

Pyrogenic carbon capture and storage

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Funding information

Bundesministerium für Bildung und Forschung, Grant/Award Number: 01LS1620A, 01LS1620B

Abstract

The growth of biomass is considered the most efficient method currently available to extract carbon dioxide from the atmosphere. However, biomass carbon is easily degraded by microorganisms releasing it in the form of greenhouse gases back to the atmosphere. If biomass is pyrolyzed, the organic carbon is converted into solid (biochar), liquid (bio-oil), and gaseous (permanent pyrogas) carbonaceous products. During the last decade, biochar has been discussed as a promising option to improve soil fertility and sequester carbon, although the carbon efficiency of the thermal conversion of biomass into biochar is in the range of 30%–50% only. So far, the liquid and gaseous pyrolysis products were mainly considered for combustion, though they can equally be processed into recalcitrant forms suitable for carbon sequestration. In this review, we show that pyrolytic carbon capture and storage (PyCCS) can aspire for carbon sequestration efficiencies of >70%, which is shown to be an important threshold to allow PyCCS to become a relevant negative emission technology. Prolonged residence times of pyrogenic carbon can be generated (a) within the terrestrial biosphere including the agricultural use of biochar; (b) within advanced bio-based materials as long as they are not oxidized (biochar, bio-oil); and (c) within suitable geological deposits (bio-oil and CO₂ from permanent pyrogas oxidation). While pathway (c) would need major carbon taxes or similar governmental incentives to become a realistic option, pathways (a) and (b) create added economic value and could at least partly be implemented without other financial incentives. Pyrolysis technology is already well established, biochar sequestration and bio-oil sequestration in soils, respectively biomaterials, do not present ecological hazards, and global scale-up appears feasible within a time frame of 10–30 years. Thus, PyCCS could evolve into a decisive tool for global carbon governance, serving climate change mitigation and the sustainable development goals simultaneously.

KEYWORDS

biochar, bio-oil, carbon sequestration, climate mitigation, permanent pyrogas, pyrolysis, tCDR

1 | INTRODUCTION

To keep global warming in the range that has sustained civilization during the past millennia, the carbon balance between emissions to the atmosphere and carbon

accumulation in the terrestrial system has to return to an equilibrium by 2050 at the latest (Obersteiner et al., 2018; Rockström et al., 2016, 2009). To achieve this, greenhouse gas (GHG) emissions need to be reduced by at least 90%

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with the world economy becoming climate neutral by 2050 (Rogelj et al., 2015; Bertram et al., 2015; Sanderson, O'Neill, & Tebaldi, 2016; Schleussner et al., 2016). However, even if the most ambitious scenarios of global GHG emission reductions were implemented within this time frame, the additional need for large-scale atmospheric carbon dioxide removal (CDR) to prevent overshooting the 1.5°C temperature threshold remains (Boysen, Lucht, Schellnhuber, et al., 2016; Hansen et al., 2017; Smith et al., 2015). Thus, most recent scenarios from integrated assessment models (IAMs) include the large-scale deployment of so-called negative emissions technologies (NETs) to achieve CDR (Fuss et al., 2014; Hansen et al., 2017; Riahi et al., 2015; Rogelj et al., 2015; Rogelj, McCollum, Reisinger, Meinshausen, & Riahi, 2013; Van Vuuren et al., 2013). Technical solutions to extract CO₂ from the atmosphere like direct air capture (Kumar et al., 2015; Sanz-Pérez, Murdock, Didas, & Jones, 2016), enhanced weathering (Koeve, Keller, & Oschlies, 2017; Moosdorf, Renforth, & Hartmann, 2014), and artificial ocean alkalization (Montserrat et al., 2017) are promising geoengineering approaches, although they are, to different degrees, either not yet mature or available at the needed scale, or the risk of large-scale implementation may still be considered too high (Hansen et al., 2017). An increase in terrestrial and marine biomass production, combined where possible with the sequestration of a significant part of its accumulated carbon, is therefore considered a CDR strategy that may be implemented most rapidly, and with the lowest risk of other geological and ecological processes (Hansen et al., 2017; Rockström et al., 2017; Smith et al., 2015).

Beside afforestation, bioenergy production with carbon capture and storage (BECCS) is the only NET included in the mitigation scenarios of the Intergovernmental Panel on Climate Change's (IPCC) Fifth Assessment Report (Allen et al., 2014). The BECCS scenario anticipates that biomass combustion could become a major pathway for clean energy production and that capturing the emitted CO₂ would become a complementary technology. Besides the known and unknown risks of fossilizing CO₂ and its high costs (>150 USD/t CO₂ (Klein et al., 2014; Smith et al., 2015)), BECCS is increasingly being recognized for potentially harming ecosystem services and the integrity of the biosphere with its extended implementation (Boysen, Lucht, Gerten, & Heck, 2016; Burns & Nicholson, 2017; Heck, Gerten, Lucht, & Popp, 2018).

Alternatively, CDR could be achieved through increased net primary productivity (NPP) of the biosphere, combined with the extension of the mean residence time (MRT) of the biogenic carbon (i.e. net C sequestration) (Erb et al., 2017; Smith et al., 2015). Increasing soil organic matter is one way forward to extend MRTs (Lal, 2011; Minasny, Malone, et al., 2017; Zomer, Bossio, Sommer, & Verchot, 2017).

