °C	1-12 h	< 66 % [a]	< 70 % [b]	≈ 0.88	(Libra et al. 2011; Tsukashi 1966)
flash carbonization	~ 300-600 °C	< 30 min	37 %	≈ 85 %	≈ 0.65	(Antal and Gronli 2003)

[a] Lower solid products yields for htc at both shorter and longer residence times are reported by (Libra et al. 2011). [b] The carbon content of 70 % of the product indicated in (Tsukashi 1966) is related to the dry, ash-free product.

The hydrothermal carbonization of biomass is realized by applying elevated temperature (180 - 220 °C) to biomass in a suspension with water under elevated pressure for several hours. It yields solid, liquid, and gaseous products (Funke and Ziegler 2010). (Libra et al. 2011) refer to hydrothermal carbonization as "wet pyrolysis". Because no oxygen is supplied to the reactor with the biomasswater suspension, this classification is justified.

For the flash carbonization of biomass, a flash fire is ignited at elevated pressure (at about 1 - 2 MPa) at the bottom of a packed bed of biomass. The fire moves upward through the carbonization bed against the downward flow of air added to the process. In total about 0.8 - 1.5 kg of air per kg of biomass are delivered to the process. The reaction time of the process is below 30 min, and the temperature in the reactor is in the range of 300 - 600 °C. The process results mainly in gaseous and solid products. In addition to that, a limited amount of condensate is formed. While the oxygen input into the carbonization process is a typical feature of gasification technologies, both process temperature and the product spectrum (distribution among solid, liquid, and gaseous outputs) of flash carbonization are uncommon for gasification processes. It should be noted that typical solid product yields obtained by gasification and fast pyrolysis processes are significantly lower as compared to the solid product yields of slow pyrolysis, flash carbonization, hydrothermal carbonization and torrefaction (see Table 2).

It is important to take into account that the development history of the different technologies reviewed varies considerably: The development of coal gasification started already a few centuries ago (Hamper 2006) whereas the development of charcoal kilns has taken place over a time span of millennia (Antal and Gronli 2003).

2.5   Technological maturity of carbonization technologies

To understand the challenges that need to be solved to ensure a high annual availability of a biochar production system, Table 3 lists technical points that need special attention to ensure a long-term operation of the respective technologies.

Table 3: Selection of technology-specific challenges

technology type	technological challenges	Reference
Pyrolysis	• achieving and maintaining high, controlled heat rates and a correct reaction temperature; a low gas-vapour residence time at a moderate temperature • a rapid removal of char and effective liquids recovery can be challenging in fast pyrolysis systems • the release of chlorine from feedstock with high Cl content may result in corrosion of the reactor containment and in formation of deposits during pyrolysis gas conversion	(Jensen et al. 2000; Bridgwater et al. 2002)

gasification	• aerosol formation • soot formation due to repolymerization • dehydration of tars in the gas phase and interaction with other contaminants on fine particles • condensation of heavier tar components on cooler surfaces • blockage of particulate filters and clogging of fuel lines / injectors in internal combustion engines • corrosion caused by tar	(Nunes et al. 2008; Buchireddy et al. 2010)
hydrothermal carbonization	• the elasticity limit of the materials used for the pressure tank may not be exceeded during operation • feeding against pressure in continuous systems is challenging regarding material and safety aspects • a heat recovery from the hot process water and post-treatment installations for the htc-char might be necessary	(Funke and Ziegler 2010; Libra et al. 2011)
flash carbonization	• sudden pressure rise in carbonization container observed at ignition under specific process conditions with certain feedstock's • the elasticity limit of the materials used for the pressure tank may not be exceeded during operation	(Wade, SR et al. 2006)

2.5.1   Pyrolysis technologies

(Bridgwater et al. 2002) assumed an overall annual availability of 85% for an electricity production process based on liquids produced by fast pyrolysis. This assumption is used in a model to calculate the electricity production costs of the process. The assumption itself is based on the precondition that a buffer storage for pyrolysis liquids limits unplanned generation shutdowns. Thus, the pyrolysis process itself can have a considerably lower availability than 85%.

2.5.2   Gasification

(Bridgwater et al. 2002) assumed a mean annual availability of 80% for an electricity production process based on a dual fuel diesel engine fed by the atmospheric gasification of wood chips and diesel as auxiliary fuel. In the model, it is assumed that the ash produced from the atmospheric gasification process contains 33% char on a weight basis. (Bridgwater et al. 2002) further assumed the same annual availability (80%) for an electricity production process based on an integrated gas turbine combined cycle fed by the pressurized gasification of wood chips. It has to be noted that this technology is still in an early development stage.

(Yin et al. 2002) described a circulating fluidized bed biomass gasification and power generation system based on rice husk installed in 1998 which has been operating for 10 000 h within two years of operation. A considerable part of the char produced in the gasifier is removed from the product gas and returned to the gasifier.

According to (Pröll et al. 2007), the 8MW$_{th}$ dual fluidized bed steam gasification plant for solid biomass in Güssing, Austria has been operated for 24 000 h between April 2002 and the end of 2006. This translates into an average plant availability of about 58%. In 2005, an average availability of about 69% was reached (6 000 operation hours in one year) (Kreuzeder et al. 2007).

(Nunes et al. 2008) described the negative effect of tar formation on the operational availability of gasification, but do not indicate quantitative numbers on the annual availability of gasification processes.

(Yassin et al. 2009) assumed an availability of an electricity production system based on the fluidized bed gasification of residual waste of 90% (329 days per year) within a model to evaluate the techno-economic performance of energy from waste fluidized bed gasification.

Table 4: Annual availability of electricity production systems

process name	annual availability	comment	Reference
fast pyrolysis	> 85%	model assumption	(Bridgwater et al. 2002)
atmospheric gasification	80%	model assumption	(Bridgwater et al. 2002)
pressurized gasification	80%	model assumption	(Bridgwater et al. 2002)
fluidized bed gasification	90%	model assumption	(Yassin et al. 2009)
circulating fluidized bed gasification	57 %	empirical data	(Yin et al. 2002)
circulating fluidized bed gasification	58 %; 69%	empirical data	(Pröll et al. 2007; Kreuzeder et al. 2007)

2.5.3 Summary

Most information is available on gasification processes; less information is available on pyrolysis technologies (Table 4). Papers on the availability and reliability of carbonization

technologies are often not based on empirical data and do not cover hydrothermal and flash carbonization technologies at all. The available knowledge is focused on systems for the production of pyrolysis oil, synthesis gas, electricity, or heat. In summary, a comparison of the technological maturity of biochar production technologies based on scientific literature in not possible at the moment. In Table 4, data on the annual availability of production processes as indicated in the reviewed papers are summarized. The difference between the assumed availability rates and the empirical data is evident.

2.6   Profitability analyses of carbonization technologies

The focus of the literature review in this section was on publications issued not earlier than the year 2000, since profitability analyses are subject to rapidly changing economic framework conditions. Apart from that, they are often only valid for a specific project in a specific region at a specific point in time. Depending on the type of technology used, biogenic energy carriers (biogenic oil, synthesis gas), electricity, or heat are produced together with the char and constitute the main product, byproduct, or residue of the biomass conversion process. A considerable part of the described processes aim primarily at the provision of bioenergy. In these cases, the indicated economic data cannot be directly used to assess the profitability of the described technologies for biochar production. However, the indicated economic data can be used as a benchmark to assess under which conditions the production of biochar would be more (or less) profitable compared to the production of a bioenergy carrier. It is important to be aware that the (bio)energy and the biochar markets compete for the same feedstock, and that biochar-based soil amendments compete with other products (e.g., peat, pure compost) and other methods used to improve soil properties. To enable a direct comparison, the published economic data has been converted to US $ at historical exchange rates and has been inflation-adjusted to the reference year 2010 (US\$$_{2010}$).

2.6.1   Pyrolysis

(Islam and Ani 2000) carried out a techno – economic assessment of fluidized bed fast pyrolysis systems with rice husk throughputs of 100 and 1000 kg/h. The systems were assumed to be installed in Malaysia in a study carried out in 2000. Since the study focuses on the production of the pyrolysis oil, production costs of 0.38 US\$ (0.5 US\$$_{2010}$) per kg primary

pyrolysis oil [at 100 kg feed/hour] and 0.18 US$ (0.23 US$$_{2010}$) per kg primary oil [at 1000 kg feed/hour] have been calculated. Because solid char is coproduced by the fluidized bed fast pyrolysis system, the sales price of the primary pyrolysis oil could be reduced if the char would be sold. Unfortunately, production costs for the solid char cannot be derived from this study. However, the energy value of char from fast pyrolysis within the process can be calculated. Based on the higher heating value of char from fast pyrolysis (about 28 MJ/kg) (DeSisto et al. 2010) and the price of wood pellets as an alternative biogenic heating fuel (0.05 €$_{2011}$/kWh; 0.0202 $$_{2010}$/MJ), the energy value of the char is as high as 560 US$$_{2010}$ /tonne. It should be noted here that the value of the char is considerably lower if a cheaper conventional fuel is replaced. For example, (Badger et al. 2011) calculate with residual heating oil as replacement at a price of 0.0109 US$$_{2010}$/MJ.

(Bridgwater et al. 2002) calculated electricity production costs of 0.091 € (0.098 US$$_{2010}$)/kWh at 20 MW$_{el}$ and 0.199 € (0.215 US$$_{2010}$)/kWh at 1 MW$_{el}$ for a modeled electricity production process in UK based on liquids produced by fast pyrolysis and diesel as auxiliary fuel. Taking into account learning effects and assuming a 50% reduction of capital costs of fast pyrolysis modules after 10 installations, they calculated electricity production costs of 0.073 € (0.078 US$$_{2010}$)/kWh at 20 MW$_{el}$ and of 0.146 € (0.157 US$$_{2010}$)/kWh at 1 MW$_{el}$. In their model it is assumed that char and off-gas produced during the pyrolysis are burned to cover the internal heat demand of the installation. As calculated already above, the energy value of the char can be as high as 560 US$$_{2010}$/tonne.

(Lin and Hwang 2009) assessed the profitability of charcoal production from discarded Cryptomeria branches and wood tops using a still-operational earthen kiln in Taiwan. This analysis was based on empirical data combined with market research. Charcoal production cost of 3707 US$ (3747 US$$_{2010}$)/tonne can be derived from the analysis. If the revenues of selling wood vinegar are subtracted from the sum of production cost, the char could be sold at a whole-sale price of 1840 US$ (1860 US$$_{2010}$) per tonne. Considering charcoal prices in Taiwan amounted to 3030 US$ (3063 US$$_{2010}$)/tonne at the time of the analysis according to (Lin and Hwang 2009) the production process was judged to be economically feasible in their publication. However, the charcoal sales price assumed in this calculation—it is not stated in the mentioned publication if the indicated sales price is a retail price or an end customer price—is extremely high and exceeds even the end customer price for retort barbecue

charcoal in Germany in 2011 (2,700 US$\$_{2010}$). Thus, it is doubtful whether the assumed sales price can be realized for the total production volume indicated in the calculation (13,000 kg charcoal / year). Whereas charcoal production might thus not be profitable in the described example, charcoal production for energy applications— both in simple charcoal kilns and in modern retort systems—is clearly profitable for many charcoal producers around the globe (Brown et al. 2011). Thus, (Lin and Hwang 2009) might overestimate charcoal production cost in earthen-kilns. For comparison, (Norgate and Langberg 2009) calculated charcoal production cost of 373 US$ (386 US$\$_{2010}$)/tonne based on a continuous charcoal retort.

In a very detailed assessment, (Roberts et al. 2010) calculated the economic viability of a modeled continuous drum kiln "slow" pyrolysis plant with a throughput of 10 tonnes dry feedstock mass per hour at a temperature of 450 °C and a drum residence time of several minutes in the United States. Aim of the process is to produce biochar for soil management and synthesis gas for heat provision. Taking into account revenues from selling the biochar (its value is calculated on basis of the potassium and phosphate content of the biochar and an improved nitrogen fertilizer use efficiency caused by the application of the char), a tipping fee for the disposal of yard waste, the sales of heat produced from the synthesis gas, avoided composting costs, and the sales of GHG offset certificates (at a price of 20 US$ per tonne CO_2), biochar produced on the basis of yard waste yields a positive return of 16 US$ per tonne dry feedstock. This calculation takes into account the opportunity costs of switching from yard waste based compost production to biochar production. Biochar produced on the basis of corn stover and switch grass cannot be produced in a profitable way under the same assumptions. For these types of feedstock, negative returns of 17 US$ to 30 US$ per tonne dry feedstock have been calculated. It should be noted here that the costs for the transportation of feedstock from dispersed locations to the pyrolysis plant can play a major role in the overall production costs of biochar. In this respect, the opportunity of sourcing biochar feedstock from a single location—e.g., from a composting collection station as assumed in the calculation cited above—can be a clear cost advantage.

Under these framework conditions, the direct production cost (not taking into account the opportunity costs for not producing and selling compost) amount to 50 US$ per tonne dry feedstock (or 172 US$ per tonne biochar at 29% wt biochar yield), while the total direct revenues (not taking into account avoided costs for composting) amount to 112 US$ per

tonne dry feedstock (or 368 US$ per tonne biochar). Of the direct revenues, 35 US$ per tonne dry feedstock (121 US$ per tonne biochar) are gained by sale of heat produced from the synthesis gas of the pyrolysis process. Only 11 US$ per tonne dry feedstock (38 US$ per tonne biochar) are associated with the agricultural value of biochar. Without the revenues from the sales of GHG offset certificates, the pyrolysis process would be just at the edge of profitability. Two aspects regarding the profitability analysis of the yard waste analysis need further examination: Is it possible to create GHG offset certificates from a biochar project? Since this is not possible on the market for legally binding GHG emission reductions, only the voluntary market would offer chances to sell GHG offset certificates from biochar projects. In addition to that, potential yield increases associated with the application of biochar—yet not connected to its potassium and phosphorus content alone—have not been included yet in the value of biochar and might improve the profitability of the analyzed system substantially.

(Brown et al. 2011) reported total annual operating costs including fixed costs, capital depreciation, and coproduct credits of about 71 million US$$_{2010}$/year for a slow pyrolysis facility with 262.000 tonnes of biochar production per year. From these figures, the production costs for one tonne biochar can be calculated at 272 US$$_{2010}$. For a fast pyrolysis facility with an output of 172 million liters of biogenic gasoline from biooil, total annual operating costs of 67,500,000 US$$_{2010}$ and biogenic gasoline production costs of 0.39 US$$_{2010}$/liter can be derived from the study. If the indicated production cost could be realized, this facility would be highly profitable. The paper assumes that only 26% of the coproduced char is used within the fast pyrolysis process to provide heat, the remaining char is sold.

2.6.2 Gasification

(Yin et al. 2002) indicated a payback period of less than two years for a circulating fluidized bed biomass gasification and power generation system installed in 1998 in the Fujian Province of China. As already stated before, a considerable part of the char produced in the gasifier is removed from the product gas and returned to the gasifier. For this system with a throughput of 1500 kg rice husk/hour providing a power output of about 800 kW, total investment costs of 510,000 US$ (625,000 US$$_{2010}$) are necessary. However, the amount of data provided in this article to underline the claimed payback period of two years is very

scarce. In addition to that, the indicated investment costs (about 640 US$ (784 US$$_{2010}$)/kW) are very low. The energy value of char from gasification within the process is calculated in the last part of this subchapter.

(Bridgwater et al. 2002) calculated electricity production costs of 0.1 € (0.11 US$$_{2010}$)/kWh at 20 MW$_{el}$ and 0.22 € (0.24 US$$_{2010}$)/ kWh at 1 MW$_{el}$ installed capacity for an electricity production process based on a dual fuel diesel engine fed by the atmospheric gasification of wood chips and diesel as auxiliary fuel. They assumed electricity production costs of about 0.09 € (0.097 US $$_{2010)}$/kWh at 20 MWel and of about 0.26 € (0.28 US$$_{2010}$)/kWh at 1MW$_{el}$ for an electricity production process based on an integrated gas turbine combined cycle fed by the pressurized gasification of wood chips. In this model, it is assumed that the ash produced from the atmospheric gasification process contains 33% wt char, resulting in an overall carbon conversion efficiency of the system of 99.5%. Thus, nearly no char is left after the biomass conversion process.

Peer-reviewed profitability analyses of gasification systems aiming at the sale of the char produced in the process are not available in the ISI to the knowledge of the authors. This can be partly explained by the development focus of this technology which is clearly set on the provision of energy, and by the technical challenges still connected with the biomass gasification technology. It is important to be aware that the operators of gasifiers will only sell the coproduced char of the gasifiers if a char price is paid which at least covers the cost for an alternative heating fuel for the gasification process. (Jorapur and Rajvanshi 1997) indicate a higher heating value of 18.9 MJ for gasifier char. This would correspond to an energy value of about 380 US$$_{2010}$/tonne gasifier char if wood pellets would be used to replace the char used as fuel in the gasifier.

2.6.3 Flash Carbonization

(Antal et al. 2007) stated that the actual capital investment incurred in the fabrication and setup of a flash carbonization demonstration reactor (1.73 m diameter x 2.74 m height) at the University of Hawaii were 270,000 US$ (290,000 US$$_{2010}$). To these costs, US$ 30,000 (32,300 US$$_{2010}$) have to be added in case a 1.27 MPa (12.7 bar) air compressor is installed to provide pressure to the reactor. In case a 2.17 MPa (21.7 bar) air compressor would be used, about US$ 120,000 (129,000 US$$_{2010}$) has to be added to the costs of the reactor. According

to the authors, the 2.17 MPa systems have an output of 8.4 tonnes/day of fixed-carbon, whereas the 1.27 MPa system has an output of 6.1 tonnes/day of fixed-carbon at 24 h of operation. A rough profitability analysis is indicated in the paper with the aim to compare the two systems from an economical point of view. This analysis—which resulted in very short payback periods of 3.7 and 1.3 years for the 1.27 and the 2.17 MPa systems, respectively—however cannot be used to assess the overall profitability of the two systems due to the limited amount of cost data included in the calculation. It is possible that only little economic information on this process has been published by the authors for confidentiality reasons.

2.6.4 Summary

Most information is available on pyrolysis (especially slow pyrolysis) processes. Though the information provided on the economics of a slow pyrolysis system aimed at the production of heat and biochar is very detailed, it is only partly based on empirical data of an already installed system. In summary, a thorough comparison of the profitability of biochar production technologies based on scientific literature is not possible at the moment.

In Table 5, data on the economic viability of the different production processes as indicated in the reviewed papers is summarized.

Table 5: Productions costs for char and energy carriers as indicated in reviewed papers

process type	production costs	comment	reference
fluidized bed fast pyrolysis	0.23 - 0.5 US$_{2010}$ per kg pyrolysis oil	no sales of co-produced char assumed	(Islam and Ani 2000)
fluidized bed fast pyrolysis	0,39 US$_{2010}$ / liter biogenic gasoline from pyrolysis oil	26% of coproduced char used within the process	(Brown et al. 2011)
electricity production based on fast pyrolysis	0.098 US$_{2010}$ /kWh$_{el}$ at 20 MW$_{el}$ 0.215 US$_{2010}$ /kWh$_{el}$ at 1 MW$_{el}$	char used to cover the internal heat demand of the process	(Bridgwater et al. 2002)
fast pyrolysis	560 US$_{2010}$ / tonne char [a]	energy value of fast pyrolysis char in the process	own calculation
slow pyrolysis (earthen Kiln)	3,747 (1860) US$_{2010}$ / tonne charcoal	sales of co-produced wood vinegar excluded (included) in the production cost	(Lin and Hwang 2009))
slow pyrolysis (Lambiotte continuous retort)	373 US$ (386 US$_{2010}$) / tonne charcoal	production costs based on wood production and wood processing (charring) cost	(Norgate and Langberg 2009)
slow pyrolysis (Drum Kiln)	51 US$_{2010}$ per tonne char from yard waste	sales of heat from syngas included in the production costs	(Roberts et al. 2010)
slow pyrolysis	272 US$_{2010}$ per tonne char from corn stover	corn stover feedstock costs: 83 $ / tonne	(Brown et al. 2011)
circulating fluidized bed gasification		investment: 510,000 US$2010 capacity: 1,500 kg feed/h	(Yin et al. 2002)
electricity production based on atmospheric gasification	0.11 US$_{2010}$ /kWh $_{el}$ at 20 MW$_{el}$ 0.24 US$_{2010}$ /kWh $_{el}$ at 1 MW$_{el}$	Only 0,5% of the carbon in the feedstock is converted to char	(Bridgwater et al. 2002)
electricity production based on pressurized gasification	0.097 US$_{2010}$ /kWh$_{el}$ at 20 MW$_{el}$ 0.128 US$_{2010}$ /kWh$_{el}$ at 1 MW$_{el}$	no information on char production and char use available	(Bridgwater et al. 2002)
gasification	380 US$_{2010}$ / tonne char [a]	energy value of gasification char in the process	own calculation
flash carbonization	no information available	investment: 419,000 US$2010; capacity: 430 kg char or 1,300 kg feedstock /h (at 2.17 MPa)	(Antal et al. 2007)

[a] The char value has been calculated based on the costs for an alternative heating fuel (wood pellets)

2.7   Greenhouse gas (GHG) balance of biochar production and application

Before discussing the value of biochar technologies for climate change mitigation, it is important to understand the overall context of mitigation strategies. Sufficiency (lifestyle changes), efficiency, and renewable fuel switch strategies help to avoid the emission of greenhouse gases before they enter the atmosphere. Biochar systems can help to mitigate global warming also after fossil CO_2 has already been released to the atmosphere. Whereas biochar systems thus offer the opportunity to act also if other climate change mitigation strategies should fail, it is important to not weaken the necessary efforts in the field of sufficiency, efficiency, and renewable fuel strategies. This risk would become very concrete if the sale of GHG certificates from biochar projects on the carbon compliance market would enable utilities to offset their fossil fuel emissions in "temporary" emission reduction projects, instead of implementing efficiency or fuel switch measures needed in an existing cap-and-trade system. In contrast to that, trading GHG certificates from biochar projects on the voluntary market would not reduce the mitigation pressure in the carbon compliance market. For a discussion of the same mechanism in the context of forestry offset projects, see (Streck et al. 2009). To fully assess the GHG balance of biochar conversion technologies, information on feedstock provision (including direct and indirect land use change effects), conversion process, byproducts use, biochar application, biochar stability in soil, influence of biochar application on soil related N_2O, CH_4, and CO_2 emissions and on plant growth—including associated impacts on land use—is needed (Libra et al. 2011; Panichelli and Gnansounou 2008; Gelfand et al. 2011). To compare the greenhouse gas impact of the production and use of biochar to a reference scenario with an alternative use of the feedstock, it is necessary to provide detailed information on this reference scenario. To comprehensively assess the climate-related effects of biochar application, insight into the impacts of biochar application on surface albedo (Verheijen et al. 2009) and on black carbon concentration in the atmosphere (Ramanathan and Carmichael 2008) is needed in addition to the information summarized above. In the following sections it is indicated to which extent these aspects have been included in the reviewed literature articles. Table 6 gives an overview of the analyzed publications which are described in the following sections. From Table 6 it is evident that biochar sequestration in the soil is one of the main factors positively influencing the GHG balance of the biochar systems. Taking into account the variety in char yields of different technologies (see Table 2) and the differences in the long-term stability of

chars made from different technologies (see Nguyen and Lehmann 2009; Steinbeiss et al. 2009), the full effect of biochar systems on the carbon cycle has to be understood.

