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Biochar potentially mitigates greenhouse gas emissions from cultivation of oilseed rape for biodiesel

Keywords: Biochar; Biodiesel; Carbon sequestration factor; Greenhouse gasses; Life cycle assessment; Oilseed rape

Abstract

Winter oilseed rape (WOSR) is the main crop for biodiesel in the EU, where legislation demands at least 50% savings in greenhouse gas (GHG) emissions as compared to fossil diesel. Thus industrial sectors search for optimized management systems to lower GHG emissions from oilseed rape cultivation. Recently, pyrolysis of biomass with subsequent soil amendment of biochar has shown potentials for GHG mitigation in terms of carbon (C) sequestration, avoidance of fossil based electricity, and mitigation of soil nitrous oxide (N₂O) emissions. Here we analyzed three WOSR scenarios in terms of their global warming impact using a life cycle assessment approach. The first was a reference scenario with average Danish WOSR cultivation where straw residues were incorporated to the soil. The others were biochar scenarios in which the oilseed rape straw was pyrolysed to biochar at two process temperatures (400 and 800°C) and returned to the field. The concept of avoided atmospheric CO₂ load was applied for calculation of C sequestration factors for biochar, which resulted in larger mitigation effects than derived from calculations of just the remaining C in soil. In total, GHG emissions were reduced by 73 to 83% in the two biochar scenarios as compared to the reference scenario, mainly due to increased C sequestration. The climate benefits were higher for pyrolysis of oilseed rape straw at 800 than at 400°C. The results demonstrated that biochar has a potential to improve the life cycle GHG emissions of oilseed rape biodiesel, and highlighted the importance of consolidated key assumptions, such as biochar stability in soil and the CO₂ load of marginal grid electricity.

1. Introduction

Oilseed rape (*Brassica napus* L.) is the main feedstock for production of biodiesel in the European Union (EU) countries (EUBIA, 2019). Life cycle assessments (LCA) of the sustainability of rapeseed biodiesel have identified the cultivation step as hotspot of greenhouse gas (GHG) emissions associated with rapeseed production and conversion to biodiesel (Boldrin and Astrup, 2015; Fischer et al., 2010; Thamsiriroj and Murphy, 2010). Further, it has been found that direct field emissions of nitrous oxide (N₂O) typically represent 33-55% of the total GHG emissions (in CO₂ equivalents, CO_{2eq}) related to the oilseed rape cultivation step (Elsgaard et al., 2013; Malça et al., 2014; Queirós et al., 2015). Therefore, to improve the GHG emission profile of biodiesel production, field managements are pursued, which hold a potential for mitigating N₂O emissions. In the EU countries, this incentive is reinforced by the EU Renewable Energy Directive (RED), which requires that GHG emissions from production of renewable biofuels, such as biodiesel, must be at least 50% lower as compared to the use of fossil fuels (European Parliament, 2009).

Recently, the use of biochar has been suggested as a management option that may lower direct field emissions of N₂O, although there are uncertainties regarding the specific mechanism(s) involved (Cayuela et al., 2014; Feng et al., 2018). Biochar is the solid carbonaceous residue resulting from thermal conversion of biomass under limited or zero oxygen conditions typically by gasification or pyrolysis (Criscuoli et al., 2014; Laird et al., 2009). Notoriously, biochar has different chemical and physical properties depending on the biomass feedstock and the conversion technology, e.g., related to process temperatures and duration of the thermal treatment (Angin, 2013; Chen et al., 2016; Wang et al., 2012). Yet, meta-analysis of empirical data showed that biochar on average reduced N₂O emissions by

54% in laboratory studies and 28% in field studies (Cayuela et al., 2015). Further, in relation to GHG mitigation, biochars collectively represent a kinetically stable carbon (C) pool (Wang et al., 2016) that may contribute to C sequestration when added to soil (Field et al., 2013). Likewise, the syngas and bio-oils produced during the thermal biomass conversion may be combusted to replace fossil energy and in this way mitigate net CO₂ emissions (Lugato et al., 2013).

Previous studies have detailed the GHG balance of oilseed rape cultivation for biofuel production without including biochar scenarios. Malça et al. (2014) and Queirós et al. (2015) addressed the role of N₂O emissions, while also considering the role of soil C stock changes, which turned out to be crucial for the overall results. Likewise, studies of pyrolysis processes and biochar in relation to other cropping systems have documented the importance of soil C sequestration in the overall GHG balances (Hammond et al., 2011; Wang et al., 2014). Wang et al. (2014) showed that increased biochar output at the expense of decreased energy production in the pyrolysis process resulted in lower net GHG emissions. Sigurjonsson et al. (2015) analyzed the consequences of utilization of wheat straw for energy in a wheat grain production system including scenarios where straw biochar was returned to the soil. They applied the concept of avoided atmospheric CO₂ load for quantifying the effect of biochar C sequestration (Sigurjonsson et al., 2015), using a methodology originally proposed by Petersen et al. (2013) for calculation of C sequestration factors in relation to lost C sequestration due to wheat straw removal. Yet, whereas the methodology may be used in the context of biochar, there is so far a lack of documented C sequestration factors derived for biochar in relation to specific biochar properties.

The aim of the present study was to provide a consolidated background for evaluating the sustainability of oilseed rape cultivation for biofuel in a future scenario with biochar-amended soil agroecosystems. This included recirculation of straw to biochar by the use of pyrolysis

technology in consideration of (i) potential N₂O mitigating effects, (ii) avoided electricity production, and (iii) avoided atmospheric CO₂ load in two biochar scenarios, hereby also addressing the consequences of different partitioning strategies between biochar, syngas and bio-oil. Notably, we aimed to provide C sequestration factors for biochar in relation to assumed, but well-defined, biochar properties as basis for comparison in future studies adopting the same methodology. The C sequestration factors derived for the two biochar scenarios were included in a life cycle assessment (LCA) regarding the global warming potential (GWP) of the average Danish winter oilseed rape (WOSR) cultivation with and without straw recirculation via biochar.