However, the capacity of soils to accumulate organic carbon is likely limited (Barré et al., 2017; Minasny, Arrouays, et al., 2017) and requires large amounts of nitrogen (van Groenigen et al., 2017). Maintaining increased soil organic matter (SOM) stocks will depend on agronomic methods and may further be hampered by the effects of climate change (Sierra, Trumbore, Davidson, Vicca, & Janssens, 2015). The MRT of SOM is 50–80 years at maximum (Schmidt et al., 2011; Wang & Chang, 2001). Thus, increasing SOM is clearly an important CDR with extensive ecological cobenefits; however, its long-term potential may not be sufficient as sole CDR technology (Boysen, Lucht, Schellnhuber, et al., 2016; Smith et al., 2015; Soussana et al., 2017; van Groenigen et al., 2017). Moreover, the conversion of plant residues (shoots, roots, and root-derived C) into SOM has low C-efficiencies of 10%–15% (Bolinder, Angers, Giroux, & Laverdière, 1999) not considering SOM saturation (Six & Jastrow, 2002). A complementary way forward to extend the MRT of biogenic C in the terrestrial system and to increase C-efficiencies is the pyrolytic treatment of biomass with subsequent sequestration in the bio-, geo-, and anthroposphere.

In pyrolysis processes, shredded biomass is heated under oxygen-deficient atmospheres to temperatures between 350 and 900°C (EBC, 2012) converting the biomass into a solid (biochar), a liquid (bio-oil), and a permanent pyrogas fraction. In most current pyrolysis systems, the pyrolysis liquids and gases are combusted for the production of thermal and electric energy releasing the carbon as GHG back to the atmosphere. While this is often considered as carbon neutral, that is “green energy” because it is made from biomass, it can only sequester the biochar carbon but not the carbon from the gaseous and liquid phases which is more than half of the initial biomass carbon. To optimize the carbon sequestration potential, the following review is focused on the material use of all pyrogenic carbon species (i.e. solid, liquid, gaseous), and to reduce the combustion of pyrolytic products to a minimum. We specifically investigate the conditions and capacity of pyrogenic carbon capture and storage (PyCCS) as a complete negative emission system, quantifying the C-sequestration potential of all three pyrolysis products including their use as bio-based materials and agronomic amendments, but also for geologic carbon storage. We review literature on biochar, bio-oil, and pyrolysis systems for the required properties of pyrolytic products and summarize production conditions optimized for material use and C sequestration. We then compare PyCCS with BECCS in terms of carbon and nutrient efficiency, costs, environmental risks, and time frame for technology implementation.

2 | PYROLYSIS TECHNOLOGY

Pyrolysis is the thermal conversion of carbonaceous materials (e.g. biomass) in a low oxygen atmosphere. During

pyrolysis, biomass evolves into biochar (solid product) and releases volatiles, the so-called pyrolytic gas or pyrogas. Cooled to ambient temperature, pyrogases mostly condense into a liquid, the bio-oil. The remaining gas is called permanent pyrogas referring to the volatiles of the pyrolysis gas that do not condense at ambient temperature. The quality and properties of the three products and their yield fraction depend on the feedstock and its properties (e.g. woody vs. herbaceous biomass, soft- vs. hard-wood, moisture content, particle size) and on the pyrolysis process conditions. These include heating rate, highest treatment temperature (HTT), residence time of the solid, residence time of the volatiles as determined by the gas flow rate in the pyrolysis reactor, direction of gas flow and pyrogas pressure, residual oxygen contact, and for biochar also quenching/activation procedures (Boateng, Garcia-Perez, Masek, Brown, & Campo, 2015; Hagemann et al., 2018; Weber & Quicker, 2018).

The solid pyrolysis product, biochar, is a highly porous material consisting mainly of polyaromatic hydrocarbons and inorganic species originally contained in the biomass. Bio-oil is a dark brown, oil-like liquid composed of water and more than 100 oxygenated condensable hydrocarbon species including acetic acid, methanol, aldehydes, ketones, phenols, oligomeric sugars, and water-insoluble lignin-derived compounds (Sanna, Li, Linforth, Smart, & a, Andrésen JM, 2011). The remaining permanent pyrogas includes CO, CO₂, CH₄, H₂, and C_xH_y; it is highly inflammable. To date, a multitude of different pyrolysis technologies exists that are usually optimized for one of the products, for example fast or flash pyrolysis for bio-oil, slow pyrolysis for biochar, or gasification for pyrolytic gases.

3 | BIOCHAR CARBON PERSISTENCE

During the last decade, biochar was increasingly discussed as a tool for carbon sequestration in soil (Fowles, 2007; Laird, 2008; Lehmann, Gaunt, & Rondon, 2006; Matovic, 2011; Woolf, Amonette, Street-Perrott, Lehmann, & Joseph, 2010; Woolf, Lehmann, & Lee, 2016). It is the most resistant form of organic carbon in soils as well as in lake and ocean sediments (Cotrufo et al., 2016; Lehmann et al., 2015; Reisser, Purves, Schmidt, & Abiven, 2016; Zimmerman & Gao, 2013). In the absence of very long-term (1,000 years) field experiments in various environments and climatic zones, the MRT can only be approximated by (a) short-term (<10 years) experimental data, combined with mathematical decay models and temperature normalization (Kuzyakov, Bogomolova, & Glaser, 2014; Lehmann et al., 2015), by (b) bottom-up assessments of fire frequencies and pyrogenic carbon (PyC) leftovers from

natural fires (Cheng, Lehmann, & Engelhard, 2008; Santín et al., 2017), or by (c) archeological evidence (Braadbaart, Poole, & Brussel, 2009; Criscuoli et al., 2014).