Table 6: Climate impacts of biochar production technologies

GHG related impacts	Color Code: Positive impacts		Color Code: Negative impacts	
(L)arge impact:	> 500 kg CO_2e emission reductions / tonne dry feedstock		> 500 kg CO_2e emission increase / tonne dry feedstock	
(M)edium impact:	> 250 kg CO_2e emission reductions / tonne dry feedstock		> 250 kg CO_2e emission increase / tonne dry feedstock	
(S)mall impact:	< 250 kg CO_2e emission reductions / tonne dry feedstock		< 250 kg CO_2e emission increase / tonne dry feedstock	
Publication	**(Woolf et al. 2010)**	**(Roberts et al. 2010)**	**(Gaunt and Lehmann 2008)**	**(Searcy and Flynn 2010)**
Process Type	Pyrolysis	Pyrolysis	Pyrolysis	Gasification
Indirect Land Use Change	Assessed, no impact assumed	(M-L), negative	Not assessed	Not assessed
Direct Land use Change	Assessed, no impact assumed	(S), positive	(S), positive	Not assessed
Feedstock Provision	(S), negative (only transport assessed)	(S), negative	Not assessed	(S), negative
Replaced Process (e.g. composting)	(S), positive	(S), positive	Not applicable	Not assessed
Conversion process	Assessed, no impact assumed	(S), negative	Not assessed	No impact
Use of byproducts (e.g. syngas)	(M), positive	(M), positive	(S-M), positive	(L), positive
Biochar Application Process	(S), negative	(S), negative	Not assessed	Not applicable
Biochar Sequestration in the soil	(L), positive	(L), positive	(L), positive	Not applicable
Increased Fertilizer Efficiency	(S), positive	(S), positive	(S), positive	Not applicable
Change of Soil CO_2 – Emissions	(S), negative	Not assessed	Not assessed	Not applicable
Change of Soil N_2O – Emissions	(S), positive	(S), positive	(M), positive	Not applicable
Change of Soil CH_4 – Emissions	Assessed, no impact assumed	Not assessed	Not assessed	Not applicable
Plant response (Carbon uptake)	Assessed, impact not included	Assessed, no impact assumed	Not assessed	Not applicable
Yield impact on land use	(S), positive	Not assessed	Not assessed	Not applicable
Non-GHG related impacts:				
Atmospheric Soot Concentration	Not assessed	Not assessed	Not assessed	Not applicable
Change of Surface Albedo	Not assessed	Not assessed	Not assessed	Not applicable

Whereas the production of char is in most cases slowing down the carbon cycling of the charred fraction of the feedstock (as compared to a reference situation with the natural decay of, e.g., forest residues or agricultural residues) (Kuzyakov et al. 2009), the release of CO_2 from the biomass conversion process will speed up the carbon cycle of the uncharred feedstock fraction compared to the reference situation (Figure 1). For a detailed discussion of this effect in the context of bioenergy and biochar use, see (Repo et al. 2011) and the supplementary information to the publication of (Woolf et al. 2010).
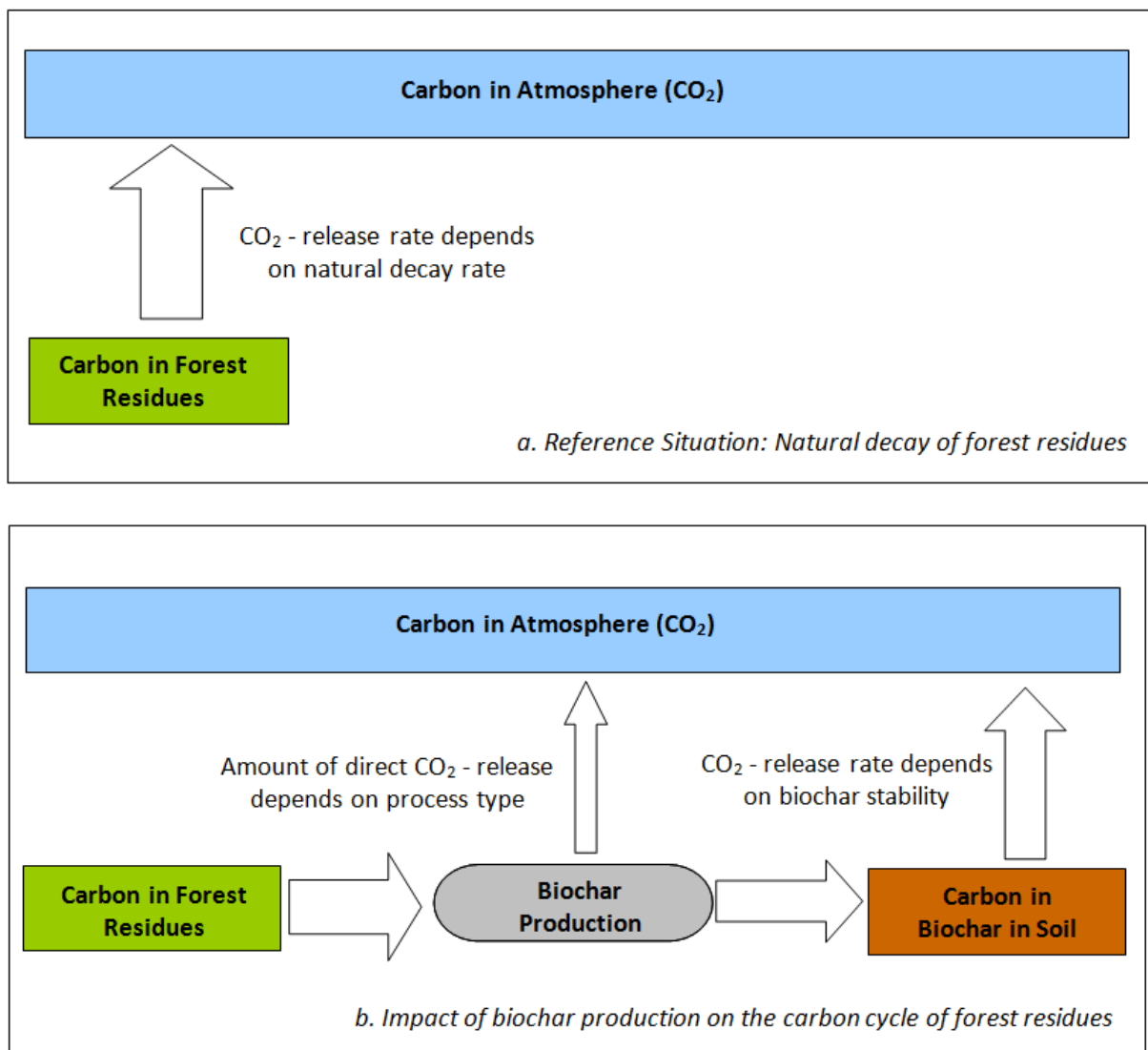
Figure 1: Impact of biochar production on the natural carbon cycle

2.7.1   Pyrolysis technologies

(Woolf et al. 2010) calculated the maximum sustainable technical global potential for the contribution of biochar systems to climate change mitigation. In this very comprehensive paper, all GHG related impacts of pyrolysis biochar production and application have been assessed. The potential impacts of biochar systems on the atmospheric soot concentration— via biomass smoke and via black carbon dust becoming airborne—and on the surface albedo are mentioned in the Supporting Information to the paper, but have not been examined in detail. In the alpha scenario of the publication, 66 Gigatonnes CO_2-C equivalent net avoided GHG emissions have been calculated over a time period of 100 years for the production and application of biochar derived from about 1.01 Gigatonnes biogenic carbon per year. Assuming an average carbon content of 50% for dry biomass, 2.02 Gigatonnes of biomass feedstock are used in the scenario for the production of biochar. As yield improvements are assumed to be triggered by biochar application, the increment in biomass production is reinvested into additional production of biochar in this scenario. Assuming a total consumption of 2.3 Gigatonnes of dry biomass feedstock for the biochar production, this scenario results in average net avoided GHG emissions of 1054 kg CO_2e/tonne dry feedstock and year.

The average avoided GHG emissions indicated above are in line with the results of a recent publication of (Hammond et al. 2011): in this paper, a carbon abatement of 0.7-1.3 t CO_2 equivalent per oven dry tonne of feedstock processed has been calculated. They also fit with the calculations of (Roberts et al. 2010) in those of their scenarios which assume that biochar is produced from unused residues.

(Roberts et al. 2010) calculated comprehensive greenhouse gas balances for the production and application of biochar produced from different feedstock in a slow pyrolysis process. The authors included most of the climate-relevant factors but did not account for impact of biochar application on soil CH_4 and soil CO_2 emissions, on the surface albedo and the soot concentration in the atmosphere. The latter two aspects do not impact on the GHG balance of biochar production and application itself, but they influence the sum of climate relevant effects of biochar application. To calculate the GHG impact of the production and use of biochar, a reference scenario has to be taken into account to describe changes in emissions when the biochar system is implemented. Under the assumption used by (Roberts et al.

2010), the following results have been calculated: Choosing a reference scenario in which yard waste is used for composting, 885 kg CO_2e per t dry biomass feedstock can be saved when switching from yard waste composting to the production and application of biochar. Choosing a reference scenario in which corn stover is left as residue on the field (thus not used to provide bioenergy in the reference scenario), 793-864 kg CO_2e per t dry biomass feedstock can be saved when switching to the production and application of biochar. The range of emission reduction depends on the moisture content of the corn stover used for biochar production. However, if corn stover were used to produce electricity (thereby replacing natural gas based electricity generation) in the reference scenario, GHG emissions would increase by 123 kg CO_2e per t dry biomass feedstock when switching to use the stover in a biochar system. Switching from a reference scenario with agricultural crop production to the cultivation of switch grass and the subsequent use of this feedstock for biochar production might either reduce GHG emission by 442 kg CO_2e per t dry biomass or increase GHG emissions by 32 $kgCO2_e$ per t dry biomass, depending on the amount of GHG emissions assumed to be triggered via indirect land use change effects. Indirect land-use change effects are caused when an existing production of agricultural goods is displaced by the cultivation of energy crops on the same plot of land. As an effect of that, other land areas, e.g., primary rain forest might be converted to arable land to compensate for the decrease in the previous production of agricultural goods.

In contrast to (Roberts et al. 2010), (Hammond et al. 2011) do not account for indirect land use change effects when assessing the GHG balance of biochar systems. Thus, the latter calculate substantial carbon abatements for biochar systems even in the case of wood chips from short rotation coppice being used for biochar production.

A less comprehensive GHG balance for a slow pyrolysis-based biochar system has been carried out by (Gaunt and Lehmann 2008). The authors did not account for indirect land-use change impacts triggered by the production of energy crops, the emissions connected to the provision and the conversion of the biomass feedstock, the energy use necessary for biochar application, the impact of biochar application on plant growth and associated land use effects, soil CH_4 and soil CO_2 emissions, the impacts on the surface albedo, and the soot concentration in the atmosphere. Based on their assumptions, they calculated GHG emission reductions of 10.7 t CO_2 ha^{-1} yr^{-1} for corn stover. For direct comparison, (Roberts et al. 2010)

calculated emissions reductions of 7 t CO_2 ha^{-1} yr^{-1} in a similar scenario for corn stover if this feedstock would have remained a field residue in the reference scenario. If corn stover and switch grass were used for pyrolysis based electricity production in the reference scenario (thereby replacing natural gas-derived electricity), switching to a pyrolysis system optimized for biochar production would reduce GHG emissions by 8.5 t CO_2 ha^{-1} yr^{-1} in the case of using corn stover as feedstock and by 7.6 t CO_2 ha^{-1} yr^{-1} in the case of using wheat straw as feedstock according to (Gaunt and Lehmann 2008). Because direct and indirect land-use change effects were not taken into account for using energy crops as feedstock, the calculated emission reductions for energy crop scenarios are not indicated here.

Whereas (Libra et al. 2011) did not calculate a complete GHG assessment of biochar systems, they observed both a reduction in soil N_2O emission and CO_2 efflux four weeks after mixing sandy loam brown earth mixed with pyrolysis biochar.

2.7.2 Gasification

(Searcy and Flynn 2010) calculated emission reductions of switching from coal-based electricity production to a straw-based integrated gasification and combined cycle electricity production system at 839 g CO_2e per kWh of produced electricity (1680 kg CO_2e/tonne dry feedstock). It should be noted that this technology is still in an early development stage. Apart from that, no extraction of biochar out of the integrated gasification and combined cycle was assumed in this study.

2.7.3 Summary

Peer-reviewed greenhouse gas balances on the production and application of biochar were identified for pyrolysis technologies only. The more recent publications in this field—(Woolf et al. 2010) and (Roberts et al. 2010)—are far more comprehensive compared to older papers since they cover more GHG related impacts of the biochar systems. Depending on the types and previous use of the biomass feedstock, both reductions and increases of GHGs have been calculated for biochar systems (Woolf et al. 2010; Roberts et al. 2010; Gaunt and Lehmann 2008). GHG reductions are often not achieved if dedicated energy crops are used as feedstock for the production of biochar or if biomass residues are already used for the provision of bioenergy in the reference scenario. From a GHG perspective alone, the most recent studies give a clear indication under which conditions biochar systems can contribute

to mitigate climate change. However, as explained above, the calculations do not yet take into account all relevant climate impacts of biochar systems: Insights into the impacts of biochar application on the surface albedo and on the black carbon (soot) concentration in the atmosphere have not been added yet to the GHG balances of the biochar systems in the publications reviewed. In this context, it should be noted that (Vaccari et al. 2011) reported positive soil temperature anomalies up to 2 °C in open field biochar plots during the initial phases of durum wheat production. These aspects should also be taken into account when comparing the full climate benefit of bioenergy vs biochar systems (see also Woolf et al. 2010). Last but not least - as already indicated - it is important to use biochar-based mitigation options complementary to existing mitigation strategies instead of replacing the latter.

2.8   Outlook

The peer-reviewed papers analyzed provided valuable insights into technical reliability, economic feasibility, and climate impact of different carbonization technologies. Most papers focus on pyrolysis technologies, less information is available on gasification processes. Publications on gasification processes often do not take into account the potential suitability of the char as a product for soil improvement. Very little information about hydrothermal and flash carbonization technologies with relevance for this review has been published yet. Two comprehensive studies on the economic profitability and the GHG balance of a slow pyrolysis process have been identified which point at economic and environmental chances of biochar systems (Roberts et al. 2010; Woolf et al. 2010). Data from pilot projects would be essential to further improve assessments on the technical reliability and economic profitability of biochar production technologies. To complement the assessments on the climate impact of biochar production technologies, additional information on the impact of biochar application on surface albedo, atmospheric soot concentration, and yield responses would be needed. The GHG balance of biochar systems itself has been already quite well examined in recent papers with promising results regarding climate mitigation opportunities.

In most of the studies, only one assessment dimension of a technology is analyzed. Comparisons between different technologies—see for example the papers of (Bridgwater et al. 2002) or (Brown et al. 2011)—are rare as well. Empirical data on the annual availability of

technologies which (co)produce biogenic chars has only been published from gasification systems aimed at the production of electricity (in this sector, annual availability rates of 60-70% were measured). A wide range of data on the costs of char production (between 51 $$_{2010}$ per tonne pyrolysis biochar from yard waste and 386 US$$_{2010}$ per tonne retort charcoal) and on the GHG balance of biochar systems (between -1,054 kg CO_2e and +123 kg CO_2e per t dry biomass feedstock) can be retrieved from the literature. A comprehensive assessment of the technical, economic, and environmental strength and weakness of biochar production technologies is unfortunately still not possible yet on the basis of the available scientific peer-reviewed literature. This is at least partly explainable by the fact that the production of biomass-based chars for the improvement of agricultural soils is still a relatively new topic of scientific interest. Further research of both the public and the private sector on the indicated knowledge gaps and its publication is necessary to support project developers, technology developers, and policy makers with a comprehensive and detailed picture on the different options to produce biochar for soil improvement and climate change mitigation.

3   Albedo impact on the suitability of biochar systems to mitigate global warming

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3.1   Summary

Biochar application to agricultural soils can change the surface albedo which could counteract the climate mitigation benefit of biochar systems. However, the size of this impact has not yet been quantified. Based on empirical albedo measurements and literature data of arable soils mixed with biochar, a model for annual vegetation cover development based on satellite data and an assessment of the annual development of surface humidity, an average mean annual albedo reduction of 0.05 has been calculated for applying 30–32 Mg ha^{-1} biochar on a test field near Bayreuth, Germany. The impact of biochar production and application on the carbon cycle and on the soil albedo was integrated into the greenhouse gas (GHG) balance of a modeled pyrolysis based biochar system via the computation of global warming potential (GWP) characterization factors. The analysis resulted in a reduction of the overall climate mitigation benefit of biochar systems by 13–22% due to the albedo change as compared to an analysis which disregards the albedo effect. Comparing the use of the same quantity of biomass in a biochar system to a bioenergy district heating system which replaces natural gas combustion, bioenergy heating systems achieve 99–119% of the climate benefit of biochar systems according to the model calculation.

3.2   Introduction

The charring of organic matter and its application to soil with the intent to improve soil properties is known as biochar technology and commonly seen as an opportunity to mitigate global warming (Glaser and Birk 2012). The carbon cycling of the charred material is slowed down compared to uncharred organic matter. In addition, the production of biochar often yields bioenergy as a coproduct which can substitute fossil fuels. Further, it was observed that the application of biochar to soil can - at least in the short term - decrease soil greenhouse gas emissions (Libra et al. 2011; Kammann et al. 2012; Singh et al. 2010) and increase fertilizer use efficiency (Steiner et al. 2008). Under certain conditions, there is evidence that black carbon (predominantly condensed aromatic and graphitic carbon structures which are, for example, formed during biochar production (Glaser und Knorr 2008) in soil can reduce the carbon mineralization of organic matter added to the soil; for example, in the form of harvest residues (Biqing Liang et al. 2010). While all of these impacts serve to reduce radiative forcings from greenhouse gases (GHGs), there are also GHG emissions during the whole lifecycle of a biochar system starting with feedstock production up to the final degradation of the biochar in the soil (see also Meyer et al. 2011). The application of biochar to soil can induce a radiative forcing (Genesio et al. 2012) by changing the surface albedo (the dimensionless relation of reflected shortwave radiation to incoming shortwave radiation) and the black carbon (soot) concentration in the atmosphere (Ramanathan and Carmichael 2008). Thus, there is also a risk that biochar systems might accelerate global warming.