2. Methods

2.1. Scope and system boundaries

This study applied an LCA approach to compare the GHG emissions of Danish WOSR cultivation in a reference scenario and two scenarios with biochar (BC) produced at 400°C (BC-400) and 800°C (BC-800). The two biochar production temperatures were included to represent two alternative strategies in feedstock C conversion, e.g., in terms of biochar quantity and properties (Karaosmanoğlu et al., 2000). All scenarios included typical Danish WOSR cultivation with related field and upstream emissions as outlined in Fig. 1 and documented in Table 1 in terms of inventory data and their sources (see also Elsgaard, 2015). The two biochar scenarios further included baling, transport to and from the pyrolysis plant (straw and biochar), biochar application, N₂O mitigating effects, and improved C sequestration compared to ploughing back the straw residues into the soil. For the latter purpose we adopted the concept of avoided atmospheric CO₂ load (Petersen et al., 2013), which is treated further in section 2.5. The analyses were performed in a 100-years time perspective. For conversion of GHG emissions to CO_{2eq}, the 100-years GWP factors of 28 for

methane (CH₄) and 265 for N₂O were used (IPCC, 2013), although older estimates are stipulated in the RED for use in national reporting to the EU (23 for CH₄ and 296 for N₂O). The seed yield was estimated based on linear regression of yields in 2006-2017 (Statistics Denmark, 2018) and adjusted to current fertilizer legislation (MFM, 2016) specifying the application levels of nitrogen (N), potassium (K) and phosphorous (P) in the growing season 2016/2017. Transportation of fertilizers were assumed to involve 1000 km of sea freight and 350 km of road transportation (Elsgaard, 2015). We ignored indirect LUC by assuming that our suggested system change could be introduced into the existing cultivation practices without any changes in yield and crop rotation. The direct LUC was considered in terms of the biochar-mediated soil organic carbon (SOC) change. Danish environmental protection legislation prohibits the cultivation of new farmland, which made other dimensions of the direct LUC irrelevant in this case. We excluded capital goods in general from the calculations in line with the RED and other studies acknowledging this to be of minor importance (Malça and Freire, 2011; Queirós et al., 2015). The functional unit in the study was 1 Mg dry seed of WOSR.

We acknowledge that other impact categories than the GWP could be relevant to include in an analysis like this. However, future standards for biochar application are expected to secure an ecologically sustainable and environmentally safe profile (EBC, 2012) and therefore the GWP would be a key impact category when biochar is considered in a WOSR cultivation scenario.

2.2. Reference and biochar scenarios

The reference scenario represented average Danish WOSR cultivation in terms of cultivation practice, irrigation, liming, fertilizer levels, yields and field emissions (Table 1), using the assumptions that fertilizers were mineral types and that straw residues were incorporated into

the soil after harvest, which is in line with the current practice of (on average) 86% oilseed rape straw incorporation in 2017 (Statistics Denmark, 2018). The straw residue incorporation in the reference scenario was assumed to maintain the SOC stock equilibrium leading to no gain or losses. Calculation of GHG emissions in the reference scenario was basically done in accordance with the RED (European Parliament, 2009).

The biochar scenarios were similar to the reference scenario in terms of fertilizer levels, liming, pesticides, the main part of the soil management, principles of N₂O emission calculation and crop yields. The biochar scenarios differed from the reference scenario in terms of harvest of straw residues as feedstock for biochar production, transportation between field and pyrolysis plant (assumed to 70 km), and soil incorporation of biochar (Fig. 1). In addition, the biochar scenarios included the GHG balance from the N₂O mitigating effect, the C sequestration, and the carbon to electricity conversion via syngas and bio-oil. Harvestable straw available for biochar production was assumed to be 90% of the seed yield on dry matter (DM) basis (Statistics Denmark, 2018). The two biochar scenarios differed by the temperatures assumed in the thermal conversion process, which influence partitioning between biochar, bio-oil and syngas yields and therefore also influence electricity production as well as biochar properties and C contents (Karaosmanoğlu et al., 2000). The biochar field application rate (approximately 1 Mg ha⁻¹) was based on the conversion of WOSR straw yield from 1 ha, hereby avoiding feedstock import from other sources (including related allocation issues). The biochar application rates corresponded roughly to a biochar/soil ratio of 0.03% (dry weight/dry weight) in the upper 20 cm soil layer assuming a soil bulk density of 1.5 g cm⁻³. An N₂O mitigating effect of 15% for both biochar scenarios (BC-400 and BC-800) was adopted in accordance with the data listed in Cayuela et al. (2014) for application rates less than 1% (biochar/soil ratio).

All scenarios were based on a single WOSR growing season to comply with RED principles and to exclude crop rotation considerations. Following this, the GHG balance changes in C stocks, due to the straw to biochar recirculation, was assigned to the WOSR-cropping year. Also, N₂O mitigating effects were only considered in this year. In general, we assumed the biochar scenarios to include many farmers delivering WOSR straw for pyrolysis plants every year, making WOSR straw biochar available at all times. Following this, we assumed the biochar to be applied to the soil before the WOSR was seeded, which allowed focusing on a single growing season. Multifunctional processes in the pyrolysis process were accounted for by a displacement method, i.e., by including avoided CO₂ emissions from displaced grid electricity instead of performing allocation between multiple pyrolysis outputs.

2.3. WOSR cultivation and N₂O emissions

For assessment of direct N₂O emissions from the field, we used the IPCC default emission factor (EF) of 1% for turnover of fertilizer N, crop residue N and N potentially mineralized from biochar (IPCC, 2006). Straw (90% of seed DM yield) was assumed to have 1.07% N (Elsgaard, 2015). We further assumed 4.4 kg N ha⁻¹ from stubble (Mikkelsen et al., 2006) and 0.9% N in the below ground biomass (IPCC, 2006), which was rated as 22% of total above ground biomass (i.e., yield + straw + stubble) (IPCC, 2006). For soil-incorporated crop residues, we assumed total N mineralization. Indirect N₂O emissions from nitrate (NO₃⁻) leaching were calculated as a combined EF for leaching to ground water, rivers and estuaries of 0.0046 kg N₂O-N/kg NO₃⁻-N (Elsgaard, 2015) based on 30% default leaching of the total N from fertilizer, crop residues, and biochar (IPCC, 2006). Indirect N₂O emissions from ammonia (NH₃) volatilization were calculated using an EF of 0.01 kg N₂O-N/kg NH₃-N (IPCC, 2006) and assuming a 2.2% volatilization rate of the applied mineral N fertilizer under Danish conditions (Mikkelsen et al., 2006).