The MRT of biochar is strongly related to its H/C_{org} ratio (which depends mainly on the pyrolysis temperature) and to the environmental conditions of its storage (Braadbaart et al., 2009; Camps-Arbestain, Amonette, Singh, Wang, & Schmidt, 2015). In a meta-analysis of 111 experiments on biochar persistence, Lehmann et al. (2015) estimated that biochars with a H/C_{org} ratio of <0.4 have, when applied to soil, a MRT of >1,000 years, corresponding to half-life ($T_{1/2}$) times of ~700 years. Similar estimates were obtained in a review by Zimmerman and Gao (2013). Another meta-analysis by Wang, Xiong, and Kuzyakov (2016) based on 24 studies with stable (¹³C) and radioactive (¹⁴C) carbon isotopes found MRTs of 556 years independent of the H/C_{org} ratio. However, the soil environment seems to play a dominant role in PyC persistence. While the majority of field and laboratory studies reveal centennial MRTs of >100 years (Lehmann et al., 2015; Rasse et al., 2017), some studies show that under certain soil (biota) conditions, biochar can be degraded biologically with much shorter MRTs (de la Rosa, Miller, & Knicker, 2018; de la Rosa, Rosado, Paneque, Miller, & Knicker, 2018). In their recent assessment of the worlds' stocks of PyC, Reisser et al. (2016) found that soil PyC stocks average 13.7% (i.e. 200 Pg C globally) of the overall soil organic carbon stocks down to 2 m depth. Soil clay content and pH were the variables with the strongest predictive value for high PyC contents in soils. However, native, fire-derived PyC in soils is chemically different to biochar produced from the same feedstock; the chemical characteristics of biochar produced from the same material point toward greater stability of the latter (Santín et al., 2017).

Once mixed into soil, PyC particles shatter into micro- and nanoparticles (Zimmerman & Gao, 2013). This is mainly a physical process, that is the chemical structure and the amount of carbon stored remain unchanged (Spokas, et al., 2014). Fine particles can be transported vertically to deeper soil horizons, groundwater, or horizontally into adjacent soils or waterbodies where it may be protected against degradation. In fact, deep soil horizons are the most important compartments for sequestration of soil organic carbon on timescales of decades to centuries (Lorenz & Lal, 2014). Over longer timescales, groundwater and sediments may be more relevant sequestration compartments due to micronized biochar-carbon species being even better preserved there from microbial and chemical degradation (Zimmerman & Gao, 2013). Micron-sized and nanostructured PyC may ultimately reach the ocean (Foerid, Lehmann, & Major, 2011; Hockaday, Grannas, Kim, & Hatcher, 2007; Jaffe et al., 2013; Major, Lehmann, Rondon, & Goodale, 2010). In the ocean floor sediments, PyC

MRTs of >6,000 years were calculated (Coppola, Ziolkowski, Masiello, & Druffel, 2014). However, to the best of our knowledge, no published study experimentally proved and quantified the transfer of PyC from topsoil applications to waterbodies and sediments (Maestrini et al., 2014). Often, a proportion of an applied biochar are just missing after several years without having left the soil system as CO₂ efflux (e.g. Major et al., 2010).

Based on the available data, it is hard to provide a globally valid leakage rate of biochar applied to soil after 80 years. Biochars produced at pyrolysis temperatures >400°C show MRTs, based on extrapolations from degradation assessments of at least three years, that range from 201 years (Singh, Cowie, & Smernik, 2012) to 4,419 years (Lehmann et al., 2015; Zimmerman & Gao, 2013), depending on the models, degradation methods, and biochar characteristics. Under a conservative estimation and considering a double-exponential decay model (Lehmann et al., 2015; Zimmerman & Gao, 2013), we assume average C-leakage rates for the first 100 years after soil application (BC₊₁₀₀) between 10% at molar H/C_{org} ratios below 0.4% and 20% above. However, caution is recommended as some soils, for example with low SOC and frequent harvest-residue fires or frequent frost–thaw cycles, may turn out to be less suitable for biochar carbon sequestration causing lower MRTs (Rosa, Rosado, et al., 2018). While more research about mechanisms of PyC degradation and the fate of the degradation products are clearly needed, three meta-analyses and all studies on biochar persistence in soil (based on >120 experiments) confirm that biochars are much more recalcitrant than their precursor materials and natural SOM and that MRTs exceed the centennial scale.

4 | BIOCHAR USES AND FURTHER CLIMATE-RELEVANT EFFECTS

Biochar can not only be used as soil amendment but also in multiple ways for industrial products like construction materials (Gupta & Kua, 2017), for wastewater treatment (Mohan, Sarswat, Ok, & Pittman, 2014), and for electronics (Gu et al., 2014). In all of these products, PyC can serve as a C-sink, as long as the product is not thermally degraded and oxidized during use, recycling, or disposal. When biochar is not used as a soil amendment but, for example, as a composite building material or stored in a long-term deep soil repositories, it can likely be protected more efficiently from microbial and chemical degradation to reach MRTs comparable to those of PyC in sediments (Coppola & Druffel, 2016).

To date, biochar is mainly used as a soil amendment, as animal feed ingredient, for manure treatment in agriculture (Schmidt & Shackley, 2016) or as a compost or planting

substrate additive (Jaiswal, Elad, Cytryn, Graber, & Frenkel, 2018; Kern et al., 2017). When applied to soil, biochar can, but does not always, improve parameters like soil nutrient retention, water retention, soil pH, cation exchange capacity, or microbial activity, with effects strongly depending on both soil and biochar characteristics (Atkinson, Fitzgerald, & Hipps, 2010; Cornelissen et al., 2013; Lehmann et al., 2011) and plant species grown on it (e.g. Guereña et al., 2015; Schmidt, Pandit, Cornelissen, & Kammann, 2017). In the longer term, for example with repeated additions of biochar organic blends, biochar will modify the original soil chemical and physical properties and cause bulk density decreases, improved water infiltration, and increased stocks of water or plant-available nutrients. Such modifications are frequent in PyC-rich anthropogenic dark earth soils worldwide (Glaser & Birk, 2012; Solomon et al., 2016) or at old charcoal-making (kiln) places (Borchard et al., 2014; Criscuoli et al., 2014).