This paper integrates the albedo impact caused by biochar application in the overall climate impact assessment of a pyrolysis-based biochar system to assess the effect of biochar systems on the climate more comprehensively. An existing, partly adapted GHG balance of a pyrolysis based biochar system compiled by (Hammond et al. 2011) was used as basis to assess the overall climate impact of a biochar system after the integration of the albedo impact assessment. Quantifications of direct radiative forcing impacts of albedo changes when biochar is applied to soil (i.e., the increase in absorbed short-wave radiation) were based on empirical measurements and literature data. Since albedo measurements of soils mixed with biochar are still rare (Genesio et al. 2012; Oguntunde et al. 2008), additional soil albedo measurements were carried out to strengthen the basis of the analysis. Indirect radiative forcing impacts of albedo changes (caused by changes in water vapor

concentration in the atmosphere and changes in cloud cover due to changes in evapotranspiration rates resulting from changes in the ratio of latent to sensible heat fluxes) are not analyzed in this article (see also Figure 1 in Kirschbaum et al. 2011). These indirect effects are difficult to assess and were not included in the scope of the present study, although they may be, under certain conditions, quantitatively as important as the direct effect of albedo changes (Bala et al. 2007). To stay in line with GHG metrics that integrate instantaneous radiative forcing - the instantaneous perturbation of the earth energy balance at the top of the atmosphere - caused by pulse emissions of greenhouse gases over a common time horizon, this analysis adapts a methodology applied by (Bright et al. 2012) to express the climate impact of albedo changes in the same unit (i.e., in Megagram of CO_2 equivalent emissions [Mg CO_2e]).

This paper also accounts for the climate impact caused by the temporal shift between pulse emissions of biogenic CO_2 during biochar production and the subsequent carbon sequestration via the regrowing biomass feedstock. A comprehensive literature review reveals that this dynamic impact has not yet been accounted for in global warming impact assessments of biochar systems (Meyer et al. 2011). In line with (Cherubini et al. 2012c), suitable GWP characterization factors for biogenic and time-distributed CO_2 emissions of the biochar system under study are developed.

Results are benchmarked to the climate impact of a standalone bioenergy heating system which substitutes the use of fossil fuels and consumes the same amount of dry biomass feedstock as the biochar system.

3.3   Materials and methods

3.3.1   Overview of the modeled biochar system

As mentioned, we are making use of existing lifecycle GHG data of (Hammond et al. 2011) to model the GHG balance of a biochar system consisting of a pyrolysis plant with an annual feedstock consumption of 2,000 Mg biomass (25% water content) and biochar application on a wheat field. Since the results presented in chapter 3.4 are related to biochar production via slow pyrolysis, they cannot be generalized to other carbonization technologies such as fast pyrolysis, gasification, hydrothermal-, or flash carbonization. We modeled two scenarios based on two types of feedstock with different regrowth periods: Wood chips from small

forestry roundwood and wheat straw. Data on GHG emissions per type of feedstock connected to the provision of biomass feedstock (including transport to the pyrolysis plants), the production of the pyrolysis plant, char transport to the field, and its application to the soil are taken directly from (Hammond et al. 2011). Wood chips were treated as a main product, wheat straw as byproduct in the LCA inventory of this publication. We deviate from the publication in the assumptions that 55% of the energy in the synthesis gas and waste heat of the process can be supplied into a district heating system with a high annual utilization factor of 75%, that transport heat losses are 5% (see also Cholewa and Siuta-Olcha 2010) and that resulting emissions saving are 0.252 kg CO_2e/kWh final energy (see Umweltbundesamt 2012) due to the replacement of natural gas heating systems. Due to the limited scientific knowledge on a discussed positive impact of biochar application on soil inherent organic matter stabilization, such an effect was not accounted for. In addition, the impact of a potential increase in biomass production after biochar application on soil humus formation was not taken into account.

To model the biochar system, it is assumed that biochar is applied to an arable field near Donndorf close to Bayreuth in Bavaria/Germany and used for wheat and rapeseed cultivation. The simulation of the albedo impact of biochar application at this location is dealt with in chapter 3.3.2. The impact of biogenic and time-distributed emissions and removal fluxes caused by the oxidation and stabilization of biochar, increases in fertilizer use efficiency, and soil N_2O reduction are discussed in chapter 3.3.3.

3.3.2   Albedo impact of biochar application

3.3.2.1 Laboratory soil albedo measurements

The following study was carried out: 16 wet soil samples (four treatments with four replicates of each treatment) were taken from a biochar field trial near Donndorf in Northern Bavaria [49°56′0.02″N, 11°31′15.77″E, World Geodetic System 1984 coordinates] on January 26, 2012 (see Figure 2). The A horizon of the field site consists mainly of sandy silt (Us) and of very sandy clay (Ls4). On the East side of the test field, the parent material is sand stone. In Table 7, the different treatment volumes which had been already tilled 10 cm deep into the arable soil in July 2010 are described.

Figure 2: Location of the field trial close to Donndorf near Bayreuth, Germany

Table 7: Donndorf field trial setup

Treatments	Compost application [Mg ha^{-1}] Dry Mass	Biochar application [Mg ha^{-1}] Dry Mass
Control	0	0
Biochar	0	31.5
Biochar-Compost	69.2	31.5
Compost	70	0

Table 8: Pot trial setup

Treatments	Compost application [Mg ha^{-1}] Dry Mass	Biochar application [Mg ha^{-1}] Dry Mass
Control	0.0	0.0
Compost 50 Mg/ha	50.0	0.0
Compost 200 Mg/ha	200.0	0.0
Biochar-Compost 50 Mg/ha	26.6	23.5
Biochar-Compost 200 Mg/ha	106.2	93.8

For a detailed description of this field trial set up in 2010, see (Fischer 2010). Two 10 cm deep tilling operations in preparation for corn and triticale cultivation were carried out in the time period between field trial setup and soil sample extraction.

The biochar used in the treatments of the field trial (application rate 31.5 Mg ha−1) was produced from wood in a slow pyrolysis plant by the company CarbonTerra in Duttenstein, Germany. The soil samples were taken from the soil surface (0–5 cm) of four randomly chosen sample sites of the respective treatments forming 4-fold replications, filled in plastic bags and transported to the micrometeorological laboratory of the University of Bayreuth. The albedo of the field trial soils samples was measured twice: One measurement per sample was carried out at the original water content of the soil samples. Subsequently, these soil samples were modestly dried in a drying oven at a temperature around 60 °C for 90 min, followed by a second soil albedo measurement of each sample. In addition to the albedo measurements, the gravimetric water content of each soil sample was analyzed.

The albedo of a second series of dry soil samples from a pot trial set up in the year 2009 (see Schulz et al. 2013) was analyzed in the laboratory as well to study the impact of very high biochar and compost applications on the soil albedo. The control treatment of this series consists of washed sand from the Kiesgrube ZAPF, Weidenberg, Germany. Three further treatments are based on very high biochar and compost amendments to the washed sand as described in

Table 8. The char used in the washed sand samples (application rates 23.5 and 93.8 Mg ha^{-1} in two different treatments) was produced from hardwood by the charcoal producer Köhlerei Wiesener in Rohr, Austria in a traditional charcoal kiln. For a detailed description of the pot trial set up in 2009, see (Schulz et al. 2013). The treatments of the pot trial had been used for greenhouse cultivation experiments for a period of two years before they were used for the albedo measurements.

In the laboratory, each of the soil samples was evenly distributed on an open flat plastic plate of 60 cm x 2 cm x 40 cm (width x height x depth)) size. A 500 Watt flood light with a halide lamp (Manufacturer: düwi) was installed 50 cm above the plastic plate. Albedo measurements of all soil samples were carried out in the lab with an ISO Second Class Kipp & Zonen Double-Pyranometer CM 3 which was installed centrally 13 cm above the respective soil samples. The albedo of the soils samples of the field trial in Bayreuth was measured

twice: The first measurement was carried out with the original water content of the soil samples. After that, these soil samples were modestly dried in a drying oven at a temperature around 60 °C for 90 minutes, followed by a second soil albedo measurement. In addition to the albedo measurements, the gravimetric water content of each soil sample was analyzed.

To account for the measurement response time of the albedometer, the albedo of the soil samples and the temperature of the albedometer were measured after lighting the soil samples for 40 seconds with the halide lamp. Since the laboratory installation did not allow for preventing that 15% of the soil sample area was covered by the shadow of the albedometer, the values of reflected shortwave radiation measured were corrected accordingly to account for the loss in reflected shortwave radiation. The albedo of a reference soil sample (white sand) was measured together with the temperature of the albedometer after every 10 albedo measurements to analyze the impact of the albedometer temperature on the measured albedometer data. Since a clear linear correlation between the albedometer temperature and the measured albedo of the white sand was observed (for each degree of instrument temperature warming above 21.7 °C, the measured albedo value increased by 0.0053), the detected albedo data was temperature-corrected for this thermal measurement error.

One way analyses of variance (ANOVA) were carried out to compare the treatment effects on the surface albedo values with Tukey's HSD as post-hoc test at a significance level of 0.05. In addition, a regression analysis with the data of the FT soil samples was carried out with the independent variables *Gravimetric water content GWC, Compost Application Mass CAM, and Biochar application Mass BAM* and the dependent variable *Surface Albedo.*

3.3.2.2   Impact of vegetation cover, snow cover, and soil humidity on the surface albedo change

The development of mean monthly surface albedo difference $\Delta\widetilde{\alpha}_s$ between arable land with and without biochar application within a year is influenced by the average monthly surface water content, the average monthly vegetation cover, and the average monthly snow cover. We derive $\Delta\widetilde{\alpha}_s$ in our simulation according to the following formula:

$$\Delta \tilde{\alpha}_s = \left[1 - \tilde{f}_g - \tilde{f}_{sc} \right] \Delta \tilde{\alpha}_{soil} \tag{1}$$

$\tilde{f}_g$ is the average monthly fraction of green vegetation and $\tilde{f}_{sc}$ is the average monthly fraction of snow cover. $\Delta \tilde{\alpha}_{soil}$ - the albedo difference between different types of soil –is dependent on the surface properties of the soil treatments which depend on the type of treatment, the change in surface properties over time, and the soil humidity (since water enforces irradiation absorption).

To model the annual development of the vegetation cover of wheat and rapeseed fields at our model location near Donndorf, the correlation between the fraction of green vegetation at a certain point in time f_g and the scaled difference vegetation index (SDVI) as suggested by (Zhangyan Jiang et al. 2006) was applied:

$$f_g = SDVI = \frac{N - R - (N_s - R_s)}{N_v - R_v - (N_s - R_s)} \tag{2}$$

R represents the surface reflectance averaged over visible regions ($\lambda \sim 0.6$ μm) and N the surface reflectance averaged over near-infrared regions ($\lambda \sim 0.8$ μm) of the spectrum. N_s and R_s represent the reflectance of bare soil, N_v and R_v represent the reflectance of dense vegetation. The bands 1 (0.62–0.67 μm) and 2 (0.84–0.87 μm) of the surface reflectance product MOD09A1 produced every 8 days by the moderate-resolution imaging spectroradiometer (MODIS) on the Terra satellite of (NASA) over the years 2010 and 2011 was used to derive f_g and $\tilde{f}_g$. Since the data set has a resolution of 500 × 500 m, the surface reflectance data from an agricultural field large enough to provide a homogeneous surface was needed to calculate f_g and $\tilde{f}_g$. For this purpose, surface reflectance data of an agricultural field close to Penkun/Germany [53° 19′ 23.46″ N, 14° 15′48.35″ E, World Geodetic System 1984 coordinates) with wheat cultivation in 2010 and rapeseed cultivation in 2011 (no intertillage crops were cultivated in both years) was obtained. The data was used to simulate the development of green vegetation cover on the modeled field site near Donndorf without taking into account differences in the vegetation phenology between fields in Donndorf and Penkun.

According to the snow cover period map of (Hochschule für Angewandte Wissenschaften FH München 2012) there were 40–60 snow cover days per year in the region of Bayreuth in the average of the years 2005–2009. Based on this information, a total of 50 days with snow cover was evenly distributed over the months from December to February in the intra-annual delta albedo simulation. The impact of surface albedo changes on the snow cover period due to increased radiation absorption (Ramanathan and Carmichael 2008) was not accounted for in our assessment.

To account for the intra-annual variation in soil humidity and its impact on $\Delta \widetilde{\alpha}_{soil}$, it was necessary to know how the humidity in the first millimeters of the soil surface of the field trial site near Donndorf develops over the year. Due to a lack of empirical data, we assumed in a simplified approach that dry surface conditions dominate on days without rainfall and wet surface conditions dominate on day with rainfall. Continuously measured rainfalls records (10 min measurement interval) for the years 2008–2011 in the Ökologisch-Botanischer Garten in Bayreuth provided by the Micrometeorological Department of the University of Bayreuth were used to derive the average amount of days with and without rainfall per month in the region of Bayreuth. For wet days, a $\Delta \alpha_{soil}$ of 0.027 between control and biochar treatments (directly after biochar incorporation in soil) was used in our annual delta albedo simulation for the field near Donndorf in line with the result from the Donndorf field trial (see Figure 3) and our assumption on the development of $\Delta \alpha_{soil}$ in time (see eq 4). In line with the results from the albedo measurements of (Genesio et al. 2012) in Pistoia, Italy (see Figure 6), a $\Delta \alpha_{soil}$ of 0.15 between control and biochar treatments (directly after biochar incorporation in soil) was used for dry days in the same simulation.

3.3.2.3 Radiative Forcing and GWP from albedo change

Methods for estimating GWP characterization factors from surface albedo changes are thoroughly discussed in (Bright et al. 2012; Cherubini et al. 2012a) and (Muñoz et al. 2010). Thus only a brief description is presented here. Monthly mean instantaneous forcing from the monthly mean surface albedo change when biochar is applied can be described by the following equation:

$$\widetilde{RF}_\alpha = -\widetilde{R}_{TOA}\, \widetilde{f}_{Atm.}\, \Delta \widetilde{\alpha}_s$$

(3)

$\widetilde{R}_{TOA}$ is the monthly mean downward solar flux at the top of the atmosphere (TOA) for our region (in W/m^2), $\tilde{f}_{Atm}$ is a two-way atmospheric transmittance parameter accounting for the monthly mean reflection and absorption of solar radiation (downward and upward) throughout the atmosphere for the same region, and $\Delta\widetilde{\alpha}_s$ is the monthly mean surface albedo change of the sample area scaled to 1 m^2. $\widetilde{R}_{TOA}$ is a function of latitude, sunset hour angle, and solar declination angle and is calculated following the methodology outlined in (Duffie and Beckman 1991) and (Kalogirou 2009). $\tilde{f}_{Atm}$ is the product of two factors: The monthly mean clearness index, K_T, or the fraction of TOA irradiance reaching Earth's surface, and, T_a the monthly fraction reaching TOA after reflection at the surface. 22-year mean monthly clearness index data for our specific region are obtained from (NASA). There is no empirical data on T_a. Since K_T and T_a are subject to equal atmospheric conditions, we estimated Ta based on a one layer atmosphere model and the following assumptions: For each transition of the atmosphere (upwards and downwards), we assume that the fraction of shortwave radiation transmitted is equal to K_T. In addition to that, we assume that 50% of the upwelling radiation not transmitted to the top of the atmosphere is reflected back to the surface (and that the remaining 50% are being absorbed by the atmosphere) in line with the global annual mean Earth's energy budget of (Trenberth et al. 2009). After accounting for the reduction of the reflected radiation by surface albedo, the fraction K_T of the remaining shortwave radiation is assumed to be transmitted again to the top of the atmosphere, 50% of the radiation not transmitted to the top of the atmosphere is assumed to be reflected back to the surface and so forth. To calculate T_a, we add all the fractions of short wave radiation (reflected on the surface) reaching the top of the atmosphere. Averaged over 22 years, K_T was 0.41 over the test field near Donndorf. According to the calculation based on our assumptions described above, T_a was 0.44 over the same site in the same time period. This value was used for the radiative forcing calculation. Since the value for the amount of upwelling radiation not transmitted to the top of the atmosphere taken from (Trenberth et al. 2009) describes a global average, the local conditions over the test field near Donndorf might deviate substantially. To test the sensitivity or our result against a second, very conservative scenario, we assumed that 90% of the upwelling radiation not transmitted to the top of the atmosphere would be reflected back to the surface (and that the remaining 10% are being absorbed by the atmosphere). Under this assumption, T_a would be 0.45. Thus, our result would change only very modestly. Monthly mean local instantaneous forcing is

averaged over the year to obtain a single value for the annual forcing associated with biochar application (Bright et al. 2012).

(Genesio et al. 2012) observed a rapid decline in $\Delta\alpha_{soil}$ within the first 18 months after biochar application on a test site in Pistoia (see Figure 6) which can be explained by subsurface biochar concentration, demobilization, clogging of the biochar surface with mineral particles and biochar degradation. The soil was tilled 10 cm deep in Pistoia as well as in Donndorf. In line with this observation, we assume that the average delta albedo in year 1 is 65% of the initial delta albedo value $\alpha-0$ directly after biochar incorporation in soil and 32% of the start value in average in year 2. In this context, it should be noted that demobilized biochar, for example by wind erosion, might decrease the surface albedo in other areas than the field site. We did not account for this effect in our climate impact assessment. The albedo measurements on the site in Pistoia did not identify a statistically significant delta albedo after the second tilling operation anymore. We are taking a conservative approach by assuming that 22% of the start value is still present in year 3 after the second tilling operation. After year 3, the delta albedo is assumed to decay exponentially at the same decay rate as the biochar decays (see chapter 3.3.3.1). Since albedo scales with forcing, the local mean annual instantaneous forcing time profile with a 1 year discretization takes the following functional form:

$$RF_\alpha(t) = \begin{cases} 0.65 RF_{\alpha-0} & \forall t = 1 \\ 0.32 RF_{\alpha-0} & \forall t = 2 \\ 0.22 RF_{\alpha-0} & \forall t = 3 \\ RF_\alpha(3)\exp(-MRT^{-1}(t-3)) & \forall t > 3 \end{cases} \tag{4}$$

t indicates a complete annual time period (365 days). MRT is the assumed mean residence time of biochar (500 years) as indicated by (Hammond et al. 2011).

By averaging the local forcing impacts from the affected area over the area of Earth's surface, we get a global instantaneous forcing time profile that can now be used to benchmark against the effect of anthropogenic CO_2 emissions. Integrating over a defined time horizon (TH) allows us to estimate the magnitude of the albedo change forcing (in global W m^{-2} yr/m^2) relative to that of a pulse emission of anthropogenic CO_2 (in W m^{-2} yr/kg):

$$GWP_{Albedo} = \frac{\int\limits_{0}^{TH} RF_{\alpha}(t)\mathrm{d}t}{\int\limits_{0}^{TH} RF_{CO_2}(t)\mathrm{d}t} \tag{5}$$

However, because GWP is meant to be an "emission" metric, we want to normalize albedo forcing impacts to biogenic CO_2 emission pulses from bioenergy and biochar production, thus rewriting eq. 5 to

$$GWP_{Albedo} = \left(\left(\frac{M_{FS} \times C_{BC} \times 1.33 \times 0.32}{M_{FS} \times C_E (44/12)} \right) \cdot \frac{\int\limits_{0}^{TH} RF_{\alpha}(t)\mathrm{d}t}{\int\limits_{0}^{TH} RF_{CO_2}(t)\mathrm{d}t} \right) \tag{6}$$

M_{FS} is the dry feedstock mass, C_E is the fraction of carbon in oven dry biomass oxidized and used to provide bioenergy and produce biochar, and C_{BC} is the fraction of carbon in oven dry biomass contained in biochar. C_E depends on the pyrolysis conditions (temperature and residence time). When wheat straw is the feedstock, $CC_{ODB} = 0.467$ and C_E is 0.533 in our scenario. When roundwood is the feedstock, CC_{ODB} is 0.501 and C_E is 0.499 in our scenario (Hammond et al. 2011; Mani et al. 2011). 1.33 is the mass of biochar per kg carbon in biochar in our scenario. 0.32 - also a constant - is the average area (in m^2) covered by 1 kg biochar at a biochar application rate of 31.5–32 Mg/ha. 44/12 is a constant and is the mass of CO_2 produced by the combustion of 1 kg carbon.

Parametric uncertainty in the forcing calculations is discussed in (Bright et al. 2012). Uncertainty of the simple albedo forcing model applied in this paper is assessed in (Cherubini et al. 2012b) who report a +2.9% forward bias of the annually averaged albedo RF at TOA when compared to outputs of a more advanced, highly parameterized plane-parallel radiative transfer model (Fu and Liou 1993; Fu and Liou).

3.3.3 The impact of biogenic and time-distributed emissions

3.3.3.1 Calculation of GWP characterization factors for biogenic emissions

We follow the approach of (Cherubini et al. 2012c) to estimate GWPs of biogenic CO_2 emissions from our modeled biochar-bioenergy system coproducing biochar and bioenergy used for the supply of heat to a district heating system. Essentially, time-distributed atmosphere-biosphere sequestration fluxes of CO_2 are integrated into the global carbon

cycle and reconciled with pulse biogenic CO_2 emission fluxes occurring at a single point in time. We refer the reader to refs (Bright et al. 2012; Cherubini et al. 2011a; Cherubini et al. 2012b; Cherubini et al. 2011b) and (Cherubini et al. 2012c) for details/ methodological elaboration.