2.4. Biochar properties and degradation

Properties of biochar produced by pyrolysis of WOSR straw were compiled from literature surveys. The pyrolysis plant considered in this study is still prospective in Denmark, but is assumed to be similar to the plant described by Yang et al. (2016) expanded by electricity generation equipment. The system has three outputs, i.e., biochar, bio-oil and syngas, with the latter two being converted to electricity on site. Further technical details is beyond the scope of this study. Based on 10 analyses of oilseed rape (or canola) biochar, produced under different conditions, we derived generic properties for biochars produced at 400 and 800°C in relation to yield, heating value, H/C ratio, and contents of C and N (Table 2 and Fig. S1). Experimental data on degradation rates of biochar produced from oilseed rape straw were unavailable. It is generally assumed, though, that biochars contain a small labile C pool with mean residence times (MRT) of weeks to few years and a larger recalcitrant C pool with MRT of decades to centuries (Singh et al., 2012; Wang et al., 2014; Zimmerman, 2010). Based on available data on degradation rates of biochar from leaf, crop, and grass feedstocks (Hammond et al., 2011; Singh et al., 2012; Wang et al., 2016; Zimmerman, 2010), we estimated conceivable values for MRT and proportions of labile and recalcitrant C from WOSR straw biochar produced at 400 and 800°C (Table 2). We adopted the assumption that high temperature biochar (as compared to low temperature biochar) should have minor proportions of labile C and longer MRT due to larger proportions of aromatic C (Singh et al., 2012). MRT of labile fractions were assumed to be 1 month.

2.5. Carbon sequestration

The effect of C sequestration is not included in the RED reporting to the EU (e.g., Elsgaard, 2015), although the directive allows for inclusion of increased soil C stocks due to improved

farm management (European Union, 2010). However, the RED is not detailed on how to include C sequestration in general or from biochar in particular. We adopted the approach by Petersen et al. (2013), combining the yearly CO₂ emissions from mineralization of crop residues with atmospheric CO₂ decay curves using the Bern Carbon Cycle model. The method was implemented in the context of biochar in our study as follows.

Firstly, we considered the lost C input due to straw harvest (removal from the field) compared to soil incorporation of straw in the reference scenario, which we defined as the equilibrium situation without any gains or losses in SOC. For this purpose, we used the residue C sequestration factors of 21.3% and 9.7% in 20 and 100-years perspectives, respectively, as reported by Petersen et al. (2013), i.e., assuming a similar degradation profile of wheat straw and WOSR straw with an expected biomass C content of 45% on dry weight basis (Chen et al., 2016; Dai et al., 2016; Karaosmanoğlu et al., 2000).

Secondly, to adopt the method to soil CO₂ emission from biochar (rather than straw), we derived emission curves from degradation of biochar in the soil and then combined these with the Bern Carbon Cycle model. The biochar C remaining in the soil after t years, $C(t)$, was calculated as (Eq. 1):

$$C(t) = C_1 \exp(-k_1 t) + C_2 \exp(-k_2 t) \quad (1)$$

where C_1 is the initial labile C content, C_2 is the initial recalcitrant C content, and k_1 and k_2 are the respective mineralization rates (1/MRT). Hence, the annual C emission in year t , $E_C(t)$, as depicted in Fig. 2, was estimated as (Eq. 2):

$$E_C(t) = C(t) - C(t-1) \quad (2)$$

The annual C emissions were then combined with the Bern Carbon Cycle model (Eq. 3) to take the gradual adsorption of atmospheric CO₂ by sinks (mainly oceans) into account:

$$f(t) = 0.217 + 0.186\exp(-t/1.186) + 0.338\exp(-t/18.51) + 0.259\exp(-t/172.9) \quad (3)$$

where $f(t)$ is the fraction of CO₂ left in the atmosphere and t is the time scale considered after the emission pulse (Petersen et al., 2013). The C sequestration factors were finally estimated by calculating the sum of the integrals of the Bern Cycle emission decay curves over time and relating this to the instantaneous combustion of biomass (an example of the calculations is shown in the Supplementary material).

Importantly, the net avoided atmospheric CO₂ load comprises the difference between the C gain due to biochar application and the C loss due to straw harvest for pyrolysis, i.e., to avoid that the same C were accounted for twice.

The C sequestration factors were calculated principally in a 100-years time perspective, but also in a 20-years perspective, since this is the timespan applied in the EU legislation in relation to C sequestration. Further, C sequestration factors for 30-years timespan was included in the Supplemental material (Table S1).

2.6. Nitrogen dynamics after biochar application

Mineralization of C and N from biochar was assumed to be proportional, i.e., allowing N mineralization to be calculated as the product of C mineralization and the inverse C/N ratio (Table 2), although there is a lack of long-term studies to substantiate this assumption (Nguyen et al., 2017). This N source was included in the calculations of direct and indirect N₂O emissions and assigned to the year of application without regarding the time perspective of the pulses.

2.7. Avoided electricity production from the pyrolysis process

Based on heating values of WOSR straw (16.3 MJ kg⁻¹; Chen et al., 2016; Karaosmanoğlu et al., 2000) and biochar (Table 2, Fig. S1), we calculated the energy content in the syngas and bio-oil yield, which were treated collectively for conversion into electricity (Table 3). We assumed 15% energy consumption in the conversion process of straw to syngas and bio-oil due to feedstock preparation and other processes related to the pyrolysis process and an additionally 10% inevitable loss according to Hammond et al. (2011). For the remaining 75% of the energy content, we assumed 32% conversion efficiency to electricity (Hammond et al., 2011; Wang et al., 2014) and no exploitation of produced heat from the pyrolysis processes except for feedstock drying. Avoided GHG emissions were set to 83.3 g CO_{2eq} kWh⁻¹ for electricity produced by the pyrolysis plant, representing the Danish average marginal electricity supply in a scenario where future increased electricity demand is met by wind power capacity change (Lund et al., 2010).