Biochar can have contrasting effects on nonpyrogenic soil organic carbon stocks (Wang et al., 2016). As shown in some studies, biochar soil application may enhance the accumulation of plant-derived carbon entering the soil (litter, root exudates) and thus increase the content of soil organic carbon beyond the addition of biochar's PyC (Amendola et al., 2017; Bruun, Petersen, Hansen, Holm, & Hauggaard-Nielsen, 2014; Ventura et al., 2014; Weng et al., 2017). In some cases, however, decomposition of already present nonpyrogenic soil organic carbon was accelerated (Wardle, Nilsson, & Zackrisson, 2008; Whithman & Lehmann, 2015). Thus, biochar can have positive or negative priming effects; particularly, the interaction with plant roots is not well understood (Cross & Sohi, 2011; Wang et al., 2016). To trace C flows, C sources must be traced by stable isotopes to three CO₂–C sources: plant-derived C, soil organic matter-derived C, and biochar-derived C. Due to the complexity of such experiments, the number of published studies is still low.

Several meta-analyses of biochar field trials indicate average yield increases of 10%–20% following amendments of more than 5 t/ha of pure, not-nutrient-enriched biochar (Crane-Droesch, Abiven, Jeffery, & Torn, 2013; Jeffery, Abalos, Spokas, & Verheijen, 2015). While yield increases (with pure biochar use) are low or absent in temperate soils, biochar application increased yields in tropical and subtropical soils by 25% on average, according to the latest extensive meta-analysis (Jeffery et al., 2017). The increase also enhances accumulated C from the atmosphere by the same percentage; if the same practice is maintained over decades, the sustained increase in NPP increases the terrestrial carbon pool by the corresponding amount. Such a “return of investment” of biochar use, that is the increase in non-PyC SOC and NPP, may be as important for PyCCS as the PyC sequestration by the biochar itself.

However, the use of large amounts of pure biochar may not become the final pathway of soil application in the future. Biochar may serve as raw material for different agricultural (fertilizer) products rather than being a final amendment product in itself. For example, biochar made from invasive weed and harvest residues improved fertilizer efficiencies and boosted yields in fertile soils in Nepal by on average 100% when used as a nutrient carrier at low dosages (<1–2 t/ha) (Schmidt et al., 2017). Moreover, biochar can be used as a tool to further reduce agronomic GHG emissions (Kammann et al., 2017) as it has been shown to reduce methane emissions in saturated soils, for example in rice agriculture (Han et al., 2016; Jeffery, Verheijen, Kammann, & Abalos, 2016), or N₂O emissions from fertilized soils by 40%–50% on average (meta-studies: Cayuela et al., 2014; Schirrmann et al., 2017).

5 | BIO-OIL, THE LIQUID PRODUCT OF PYROLYSIS

While biochar is well established as a means of carbon sequestration (Brassard, Godbout, & Raghavan, 2016), bio-oil was not yet discussed as such. Bio-oil, also known under the names pyrolysis liquids, pyroligneous acid, or (more historically) wood vinegar, is a very complex liquid mixture composed of hundreds of different oxygenated hydrocarbons and water. It is an obligate by-product of all kinds of pyrolysis. When bio-oil is the main intended pyrolysis product, optimal production parameters are fast (<1 s) pyrolysis at 500°C (Xie, Xu, Fang, Luo, & Ma, 2013).

Fast pyrolysis, bio-oil is typically viscous but free-flowing and dense (~1.2 kg/L), has usually a dark brown color, is acidic (pH ~2.5), and has a low net calorific value (NCV <20 MJ/kg) due to the high oxygen content and moisture (Mohan, Pittman, & Steele, 2006; Oasmaa, Beld, Saari, Elliott, & Solantausta, 2015). It is a micro-emulsion, in which pyrolytic lignin and other water-insoluble organic compounds are dispersed. Pyrogenic organic compounds dissolved in the aqueous phase serve as emulsifiers, though it has a strong tendency for phase separation. A decanted heavy oil phase at the bottom, rich in nonpolar compounds (mainly pyrolytic lignin), can be distinguished from an upper aqueous phase rich in polar compounds (light organic compounds and heavy sugars) (Oasmaa, Fonts, Pelaez-Samaniego, Garcia-Perez, & Garcia-Perez, 2016). Additionally, a distinctive upper layer rich in extractives (mainly waxes, fatty acids, phenolics) may form.

A typical composition of bio-oil made from woody biomass by fast pyrolysis at 500°C includes, in mass percentage, 25% water, 20% pyrolytic lignin, 55% of organic water-soluble compounds (around 30% of sugars produced from cellulose and hemicellulose and 20% of carbonyls and

alcohols), and small amounts of solid particles including char, ash, or sand (Bayerbach & Meier, 2009; Oasmaa et al., 2016, 2015).

Bio-oil can be also obtained from slow pyrolysis processes over the whole pyrolysis temperature range (350–900°C) and from all types of biomass feedstocks (Sanna et al., 2011). Thus, pyrolysis optimized for biochar production still yields bio-oil, though at considerably lower amounts and with some distinct differences in composition. At a given temperature, slow pyrolysis bio-oil has similar elemental composition on a dry basis, although with the following differences:

- The water content is increased, which leads to enhanced phase separation.
- The sugar content is significantly reduced due to secondary reactions (Anca-Couce, Mehrabian, Scharler, & Obernberger, 2014; Branca, Giudicianni, & Blasi, 2003).
- The pyrolytic lignin yield is reduced.
- The production of benzene, toluene, and xylene isomers (BTX) and polycyclic aromatic hydrocarbons (PAH) is enhanced to significant values, which can be a concern for some applications due to their toxicity (Fagernäs, Kuoppala, & Simell, 2012; Milhé et al., 2013).

6 | BIO-OIL USES AND ITS SEQUESTRATION

Bio-oil can be employed for heat and power generation in gas turbines or furnaces and, after an upgrading, as biofuel for internal combustion engines (Elliott, 2007; Fagernäs, Kuoppala, Tiilikkala, & Oasmaa, 2012; Kauffman, Dumortier, Hayes, Brown, & Laird, 2014). Here, however, we do not consider the purpose of energetic use which is of course possible but would release the carbon back to the atmosphere. We rather consider applications and uses that maintain the bio-oil's carbon sequestered. Instead of combusting the nonsolid by-products of biomass pyrolysis as suggested by Woolf et al. (2016), the bio-oil could be either used in a biorefinery approach (Table 1) or sequestered in geological repositories as discussed below.