For our biochar-bioenergy systems, roughly one-half of the carbon in the biomass feedstock is embodied in useable biochar ready for field application. 15% of C in biochar is oxidized at the start of the second year and the remaining 85% exponentially thereafter with a mean residence time of 500 years (Hammond et al. 2011). This rate gives us field carbon emissions from biochar oxidation as a function of time, or $e_{BC}(t)$. Carbon sequestration fluxes are linked to the biomass feedstock growth rate, $g(t)$, to which a simple Gaussian function is used, and subsequently normalized over the rotation length such that 100% of the initial carbon pulse is sequestered at the end of the rotation period. Following (Cherubini et al. 2012c), the function for distributed emission and sequestration fluxes in time used to derive a single concentration time profile for distributed field emissions from biochar oxidation, $f_{BC}(t)$ takes the following form:

$$f_{BC}(t) = \int_0^t e_{BC}(t')y(t-t')dt' - \int_0^t g(t')y(t-t')dt'$$ (7)

where $y(t)$ is a CO_2 impulse response function (IRF) representing the fraction of CO_2 remaining in the atmosphere after a single pulse emission/pulse sequestration depending on the interactions between the atmosphere, oceans, and the terrestrial biosphere (Joos and Bruno 1996), (Joos et al. 2001). This IRF $y(t)$ has the following analytic form (Forster and Venkatachalam 2007):

$$y(t) = A_0 + \sum_{i=1}^{3} A_i e^{-t/\beta_i}$$ (8)

where $A_0 = 0.217$, $A_1 = 0.259$, $A_2 = 0.338$, $A_3 = 0.186$, $\beta_1 = 172.9$, $\beta_2 = 18.51$, and $\beta_3 = 1.186$. Because our system produces biochar and bioenergy jointly using the carbon in biomass, we choose to normalize all emission and sequestration fluxes to a unit pulse emission from biochar and bioenergy production which gives the following concentration profile as a function of time:

$$f_{BC/E}(t) = \frac{C_E y_{CO_2}(t)}{C_E} + \frac{C_{BC} \int_0^t e_{BC}(t') y_{CO_2}(t-t')dt'}{C_E} - \frac{(C_{BC}+C_E) \int_0^t g(t') y_{CO_2}(t-t')dt'}{C_E} \qquad (9)$$

"GWP$_{bio}$" characterization factors for biogenic CO2 emissions from our combined bioenergy-biochar system for any given TH can now be estimated:

$$GWP_{bio}(TH) = \frac{\int_0^{TH} RF_{BC/E}(t)dt}{\int_0^{TH} RF_{CO_2}(t)dt} = \frac{\int_0^{TH} k_{CO_2} f_{BC/E}(t)dt}{\int_0^{TH} k_{CO_2} y_{CO_2}(t)dt} \qquad (10)$$

where k_{CO2} is the radiative efficiency of CO_2 in the atmosphere given a background CO_2 concentration of 378 ppmv (Forster and Venkatachalam 2007). For comparison, GWP characterization factors for biogenic CO_2 emissions from stand-alone bioenergy production are shown in Table 9.

Table 9: GWP characterization factors (for a TH of 20, 100 and 500 years) of a stand-alone bioenergy system per kg biogenic CO_2 emission from bioenergy production when 1-yr. rotation and 50-yr. rotation biomass is used as feedstock

Biomass procurement losses	GWP20	GWP100	GWP500
50-yr. rotation feedstock	0.88	0.20	0.04
1-yr. rotation feedstock	0.02	0.004	0.00074

These factors are applied to biogenic CO_2 emissions that occur upstream in the supply chain due to carbon oxidation associated with biomass procurement losses. These emissions are treated as pulses occurring in year 0. It was assumed that there are 5% (related to the feedstock) procurement losses for wheat straw and 9% (related to the feedstock) procurement losses for round wood.

3.3.3.2 Calculation of GWP characterization factors for avoided fertilizer use and soil N$_2$O emissions.

In line with (Hammond et al. 2011), a constant 10% decrease in N fertilizer requirement and a constant 5% decrease in P and K fertilizer requirement was assumed to result from biochar

application. While (Woolf et al. 2010) assumed that the increase in the fertilizer use efficiency of the soil remains constant for 100 years after biochar application, we assume a more conservative time period of 20 years following char application in our model in line with (Hammond et al. 2011). The fertilizer reduction impact has been quantified previously by Hammond and colleagues amounting to −1.7 kg-CO_2e/odt biomass feedstock and year in terms of avoided 100 year CO_2-eq. emissions for biochar systems in the UK (Hammond et al. 2011). We use the UBA ProBas LCA database (Umweltbundesamt 2012) in order to disaggregate CO_2e into their relative GHG constituents: Anthropogenic CO_2, CH_4, and N_2O. These are then divided by their 100 year. GWP characterization factors indicated in (Forster and Venkatachalam 2007) to obtain absolute values for avoided GHG emissions of type x per Mg dry feedstock and year, or $e_x(t)$.

A similar approach is followed to obtain absolute avoided emission values for soil direct N_2O. Due to a recent publication of (Kammann et al. 2012) based on laboratory experiments, we deviate from (Hammond et al. 2011) with our assumption that a constant 50% suppression of soil N_2O emissions can be achieved for a time period of 5 years after biochar application.

Taking into account earlier experiment results published by (Libra et al. 2011), the 50% reduction should be seen as an upper range estimate. We assumed that the reduction in soil N_2O emissions decreases linearly from year 5 after biochar application to zero in year 15 after biochar application. Avoided direct soil N_2O emission amount to −24.9 kg-CO_2e/odt and year in the years 1−5 under the assumptions described above.

We customized additional GWP characterization factors that take these avoided time-distributed emission savings into account. For these avoided emission scenarios, "negative" emissions −e occurring at specific points in time t' as single pulses (represented by the distribution ε(t')) are normalized to biogenic CO_2 emission pulses from biochar and bioenergy production using the factor C_E, the factor CC_{odb}, the constant 1000 (kg/Mg dry feedstock), and the constant 44/12 (kg CO_2 /kg C). Subsequently, they are convoluted with the corresponding decay function $y_x(t)$ of greenhouse gas type x and integrated to obtain an atmospheric CO_2 concentration profile associated with the scenario. Radiative efficiencies k_x of a substance x from (Kirschbaum et al. 2011) are multiplied by the derived concentration time profiles to obtain instantaneous forcing time profiles, integrated to TH, and divided by the cumulative forcing of anthropogenic CO_2 for the same TH. These operations are

combined to yield the following equation which is repeated for each of the avoided emission scenarios:

$$GWP_{-e_x}(TH) = \left(\frac{\int_0^{TH} k_x \left[\int_0^t \left[\left(\frac{-e_x}{1000 \cdot CC_{odb} \cdot C_E \cdot (44/12)} \right) \varepsilon(t') \right] y_x(t-t') dt' \right]}{\int_0^{TH} RF_{CO_2}(t) dt'} \right) \qquad (11)$$

3.4 Results

In the Top of Figure 3, the arithmetic means of the albedo of the different treatments from the field trial soil samples are shown. The gravimetric water content of the soil samples before drying was in the range of 25–36%. It should be noted that the soil samples were still quite wet (gravimetric water content: 15–27%) after drying. In the bottom of Figure 3, the arithmetic means of the different treatments of the albedo measurement for the pot trial series samples are shown. The gravimetric water content of these very dry soil samples was in the range of 0.1–0.4%. The standard errors indicated in the bottom of Figure 3 are lower compared to the standard errors indicated in the top of Figure 3. This can be partly explained by the fact that variations of field test samples are more heterogeneous compared to pot test samples. The maximum absolute difference in the arithmetic mean of the measured albedo values of the fresh (modestly dried) field trial soil samples was obtained between the control and the biochar-compost treatment which amounted to 0.0091 (0.0147). The difference is slightly lower (0.0090 for wet soil samples and 0.011 for modestly dried soil samples) when the control is compared to the biochar treatment.

For the dry pot trial series samples, the maximum difference obtained between the control and the biochar-compost 200 Mg/ha treatment (0.146) is much higher compared to the field trial soil samples. In general, all pot trial albedo values are much higher compared to the field trial samples which cannot be explained by the difference in water contents alone: The albedo of the bright control soil of the pot trial is higher than the albedo of the darker control soil of the field trial. This is not surprising, as both albedo and color of soils are determined by surface properties.
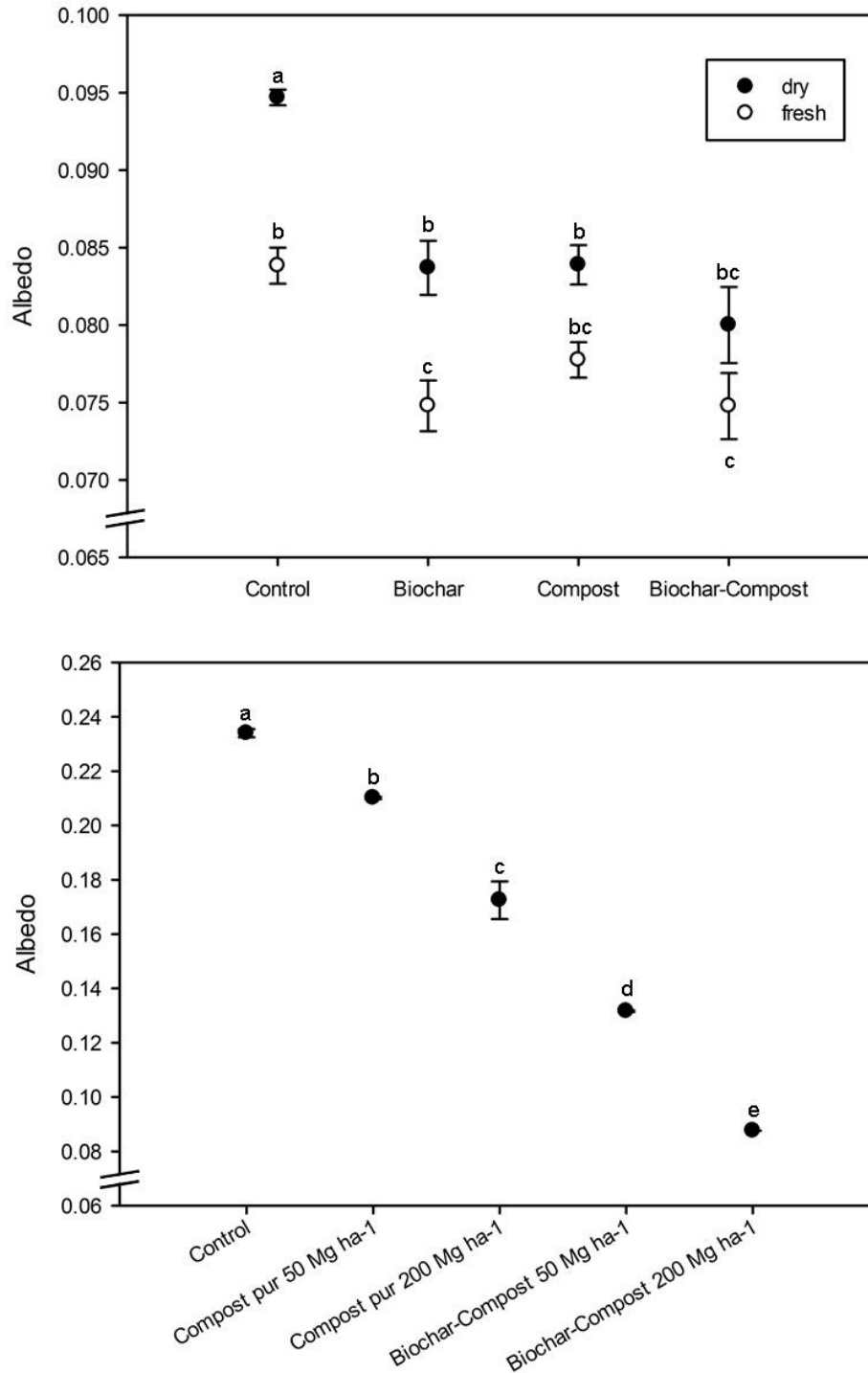
Figure 3: (Top) Albedo of FT soil samples before (black circles) and after (empty circles) modest drying. (Bottom). Albedo of the PT series soil samples. Significant differences of the treatment means (p<0.05 with n=4) are indicated by different lower case letters. Error bars indicate the standard error (n=4) of the albedo values obtained from the respective treatments.

Multiple linear regression analysis of the results of the field trial soil samples resulted in the equation: Surface Albedo = $0.103 - 0.0002141$ *BAM* (*Biochar Application Mass* in Mg ha^{-1}) $-$ 0.00009018 *CAM* (*Compost Application Mass* in Mg ha^{-1}) $- 0,58$ *GWC* (*Gravimetric Water*

Content in %); the zeroth-order partial correlation coefficients -0.502 for *BAM*, -0.383 for *CAM* and 0.291 for *GWC*; and the partial correlation coefficients -0.599 for *BAM*, -0.562 for *CAM* and 0.491 for *GWC*. The regression analysis showed a significant impact of all three variables entered on albedo values: *BAM* showed the lowest negative standardized regression beta (-0.504) followed by *CAM* (-0.469) and *GWC* (-0.389). The regression analysis resulted in an adjusted coefficient of determination of 0.497. This analysis underlines the impact of these variables on the soil albedo.

In Figure 4, $\Delta\widetilde{\alpha}_s$, $\widetilde{R}_{TOA}$, $\widetilde{f}_{Atm}$ and $\widetilde{RF}_\alpha$ values resulting from the intra-annual delta albedo simulation for both wheat and rapeseed cultivation are presented.
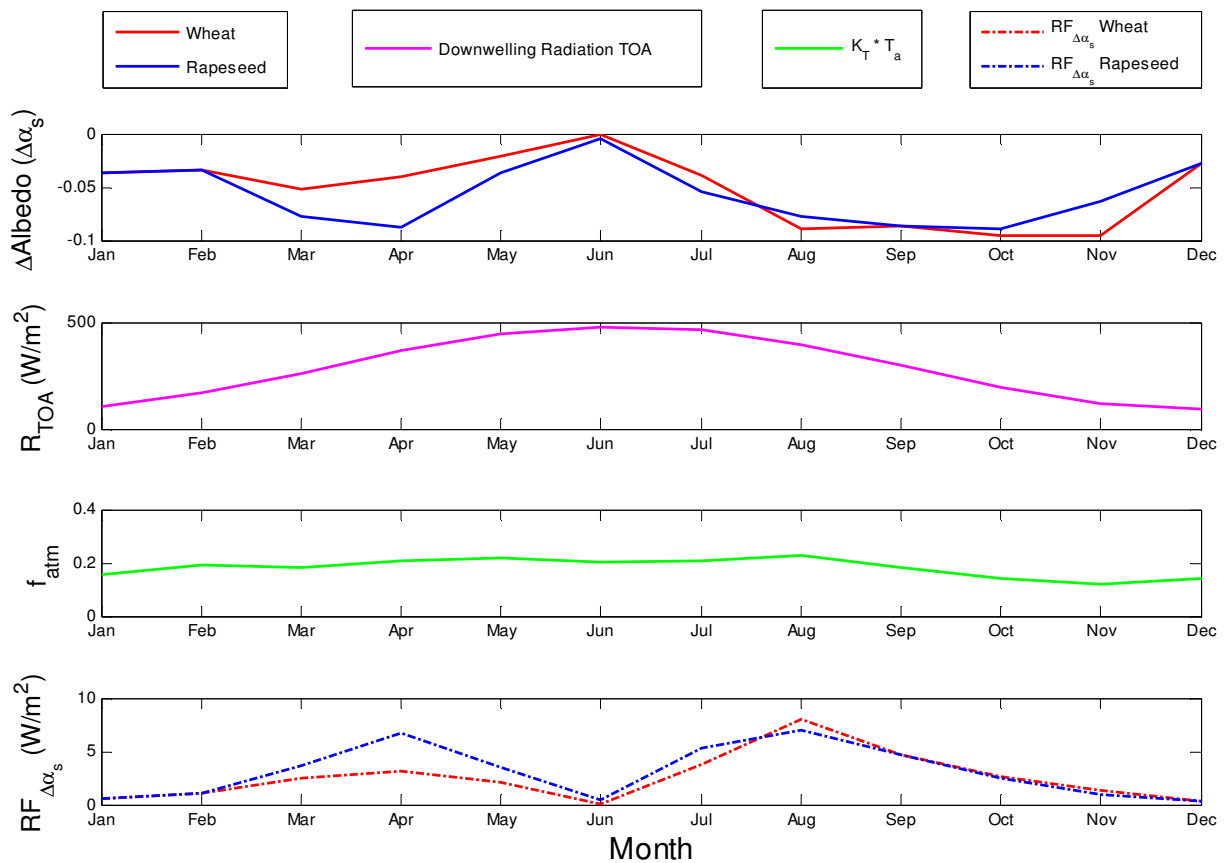
Figure 4: (Top) Monthly changes in surface albedo in the first year after biochar application to Wheat and Rapeseed fields near Donndorf, Germany. (Upper Middle) Monthly incoming solar radiation at the top of the atmosphere ("TOA"). (Lower Middle) Monthly mean two-way transmittance ("f_{atm}") of solar radiation throughout the atmosphere. (Bottom) Instantaneous local radiative forcing ("RF") associated with changes to surface albedo for the two cases. All graphs show the parameters for the same location.

The climax of vegetation coverage in June as well as the harvesting operations in the end of July and in August are clearly reflected in the top of Figure 4: While the dense vegetation

cover cancels out any albedo differences of the soil in June, the biochar effect on the surface albedo change is evident after crop harvest and grubbing. Snow coverage reduces albedo differences in the winter months. Please note that the delta albedo decrease within in the first year (see eq. 4) is not accounted for in Figure 4 to reduce the complexity for the interpretation of the graph.

If the biochar is applied to a wheat field (values for an application on a rapeseed field in brackets), the resulting GWP albedo characterization factors for a time horizon of 100 years are 0.14 (0.17) for a biochar feedstock with 50-year rotation period - roundwood (RW) - and 0.12 (0.14) for biochar feedstock with 1 year rotation period, straw. The GWP characterization factors resulting for 20, 100 and 500 year time horizons are presented in Table 10.

Table 10: GWP albedo characterization factors for a time horizon of 20, 100 and 500 years

ΔAlbedo, wheat field (rapeseed field)	GWP20	GWP100	GWP500
Feedstock: 50-year rotation roundwood	0.11 (0.14)	0.14 (0.17)	0.14 (0.17)
Feedstock: Annual crop	0.10 (0.12)	0.12 (0.14)	0.12 (0.15)

Figure 5 visualizes the (positive and negative) integrated radiative forcing caused by the temporal shift between biogenic CO_2 emissions during biochar/bioenergy production and the subsequent carbon sequestration in soil and vegetation. Figure 5 reflects increases in the iRF (Time-integrated radiative forcing) due to the radiative forcing triggered by biogenic and fossil CO_2 emissions (upper part of the graph). The very low, but positive iRF of the straw bioenergy system is a result of the rapid absorption of the emitted carbon due to the fast regrowth of the annual crop. Decreases in the iRF displayed in the lower part of the figure result from the net removal of CO_2 from the atmosphere via carbon sequestration in soils. The derived GWP characterization factors of the combined bioenergy/biochar system for roundwood (values for straw in brackets) over a 100-year time horizon amount to −0.36 (−0.67) for biogenic CO_2 emissions and biogenic carbon stabilization, −0.04 (−0.04) for avoided fertilizer emissions and −0.14 (−0.14) for avoided soil N_2O emission according to eqs 10 and 11. The GWP characterization factors resulting for 20, 100 and 500 year time horizons are presented in Table 11 and Table 12.
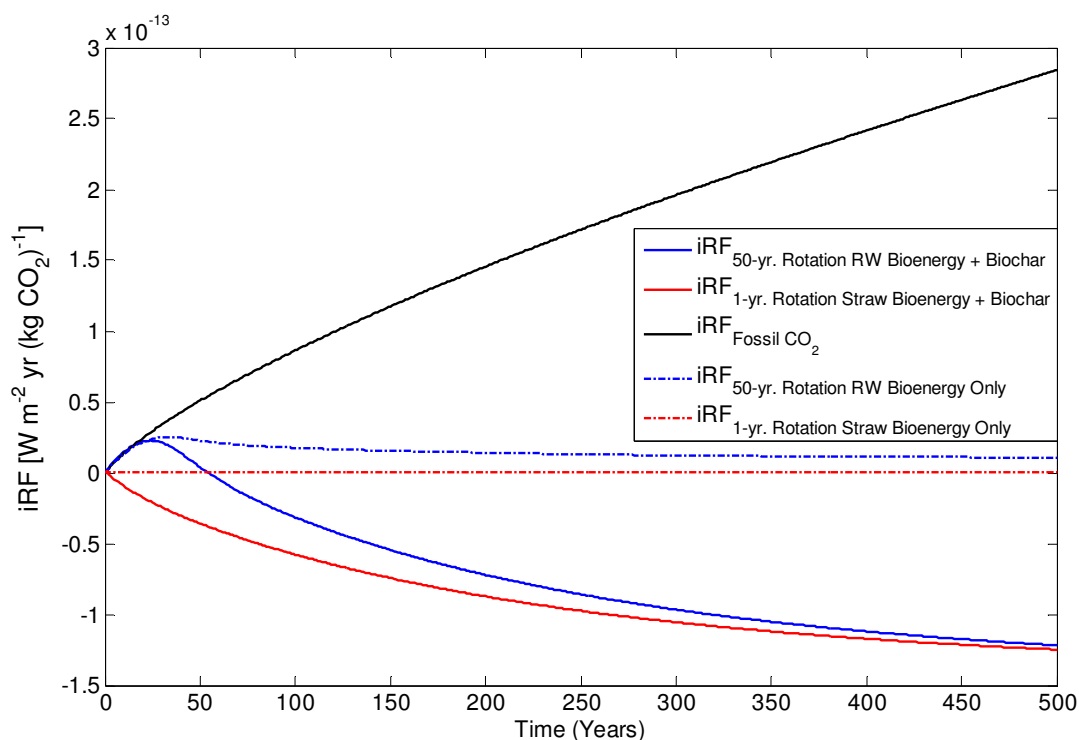
Figure 5: Time-integrated radiative forcing ("iRF") per 1 kg CO_2 pulse emission of bioenergy and biochar production compared to iRF per 1 kg CO_2 from stand-alone bioenergy production and to iRF per 1 kg CO_2 from fossil CO_2 emissions. Blue lines represent cases where 50-yr. rotation biomass is used as feedstock; red lines are used for cases where annual crops are used.