2.8. Sensitivity analyses

Sensitivity analyses were performed in order to quantify potential impacts of specific key assumptions. Firstly, uncertainty exists regarding the degradation rate of biochar. Lutfalla et al. (2017) studied degradation rates of pyrogenic C in different soils and reported 42 years as the minimum MRT across the studied sites. The consequences of adopting such (unusually) low MRT were analyzed. Secondly, if the responding marginal producer of Danish electricity supply was power plants based on natural gas, then the avoided GHG emissions due to electricity production at the pyrolysis plant would be 578 g CO_{2eq} kWh⁻¹ (Lund et al., 2010), and the effects of this was tested. Thirdly, uncertainty of N₂O mitigating effects following biochar application at rates less than 1% (Cayuela et al., 2014) were addressed by assuming

the case of no mitigating effect. Fourthly, we analyzed the impact of taking the remaining biochar C in soil (Eq. 1), rather than the C sequestration factors, as basis for the C sequestration in the LCA. Fifthly, we considered an alternative time perspective of 20 years (rather than 100 years), by using the derived C sequestration factors for this timespan. For other aspects of the latter analysis, the 100-years GWP factors were used equivalent to the main analysis in order to comply with agreed LCA practice (IPCC, 2013).

3. Results

3.1. Carbon sequestration factors for biochar

Based on the compiled biochar properties (Table 2), the degradation of BC-400 and BC-800 resulted in remaining proportions of biochar C in soil of 85.1% and 93.2%, respectively, after 20 years and 57.0 and 79.4%, respectively, after 100 years (Table 4). Applying the concept of avoided atmospheric CO₂ load resulted in consistently higher C sequestration factors as compared to the remaining proportions of biochar C in soil. The difference between the two methods increased with increasing time perspective and decreasing MRT (Table 4). For the 20-years perspective, the C sequestration factors for BC-400 and BC-800 were 88.9% and 94.8%, respectively and for the 100-years perspective, they were 71.5% and 86.7%, respectively (Table 4).

3.2. GHG emissions from WOSR cultivation in reference and biochar scenarios

For oilseed rape cultivation in the reference scenario, the GHG emission summed up to 638 kg CO_{2eq} Mg⁻¹ dry seed (Fig. 3, Table S2). The biochar scenarios resulted in cumulative emissions of 171 and 111 kg CO_{2eq} Mg⁻¹ dry seed for BC-400 and BC-800, respectively, reflecting a substantial reduction of GHG emissions when biochar was included in the WOSR cultivation system. The effects of C sequestration accounted for the main part of the

differences between the biochar and the reference scenarios with mitigating contributions of -392 and -429 kg CO_{2eq} Mg⁻¹ dry seed in the BC-400 and BC-800 scenarios, respectively (Fig. 3). Mitigating effects related to lower direct field emissions of N₂O represented -73 to -77 kg CO_{2eq} Mg⁻¹ dry seed and was a minor contribution to the total reduction of GHG emissions of the biochar scenarios compared to the reference scenario (Fig. 3). Even smaller differences between the scenarios (biochar versus reference) included lower indirect N₂O emissions (-4 to -5 kg CO_{2eq} Mg⁻¹ dry seed), higher fuel consumption due to extra field operations and transportation of straw and biochar (35 to 33 kg CO_{2eq} Mg⁻¹ dry seed), and avoided electricity production to the national grid (-33 to -48 kg CO_{2eq} Mg⁻¹ dry seed).

3.3 Sensitivity analyses

The first sensitivity analysis (Sa #1) showed that changing the assumed MRT to 42 years had a strong negative effect on the GHG mitigation related to biochar application, although the biochar scenarios still emitted 26-27% less CO_{2eq} than the reference scenario (Table 5). However, even when the MRT was reduced to 42 years (Table 4), a C sequestration factor of 33.1% of the biochar C was still obtained in a 100-years perspective with the present calculation method as compared to only 9.2% biochar C remaining in soil according to Eq. (1).

In the second sensitivity analysis (Sa #2), the marginal electricity supply was assumed to be natural gas fueled power plants with a GHG load of 578 g CO_{2eq} kWh⁻¹. Under these conditions, the calculated total WOSR emissions turned negative (Table 5), indicating that the total emissions from the WOSR cultivation system were reduced by more than 100%.

Disregarding the possible N₂O mitigating effect of biochar (Sa #3), showed that the total GHG emissions were increased by 40 kg CO_{2eq} Mg⁻¹ dry seed for both biochar scenarios (Table 5). This showed that the contribution of the direct N₂O mitigation corresponded to

only 8-9% of the total GHG mitigation obtained in the biochar scenarios.

Using remaining biochar C in soil as the measure of C sequestration (Sa #4) resulted in biochar scenarios with GHG mitigation effects of 56% (BC-400) and 75% (BC-800) as compared to respective mitigation effects of 73% and 83% in the main analysis (Table 5). This underpinned that the two methods of C sequestration calculation clearly influenced the results, although similar overall conclusions could be reached.

The fifth sensitivity analysis (Sa #5) indicated that the GHG mitigation was weaker when taking a 20-years rather than a 100-years perspective both for the BC-400 and BC-800 scenarios (Table 5). Moreover, in the 20-years time-perspective, the BC-400 scenario changed to be more beneficial than the BC-800 scenario, although the difference between the two scenarios was moderate (21 kg CO_{2eq} Mg⁻¹ dry seed).

4. Discussion

4.1. Carbon sequestration

The present study identified biochar C sequestration, linked to biochar MRT, as the most important factor for the overall GHG emission in the WOSR cultivation scenarios. This finding is in line with other studies analyzing the consequences of pyrolysis processing of feedstocks and soil application of the biochar residue, when effects of indirect LUC are excluded (Hammond et al., 2011; Ibarrola et al., 2012; Roberts et al., 2010; Sigurjonsson et al., 2015). Yet, the results call for a discussion of the reliability of assumed biochar degradation properties. Empirical long-term data on biochar persistence following field amendment are still sparse (Wang et al., 2016) and most assessments rely on extrapolation of shorter-term laboratory studies. Thus, suggested estimates should be treated with caution in order to avoid potentially unrealistic estimates of C sequestration. Zimmerman (2010) found an average biochar C stability of 89.7% in a 100-years perspective, which is above any of our

assumed values in the corresponding period. Similar to our approach, Lugato et al. (2013) also estimated biochar degradation rates by considering literature values and they arrived at degradation of 32% and 7.3% in a 100-years perspective as representative fast and slow mineralization scenarios, respectively. Corresponding degradation values in our study (100% - remaining C in soil), in a 100-years perspective were 43% and 21% for the BC-400 and BC-800 scenarios, respectively, meaning that we assume faster mineralization (i.e., lower stability) in our study as compared to Lugato et al. (2013). Kuzyakov et al. (2014) reported MRT of 400 years for grass-based biochar produced at 400°C when decomposing in soil under laboratory conditions; these data were suggested to imply that MRT under field conditions could be in the range of 4000 years in temperate soils. In summary, therefore, we expect that our present estimates for BC-400 and BC-800 do not overemphasize the stability of biochar under field conditions.