Before the advent of fossil fuel extraction in the early 20th century, main raw materials for the chemical industry were produced by wood distillation, which is a historical name for pyrolytic bio-oil production. Besides tar and pitch for building ships and roads, basic chemicals like naphthalene, anthracene, aniline, phenol, benzene, methanol, acidic acid, and acetone were produced with pyrolysis systems for the nascent chemical industry (Aftalion, 2001). Until 1950, methanol was still mainly produced through wood pyrolysis, though by then the much cheaper and more homogeneous fossil oils replaced the biomass materials as important resource for the chemical industry (Soltes

TABLE 1 Suggested and tested uses of bio-oil-based products

| Bio-oil-based product and use | References |
|----------------------------------|---|
| Bioplastics | Crombie and Mašek (2014) |
| Asphalt amendment | Raman et al. (2015) |
| Amendment for building materials | Czernik and Bridgwater (2004) and Xie et al. (2013) |
| Wood preservative | Czernik and Bridgwater (2004) and Tiilikkala, Fagermäs, and Tiilikkala (2010) |
| Biocide and crop protection | Tiilikkala et al. (2010) |
| Feed additive | Yamauchi, Ruttanavut, and Takenoyama (2010), Cai, Jiang, and He (2011) and Chu et al. (2013) |
| Plant growth enhancer | Ratanapisit, Apiraksakul, Rerngnarong, Chungsiriporn, and Bunyakarn (2009), Tiilikkala et al. (2010) and Hagner, Penttinen, Tiilikkala, and Setälä (2013) |

& Elder, 2017). Currently, 10% of annually produced fossil oils are used as raw material by the chemical industry (Keim, 2014). If humanity succeeds in limiting mean global warming to 1.5°C or 2°C as specified in the Paris Agreement (Schleussner et al., 2016, Rockström et al., 2017), carbon emissions will have to be reduced by 90% until 2050. Emission reduction of this order can only be achieved with rapid and complete phasing-out fossil fuels within the next 30 years (Rogelj et al., 2015, Bertram et al., 2015; Sanderson et al., 2016; Schleussner et al., 2016). This, however, implicates that the 440 million tons of fossil oil (OECD, 2018) that are currently extracted and used as raw material for the chemical industry would have to be replaced by biomass-derived raw chemicals, that is bio-oil, cellulose, starch, lactic acid monomers.

Most chemical products that are currently produced from fossil fuels can as well be produced from bio-oils in a biorefinery approach (see Table 1) though today (until CO₂ emissions are properly taxed) at higher costs.

The most pertinent industrial C-storing use of bio-oil is certainly its blending to asphalt binder for road construction. Raman, Hainin, Hassan, and Ani (2015) have shown that the addition of 5%–20% of bio-oil to the asphalt mixture improves asphalt quality like stiffness and durability. If 10% bio-oil by weight were added as binder additives and/or aggregates to 1.8 billion tons of asphalt poured each year, 180 million tons of carbonized material would be entombed annually. With a carbon content of 55%, the amount of sequestered C in asphalt could be 100 million tons per year. Bio-oil could further be added to concrete and other building materials (Czernik & Bridgwater, 2004; Xie et al., 2013), which would also become long-term

carbon storage deposits, as those materials would end their material life cycle in other construction works or landfills. Those applications could be realized already within years, that is short to mid term.

More challenging is the use of bio-oil as raw material for bioplastics and other types of composite materials (Crombie & Mašek, 2014), which will need advanced chemical engineering. Depending on the life cycle of the plastic materials, carbon fibers and carbon composites, the persistence of the carbon in the terrestrial system would vary between short, mid, and long term. With the increasing public and political pressure on recycling plastic materials (instead of waste combustion and landfill dumping), the carbon contained in the advanced biomaterials could be stored for much longer timescales in the terrestrial system, so that the material use and recycling would become a long-term carbon sink.

Research and development in regard to biorefinery of bio-oil is, although based on a long history, currently only at the beginning though, from the theory, it is rather clear that bio-oil could well become a decisive raw material for the chemical industry once the production of fossil fuels would be banned. Further possible fields of bio-oil application include agronomy, animal husbandry, pharmaceutical industry, or wood preservation (Table 1). However, those latter applications would have a rather short carbon storage capacity.

As long as the chemicals or materials using bio-oil carbon are not combusted or otherwise oxidized, the carbon remains sequestered, augmenting the terrestrial carbon pool. With advanced end-of-life product management, the carbon of these bio-oil based products could be recycled or sequestered in protected deposits at the end of its lifetime, then still serving as a C-sink.

7 | GEOLOGICAL STORAGE OF BIO-OIL

Compared to fossil crude oil, bio-oil is characterized by a higher moisture and oxygen content, lower viscosity, and lower caloric value. However, both liquids are similar in regard to pumping, transportation, and storage (Czernik & Bridgwater, 2004; Gueudré et al., 2017; Staš, Chudoba, Kubicka, Blazek, & Pospíšil, 2017). It can be assumed that the environmental toxicity of fossil crude and bio-oil is similar (Fermoso, Pizarro, Coronado, & Serrano, 2017; Louwes et al., 2017; Varma & Mondal, 2017; Zhang, Chang, Wang, & Xu, 2007) though direct comparisons and ecotoxicological assessments were not yet done. It is clear that both should not be applied to soil. However, bio-oil carbon could, as crude oil was for millions of years, be sequestered for the long term (>1,000 years) when pumped into depleted fossil oil deposits (Werner, Schmidt, Gerten,

Lucht, & Kammann, 2018). Those deposits would have the advantage that they are typically deeper than 1,000 m below the surface, that is deep below the groundwater zone (Philp, 1985). They would thus be protected from oxygen and microbial degradation. Any risk of leaching would be avoided. The bio-oil carbon could thus, in theory, be sequestered without any apparent environmental risk while being protected from decomposition. The geological integrity of the sequestration deposits was demonstrated by the ability to hold fossil oil for millions of years without leakage. Risks of volatilization to the atmosphere, except for the transportation to the final geological deposit, could be assumed to be minimal considering that bio-oil has a poor volatility compared to fossil oil (Czernik & Bridgwater, 2004).