Table 11: GWP characterization factors (for a TH of 20, 100 and 500 years) of the combined biochar – bioenergy system per kg biogenic CO_2 emission from bioenergy production when 50-yr. rotation is used as a feedstock

Feedstock: 50-year rotation roundwood	GWP20	GWP100	GWP500
Energy + biochar production, direct	0.91	-0.36	-0.42
Energy + biochar production, avoided fertilizer emissions	-0.02	-0.04	-0.03
Energy + biochar production, avoided soil N2O	-0.13	-0.14	-0.07

Table 12: GWP characterization factors (for a TH of 20, 100 and 500 years) of the combined biochar – bioenergy system per kg biogenic CO_2 emission from bioenergy production when straw from an annual crop is used as a feedstock

Feedstock: Annual crop	GWP20	GWP100	GWP500
Energy + biochar production, direct	-0.71	-0.67	-0.44
Energy + biochar production, avoided fertilizer emissions	-0.02	-0.04	-0.03
Energy + biochar production, avoided soil N2O	-0.13	-0.14	-0.07

In Table 13, the synthesis of the overall results of our model is presented.

Table 13: Overall climate impact of the biochar system for wheat cultivation (TH = 100). Values for rapeseed cultivation are shown in parentheses.

Type of impact	Feedstock		Indicated data based on:
	Straw	Small Round Wood	
	Mg CO_2e/ t DM	Mg CO_2e/ t DM	
Provision of biomass feedstock	0.268	0.035	(Hammond et al. 2011)
Transport of biomass to pyrolysis plants	0.001	0.002	(Hammond et al. 2011)
Emissions from the pyrolysis plant construction	0.020	0.020	(Hammond et al. 2011)
Heat offset	-0.328	-0.315	Chapter 3.3.1
Char transport to farm	0.000	0.000	(Hammond et al. 2011)
Char transport to fields	0.001	0.001	(Hammond et al. 2011)
Char application to soils	0.000	0.000	(Hammond et al. 2011)
Albedo impact for wheat field (rapeseed field)	0.107 (0.124)	0.128 (0.156)	Table 10
Temporal impact of biomass procurement	0.000	0.033	Table 9
Temp. impact of biochar system on carbon cycle	-0.595	-0.330	Table 11,Table 12
Avoided fertilizer life cycle emissions	-0.034	-0.034	Table 11,Table 12
Avoided soil N_2O emissions	-0.124	-0.128	Table 11,Table 12
Overall Impact for wheat field (rapeseed field)	**-0.685 (-0.667)**	**-0.587 (-0.560)**	

We compare the combined biochar-bioenergy system outlined above to a stand-alone bioenergy system - a biomass heating plant - which consumes the same amount of dry biomass feedstock. Regarding the stand-alone bioenergy system, we assume that 85% of the produced heat can be supplied into a district heating system with a high annual utilization factor of 75%, transport heat losses of 5%, and resulting lifecycle emissions saving of 0.254 kg CO_2e/kWh final energy (Umweltbundesamt 2012) due to the replacement of natural gas heating systems. In contrast to the biochar system, we assume that the biomass heating plant will not run at constant heat output throughout the year, but adapts the heat output to the heat demand in the district heating system. Thus, the standalone bioenergy system is assumed to produce not more than 5% of unusable waste heat. The specific lifecycle emissions from the construction of the biomass heating plant - if related to one ton of dry biomass input - were assumed to be equal to the life cycle emissions of the construction of a pyrolysis plant.

Table 14 indicates the overall result of our model:

Table 14: Overall climate impact of the stand-alone bioenergy system (TH = 100)

Type of impact	Feedstock		Indicated data based on:
	Straw	Small round wood	
	Mg CO_2e/ t DM	Mg CO_2e/ t DM	
Provision of biomass feedstock	0.268	0.035	(Hammond et al. 2011)
Transport of biomass to pyrolysis plants	0.001	0.002	(Hammond et al. 2011)
Emissions from the heating plant construction	0.020	0.020	Chapter 3.4
Heat offset	-1.084	-1.041	Chapter 3.4
Temporal impact of biomass procurement losses	0.000	0.033	Table 9
Temp. impact of bioenergy system on carbon cycle	0.000	0.367	Table 9
Overall impact:	**-0.795**	**-0.584**	

3.5   Discussion

The albedo values measured in the laboratory reflects field conditions only to limited extent: the radiation spectrum of the halide lamp is not fully congruent with the radiation spectrum of the sun, the area covered by the soil samples in the lab (0.24 m²) did not fully cover the light cone of the flood light - thus, a part of the shortwave radiation of the flood light was reflected by materials with different surface properties compared to the soil sample - and the necessary data corrections applied to account for the temperature and the shadow error involve the risk of modeling errors. While field albedo measurement would be very helpful to reduce this uncertainty, they were unfortunately not feasible in the scope of our assessment due to the crop cover of the test field in summer (field albedo measurements need to be carried out during the summer season with substantial irradiation to reduce measurement errors).

While the absolute albedo of agricultural soils is strongly affected by the background soil type, the obtained differences in albedo values of treatments with the same background soil resulted mainly from the influence of biochar amendments, followed by the impact of compost amendments and varying soil water contents (see result of the statistical analysis in chapter 3.4). It is most reasonable to compare the albedo values obtained from the soil

samples from Donndorf with the values measured in Pistoia (18 months after biochar application) due to a similar amount of biochar application, similar background soils, same tilling depth and equal time period between biochar application and albedo measurement in both trials. However, the soils measured in Pistoia were very dry when analyzed as compared to the wet soils analyzed in Donndorf. The measurements of soil samples in Bayreuth resulted in larger absolute albedo differences when drier soil samples were compared. This is in line with the higher absolute soil albedo difference ($\Delta\alpha_{soil}$) measured on the dry soils in Pistoia as compared to the values obtained from the wet soil samples of Donndorf. The measured albedo differences are compared to published literature about biochar impacts on soil albedo and are discussed in greater detail in the following section:

(Oguntunde et al. 2008) measured an absolute albedo difference between wet soils previously situated under charcoal kilns in Ghana and wet soils of adjacent field areas of 0.032. The absolute difference in albedo between the same soil samples increased to 0.062 under dry conditions. The area where the measurements were carried out is dominated by Haplic Acrisols with a high sand content (mean value of about 72%) in the topsoil (0–15 cm). As already mentioned, (Genesio et al. 2012) measured an absolute albedo difference between treatments with (at a rate of 30 [Mg ha^{-1}]) and without biochar application of about 0.15 in December 2009 shortly after biochar application on dry arable silty loam soils near Pistoia, Italy. The biochar was tilled 10 cm deep into the arable soil. The absolute albedo difference between dry treatments with and without biochar application decreased to 0.08 seven months after application. On a parallel field trial at the same location, the authors measured an absolute albedo difference of only 0.05 around 18 months after biochar application. They were not able anymore to identify a statistically significant albedo difference between the same treatments after the second tillage (which was carried out only a few weeks after latest measurement described above). In Figure 6, the measured absolute soil albedo differences are summarized.
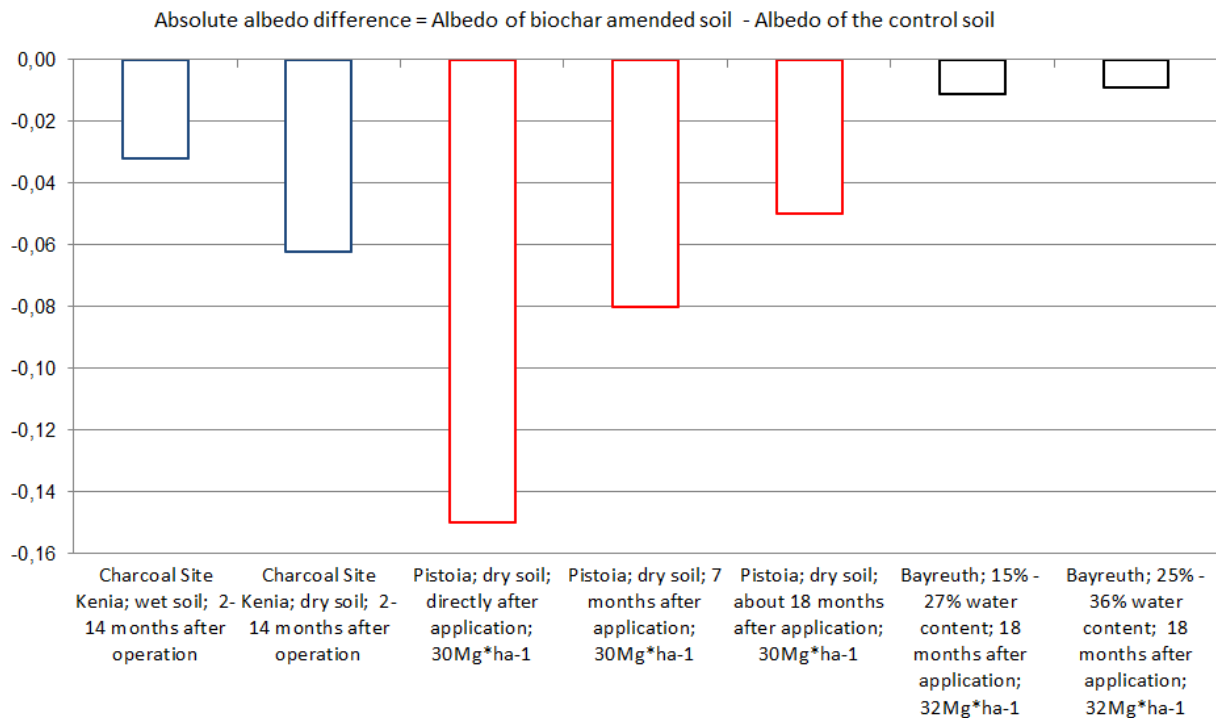
Figure 6: Absolute Albedo Differences between control soil and (bio)char treatment from Oguntunde et al. 2008 (left), Genesio et al. 2012 (middle) and field trial soil samples (right)

The measurement uncertainties as described in the beginning of this chapter need to be taken into account for the interpretation of the albedo differences between control and (bio)char treatment in the field trial in Donndorf. The impact of the uncertainties described have a larger relative impact on the absolute albedo values of the samples as compared to their relative impact on the difference in the albedo values of the different treatments. For our simulation, not the absolute albedo values of the samples, but the difference in the albedo values of the different treatments was used. In addition to that, literature values on the albedo of dry soil treatments from field albedo measurements by (Genesio et al. 2012) were used to complement our simulation.

Additional albedo field measurements on biochar sites under both wet and dry surface conditions in annual intervals would be helpful to complement the existing data and to better understand albedo development in time. It should be noticed in this context that the GWP albedo characterization factors are reduced by 1 order of magnitude if the delta albedo would completely vanish within two years after biochar application (see eq 4). Based on the modeled slow pyrolysis biochar system, we calculated that the overall climate impact of biochar systems is reduced by 13–22% due to the albedo impact of biochar application,

depending on the type of biochar feedstock and crop cultivated on the soil. Since the albedo impact is linearly correlated to the field vegetation cover, agricultural systems with a large share of dense and year-round vegetation cover can minimize this impact. The albedo impact is also reduced when dark background soils are amended with biochar. To minimize the uncertainty connected to the modeling of the annual development of vegetation cover on basis of satellite data as carried out in this assessment, further field validations of the applied SDVI- methodology over heterogeneous surfaces divided into very small sections are necessary. In addition, further research should focus on the indirect impacts of albedo changes and the impacts of biochar application on the annual development of vegetation cover and near surface exchanges of water and energy. As GWP_{albedo} is directly proportional to T_a, the monthly fraction of short wave radiation reaching TOA after reflection at the surface, it is very important to know realistic local T_a values. Due to a lack of empirical measurements available, we estimated T_a based on a simple one layer atmosphere model and average global values for short wave radiation absorption. If achievable, empirical measurements of T_a would be very helpful to improve the assessment of GWP_{albedo}.

Due to the scarcity in globally available biomass (if biomass is used for biochar production, it cannot be used in standalone bioenergy systems to save fossil fuel emissions), we compared the climate impact of using one ton of dry wood (and straw respectively) in biochar systems and in stand-alone bioenergy systems. While we calculated overall CO_2e emission savings with our model for both systems and feedstock types, bioenergy systems achieve 99–119% of the climate benefit of biochar systems according to our analysis. This can be mainly explained by the lower energy provision of the pyrolysis plant due to the lost energy contained in the biochar, the lower energy efficiency, and the lower heat use efficiency caused by the continuous operation of the pyrolysis plant. According to our assessment, a considerable fraction (23–29%) of the emissions savings of the biochar system is a result of avoided soil N_2O emissions and avoided fertilizer life cycle emissions. Long-term measurements of avoided soil N_2O emissions and more practical experience on the achievable fertilizer reductions after biochar application are necessary to reduce the uncertainty connected to this part of our assessment. The need to account for the climate impact of temporal shifts of the carbon cycle was clearly demonstrated by the assessment of both systems. Since we did not account for the impact of biochar application on biomass yields, soil methane emissions, soil inherent organic carbon content, and atmospheric soot

concentration, additional research is necessary to complement the current assessment. If the biomass provision was to trigger indirect land use change via displacement effects, the resulting climate impact would have to be accounted for in the overall climate impact assessment. While this analysis focuses on a climate impact assessment, one should not loose sight of the opportunities of biochar application for soil amelioration (Fischer and Glaser 2012).

4   Thermal removal of polycyclic aromatic hydrocarbons from gasification biochars

Sebastian Meyer, Bruno Glaser, Daniel Fischer, Peter Quicker, Yves Noel and Georg Kuffer

4.1   Introduction

The number of small-scale (< 200 kW electrical capacity) wood gasifiers used for electricity and heat provision in Central Europe is increasing. After the wood gasification process, about 10% of the dry-mass of the wood feedstock input are left in form of wood gasification residues (Meyer et al. 2011) consisting of a mixture of char and ash. Inspired by the Terra preta phenomenon and the intention to generate own humus rich black earths (Glaser et al. 2001), especially farmers are interested in the opportunity to use the carbonaceous and nutrient-rich gasification residues produced by their own gasifiers for farm fertilizer production, soil amelioration and for carbon sequestration (Kuzyakov et al. 2009).

However, gasification residues are known for their high content in polycyclic aromatic hydrocarbons (PAH) (Schimmelpfennig and Glaser 2012). PAH are carcinogenic, persistent, accumulate in organisms and partly inhibit reproduction (Bruno Veyrand et al. 2013). Due to that, gasification residues with very high PAH contents need to be classified as hazardous waste. As a moderate increase in temperature substantially increases the vapor pressure of PAH, thermal processes can be used to volatize and subsequently remove PAH from background matrixes (Harmon et al. 2001). To reduce the PAH content in gasification residues, a thermal process – the so called PAH volatilization unit - has been developed by a

German wood gasifier manufacturer. In the following, a critical assessment of the functional efficiency of this patented process is described.

The research work was carried out with the objective to evaluate the effectiveness of the PAH volatilization unit in reducing the PAH content in gasification residues. This objective was chosen to better assess the environmental suitability of using gasification residues as soil amendment. Our working hypothesis was that it is possible to technically reduce the PAH content in gasification residues to a level which allows for an agricultural use of the gasification residues in line with the soil protection regulations in Germany. As a precondition for this evaluation, the suitability of the analysis methods DIN 13877:A and DIN 13877:B for the determination of the PAH content in wood gasification residues had to be checked. Based on the results of (Hilber et al. 2012), our working hypothesis in this regard was that analysis method DIN 13877:B would be more suitable for the analysis task as compared to analysis method DIN 13877:A.

4.2   Materials and methods

4.2.1 Comparison of PAH analysis methods for gasification residues (1st experiment)

(Hilber et al. 2012) demonstrated that the selection of an appropriate solvent is crucial to determine the PAH content in biochars. They recommend a Soxhlet-extraction with toluene for the PAH analysis of biochars. To complement and to reassess this work, the PAH content (sum of the 16 PAH defined by the US Environmental Protection Agency EPA) of three samples of the same production batch of gasification residues was determined using two different extraction methods (cold extraction with acetone according to DIN 13877:A and Soxhlet extraction with toluene for 5 hours according to DIN 13877:B). The gasification residues had been produced from poplar wood chips in a commercially operated fixed-bed Joos-Spanner biomass gasifier (30 kW electrical capacity) of the German manufacturer Spanner Re² GmbH. The PAH analyses of all experiments described on the following pages were carried out by the commercial laboratory Görtler Analytical Services GmbH in Vaterstetten, Germany.

4.2.2 Testing the functional efficiency of the PAH volatilization unit (2nd and 3rd experiment)

In a next step, the functional efficiency of a PAH volatilization unit developed by a cooperation of the RWTH Aachen and the German manufacturer Spanner Re² GmbH was assessed. Gasification residues produced under identical process conditions as described in the first experiment were treated in the PAH volatilization unit as illustrated in Figure 7:
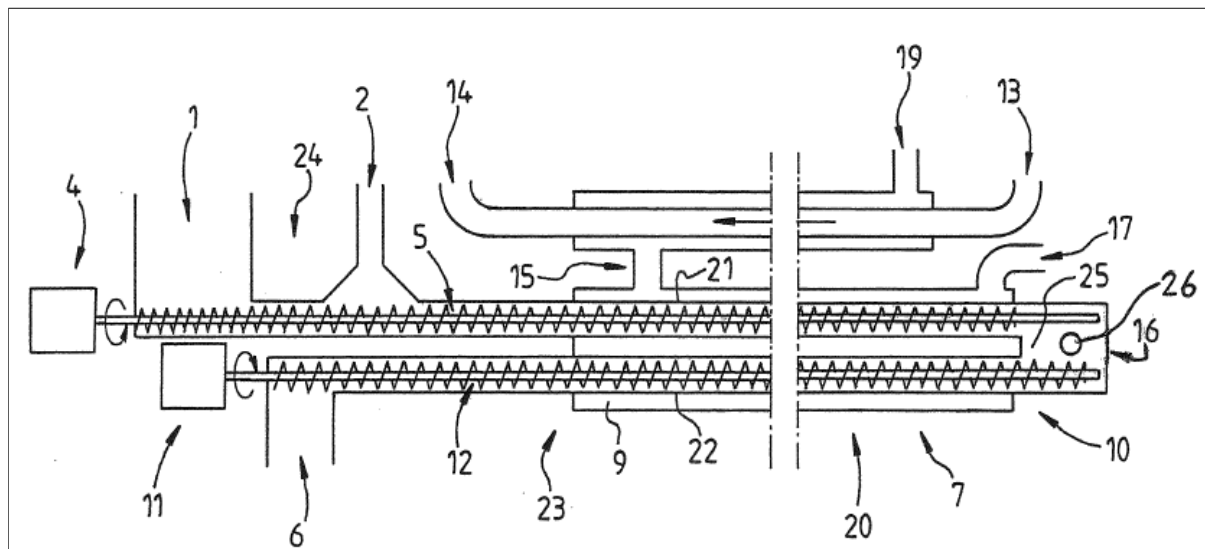
Figure 7: PAH volatilization unit (Source: Patent Specification)

The gasification residues entered the unit on the left side (1) and were being transported by a motor- (4) driven long conveyor screw (5) in an upper tube (24) through a heat exchanger (23) until the heating chamber (16) on the far right side of the unit. From this point, they were transported back through the heat exchanger by a motor- (11) driven second long conveyor screw (12) in a second tube (22) on the bottom side of the unit until the exit (6) on the bottom left site of the unit. Both conveyor screws were operated according to the following time schedule: 15 seconds operation, 30 seconds stop, 15 seconds operation and so forth... Within the heating chamber, the gasification residues got in contact with the outer side of a hot (surface temperature: about 600 °C) tube (26) transporting hot wood gas produced in the wood gasifier (not shown in the figure). It is technically possible to supply air from an external source (16) to the gasification residue stream inside the heating chamber. However, this option was not used for the 2nd experiment. A hot external air stream used for the air supply of the wood gasifier entered (13) the heat exchanger at a temperature of about 300 °C and left (14) the heat exchanger at a temperature of about 375 °C, thereby

effectively cooling the wood gasification residues on their way through the heat exchanger. Sealing air from the same external source as the heating chamber air stream was blown into the left side (6) of the bottom tube of the PAH volatilization unit in counter flow principle and left the unit on the top left side (1) of the unit. This counter current air flow was introduced to prevent volatized PAH from leaving the PAH volatilization unit through the exit for the processed gasification residues. In this technical design version of the process, about 5% of the air leaving the unit through was recirculated back into the sealing air stream.