Another important factor is the use of the concept of avoided atmospheric CO₂ load (Petersen et al., 2013), which increased the C sequestration factor to be included in the LCA analysis following biochar amendment as compared to the actual soil C sequestration (Eq. 1). The method integrates the annual dynamics of C degradation pulses, and we argue that this is a righteous method for calculations of the climate impact of long-term biochar effects compared to the focus merely on the fraction of biochar that is left after the entire time horizon considered, e.g., 20 or 100 years.

The sensitivity analysis Sa #5 counterintuitively indicated that the shorter (20-years) time perspective resulted in higher GHG emissions (i.e., less C sequestration) than the longer (100-yr) time perspective. However, this was explained by the lost C sequestration caused by straw harvest (first step in straw recirculation). Despite that a larger proportion of the biochar evidently degrades after 100-years compared to 20-years, this proportion of C degradation was more than counterbalanced by the decreasing effect of lost C sequestration due to straw

harvest, which decreased from 317 kg CO_{2eq} Mg⁻¹ dry seed after 20 years to 144 kg CO_{2eq} Mg⁻¹ dry seed after 100 years. Thus, inclusion of both gained and lost C sequestration in terms of biochar application and feedstock collection, respectively, should be included when analyzing the net C sequestration, and shorter and longer time horizons should be considered to uncover the actual GHG mitigating potential.

4.2. Optimization of biochar yield and properties

The tradeoff between biochar yield, biochar degradation properties, and energy yield (electricity production) - as influenced by the choice of thermal conversion technology - is exemplified by the two biochar scenarios (BC-400 and BC-800). The main analysis (100-years perspective) revealed an advantage for the BC-800 scenario, while Sa #5 showed a marginal difference in total GHG emissions in favor of the BC-400 scenario in the 20-years perspective. In line with the Sa #5 result, Sigurjonsson et al. (2015) found that an increased biochar yield at the expense of decreased electricity production provided the best overall GHG mitigating strategy. Likewise, Brownsort (2009) found that lower pyrolysis process temperature resulted in larger GHG mitigation despite less electricity production. However, Brownsort (2009) assumed similar properties for biochars produced at different temperatures, whereas we assumed that biochars produced at higher temperatures were more recalcitrant, thus resulting in a larger GHG mitigation in the high-temperature scenario in the 100-years time perspective.

As shown by sensitivity analysis (Sa #2), the CO_{2eq} emissions from the chosen marginal electricity heavily influences the tradeoff between biochar yield and energy production, in line with the findings of Hammond et al. (2011) and Sigurjonsson et al. (2015). In our study, the seven-fold higher CO_{2eq} emissions related to marginal electricity from natural gas power plants than from wind power changed the WOSR biochar scenarios from net GHG sources

(171 and 111 kg CO_{2eq} Mg⁻¹ dry seed) to net sinks (-26 to -176 kg CO_{2eq} Mg⁻¹ dry seed).

Thus, to secure consistency in GWP analyses of energy systems that includes electricity production, the marginal electricity should be a well-defined official value within the relevant geographical area in order to secure comparability of studies.

4.3. Nitrous oxide mitigating effects

The assumed 15% mitigating effect of biochar on direct field emissions of N₂O must be considered uncertain, since the biochar application rate in this study corresponded to approximately 1 Mg ha⁻¹ and, to our knowledge, no experimental field data exist for such low application rates. Yet, the biochar-mediated N₂O mitigation only contributed marginally to the total mitigating effects in the biochar scenarios, which were largely dominated by the effect of C sequestration. Thus, when investigating overall yield-scaled GHG consequences of returning crop residues to the soil as biochar in cropping systems, the C sequestration effect, rather than N₂O mitigation, should be in focus. Nevertheless, any reductions in N₂O emissions would still be advantageous in a climate perspective, and further studies on the interactions between biochar and N₂O emissions should be encouraged (Ameloot et al., 2016).

4.4. Perspectives for inclusion of biochar in oilseed rape cultivation for biodiesel

In order to interpret our results in relation to the sustainability of biodiesel produced from rape seed, we used the Biograce conversion method (Biograce, 2015) from oilseed rape to rape methyl esters (RME) as described in Table S3. The resulting emission load in the main analyses corresponded to 24.5, 6.6 and 4.3 g CO_{2eq} MJ⁻¹ RME for the reference, BC-400 and BC-800 scenarios, respectively. In comparison, the disaggregated Danish values reported to the EU according to the RED (Elsgaard, 2015) were in the range from 21.4 to 24.4 g CO_{2eq} MJ⁻¹ RME. However, since these values were reported, there have been certain changes in the

Danish WOSR cultivation conditions, such as the fertilizer legislation, and also Elsgaard (2015) used another allocation factor between the RME and other process outputs than suggested by the Biograce (2015) guidelines. Yet, it can be concluded that the present results for Danish average WOSR cultivation are in line with previous estimates, which substantiate the importance of the marked reductions obtained in the biochar scenarios arriving at 6.6 and 4.3 g CO_{2eq} MJ⁻¹ RME.

The high GHG emission reductions related to biochar in the cultivation system in principle could improve future biodiesel sustainability. This finding is not only relevant for Danish WOSR cultivation, but is transferable to other countries with existing WOSR cultivation, where direct LUC, besides the SOC increase following biochar amendment, can be ignored. Yet, before adopting such a conclusion, a stepwise number of actions should be performed. The first step should be to study an operational experimental pyrolysis plant including electricity production equipment. This may enable verification of assumptions related to the pyrolysis plant in terms of biochar properties, yield partitioning between outputs, syngas/bio-oil to electricity conversion efficiency, and maintenance related emissions. Also, long-term field experiments of biochar degradation and stability in soil should be encouraged to document the C sequestration of the specific WOSR straw biochar as well as any potential toxic side effects in the soil agroecosystem. These actions will substantiate whether the results presented here could prospectively be utilized for straw management in future cropping systems with biochar.