The carbon density of bio-oil (590–750 kg C/m³ (Neves, Thunman, Matos, Tarelho, & Gómez-Barea, 2011)) is slightly lower than that of fossil oil (800 kg C/m³ (Czernik & Bridgwater, 2004)) though more than three times higher than that of liquefied CO₂ (135–220 kg C/m³ (IPCC, 2005)), which is proposed to be used for BECCS. Geologic sequestration of bio-oil would therefore take less volume than CO₂-CCS. Moreover, it would avoid most of the known and unknown short- and long-term risks associated with geological storage of CO₂ (CO₂ leakage, alteration of groundwater chemistry, seismic activity, etc. (Vaughan & Gough, 2016; Burns & Nicholson, 2017)). In Werner et al. (2018), the carbon leakage during transportation of the bio-oil to the final repository and the millennial underground storage was assumed to be 2% over 80 years for the geological bio-oil storage pathway.

Today, the geological storage of bio-oil can only be considered a thought experiment. It certainly seems counterintuitive to replenish fossil oil reservoirs with bio-oil, when today's fossil oil extraction continues unabated at 4.4 Gt per year (OECD, 2018). However, it might become one of the options of last resort when, as it appears today, the phasing out of fossil fuels will be delayed by one or more decades. To return atmospheric CO₂ concentrations to a safe level, humanity might be soon forced (Rockström et al., 2016) not only to stop fossil fuel extraction but also to reverse the direction of liquid-C movement to geological stores using the same pipelines. In the meantime, bio-oil may reduce the dependency on fossil fuels by being used as energy carrier or raw material for the chemical industry.

The bio-oil can either be stored as one mixed liquid substance or it can be stored in different fractions, which are obtained either by phase separation or by fractional condensation. Fractional condensation of bio-oil would be controlled by a liquid–vapor equilibrium separating the heavy tars (polar and nonpolar, including pyrolytic lignin and heavy sugars) which condense at higher temperatures and an aqueous phase with light organic molecules which

condense at lower temperatures (Oasmaa et al., 2016). The composition of each phase can be controlled by the temperature in the fractional condensation when cooling down the pyrolysis volatiles or by stepwise distillation of biomass (i.e. recovering volatiles when heating the biomass at 250, 350, 400°C). It would thus be possible to recover first those parts of the pyrolytic oil that are, already today, economically valuable for bio-based chemical materials (C sequestration in economically valuable products) and to sequester the remaining fractions in geological deposits.

While the aqueous phase of the oil is well pumpable but has a low pH (<3), the heavy tar fraction is not well pumpable but has a more neutral pH, which would facilitate the intermediate storage of that fraction. The following bio-oil properties should further be considered when planning for transport and storage:

- Bio-oils are incapable of sustaining combustion and can be classified as nonflammable liquids (Oasmaa et al., 2012).
- Bio-oil is slightly corrosive, and toxicity increases from fast to slow pyrolysis bio-oils, which is associated with a higher concentration of PAHs (Blin, 2005).
- Bio-oil has a high viscosity, commonly in the order of tens of centistokes, and the viscosity increases during storage (Mohan et al., 2006).
- Short-term storage should be conducted in the type of containers recommended for fast pyrolysis oil (Oasmaa et al., 2016), which are composed of corrosion-resistant steel and materials such as AISI 304, AISI 316, polytetrafluoroethylene (PTFE), high-density polyethylene (HDPE), and polyvinyl chloride (PVC).

It can be expected that dedicated research and engineering could solve the mentioned storage and displacement issues. However, more research is clearly needed, especially for value-generating and cascading uses of bio-oil for C-sequestering and its environmentally safe long-term storage.

8 | OXIDATIVE USE AND SEQUESTRATION OF THE GASEOUS CARBON (CO₂-CCS)

Depending on the process parameters, the carbon contained in the permanent pyrogas accounts for 15%–45% of the total carbon of the initial biomass (Table 2). To ensure a high C-sequestration efficiency of PyCCS, the gaseous carbon should be included in the sequestration scenarios (Figure 1). Usually, the gas is combusted to produce thermal energy to drive the pyrolytic process (Crombie & Mašek, 2014) or to produce electricity. However, in conventional combustion where air is used as oxidizing agent, the flue