This experimental setting was slightly modified for a 3rd experiment: The sealing air stream was reduced. In addition to that, air from the external source (17) was intermittently (within the standstill periods of the conveyor screws) blown into the gasification residue stream within the heating chamber to supply oxygen to the hot gasification residues. In this technical design version of the process, about 4% of the flue gas from the PAH volatilization unit was recirculated back into the air stream which supplied both the combustion chamber and the sealing air stream.

The PAH content of three samples of the processed batches of gasification residues was analyzed according to DIN 13877:B in both experiments.

4.2.3   Redesign of the PAH volatilization unit (4th experiment)

In a redesigned version of the PAH volatilization unit, the manufacturer prevented the recirculation of PAH into the PAH volatilization unit by blowing clean air from an external source in the sealing air nozzle and by discharging the airstream with the volatized PAH in the gas engine where the wood gas of the gasifier was burned. Further modifications of the redesigned PAH volatilization unit included larger conveyor screw diameters and conveyor screw tube diameters. Gasification residues from a 45 kWel wood gasifier fed by a mixture of chips from different sort of woods were treated in this modified PAH volatilization unit in a 4th experiment. The sealing air stream and the heating chamber air stream volumes were increased as compared to the 2nd and 3rd experiment. The PAH content of one sample of the processed batch of gasification residues was analyzed according to DIN 13877:B.

4.2.4   PAH volatilization in a laboratory scale experiment (5th experiment)

To evaluate the general capability of thermal processes to volatize and subsequently remove PAH from gasification residues, the following experiment was carried out:

20 gram samples of gasification residues from a 45 kWel wood gasifier fed by a mixture of chips from pine trees and spruce were filled in an open steel container (20mm width x 20mm depth x 100mm height). This container was placed in an electrical box furnace (Nabertherm, Model LH 30/14) which had been heated to specified temperature levels (550° C, 650° C and 700° C in three consecutive trials). During the experiments, the box furnace was purged by inert gas of type Argon 4.6. After 30 minutes, the container was removed from the furnace and immediately cooled down in a water quench. During the cooling process, the container was purged from above with Argon 4.6. Due to that, the complete heating and cooling procedure took place in an oxygen-free environment.

The PAH content of the three samples (one for each temperature level) was analyzed according to DIN 13877:B.

4.2.5   Statistical Analysis

All statistical tests were conducted with the open source software R 3.0.1 (R CORE TEAM 2012). Due to the low number of samples per treatment (n=3), particular care and attention was paid to the statistical requirements and assumptions. In this respect, our treatments did show neither a normal distribution nor homogenous variances among groups so that the Student's t-test couldn't be applied. Therefore, we applied a permutation version of ANOVA according to (Kabacoff 2011) for the statistical analysis of the obtained results from the experiments 1, 2 and 3. For this purpose we used the package "ImPerm" (Wheeler).

4.3   Results

4.3.1 Comparison of PAH analysis methods for gasification residues (1st experiment)

Table 15 summarizes the Σ EPA16 PAH content in the three gasification residue samples in mg/kg dry mass (DM) as determined by the two different analytical methods. On average, the analysis according to DIN 13877:B resulted in PAH contents more than 4 times higher

compared to the analysis according to DIN 13877:A. The standard errors of the mean (SEM) are indicated after the average values. The difference between the sample means (n=3) of the two analysis methods is significant ($p < 0.001$) according to the applied permutation version of ANOVA.

Table 15: Comparison of the two PAH analysis methods using either acetone or toluene for extraction (1st experiment). SEM indicates standard error of the mean**.**

Gasification Residues (untreated)	**Extraction with acetone** according to DIN 13877:A Σ EPA16 PAH content mg/kg DM	**Extraction with toluene** according to DIN 13877:B Σ EPA16 PAH content mg/kg DM
sample 1	542	3,056
sample 2	571	1,009
sample 3	504	2,702
Average	**539 ± 16 (SEM)**	**2,255 ± 516 (SEM)**

Figure 8 depicts the results from Table 15 in two box-and-whisker plots:

Figure 8: Boxplots indicating the median (central black bar), the minimum and maximum (lower and upper whisker) and the lower and upper quartile (lower end upper end of the box) of the Σ EPA16 PAH contents in mg/kg DM in three gasification residue samples after application of the analysis method DIN 13877:A (left) and DIN 13877:B (right).
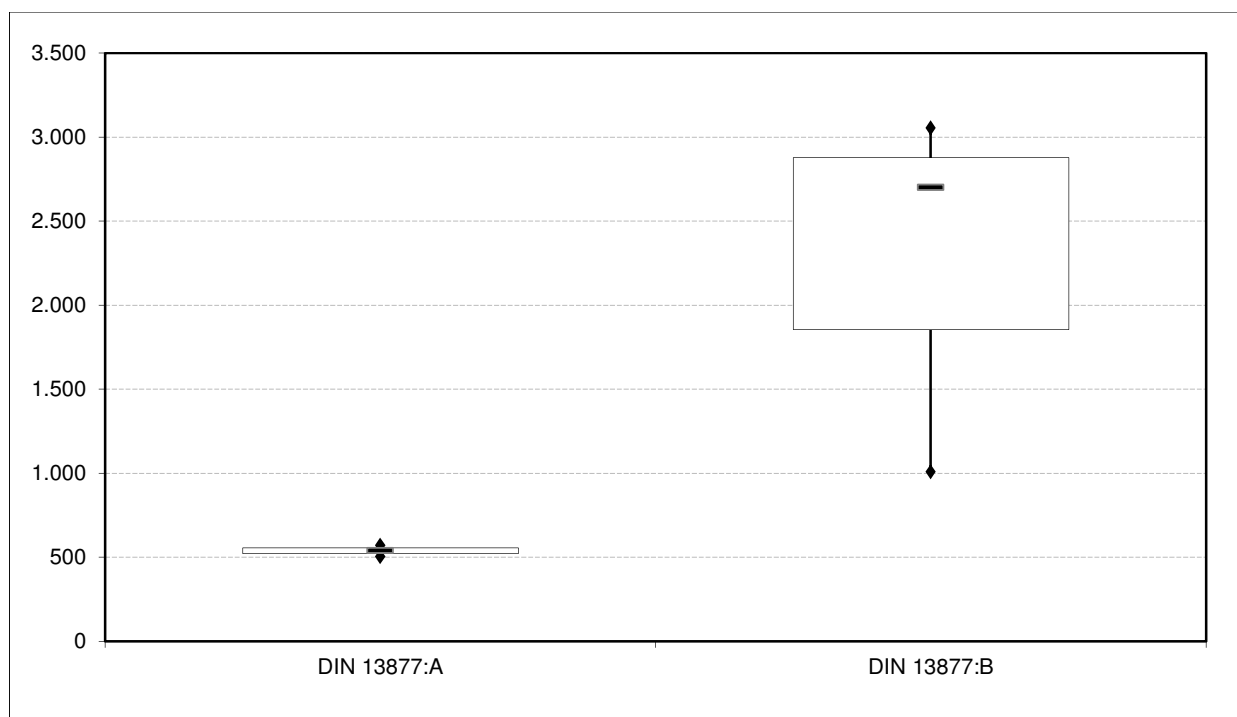
Table 16: Comparison of the two PAH analysis methods using either acetone or toluene for extraction (1st experiment). Detailed results.

Gasification Residues (untreated)	Extraction with acetone according to DIN 13877:A Σ EPA16 PAH content			Extraction with toluene according to DIN 13877:B Σ EPA16 PAH content		
	Sample 1	Sample 2 mg/kg DM	Sample 3	Sample 1	Sample 2 mg/kg DM	Sample 3
Naphthalene	460	480	420	1,200	570	1,200
2-Methylnapthalene	63	66	61	490	130	330
1-Methylnapthalene	63	67	62	470	100	260
Acenaphtylene	43	47	43	580	120	340
Acenapthene	14	15	14	110	15	54
Flourene	8,5	8,4	8,9	180	38	120
Phenanthrene	12	15	13	690	170	580
Anthracene	1,8	2,4	2	120	32	120
Flouranthen	1,5	1,9	1,7	94	31	140
Pyrene	1,4	1,6	1,5	70	27	110
Benzo(a)anthracene	< 0,01	< 0,01	< 0,01	4,5	2,4	12
Chrysene	< 0,01	< 0,01	< 0,01	4,8	2,4	18
Benzo(b)flouranthene	< 0,01	< 0,01	< 0,01	1,5	0,43	3,4
Benzo(k)flouranthene	< 0,01	< 0,01	< 0,01	0,24	0,05	0,64
Benzo(a)pyrene	< 0,01	< 0,01	< 0,01	0,65	0,19	1,9
Indeno(1,2,3.cd)pyren	< 0,01	< 0,01	< 0,01	0,25	0,11	0,9
Dibenz(a,h)anthracene	< 0,01	< 0,01	< 0,01	0,05	< 0,01	0,31
Benzo(g,h,i)perylene	< 0,01	< 0,01	< 0,01	0,16	0,16	0,4
Σ EPA16 PAH	**542**	**571**	**504**	**3,056**	**1,009**	**2,702**

4.3.2 Functional efficiency of the PAH volatilization unit (2nd and 3rd experiment)

Table 17 summarizes the Σ EPA16 PAH content in the gasification residue samples of the production batch after the treatment in the PAH volatilization unit (PAH-VU) in the 2nd experiment. On average, the PAH content of the processed gasification residues was 58% lower as compared to the unprocessed residues from the 1st experiment. The difference between the sample means (n=3) of the two analysis methods is significant ($p < 0.001$)

according to permutation version of ANOVA applied. The standard errors of the mean are indicated after each average value

Table 17: PAH reduction in PAH volatilization unit (2nd experiment). SEM indicates standard error of the mean.

Gasification Residues	Production batch without treatment from 1st experiment	Production batch with treatment in the PAH-VU from 2nd experiment
	Σ EPA16 PAH content (DIN 13877:B, extraction with toluene)	Σ EPA16 PAH content (DIN 13877:B, extraction with toluene)
	mg/kg DM	mg/kg DM
sample 1	3,056	1,291
sample 2	1,009	731
sample 3	2,702	806
Average	**2,255 ± 516 (SEM)**	**943 ± 143 (SEM)**

Figure 9 depicts the results from Table 17 in two box-and-whisker plots:

Figure 9: Boxplots indicating the median (central black bar), the minimum and maximum (lower and upper whisker) and the lower and upper quartile (lower end upper end of the box) of the Σ EPA16 PAH contents in mg/kg DM in three gasification residue samples after application of the analysis method DIN 13877:A (left) and DIN 13877:B (right).

Table 18: PAH reduction in PAH volatilization unit (2nd experiment). Detailed results.

Gasification Residues (processed)	Σ EPA16 PAH content (DIN 13877:B)		
	Sample 1 mg/kg DM	Sample 2 mg/kg DM	Sample 3 mg/kg DM
Naphthalene	850	370	510
2-Methylnapthalene	41	15	17
1-Methylnapthalene	32	14	14
Acenaphtylene	14	4.3	7.9
Acenapthene	3.4	1.4	1.1
Flourene	3.6	4	0.94
Phenanthrene	330	250	200
Anthracene	40	37	32
Flouranthen	26	32	33
Pyrene	19	26	18
Benzo(a)anthracene	1.5	2	1.2
Chrysene	2.4	3.4	1.9
Benzo(b)flouranthene	0.27	0.54	0.23
Benzo(k)flouranthene	0.05	0.04	0.05
Benzo(a)pyrene	0.06	0.1	0.06
Indeno(1,2,3.cd)pyren	0.18	<0.01	0.03
Dibenz(a,h)anthracene	<0.01	<0.01	<0.01
Benzo(g,h,i)perylene	0.04	0.07	0.05
Σ EPA16 PAH	**1,291**	**731**	**806**

Table 19 summarizes the Σ EPA16 PAH content in the gasification residue samples of the production batch after the treatment in the PAH volatilization unit in the 3rd experiment. On average, the PAH content of the processed gasification residues was 36% lower as compared to the unprocessed residues from the first experiment. The difference between the sample means (n=3) of the two analysis methods is not significant ($p < 0.05$) according to permutation version of ANOVA applied. The standard errors of the mean are indicated after each average value.

Table 19: PAH reduction in PAH volatilization unit (3rd experiment). SEM indicates standard error of the mean.

Gasification Residues	Production batch without treatment from 1st experiment	Production batch with treatment in the PAH-VU from 3rd experiment
	Σ EPA16 PAH content (DIN 13877:B, extraction with toluene)	Σ EPA16 PAH content (DIN 13877:B, extraction with toluene)
	mg/kg DM	mg/kg DM
sample 1	3,056	1,713
sample 2	1,009	1,292
sample 3	2,702	1,298
Average	**2,255 ± 516 (SEM)**	**1,434 ± 113 (SEM)**

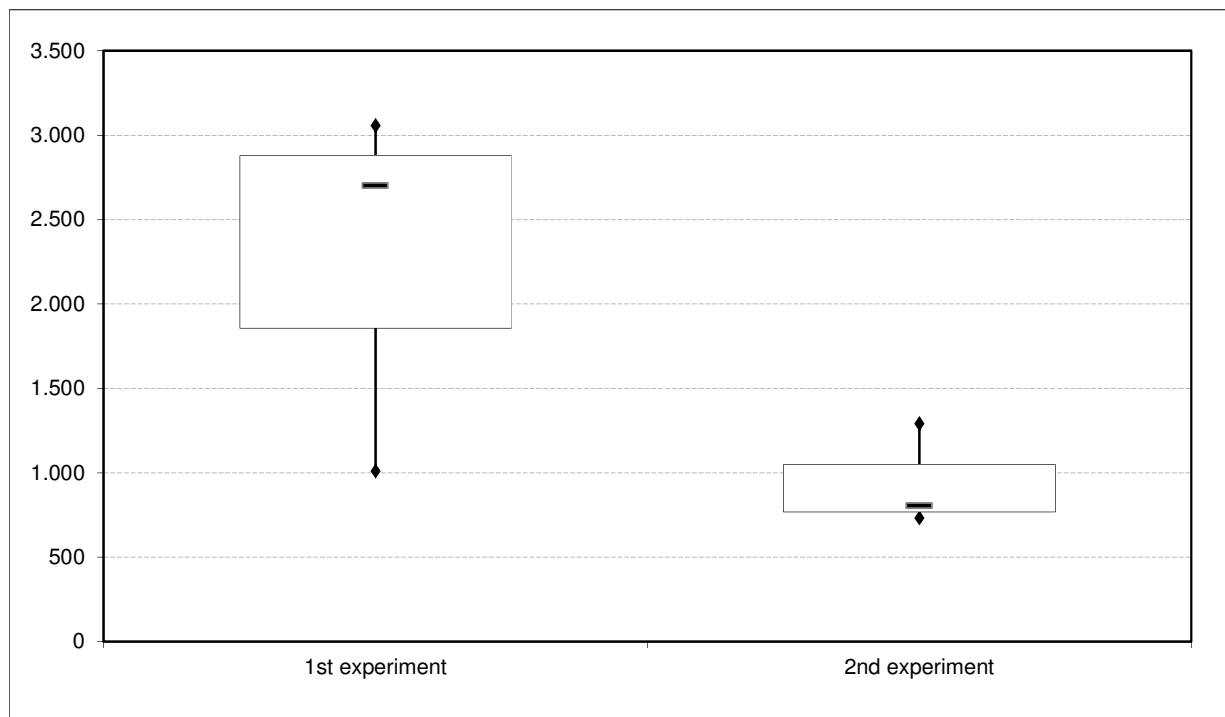Figure 10 depicts the results from Table 19 in two box-and-whisker plots:
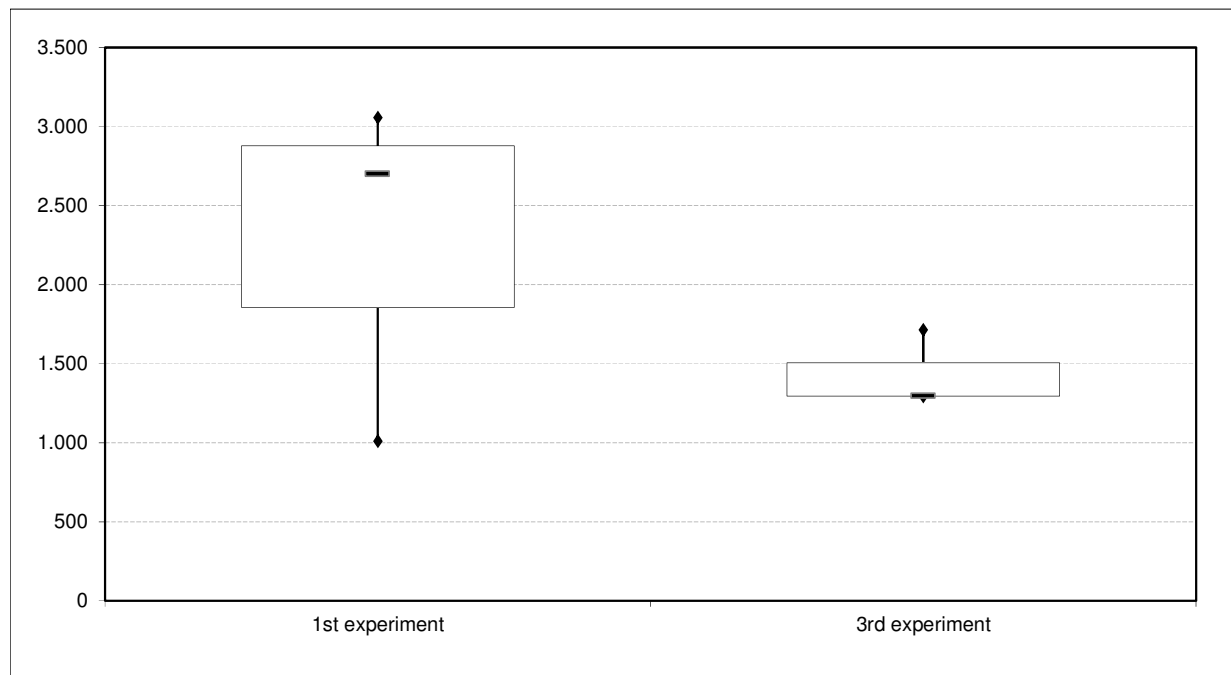
Figure 10: Boxplots indicating the median (central black bar), the minimum and maximum (lower and upper whisker) and the lower and upper quartile (lower end upper end of the box) of the Σ EPA16 PAH contents in mg/kg DM in three gasification residue samples from the 1st experiment (left) and from the 3rd experiment (right).

Table 20: PAH reduction in PAH volatilization unit (3rd experiment). Detailed results.

Gasification Residues (processed)	Σ EPA16 PAH content (DIN 13877:B)		
	Sample 1 mg/kg DM	Sample 2 mg/kg DM	Sample 3 mg/kg DM
Naphthalene	1,000	860	980
Acenaphtylene	1.1	0.47	0.52
Acenapthene	0.06	0.05	0.03
Flourene	<0.01	<0.01	<0.01
Phenanthrene	480	390	240
Anthracene	86	23	34
Flouranthen	87	12	26
Pyrene	59	6.8	17
Benzo(a)anthracene	<0.01	<0.01	<0.01
Chrysene	<0.01	<0.01	<0.01
Benzo(b)flouranthene	<0.01	<0.01	<0.01
Benzo(k)flouranthene	<0.01	<0.01	<0.01
Benzo(a)pyrene	<0.01	<0.01	<0.01
Indeno(1,2,3.cd)pyren	<0.01	<0.01	<0.01
Dibenz(a,h)anthracene	<0.01	<0.01	<0.01
Benzo(g,h,i)perylene	<0.01	<0.01	<0.01
Σ EPA16 PAH	**1,713**	**1,292**	**1,298**

4.3.3   Redesign of the PAH volatilization unit (4th experiment)

Table 21 summarizes the Σ EPA16 PAH content in the gasification residue sample of the production batch after the redesign of the PAH volatilization unit (PAH-VU) in the 4th experiment. The PAH content of the processed gasification residues was 82% lower as compared to the average PAH content in the unprocessed residues from the 1st experiment.