5. Conclusions

We analyzed the consequence of biochar inclusion in an existing Danish WOSR cultivation system and found that the potential GHG emissions were substantially reduced. This was mainly due to C sequestration resulting from biomass C stabilization conferred by the thermal

conversion process, which point at the biochar MRT as the most essential factor determining whether increased sustainability are achieved or not. For calculation of the C sequestration effect, the concept of avoided atmospheric CO₂ load was applied and C sequestration factors of 71.5% and 86.7% of the added biochar C were derived for the BC-400 and BC-800 scenarios, respectively, in a 100-years time perspective. In addition, assumptions on marginal electricity supply were shown to strongly affect the optimal partitioning between pyrolysis outputs in the form of biochar versus bio-oil and syngas. Thus consolidated and certified values for main assumptions, such as biochar stability in soil and CO₂ emissions of marginal electricity, were documented to be essential. Policy-makers, industry, researchers and the agricultural sector should aim for well-defined assumptions combined with knowledge gained from an operating test pyrolysis plant. This will provide the possibility for system optimization and identify the potential for increased sustainability of future energy crop cultivation.

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Fig. 1. A: The reference scenario for winter oilseed rape (WOSR) cultivation. Input includes fertilizer, electricity for irrigation, diesel (incl. lubrication oil), lime and pesticides as well as transportation of fertilizer and lime. Field emissions include direct and indirect N_2O emissions and CO_2 emissions due to liming. The reference scenario refers to Danish average cultivation of WOSR with the assumptions that (i) only mineral fertilizer is applied and (ii) all straw residue is incorporated to the soil. B + C: The two biochar scenarios with biochar produced at 400°C (BC-400) and 800°C (BC-800). The biochar scenarios differ from the reference in terms of straw harvest and transportation to the pyrolysis plant, electricity production at the pyrolysis plant, transportation of biochar to the field, biochar application and incorporation, direct and indirect N_2O emissions and C sequestration. The biochar scenarios differ from each other by thermal conversion temperatures (400 and 800°C), which influence the yield partitioning between biochar, bio-oil and syngas, as well as biochar properties and C content leading to differences in C sequestration.

Fig. 2. Annual emission of biochar C (in percent of added) after biochar amendment to arable soil in (A) the BC-400 scenario and (B) the BC-800 scenario. Calculations were done according to Eq. (2). For BC-400, it was assumed that 94% of the biochar C was in the recalcitrant fraction with a mean residence time (MRT) of 200 years. For BC-800, it was assumed that 97% of the biochar C was in the recalcitrant fraction with a MRT of 500 years. Labile C fractions (100% - recalcitrant fractions) were assumed to be depleted (and emitted) during Year 1. Numbers in parentheses indicate the total emissions in Year 1.

Fig. 3. Yield-scaled greenhouse gas balances ($\text{kg CO}_{2\text{eq}} \text{Mg}^{-1}$ dry seed) of oilseed rape cultivation in the reference system and the two biochar scenarios (BC-400 and BC-800) in a 100-years time perspective. Sources and sinks are divided into five categories: (i) energy and other supplies, (ii) fertilizer production and transportation, (iii) direct and indirect N_2O field emissions, (iv) carbon sequestration, and (v) CO_2 avoidance due to electricity production. The two latter categories (sinks) were only relevant for the biochar scenarios. Hatched white bars show the net emissions from each scenario. Further details are presented in Table S2.

Table 1. Inventory data for input, output and N₂O emissions from the cultivation step of Danish average winter oilseed rape (WOSR) cultivation.

	Value	Unit	kg CO _{2eq} unit ⁻¹	kg CO _{2eq} ha ⁻¹	Explanation/Source
Input:					
N fertilizer	218	Kg N ha ⁻¹	3.1	676	MFM (2016); Elsgaard (2015)
K fertilizer	84	kg K ha ⁻¹	0.46	39	MFM (2016); LowCVP (2004)
P fertilizer	26	kg P ha ⁻¹	0.71	18	MFM (2016); LowCVP (2004)
Fertilizer total weight	1100	kg ha ⁻¹			Calculated
Transportation (truck)	385	Mg × km	0.23	87	Elsgaard (2015)
Transportation (ship)	1100	Mg × km	0.01	10	Elsgaard (2015)
Liming ^a	170	kg ha ⁻¹		78	Elsgaard (2015)
Irrigation	2.4	mm ha ⁻¹	1.41	3	Calculated ^b ; Elsgaard (2015)
Pesticides	1.7	kg ha ⁻¹	5.37	9	Elsgaard (2015)
Diesel (including lubrication oil)	55	L ha ⁻¹	3.36	183	Calculated ^c ; Elsgaard (2015)
Output:					
Oil seed (DM)	3799	kg ha ⁻¹			(Statistics Denmark, 2018)
Straw (DM)	3423	kg ha ⁻¹			90% of seed yield Statistics Denmark (2018)
Field emissions:					
Direct N ₂ O emissions	4.3	kg ha ⁻¹	265	1142	Calculated ^d ; IPCC (2006)
Indirect N ₂ O emissions	0.7	kg ha ⁻¹	265	178	Elsgaard (2015); IPCC (2006)

^a Direct emissions, transportation and excavation.

^b The value of 2.4 mm ha⁻¹ is calculated as the national average. The major part of Danish WOSR is not irrigated, which causes the low average. The estimate is based on personal communication (Søren Kolind Hvid, SEGES).

^c Based on Jørgensen (2014).

^d N₂O emissions are calculated by using the 1% IPCC default value of added N, including fertilizer, crop residue, and mineralized biochar N.

Table 2. Biochar properties used in this study and the data sources. The BC-400 and BC-800 biochar properties were derived using linear regression on source data (Fig. S1).

Properties	BC-400	BC-800	Data sources ^b
Yield (% , w/w)	36	25	1,2,4,10
Yield (kg)	1232	856	Calculated ^c
Carbon (% , w/w)	63	80	1-10
Nitrogen (% , w/w)	1.3	1.3	1-10
C/N ratio (weight)	48	62	Calculated
H/C ratio (molar)	0.67	0.03	1,2,5,6,7,9,10
Heating value (MJ/kg)	26.9	26.6	1,10
Mean residence time (years)	200 ^a	500 ^a	11,12,13,14
Labile fraction (% , w/w)	6.0 ^a	3.0 ^a	11,12,13,14

^a Values are derived from the listed sources by selecting feedstock and pyrolysis temperature comparable to the requirements of this study.