TABLE 2 Pyrolysis product properties for five PyCCS scenarios

| | Units | Slow pyrolysis 400°C | Slow pyrolysis 500°C | Slow pyrolysis 650°C | Slow pyrolysis 800°C | Fast pyrolysis 500°C |
|-----------------------------|-------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Ash content | % d.b. | 1 | 1 | 1 | 1 | 1 |
| Initial moisture | % w.b. | 25 | 25 | 25 | 25 | 5 |
| Char yield | % w.b. | 26.1 | 22.4 | 17.9 | 14.4 | 20.0 |
| C char | % | 74.6 | 79.8 | 83.8 | 85.4 | 78.6 |
| H char | % | 3.4 | 2.5 | 1.6 | 1.0 | 2.5 |
| O char | % | 19.1 | 14.4 | 10.4 | 8.4 | 14.1 |
| Ash char | % | 2.9 | 3.3 | 4.2 | 5.2 | 4.8 |
| H/C ratio | – | 0.54 | 0.38 | 0.23 | 0.14 | 0.38 |
| Liquids yield | % w.b. | 52.8 | 56.1 | 54.3 | 49.2 | 61.2 |
| C liquids | % d.b. | 56.3 | 56.3 | 59.9 | 63.6 | 56.3 |
| H liquids | % d.b. | 6.1 | 6.1 | 6.4 | 6.7 | 6.1 |
| O liquids | % d.b. | 37.6 | 37.6 | 33.6 | 29.7 | 37.6 |
| Moisture liquids | % w.b. | 66.4 | 62.4 | 64.5 | 71.2 | 28.9 |
| Permanent gas yield | % w.b. | 21.1 | 21.4 | 27.7 | 36.5 | 18.9 |
| C gases | % | 37.1 | 35.1 | 38.6 | 44.0 | 37.5 |
| H gases | % | 7.1 | 7.4 | 6.9 | 6.5 | 6.5 |
| O gases | % | 55.8 | 57.5 | 54.5 | 49.5 | 56.0 |
| LCV biomass | MJ/kg w.b. | 13.4 | 13.4 | 13.4 | 13.4 | 17.7 |
| LCV char | MJ/kg | 27.2 | 28.7 | 29.7 | 29.8 | 28.3 |
| LCV liquids | MJ/kg w.b. | 5.6 | 6.6 | 6.8 | 5.6 | 14.7 |
| LCV gases | MJ/kg | 13.9 | 13.4 | 14.5 | 16.4 | 13.5 |
| C-density of char | kg/m ³ | | 239 | | 298 | 235 |
| C-density of liquids | kg/m ³ | | 672 | | 590 | 734 |
| C in char | % | 52.1 | 48.0 | 40.3 | 32.9 | 33.2 |
| C in liquids | % | 26.8 | 31.9 | 31.0 | 24.1 | 51.9 |
| C in gases | % | 21.0 | 20.2 | 28.7 | 43.0 | 15.0 |
| Leakage BC ₊₁₀₀ | % | 20 | 10 | 10 | 10 | 10 |
| CSE without CO ₂ | % | 70 | 74 | 67 | 53 | 81 |
| CSE | % | 88 | 94 | 94 | 94 | 95 |

Note. BC+100: biochar carbon that remains after 100 years after soil amendment; CSE without CO₂: CSE of the PyCCS pathway with biochar and bio-oil sequestration only; CSE: total carbon sequestration efficiency of the complete PyCCS pathway; d.b.: based on dry matter; LCV: low calorific value; w.b.: based on wet matter; PyCCS: pyrolytic carbon capture and storage.

Biomass feedstock for all considered scenarios is woody biomass. The correlations are derived from pyrolysis process parameters, and they are based on the assumptions and formula presented in the SI.

gas contains beside CO₂ and H₂O more than 50% N₂. Separating the flue gas from the N₂ to obtain pure CO₂ for CCS purposes would be a complex and expensive process increasing the cost of CO₂–CCS heavily. It would therefore only be economically viable in large-scale industrial devices (Reynolds, Ebner, & Ritter, 2006). As one important advantage of PyCCS is the option for decentralized,

small-scale production units (e.g. one unit per farm or village), this may exclude CO₂–CCS from gas combustion. A recent alternative that could well be set up in small-scale devices is chemical-looping combustion (CLC). In CLC, a solid oxygen carrier is used for combustion instead of air (Adanez, Abad, Garcia-Labiano, Gayan, & Diego, 2012). The oxygen carrier, most often based on nickel, iron, or

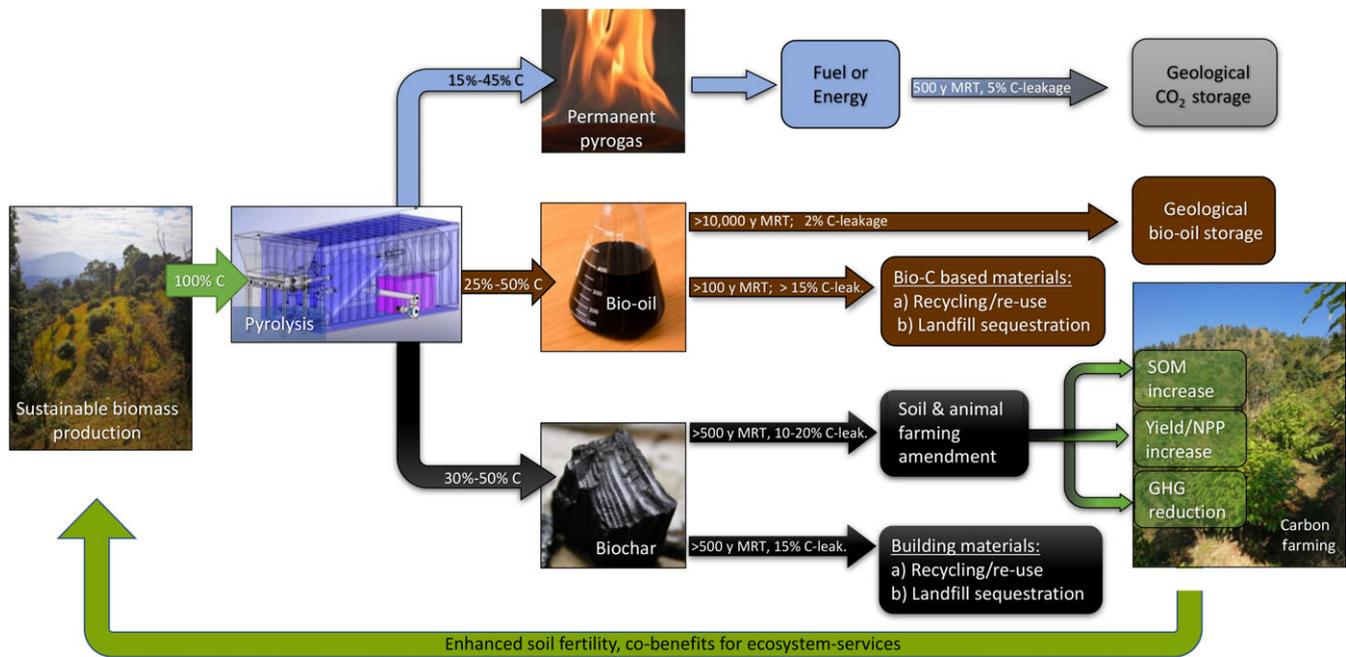


FIGURE 1 General pyrolytic carbon capture and storage scheme for pyrolytic treatment of biomass, the pathways of solid, liquid, and gaseous products, their use and sequestration scenarios, the respective C-leakage rates, and the circular effect on carbon farming systems and sustainable biomass production