Table 21: PAH reduction in PAH volatilization (4th experiment). SEM indicates standard error of the mean.

Gasification Residues	Production batch without treatment from 1st experiment	Production batch with treatment in the PAH-VU from 4th experiment
	Σ EPA16 PAH content (DIN 13877:B, extraction with toluene)	Σ EPA16 PAH content (DIN 13877:B, extraction with toluene)
	mg/kg DM	mg/kg DM
sample 1	3,056	396
sample 2	1,009	
sample 3	2,702	
Average	**2,255 ± 516 (SEM)**	

Table 22: PAH reduction in PAH volatilization (4th experiment). Detailed results.

Gasification Residues (processed)	Σ EPA16 PAH content (DIN 13877:B)
	Sample 1
	mg/kg DM
Naphthalene	160
Acenaphtylene	58
Acenapthene	2.8
Flourene	12
Phenanthrene	74
Anthracene	14
Flouranthen	35
Pyrene	32
Benzo(a)anthracene	2.5
Chrysene	3.2
Benzo(b)flouranthene	0.96
Benzo(k)flouranthene	0.32
Benzo(a)pyrene	0.59
Indeno(1,2,3.cd)pyren	0.49
Dibenz(a,h)anthracene	0.1
Benzo(g,h,i)perylene	0.5
Σ EPA16 PAH	**396**

4.3.4   PAH volatilization in a laboratory scale experiment (5th experiment)

Table 9 summarizes the Σ EPA16 PAH content in the gasification residue samples treated in the laboratory scale experiment in an oxygen-free environment. Following a temperature treatment of at least 650 °C, the PAH contents in the gasification residues decreased drastically.

Table 23: PAH content in gasification residues from the laboratory scale experiment (5th experiment)

Gasification Residues	Σ EPA16 PAH content (DIN 13877:B, extraction with toluene)
	mg/kg DM
550 °C	1,000
650 °C	1.3
700 °C	0.28

Table 24: PAH content in gasification residues from the laboratory scale experiment (5th experiment). Detailed results.

Gasification Residues (processed)	Σ EPA16 PAH content (DIN 13877:B)		
	550 °C	650 °C	700 °C
	mg/kg DM	mg/kg DM	mg/kg DM
Naphthalene	590	0.77	0.18
Acenaphtylene	0.3	0.19	< 0.01
Acenapthene	1.3	< 0.01	< 0.01
Flourene	0.2	< 0.01	< 0.01
Phenanthrene	230	0.23	< 0.01
Anthracene	43	0.04	< 0.01
Flouranthen	57	0.02	< 0.01
Pyrene	57	0.03	< 0.01
Benzo(a)anthracene	6.6	< 0.01	< 0.01
Chrysene	13	< 0.01	< 0.01
Benzo(b)flouranthene	3,6	< 0.01	< 0.01
Benzo(k)flouranthene	1,3	< 0.01	< 0.01
Benzo(a)pyrene	0.95	< 0.01	< 0.01
Indeno(1,2,3.cd)pyren	2.5	< 0.01	< 0.01
Dibenz(a,h)anthracene	0.1	< 0.01	< 0.01
Benzo(g,h,i)perylene	0.56	< 0.01	< 0.01
Σ EPA16 PAH	**1,000**	**1.3**	**0.28**

4.4   Discussion

The comparison of the PAH analysis methods described in section 4.3.1 confirms the recommendation of (Hilber et al. 2012): Soxhlet extraction with toluene resulted in a much higher extraction of PAH from the gasification residues as compared to the extraction with acetone (see Table 15). Thus, analysis method DIN 13877:B was applied for the PAH analysis in the subsequent experiments 2-5.

(Min Wu et al. 2013) observed a positive correlation between the pyrolysis temperature (between 200 °C and 500 °C in the experiment carried out) applied for the production of biochars from lake sediments and the sorption of Phenanthrene to these biochars. As gasification temperatures are higher (see Meyer et al. 2011) than the pyrolysis temperatures applied in this experiment, we explain our analysis results by a strong sorption of PAH to the carbonaceous matrix of the gasification residues.

(Fabbri et al. 2013) recently compared recovery rates after reflux extraction with toluene and a 1:1 acetone/cyclohexane mixture of the three surrogate PAH Acenaphtene-d10, Phenanthrene-d_{10} and Chrysene-d_{10} which had been previously added to a pyrolysis char made form orchard pruning. The experiment resulted in higher recovery rates with the solvent toluene as compared to the solvent mixture acetone/cyclohexane for the high molecular weight PAH Phenanthrene-d10 (68% compared to 41%) and Chrysene-d10 (58% compared to 7%). The recovery rate with the solvent toluene was though lower as compared to the acetone/cyclohexane mixture for the low molecular weight PAH Acenaphtene-d_{10} (68% compared to 80%).

The differences in the recovery rates stated above are yet small if compared to our analysis results (see Table 15). Reflux extractions are usually carried out at temperatures close to the boiling point of the solvent applied. We thus presume that the strong difference in our analysis results after applying the analysis methods DIN 13877:A (low temperature extraction) and 13877:B (high temperature extraction) can be mainly explained by the temperature difference between the two extraction methods. We recommend to directly compare Soxhlet extractions with the solvents toluene and a 1:1 acetone/cyclohexane mixture for the determination of the Σ EPA16 PAH content of gasification residues for future research.

Based on the results described above, the effectiveness of the legal provisions of the German Federal Soil Protection Act (Bundesbodenschutzgesetz [BBodSchG, (Bundesministeriums der Justiz 1998)], and the German Federal Soil Protection and Contaminated Sites Ordinance (Bundesbodenschutzverordnung [BBodSchV], Bundesministeriums der Justiz 1999) for the protection of agricultural soils against PAH pollution in Germany was analyzed. Special attention was paid to the suitability of the PAH analysis methods specified in these regulations. The German Federal Soil Protection and Contaminated Sites Ordinance defines precautionary values for the PAH content of soils. These precautionary values are set at 10 mg/kg DM for the Σ EPA16 PAH content in the finely granulated part of soils with humus contents larger than 8% and at 3 mg/kg DM for the Σ EPA16 PAH content of soils with humus contents of less or equal 8%. The German Federal Soil Protection and Contaminated Sites Ordinance specifies a number of analysis methods which may be used to determine the PAH content of soils in accordance with this ordinance. Among them are the analysis methods DIN 13877:A (cold extraction with acetone) and DIN 13877:B (Soxhlet extraction with toluene). However, our analysis results in chapter 4.3.1 have clearly shown that DIN 13877:A is not suitable to determine the PAH content in gasification residues. Thus, the regulations of the German Federal Soil Protection Act and the German Federal Soil Protection and Contaminated Sites Ordinance currently cannot prevent the application of gasification residues with high PAH contents to agricultural soils, if the cold extraction with acetone is applied for their characterization. It is recommended to close this legislative loophole. Apart from that, it should be noted that there is no boundary value for PAH loads added to soil (however for the PAH content in the soil) in the German soil legislation.

While thermal processes are already used to remove PAH from contaminated soils (Harmon et al. 2001), this principle was applied for the PAH removal from wood gasification residues for the first time to our knowledge. The results displayed in Table 17, Table 19 and Table 21 indicate a reduction of the Σ EPA16 PAH content of the gasification residues by 36% to 82% after the treatment in the PAH volatilization unit. Still, the residual PAH contents in the gasification residues are too high to allow for an agricultural use.

The residual PAH content in the gasification residues was higher in the third experiment as compared to the second experiment. This result might be explained by a difference in the

PAH content of the untreated gasification residues (although these were produced under the same production conditions) or by a change in the airflow conditions within the PAH volatilization unit caused by modifications of the sealing air stream and the heating chamber air stream volumes. As already mentioned, gasification residues which had already passed through the hot heating chamber got in contact with the volatilized PAH contained in the sealing air which was blown into the lower conveyor screw. We assume that this is one of the reasons for the high residual PAH content of the gasification residues in the 2nd and 3rd experiment.

This hypothesis is supported by the comparably low PAH content of 396 mg/kg DM which was reached after the redesign of the PAH volatilization unit which prevented the recirculation of volatized PAH. Independent from the avoided recirculation effect, the increase in the air supply to the heating chamber in the 4th experiment has with high probability promoted the oxidation (combustion) of gasification residues in the heating chamber. The resulting temperature increase might have supported a more complete volatilization of the PAH from the gasification residues as compared to the 2nd and 3rd experiment.

The 5th experiment proves that thermal volatilization processes are capable in reducing the PAH content of gasification chars to levels which are acceptable for agricultural applications. It can be derived from the data presented in Table 23, that minimum process temperatures of about 650 °C are necessary for an effective removal of PAH from gasification residues.

Based on the laboratory scale experiment, the following additional technical design modifications are suggested to further improve the functional efficiency of the PAH volatilization unit:

- The gasification residues need to be sufficiently hot to allow for a complete volatilization of the PAH sorbed to the residue surfaces. In a modified heat exchanger, the hot wood gas should be used to heat the gasification residues in counter-flow principle. It should be noted in this context that the boiling temperatures of the analyzed PAH are in the range of 218 °C (naphthalene) to 536 °C (Indeno(1,2,3-cd)pyrene) (Harmon et al. 2001), (A.K. Haritash and C.P. Kaushik 2009).

- The aim of the PAH volatilization unit is to reduce the PAH content in the gasification residues. If the gasification residues can be sufficiently heated in the heat exchanger, it is not necessary anymore to supply oxygen into the PAH volatilization unit to burn a part of the residues. In this case, cheating chamber air (and perhaps sealing air as well) would not be needed anymore.

- The volatilized PAH need to be efficiently removed from the gasification residues before condensing again to the surface of the residues. If the sealing air stream is removed, there is a need for another transport method to remove the volatized PAH. It is suggested to vacuum the volatized PAH through a heat-resistant filter installed at the hottest point of the heat exchanger and thus separate them from the hot gasification residues.

Since the use of biochars in agriculture promises beneficial effects for soil amelioration and climate change mitigation (see Fischer and Glaser 2012, Meyer et al. 2012), it is recommended to continue the technical development to obtain gasifier residues with low PAH contents which might subsequently be used as soil amendment. The joint composting of gasification residues and organic feedstock sources could help to further reduce any remaining PAH in the gasification residues via biodegradation (A.K. Haritash and C.P. Kaushik 2009) and to prevent nutrient losses in the composting process. In case further experiments would affirm the viability of the preparation of gasification residues with very low PAH contents which also meet all other applicable environmental standards for soil amendments, a disposal problem could be turned into the valuable resource supply option for the agricultural sector.

4.5   Conclusion

The results endorse the suitability of PAH analysis method DIN 13877:B for the determination of the PAH content in gasification residues. Related to that, our findings give evidence that DIN 13877:A is not suitable to determine the PAH content in gasification residues. Thus, the regulations of the German Federal Soil Protection Act and the German Federal Soil Protection and Contaminated Sites Ordinance currently cannot prevent the application of gasification residue with high PAH contents to agricultural soils. It is recommended to close this legislative loophole.

A reduction of the Σ EPA16 PAH content in gasification residues by 36% to 82% was achieved by the tested PAH volatilization unit. However, the residual Σ EPA16 PAH content in the gasification residues (between 396 and 1,713 mg/kg DM) is still far too high to allow for an agricultural use of the residues. There are though promising technical redesign options available to further improve the effectiveness of the examined thermal process. In a laboratory scale experiment, the Σ EPA16 PAH content of gasification residues was reduced to values below 2 mg/kg DM following thermal processing at temperatures of 650 °C and more.

5   General Discussion

For the presented three studies, the used materials and methods and the gained results have already been discussed separately in the following chapters:

• Technical, Economical and Climate Related Aspects of Biochar Production Technologies: A Literature Review (see chapters 2.5.3, 2.6.4, 2.7.3 and 2.8)

• Albedo Impact on the Suitability of Biochar Systems to Mitigate Global Warming (see chapter 3.5)

• Thermal Removal of PAH from Gasification Biochars (see chapter 4.4)

In the following subchapters, the discussion and the subsumption of the overall results of this thesis into the current state of scientific knowledge is presented.

5.1   The development status of carbonization technologies

It is inevitable that the information presented in the literature review on the technical, economic and climate related development status of a new and rapidly evolving technology sector (see chapter 2) is limited to the identified and analyzed literature sources and that the collected information has a short half live time. For this reason, the findings of the literature review published in 2011 are compared to the most recent information published in the field in the ISI Web of Knowledge.

(Eberhardt et al. 2011) concluded that the production of HTC coal from straw and wood for energy applications is not profitable 33er the assumptions used in their ex-ante evaluation of the production cost of HTC coal in Brandenburg.

In a Taiwanese case study, (Chih-Chun Kung et al. 2013) calculated negative net margins for the operation of slow and fast pyrolysis plants fed by wood from poplar grown on set aside land when taking into account revenues from electricity sales and the agricultural value of the produced biochar.

In line with the results presented in chapter 2.6.4, (Field et al. 2013) draw the conclusion that the use of char for energy provision yields higher revenues as compared to its use as soil amendment under the assumptions used in their model calculation. As prices for fossil

energy carriers are expected to further increase in future and bioenergy and biochar producers in many cases depend on the same resource basis, the bioenergy sector thus will with high probability remain a strong competitor for the biochar production sector.

(Wiedner et al. 2013) presents principal technical parameters about commercial pyrolysis units, gasifiers and htc units of five different European technology providers which aim at the production of chars for agricultural applications. This publication stresses the lower black carbon content of chars from hydrothermal carbonization (hydrochars) as compared to the chars from pyrolysis and gasification processes. As the black carbon content of char correlates with the stability of the chars, it is expected that the hydrochars examined are less stable compared to the chars from pyrolysis and gasification. This was confirmed by a direct comparison between the $^{13}CO_2$ efflux of soils added with pyrolysis biochar and hydrochar (both made from Miscanthus) as carried out by (Bai et al. 2013). Similar results regarding the stability difference between pyrolysis chars and chars from hydrothermal carbonization have been obtained by (Malghani et al. 2013).

Since the publication of the literature review in 2009 (see chapter 2), no additional scientific information on the flash carbonization technology has been published. It is not clear whether this technology is still being further developed.

In summary, published scientific information on the technical maturity and the economical probability of carbonization technologies is still scarce. This can be partly explained by the interest of technology manufactures to protect their technology expertise. The information presented in scientific case studies is only valid for the selected assumptions and cannot be generalized over regions, technologies and time. While the number of commercial installations for biochar production in Central Europe has been increasing over the last three years, the biochar market expansion is still substantially limited by the technical maturity and the economic competitiveness of biochar production technologies.

5.2   PAH levels in gasification biochars

(Wiedner et al. 2013) found comparably low PAH contents (up to 15 mg/kg Σ EPA16-PAH) in gasification biochars. As the analysis method DIN 13877:A (cold extraction with a mixture of acetone and cyclohexane) was used for this assessment, this fits with the results presented in chapter 4.3. It is expected that higher PAH contents would have been found in the same

gasification biochar samples, if analysis method DIN 13877:B (Soxhlet extraction with toluene) would have been applied.

In a Tradescantia genotoxicity assay, (Busch et al. 2013) observed a highly significant increase in the mean percentage of micronuclei from Tradescantia pollen cells after exposing Tradescantia flowers to a filtrate from the mixture of distilled water and a pyrolysis biochar produced at a temperature of ~450 °C with a high PAH content (62,7 mg/kg Σ EPA16-PAH, PAH analysis method: Soxhlet extraction with toluene, Hilber et al. 2012). While the observed genotoxic effects of the pyrolysis biochar on the Trandescantia plants cannot be attributed to the high PAH content of the biochar with certainty, this test clearly indicates the presence of mutagenic pollutants in the filtrate. In the same study, no statistically significant increase in the mean percentage of micronuclei was observed after exposing Tradescantia flowers to a filtrate from the mixture of distilled water and gasification residues (from gasifiers of the company A.G.T. in Arioso, Italy). The PAH contents of these gasification residues have not been examined in this publication, but they have been published in (Wiedner et al. 2013): The gasification residues contained up to 2 mg/kg Σ EPA16-PAH (PAH analysis method: cold extraction with a mixture of acetone and cyclohexane according to DIN 13877:A). As already stated above, the low identified PAH contents in the gasification residues might partly result from the application of the cold extraction method.

(Patryk Oleszczuk et al. 2014) discovered high PAH contents (between 1.8 and 101.3 mg Σ EPA16-PAH / kg soil) in soils close (5-10m distance) to portable charcoal ring kilns without exhaust gas combustion / cleaning unit. Due to a large variation in the PAH contents of the soil sample, the authors assume that at least a part of the soil samples might have gotten in direct contact with charcoal particles or the liquid byproducts of the pyrolysis process.

The cited publication underline the necessity to choose appropriate methods for the analysis of the PAH content in carbonaceous analysis samples and to be aware of all potential PAH emissions streams of biochars systems. With respect to the PAH volatilization unit examined in chapter 4, this implies that the gas stream with the volatized PAH need to be fed into a high temperature zone to enable a complete break-up / combustion of these PAH.

5.3   The overall climate impact of biochar systems

(Jorge Laine 2012) proposes to use coke by-products from the refinement of nonconventional fossil hydrocarbon reserves to change the surface albedo in arid regions in the hope that a large scale regional albedo change would increase the annual precipitation over this area. While the effectiveness of the presented concept with regard to the local climate shall not be discussed here, the suggested approach would have an adverse effect on the global climate: The decrease in the surface albedo would increase the radiative forcing (see chapter 3.3.2.3), thereby directly enforcing climate change. Besides of that, the use of the coke might provide additional financial returns to fossil fuel industry. This underlines the necessity to take into account albedo changes if the climate impact of large scale surfaces changes shall be assessed.

The climate impact of the albedo change associated with biochar application is not yet sufficiently reflected in the sustainability discussion of biochar systems. In a recent publication with the title *"Biochar as a Geoengineering Climate Solution: Hazard Identification and Risk Management"* by (Downie et al. 2012), the albedo impact of biochar systems is not even mentioned. It seems that the current focus on the GHG balance of biochar systems obstructs the perception of the other radiative forcing impacts of biochar systems. In this respect, the scientific understanding of the climate impacts of bioenergy systems is already more advanced (see Bright et al. 2012).

It should however be mentioned that the very recently published work of (Verheijen et al. 2013) confirms the (negative) impact of albedo changes on the climate mitigation potential of biochar systems: In this article, the authors calculated a reduction of the negative radiative forcing impact of biochar systems by 5 to 95% after accounting for the albedo impact of the biochar application.

The work of (Geoffrey Guest et al. 2013) underlines the need to take the rotation period of the biomass crops used for biochar production into consideration when the climate impact of biochar systems is evaluated (see the approach as taken in chapter 3.3.3.1):
<u>Carbon neutrality does not equal climate neutrality</u> in case there is a longer time period between the emission and the sequestration of biogenic carbon.

In spite of that, the recent publication of (Chih-Chun Kung et al. 2013) calculates the GHG balance of a modeled pyrolysis biochar system in Taiwain without taking into account the climate impact of the temporal shift between biogenic carbon emissions and the carbon sequestration.

In retrospect, it also has to be stated that none of the GHG balances presented in chapter 2.7 have considered the climate impact of this temporal shift. Thus, the GHG balances presented in chapters 2.7 and 2.1 need to be complemented if the net GHG emission equivalent impact (as calculated over a 100 year time horizon) resulting from biochar production and application within the analyzed biochar systems shall be correctly assessed. This holds as well for climate impact assessments of reductions in soil GHG emissions and of GHG reductions connected to avoided fertilizer use, in case these GHG reductions are distributed over time.

(Saadatullah Malghani et al. 2013) reported that the addition of slow pyrolysis char made from corn to agricultural soils slightly decreased the reference soil CO_2 - emissions (from agricultural soils without biochar addition) within the observed incubation period of 105 days. In the same experiment, htc char made from corn increased the reference soil CO_2 - emissions by 266 percent. This is in line with earlier observations of Kammann 2012 #107 already mentioned in chapter 3.2. Interestingly, (Case et al. 2013) found out that soil CO_2 - emissions of a pyrolysis char-amended Miscanthus cropping system decreased by 33% compared to the control within a time period of two years. If this trend would continue in the long term, the climate impact of biochar system might be even more favorable as presented in chapter 3 (see also Table 13), since a positive impact of biochar addition on the soil inherent organic carbon content has not been taken into account in the presented assessment.

(Bai et al. 2013) estimated comparably low half-live periods (about 18-45 years) for the decay of pyrolytic biochars from Miscanthus in temperate soils in an empirical model. While lower residence times reduce the cumulated albedo impact of biochar systems, they clearly also reduce the carbon sequestration benefit of biochar systems. The impact of half-live periods of the decay of biochar on the overall climate impact of biochar systems thus may not be underestimated.