^b Data sources: (1) Karaosmanoğlu et al. (2000); (2) UKBRC (2014); (3) Mehmood et al. (2017a); (4) Mehmood et al. (2017b); (5) Zhao et al. (2016); (6) Dai et al. (2016); (7) Yang et al. (2015); (8) Masud et al. (2014); (9) Dai et al. (2014); (10) Chen et al. (2016); (11) Wang et al. (2016); (12) Singh et al. (2012); (13) Zimmerman (2010); (14) Hammond et al. (2011).

^c Calculated from a straw yield of 3423 kg DM ha⁻¹.

Table 3. Assumptions for energy conversion of the two biochar types produced at 400°C (BC-400) and 800°C (BC-800). Values on energy content (heating value) are shown in Table 2.

	BC-400	BC-800	Unit
Energy content in straw	55,802	55,802	MJ ha ⁻¹
Energy content in biochar	33,152	22,766	MJ ha ⁻¹
Potential energy content in syngas and bio-oil including losses (by difference)	22,650	33,036	MJ ha ⁻¹
Energy for feedstock drying and other processes ^a	15	15	% (of energy)
Additional loss ^a	10	10	% (of energy)
Energy conversion efficiency from remaining energy in gas/oil to electricity ^b	32	32	%
Electricity produced	5,436	7,929	MJ ha ⁻¹
MJ to kWh	0.278	0.278	kWh MJ ⁻¹
Electricity produced	1,511	2,204	kWh ha ⁻¹
CO _{2eq} avoided (area based) ^c	126	184	kg ha ⁻¹
CO _{2eq} avoided (yield-scaled) ^c	33	48	kg Mg ⁻¹ dry seed

^a Hammond et al. (2011)

^b Wang et al. (2014)

^c Based on a value of 83.3 g CO_{2eq} kWh⁻¹ electricity (Lund et al., 2010).

Table 4. Remaining biochar carbon (C) in soil and biochar C sequestration factors after 20 and 100 years. Remaining biochar C in soil was calculated from Eq. 1 using the specific biochar properties shown in Table 2. Biochar C sequestration factors were calculated according to Petersen et al. (2013) as detailed in section 2.5. Numbers in square brackets (left column) indicate the percentages of labile versus recalcitrant biochar assumed in each scenario. MRT, mean residence time.

Scenario	Remaining biochar C in soil (%)		Biochar C sequestration factor (%)	
	20 years	100 years	20 years	100 years
BC-400 MRT = 200 years; [6%, 94%]	85.1	57.0	88.9	71.5
BC-800 MRT = 500 years; [3%, 97%]	93.2	79.4	94.8	86.7
Sensitivity analysis, Sa #1 MRT = 42 years; [0%, 100%]	62.1	9.2	77.2	33.1

Table 5. Sensitivity analyses of key assumptions in the GHG life cycle assessment showing the yield-scaled emissions from oilseed rape cultivation derived from the main analysis and sensitivity analyses (Sa) for the reference, BC-400, and BC-800 scenarios.

Ana- lysis	Investigated change	GHG emission (kg CO _{2eq} Mg ⁻¹ dry seed)		
		Reference	BC-400	BC-800
Main analysis		638	171	111
Sa #1	Mean residence time (MRT) of recalcitrant biochar fraction of 42 years (rather than 200 years for BC-400 or 500 years for BC-800)	638	467	474
Sa #2	Avoidance of 578 g CO _{2eq} kWh ⁻¹ electricity (rather than 83.3 g CO _{2eq} kWh ⁻¹ electricity)	638	-26	-176
Sa #3	No mitigating effect of biochar on direct field N ₂ O emissions (rather than 15% N ₂ O mitigation)	638	211	151
Sa #4	Calculation based on remaining biochar C in soil (rather than using the concept of avoided atmospheric CO ₂ load)	638	279	160
Sa #5	Analysis in 20-years time perspective (rather than 100 years)	638	208	229

Appendix A. Supplementary material for the paper:

Biochar potentially mitigates greenhouse gas emissions from cultivation of oilseed rape for biodiesel

Thers, H., Sylvestre, N.D., Elsgaard, L., Knudsen, M.T. (2019)

Fig. S1. Linear regression between thermal conversion temperatures and biochar properties (based on data sources listed in Table 2 of the main paper). Regressions were used to derive the values for biochar produced

at 400 and 800°C as used in the BC-400 and BC-800 scenarios. A: Biochar yield, B: Biochar carbon content, C: Biochar nitrogen content, D: Biochar H/C ratio, E: Biochar heating value.

Example of calculation of avoided atmospheric CO₂ load

By using the BC-400 properties (Table 2, main paper) of 6% carbon (C) in the labile fraction (MRT, 1 month) and 94% C in the recalcitrant fraction (MRT, 200 years), it is calculated from Eq. (1) in the main paper that 85.1% of the biochar C remains in the soil after 20 years. This is how C sequestration often is considered in LCA studies.

We here provide an example of the stepwise procedure in order to explain and highlight the impact of each step in the calculation of avoided atmospheric CO₂ load according to Petersen et al. (2013). The idea is to address the CO₂ impact to the atmosphere instead of focusing on soil C in studies regarding climate issues. In other words, we want to calculate the actual climate benefit from the biochar management actions, which might not be properly measured when expressed as a final proportion of C remaining in the soil.

The first step is to take integrals of annual pulses into account (Fig. S2). Equation S1 calculates the time dependent impact of emitted biochar C by summing the one-year areas of the cumulated emissions across the 20-years timespan and relating it to the integral of the 100% initial oxidation across 20 years.

$$\text{Time dependent impact of emitted biochar C} = \frac{Ta_t - Aa_t}{Ta_t} \quad (S1)$$

where Ta_t is the integral of an initial 100% biochar oxidation across a timespan (20 years in this example) and Aa_t is the summed area of cumulated emissions. Example values ($Ta_t = 2000$ and $Aa_t = 200.5$) treated by Eq. (S1) equals 90.0%. Thus, considering the gradual degradation across the 20 years increase the value (from 85.1% to 90.0%) that can be imported as C sequestration to the LCA

analysis. However, it is crucial to remember that the actual non-degraded proportion of the C (remaining C in soil) is unchanged (85.1%).