The approved summary for policymakers of the Working Group I Contribution to the IPCC Fifth Assessment Report Climate Change 2013 (Intergovernmental Panel on Climate Change 2013) outlines the radiative forcing impact resulting from black carbon particles in the atmosphere. A scientific quantification of the radiative forcing impact of atmospheric carbon particle emissions from the production and handling of biochar is not available yet. However, atmospheric carbon particle emissions from biochar system can be minimized if modern production technologies are used and if the handling processes are optimized (e.g. the combined composting of biomass and biochar reduces the risk for atmospheric carbon particle emissions when the final product is applied to the field).

All in all, it can be concluded that a comprehensive analysis of the climate impact of biochar systems needs to take into account additional climate impact factors which have mostly not been accounted for in earlier GHG balances.

5.4 Expanding the point of view

Downie 2012 #162 /textcit lists a variety of ecological risks of biochar systems, which need to be mitigated, but have not been discussed in this thesis:

- Adverse environmental impacts connected with direct and indirect effects of the biomass provision for biochar production
- Feedstock contamination and biochar contamination with heavy metals and organic compounds (except of PAH which have been discussed in this thesis)
- Air pollution and health hazards connected to biochar production, transport and biochar handling.

On the other hand, the following additional ecological benefits of biochar systems not discussed in this thesis shall be mentioned as well:

- Biochar addition to composting processes can help to reduce nutrient losses during composting
- Reductions in fertilizer use due to the prevention of nutrient losses help to reduce resource and energy consumption
- There is evidence from field trials that the soil inherent organic carbon content of arable soils increased after the application of compost-biochar mixtures.

6   Overall Conclusions

The introduction of new concepts and technologies aiming for the protection of the environment is often accompanied by great hope and high expectations connected with the propagated ecological benefits. The situation has not been different in the early years of "biochar boom" (see for example Lehmann 2007). After the first time of enthusiasm, typically more critical research results are published and critics are eager in highlighting the pitfalls of the well-intended "green revolution". Yet with the progress of time, the scientific knowledge on the numerous and complex interactions of biochar systems with their environment has been increasing and a more precise – though far from being complete – assessment of the ecological benefits and risks of biochar systems is possible today. In this chapter, the overall conclusions of this thesis are structured by the research scopes of the three research articles presented in this thesis.

The following conclusions can be drawn from the literature review on the technical, economical and climate-related aspects of biochar production technologies (see chapter 2):

- Theoretical model assumptions on the availability of carbonization technologies tend to overestimate empirical availability data.

- The financial benefits of biochar application occur over a long period of time. In a short term perspective, biochar systems often struggle to reach a profitable operation. For this reason, market niches and cascade applications are important for the further development of biochar markets.

- The bioenergy sector is strong competitor for the use of biochar products due to the high prices paid on the energy markets.

- The use of biomass residues for biochar production increases the profitability and reduces the ecological footprint of biochar production.

- The reviewed GHG balances of biochar systems mainly calculate net GHG savings for biochar systems, however, the considered GHG sources and sinks vary considerably.

- None of the reviewed GHG balances considered the following climate impact factors in their assessment: The climate impact of the temporal shift between biogenic carbon emissions and the carbon sequestration, the albedo impact of biochar

application and the impact of biochar application on the atmospheric soot concentration.

The following conclusions can be drawn from the assessment of the albedo impact on the suitability of biochar systems to mitigate global warming (see chapter 3):

- An annual average mean surface albedo reduction of 0.05 was simulated following the application of 30-32 Mg/ha^{-1} biochar to arable land under wheat cultivation near Bayreuth.

- The climate impact of the albedo change reduced the overall climate benefit (0.5 – 0.7 t CO_2e / t dry biomass input) of our modeled biochar system by 13 - 22%.

- The climate impact of the albedo change induced by biochar application strongly depends on the development of the surface albedo in time.

- The albedo impact of agricultural systems (with and without biochar use) on the climate can be reduced when periods without vegetation cover on the fields are minimized.

- The temporal impact of biochar and bioenergy systems on the carbon cycle needs to be addressed in climate impact assessments.

- The impact of biochar application on soil N_2O emissions plays an important role for the overall climate impact of biochar systems.

- The (positive) climate impact of biochar systems was in the same order of magnitude as compared to the climate impact of bioenergy system under the assumptions used in our model calculation.

- Additional research is needed to determine the impact of biochar application on biomass yields, soil methane emissions, soil inherent organic carbon content and atmospheric soot concentration to complement the climate impact assessment carried out.

The following conclusions can be drawn from the analysis of the thermal removal of polycyclic aromatic hydrocarbons from gasification biochars (see chapter 4):

- The selection of the appropriate PAH analysis method is crucial when analyzing gasification residues.

- DIN 13877:A (cold extraction with acetone) is not suitable to comprehensively determine the PAH content in gasification residues. The hot Soxhlet extraction method (as applied in DIN 13877:B) is better suited for PAH analysis of gasification residues.

- There is a loophole in the German soil protection legislation with regard to the permitted PAH analysis methods which needs to be closed.

- PAH contents in wood gasification residues can be very high (up to a Σ EPA16-PAH content of more than 3 000 mg/kg dry mass.

- Wood gasification residues are available at negative costs, if they have to be disposed due to their PAH contamination.

- In laboratory experiments, it was proven that the PAH content of heavily polluted gasification residues can be reduced to Σ EPA16-PAH values below 1 mg/kg dry mass by a thermal volatilization process.

- This process has not yet been successfully scaled up to be implemented as an add-up to commercial wood gasifiers. However, there are promising technical redesign option available for this purpose.

- If a standardized PAH volatilization unit in form of an add-up for small-scale wood gasifiers is developed, special care has to be taken to guarantee the effectiveness of the PAH cleaning process under a broad range of operation conditions.

To draw a single main conclusion of this thesis: biochar systems can play a very helpful role for the management of the environment if its risks are mitigated and if the application of biochar systems is not abused as an excuse for delayed action in other areas.

Due to the diversity of interactions between biochars systems and the environment and due the limitations of this thesis with regard to its scope and with regard to the present state of scientific knowledge, future research activities are necessary to continuously re-evaluate and complement the conclusions presented here.

7   Summary

The concept of carbonizing biomass and using the obtained product for soil amelioration and carbon sequestration – the so called "biochar system" - has gained much attention in the research community as well as in the media in the last years. The attractiveness of this concept can be explained by its promise to contribute to climate change mitigation and to foster food security at the same time. It is though foreseeable that an increase in biochar production will trigger critical questions on the realizable ecological benefits and the potential negative environmental effects of biochar systems. Answering these questions in an early stage of the market development might both help to avoid steering into an ecological dead-end and to optimize potential future support schemes for biochar systems. The objective of this thesis is thus an evaluation of ecological benefits and risks of biochar systems. The scope of the thesis was limited to impacts of biochar systems on the climate system and on the potential impact of biochar systems on the polycyclic aromatic hydrocarbons (PAH) level in soils. This thesis contains three separate studies which are summarized below.

In the first study, peer-reviewed scientific articles on carbonization technologies (pyrolysis, gasification, hydrothermal carbonization, and flash carbonization) have been analyzed. It is evident that theoretical model assumptions on the technical availability of carbonization technologies stated in the reviewed articles tend to overestimate empirical availability data. A wide range of data on the costs of char production (between 51 US$ per tonne pyrolysis biochar from yard waste and 386 US$ per tonne retort charcoal) has been published. The financial benefits of biochar application generally occur over a long period of time. When evaluated on a short term perspective, biochar systems thus often struggle to reach a profitable operation. In addition to that, the bioenergy sector is strong competitor for the use of biochar products due to the high prices paid on the energy markets. For this reason, market niches and cascade applications are important for the further development of biochar markets. Besides of that, the use of biomass residues for biochar production increases the profitability and reduces the ecological footprint of biochar production. The reviewed greenhouse gas (GHG) balances of biochar systems mainly calculate net GHG savings for biochar systems, however, the considered GHG sources and sinks vary considerably. The reviewed results are in a range of 1,054 kg CO_2e emission savings per t dry

biomass feedstock up to an emission increase of +123 kg CO_2e per t dry biomass feedstock. However, none of the reviewed GHG balances has considered the factors in their assessment: the climate impact of the temporal shift between biogenic carbon emissions and carbon sequestration, the albedo impact of biochar application and the impact of biochar application on the atmospheric soot concentration. Thus, at the time of publication of the first study, it could not be ruled out that a decrease in the surface albedo caused by biochar field application might overcompensate the climate mitigation benefits of biochar systems.

To quantify this risk, the second study was carried out: Based on empirical albedo measurements and literature data of arable soils mixed with biochar, a model for annual vegetation cover development (wheat cultivation) based on satellite data and an assessment of the annual development of surface humidity, an average mean annual albedo reduction of 0.05 has been calculated for applying 30–32 Mg ha^{-1} biochar on a test field near Bayreuth, Germany. The impact of biochar production and application on the carbon cycle and on the soil albedo was integrated into the greenhouse gas balance of a modeled pyrolysis-based biochar system via the computation of global warming potential (GWP) characterization factors. The analysis resulted in a reduction of the overall climate mitigation benefit of biochar systems by 13–22% due to the albedo change as compared to an analysis which disregards the albedo effect. Comparing the use of the same quantity of biomass in a biochar system to a bioenergy district heating system which replaces natural gas combustion, bioenergy heating systems achieve 99–119% of the climate benefit of biochar systems according to the model calculation. It was found out that the climate impact of the albedo change induced by biochar application strongly depends on the development of the surface albedo in time. In general, the albedo impact of agricultural systems (with and without biochar use) on the climate can be reduced when periods without vegetation cover on the fields are minimized. It also can be concluded from the model calculation that the impact of biochar application on soil N_2O emissions plays a decisive role for the overall climate impact of biochar systems. While a comprehensive consideration of temporal impact of biochar systems on the carbon cycle is essential to assess the overall climate impact of these systems, this impact is still very insufficiently reflected in the present scientific sustainability literature about biochar systems. Additional research is needed to determine the impact of biochar application on biomass yields, soil methane emissions, soil inherent organic carbon

content and atmospheric soot concentration to complement the climate impact assessment carried out.

Since the results of the literature review highlighted the economic and climate-related advantages of using biogenic residues for biochar production, a critical evaluation of the opportunity of utilizing carbonaceous wood gasification residues as soil amendment was set in the focus of the third study. Since wood gasification residues often contain large amounts of persistent and carcinogenic polycyclic aromatic hydrocarbons, this study evaluated the efficiency of a recently developed thermal process (called PAH volatilization unit) designed to remove PAH from gasification residues. As a precondition for this evaluation, the suitability of the PAH analysis methods DIN 13877:A and DIN 13877:B for the determination of the PAH content in wood gasification residues had to be checked. The results endorse the suitability of PAH analysis method DIN 13877:B for the determination of the PAH content in gasification residues. Related to that, the findings gave evidence that DIN 13877:A is not suitable to determine the PAH content in gasification residues. As the latter analysis method is legally applicable under the German Federal Soil Protection and Contaminated Sites Ordinance, this regulation cannot prevent the application of gasification residue with high PAH contents to agricultural soils. It is thus recommended to close this legislative loophole. A reduction of the Σ EPA16 PAH content in gasification residues by 36% to 82% was achieved by the tested PAH volatilization unit. However, the residual Σ EPA16 PAH content in the gasification residues (between 396 and 1,713 mg/kg DM) is still far too high to allow for an agricultural use of the residues. There are though promising technical redesign options available to further improve the effectiveness of the examined thermal process. In a laboratory scale experiment, the Σ EPA16 PAH content of gasification residues was reduced to values below 2 mg/kg DM following thermal processing at temperatures of 650 °C and more.

The overall results of this thesis suggest that biochar systems can play a very helpful role for the management of the environment if its risks are mitigated and if the application of biochar systems is not abused as an excuse for delayed action in other areas.

8 Zusammenfassung

Die Herstellung von biogener Kohle und ihr Einsatz zur Aufwertung landwirtschaftlicher Böden sowie zur Kohlenstoffsequestrierung im Rahmen sogenannter Biokohle-Systeme hat in den letzten Jahren viel Aufmerksamkeit in der wissenschaftlichen Forschung und in den Medien erhalten. Die Attraktivität dieses Konzepts lässt sich damit erklären, dass Biokohle-Systemen die Fähigkeit zugeschrieben wird, dem anthropogenen Klimawandel entgegenzuwirken und zugleich einen Beitrag zur Ernährungssicherheit zu leisten. Schon heute ist jedoch absehbar, dass ein Anstieg der Biokohleproduktion kritische Fragen zu dem dadurch tatsächlich erzielbaren ökologischen Nutzen sowie zu den möglichen ökologischen Nebenwirkungen von Biokohlesystem hervorrufen wird. Eine frühzeitige Beantwortung dieser Fragen kann dazu beitragen, ökologische Sackgassen zu vermeiden und mögliche zukünftige Förderprogramme für Biokohle-System optimal auszugestalten.

Die Bewertung der ökologischen Chancen und Risiken von Biokohle-Systemen ist daher Forschungsgegenstand dieser Dissertation. Der Forschungsfokus wurde hierbei auf die Auswirkungen von Biokohlesystemen auf den Treibhauseffekt und auf die Akkumulierung von polyzyklischen aromatischen Kohlenwasserstoffen in landwirtschaftlichen Böden gesetzt. Diese Dissertation besteht aus drei Einzelstudien, die aufeinander aufbauen und im Folgenden zusammengefasst werden.

Im Rahmen der ersten Studie wurden wissenschaftliche Peer-Review-Veröffentlichungen zu den Karbonisierungsverfahren Pyrolyse, Vergasung, Hydrothermale Karbonisierung und Flash-Karbonisierung systematisch ausgewertet. Die in den Veröffentlichungen dargestellten Treibhausgasbilanzen des Einsatzes der Biokohlesysteme resultieren (insbesondere beim Einsatz von biogenen Reststoffen) meist in einer Nettominderung der Treibhausgas-konzentration in der Atmosphäre. Hierbei ist jedoch anzumerken, dass zwischen den Studien eklatante Unterschiede in Bezug auf die berücksichtigten Treibhausgasquellen und Treibhausgassenken bestehen. Die Bandbreite der analysierten Treibhausgasbilanzen reicht von einer Nettoemissionsminderung in Höhe von 1054 kg CO_2e pro Tonne biogener (Input)-Trockenmasse bis zu einer Nettoemissionssteigerung in Höhe von 123 kg CO_2e pro Tonne biogener (Input)-Trockenmasse. Es muss allerdings konstatiert werden, dass keine der analysierten Treibhausgasbilanzen die folgenden klimarelevanten Faktoren in die Bewertung der Biokohlesysteme mit einbezogen hat: Die klimatischen Auswirkungen der zeitlichen

Differenz zwischen der Emission und der Sequestrierung biogenen Kohlenstoffs, die Auswirkungen von Albedoänderungen, die durch die Biokohleapplikation hervorgerufen werden; sowie den Einfluss der Biokohleanwendung auf den atmosphärischen Gehalt an Black Carbon. Zum Zeitpunkt der Veröffentlichung der ersten Studie konnte daher nicht ausgeschlossen werden, dass der positive Effekt von Biokohle-System auf die Treibhausgaskonzentration (und damit auf den Treibhauseffekt) nicht durch die (den Klimawandel verstärkende) Abnahme der Oberflächenalbedo aufgrund von Biokohleapplikationen ins Gegenteil verkehrt wird.

Um dieses Risiko quantifizieren zu können, wurde die zweite Studie durchgeführt. Anhand von eigenen Albedomessungen und von Literaturdaten zu Ackerflächen, die mit Biokohle vermischt worden waren, wurde eine durchschnittliche jährliche Minderung der Oberflächenalbedo in Höhe von 0,05 auf einem Versuchsfeld (nach einer Biokohleapplikation in Höhe von 30-32 Mg ha^{-1}) nahe Bayreuth in Deutschland berechnet. Hierbei wurden der jährliche Verlauf der Vegetationsentwicklung (Weizenanbau) anhand einer Auswertung von Satellitendaten und der Jahresverlauf der Entwicklung der Bodenfeuchtigkeit anhand von meteorologischen Messdaten berücksichtigt. Der Einfluss der Biokohleproduktion auf den Kohlenstoffkreislauf sowie auf die Oberflächenalbedo wurde in die Treibhausgasbilanz eines modellierten Pyrolyse-Biokohle-Systems anhand der Berechnung von Treibhausgas-Charakterisierungsfaktoren mit einbezogen. Diese Analyse ergab eine Reduktion des Treibhausgasminderungspotenzials von Biokohlesystemen um 13-22%, wenn der Albedo-Effekt in die Berechnung mit einbezogen wurde. Bei einem direkten Vergleich zwischen der Produktion von Biokohle und der Bereitstellung von Bioenergie für ein Erdgas-befeuertes Fernwärmenetz erzielte das Bioenergiesystem unter den gewählten Annahmen 99–119% des Treibhausgasminderungspotenzials des Biokohlesystems. Es zeigte sich, dass die Klimawirkung von Albedominderungen aufgrund von Biokohleapplikationen sehr stark von der langfristigen Entwicklung der Oberflächenalbedo abhängig ist. Allgemein gilt, dass die Klimawirkung der (oftmals niedrigen) Albedo landwirtschaftlichen Böden durch Bewirtschaftungsverfahren mit ganzjähriger Bodenbedeckung optimiert werden kann. Die Berechnungen ergaben weiterhin, dass der Einfluss von Biokohlegaben auf die Lachgasemissionen der Böden eine entscheidende Rolle für Gesamtklimabilanz von Biokohlesystemen spielt. Obwohl die Berücksichtigung der klimatischen Auswirkungen der zeitlichen Differenz zwischen der Emission und der Sequestrierung biogenen Kohlenstoffs

(„CO_2-neutral ist nicht zwingend auch klimaneutral") essentiell für die Bewertung der Klimawirksamkeit von Biokohlesystemen ist, findet dieser Einflussfaktor bislang nur eine unzureichende Berücksichtigung in der derzeit veröffentlichten wissenschaftlichen Literatur zu diesem Themenkomplex.

Da die Ergebnisse der Literaturauswertung die ökonomischen und ökologischen Vorteile einer Biokohleproduktion auf Basis biogener Reststoffe in den Vordergrund gerückt hatten, wurde der Fokus der dritten Studie auf eine kritische Bewertung der Option des Einsatzes von Holzvergaserrückständen als Bodenhilfsstoff gesetzt. Da Holzvergaserkohlen oftmals hohe Gehalte an persistenten und krebserregenden PAK aufweisen, wurde in dieser Untersuchung die Effektivität eines kürzlich entwickelten thermischen Verfahrens zur Reinigung von Vergaserkohlen untersucht. Im Vorfeld für diese Bewertung wurde die Eignung der PAK-Analysemethoden DIN 13877:A und DIN 13877:B für die Bestimmung der PAK-Gehalte in Vergaserkohlen untersucht. Hierbei zeigte sich, dass DIN 13877:A für diesen Zweck nicht geeignet ist. Da diese Methode derzeit jedoch noch für Analysen gemäß der Bundesbodenschutzverordnung zulässig ist, wird empfohlen, diese Gesetzeslücke zu schließen. Durch das getestete thermische Verfahren konnte eine Minderung des Σ EPA16 PAK - Gehaltes in Vergasungsrückständen um 36 - 82% erzielt werden. Die verbleibenden PAK-Gehalte in den Vergasungsrückständen waren jedoch immer noch viel zu hoch (zwischen 396 und 1.713 mg/kg Trockenmasse), um eine landwirtschaftliche Verwertung der Rückstände zuzulassen. Allerdings sind vielversprechende technische Verfahrensanpassungen verfügbar, um die Effektivität des Prozesses weiter zu steigern. Im Labormaßstab ist es durch eine thermische Behandlung der Vergasungsrückstände bei Temperaturen über 650 °C gelungen, den Σ EPA16 PAK – Gehalt in den Rückständen auf Werte unter 2 mg/kg Trockenmasse zu reduzieren.

Die Forschungsergebnisse dieser Dissertation deuten darauf hin, dass der Einsatz von Biokohle-Systemen eine hilfreiche Rolle bei der Bewältigung drängender ökologischer Herausforderungen spielen kann, wenn die Umweltrisiken der Biokohleproduktion minimiert werden und der Einsatz von Biokohlesystemen nicht als Vorwand für die Verschleppung der ökologischen Transformation in anderen Handlungsfeldern verwendet wird.

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10 Appendix

Erklärung

Hiermit erkläre ich, dass ich meine Arbeit selbständig und ohne fremde Hilfe verfasst habe, keine anderen als die von mir angegebenen Quellen und Hilfsmittel benutzt habe und die den benutzten Werke wörtlich oder inhaltlich entnommenen Stellen als solche kenntlich gemacht habe.

Ich habe weder vergebliche Promotionsversuche unternommen noch die Dissertation in der gegenwärtigen bzw. in einer anderen Fassung bereits einer anderen Fakultät vorgelegt.

Des Weiteren erkläre ich, dass keine Strafverfahren gegen mich anhängig sind.

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