Fig. S2. Cumulated annual emission pulses (time dependent). The summed degraded fraction of 14.9% is reached at the end and corresponds to the value of remaining C in soil calculated by Eq. (1) in the main paper ($100\% - 14.9\% = 85.1\%$). The red dotted line represents the initial 100% combustion to CO_2 . Example values are: $Ta_t = 2000$ and $Aa_t = 200.5$. Ta_t is the integral of an initial 100% biochar oxidation across a timespan (20 years in this example) and Aa_t is the summed area of cumulated annual emissions.

The next step in the procedure is inclusion of the Bern Cycle presented by Fig. S3 and defined as the C sequestration factor (Eq. S2).

$$\text{C sequestration factor} = \frac{Ta_{tB} - Aa_{tB}}{Ta_{tB}} \quad (\text{S2})$$

where Ta_{tB} is the integral of an initial 100% biochar oxidation multiplied by Eq. (3) (main paper) across a timespan (20 years in this example) and Aa_{tB} is the summed area of emission pulses where

each of the pulses follow the Bern Cycle atmospheric CO₂ decay defined by Eq. (3) in the main paper. Example values ($T_{atB} = 1358.5$ and $A_{atB} = 150.8$) treated by Eq. (S2) equals 88.9% (Fig. S3), which is the C sequestration factor for the specific biochar. Thus, the inclusion of the Bern Cycle results in less C sequestration effects compared to computation of the time dependent proportion of non-degraded biochar C without considering the Bern Cycle. The final step in the calculation of avoided atmospheric CO₂ load is to multiply the C sequestration factor by the biochar C stock and by 44/12 to convert the numbers to CO₂ equivalents.

Fig. S3. Cumulated annual emission pulses (time dependent), which are treated by the Bern Cycle function. Example values are: $T_{atB} = 1358.5$ and $A_{atB} = 150.8$. T_{atB} is the integral of an initial 100% biochar oxidation in consideration of the Bern Cycle decay curve across a 20-years timespan and A_{atB} is the summed area of emission pulses, where each of the pulses are decaying according to

the Bern Cycle.

Table S1. Results for remaining biochar C in soil (as percent of initial biochar C) and the C sequestration factors following the concept of avoided atmospheric CO₂ load in 20, 30 and 100 years time perspectives. Calculations were performed for the two biochar types analyzed in the main paper as well as for one sensitivity analysis. Numbers in square brackets (left column) are percentages of labile and recalcitrant C fractions of the specific biochar scenarios.

Scenario	Remaining biochar C in soil (%)			Biochar C sequestration factor (%)		
	20 yrs	30 yrs	100 yrs	20 yrs	30 yrs	100 yrs
BC-400						
MRT = 200 yrs; [6%; 94%]	85.1	80.9	57.0	88.9	86.5	71.5
BC-800						
MRT = 500 yrs; [3%; 97%]	93.2	91.4	79.4	94.8	93.9	86.7
Sensitivity analysis, Sa #1						
MRT = 42 yrs; [0%; 100%]	62.1	49.0	9.2	77.2	68.4	33.1

Table S2. Results of main calculations of the reference system (upper row) and the two biochar scenarios (BC-400 and BC-800) in 100-years time perspective by using the unit of kg CO_{2eq} Mg⁻¹ dry seed. In addition, results are shown for corresponding values for the biochar scenarios in a 20-years time-perspective. Emissions were divided into the five categories: Energy and other supplies, Fertilizer production and transportation, N₂O field emission (direct and indirect emissions), carbon sequestration and CO₂ avoidance due to electricity production, with the two latter only being relevant for the biochar scenarios.

Greenhouse gas emissions (kg CO _{2eq} Mg ⁻¹ dry seed)						
Scenario	Energy and other supplies	Fertilizer production and transport	N ₂ O emission	Carbon sequestration	CO ₂ avoidance due to electricity production	Net emissions
Reference	72	219	347	0	0	638
BC-400; 100 years	107	219	270	-392	-33	171
BC-800; 100 years	105	219	265	-429	-48	111
BC-400; 20 years	107	219	265	-349	-33	208
BC-800; 20 years	105	219	263	-310	-48	229

Table S3. Results of main calculations of the reference system (upper row) and the two biochar scenarios (BC-400 and BC-800) in 100-years time perspective by using the unit of g CO_{2eq} MJ⁻¹ RME (rape methyl ester). In addition, the results are shown for corresponding values for the biochar scenarios in a 20-years time perspective. Emissions are divided into the five categories: Energy and other supplies, fertilizer production and transportation, N₂O field emission (direct and indirect emissions), carbon sequestration and CO₂ avoidance due to electricity production, with the two latter only being relevant for the biochar scenarios. The two step conversion from kg CO_{2eq} Mg⁻¹ dry seed to g CO_{2eq} MJ⁻¹ RME includes a factor of 15.27 MJ RME per kg of dry WOSR seeds and an allocation between glycerin, rape meal and RME (the latter being 58.66%). The conversion factors were derived from Biograce (2015). We acknowledge that this conversion ignores the principles of consequential LCA. Nevertheless, it is a pragmatic conversion allowing comparison of the present results to reported values in the context of the RED directive (European Parliament, 2009). We stress that the reported values are still only covering the GHG emissions categories already treated in this analysis and do not include RME processing or distribution.

Greenhouse gas emissions (g CO _{2eq} MJ ⁻¹ RME)						
Scenario	Energy and other supplies	Fertilizer production and transport	N ₂ O emission	Carbon sequestration	CO ₂ avoidance electricity productions	Net emissions
Reference	2.75	8.39	13.34	0	0	24.5
BC-400; 100 years	4.09	8.39	10.37	-15.04	-1.27	6.6
BC-800; 100 years	4.01	8.39	10.18	-16.47	-1.86	4.3
BC-400; 20 years	4.09	8.39	10.19	-13.43	-1.27	8.0
BC-800; 20 years	4.01	8.39	10.12	-11.90	-1.86	8.8

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