manganese oxides, is moved through the permanent pyrogas stream in a countercurrent process where the metal-bound oxygen reacts with the gas. Once the oxygen carriers are reduced, they are conveyed out of the combustion reactor into another reactor where they get reoxidized with air before being reused. This chemical looping can be repeated for countless cycles without losing its efficiency (Adanez et al., 2012). The reaction products of permanent pyrogas CLC are nearly pure CO₂ and water, which can easily be separated by condensation. The CO₂ could then be treated as in conventional CO₂-CCS scenarios (Zakkour, Kemper, & Dixon, 2014).

Alternatively, the gases could also be treated with a chemical-looping reforming (CLR) process that results in CO₂ and H₂ as reaction products (Adanez et al., 2012; de Diego et al., 2008). While the resulting H₂ will be a carbon-neutral energy carrier, the pure CO₂ could be processed for geological sequestration. As this process would not generate the heat needed for pyrolysis, the required energy input needs to be generated from renewable electricity (i.e. E-pyrolysis). This approach should be investigated as a new option for power to gas.

CLC and CLR are considered as the most promising alternative to reduce the costs of CO₂ capture (Kerr, 2005) and are fitting technical opportunities to increase the C-transformation efficiency of the PyCCS technology. However, CLC and CLR in combination with pyrolysis are not yet widely tested or mature technologies. Hence, they need further development and up-scaling before being implemented at larger scales.

Following Kemper (2015) and Vaughan and Gough (2016) and assuming that captured CO₂ is harder to contain than bio-oil and biochar, we assume leakage rates of 5% over 80 years for the geological CO₂ storage.

9 | MINERAL NUTRIENT BALANCES

Biomass contains a wealth of elements beyond CHO. Although present only in lower concentrations, they are of high relevance due to their role as plant macro- and micronutrients. After harvest, essential nutrients bound in biomass should be returned to biomass-producing agroecosystems. Otherwise, soil fertility deteriorates over time (Hänsch & Mendel, 2009; Ingerslev, Skov, Sevel, & Pedersen, 2011). Already today, the mineral depletion of agronomically used soils is a point of concern, affecting global food security (Jones et al., 2013). This would be further accelerated when biomass is extracted without returning the minerals it contains to the soil. The latter is the case in BECCS scenarios where biomass is combusted to produce energy, and the resulting ashes cannot or can only partially be returned back to soils due to heavy metal, PAH, and dioxin contamination (Ingerslev et al., 2011) or to toxic ash transformation reactions during combustion (Boström et al., 2012). On the other hand, returning the ashes and minerals to the soil with the biochar will likely deliver a “mineral weathering” CCS contribution to CDR, which would need to be further explored and quantified.

Nitrogen is an important nutrient of plants, and its availability is often limiting for plant growth. In biomass, it is mainly present in the form of proteins. The main primary pyrolysis product of proteins at temperatures around 500°C is amides, which are present in the bio-oil. Nitrogen is further retained to a lower extent in the biochar but also released in small amounts as NH₃ and HCN with the gas phase (Nussbaumer, 2003). At higher temperatures, tars crack, reducing the N-content in the bio-oil and enhance the production of NH₃ and HCN in the permanent pyrogas. NH₃ and HCN are precursors of nitrogen oxides (NO_x), which can form during combustion of the volatiles depending on the combustion technology employed (Vermeulen, Block, & Vandecasteele, 2012). However, using a proper combustion approach, harmful emissions can be minimized (Nussbaumer, 2003) to near zero (i.e. N₂ release), in accordance with the clean air regulations that are in place in industrialized countries such as Germany.

Several elements such as Ca, Si, Mg, Al, Fe, or Ti are almost entirely retained in the solid fraction due to their nonvolatile nature. At pyrolysis temperatures of up to 700°C, alkali metals (K and Na) are mainly retained in the char, but they are partially released to the gas phase above 700°C (van Lith, Jensen, Frandsen, & Glarborg, 2008). Most of the chlorine and a considerable proportion of sulfur are released to the gas phase at temperatures above 400°C where it can be easily scrubbed off (Van Lith, Jensen, Frandsen, & Glarborg, 2008). Cl and S-bearing organic compounds are further present in the bio-oil. However, the sulfur and chlorine content of bio-oil made from woody biomass are lower than 100 ppm (Oasmaa et al., 2015), which is considerably lower than the sulfur content in crude oil.

Thus, most of the biomass nutrients are retained in the biochar when slow pyrolysis technology is used at temperatures below 700°C. The bio-oil is mainly composed of carbon, hydrogen, and oxygen, with a minor content of nitrogen, still smaller amounts of sulfur and chlorine, and only traces (in the ppm range) of all other elements (Oasmaa et al., 2015). The nutrient concentrations in biochar and bio-oil mainly depend on the initial biomass composition with woody feedstock having lower and annual harvest residues have much higher mineral contents, particularly graminoid species (e.g. switchgrass, miscanthus, or crop residue of rice, wheat, maize, or others) with their comparably high silicon content.

10 | CARBON BALANCES AND OPTIMIZED PYROLYSIS PARAMETERS FOR PYCCS

The overarching aim of PyCCS is to enable low-cost high C-transformation rates (i.e. minimum losses of carbon to

the atmosphere) and products with a long-term C-stability. As biochar is the pyrolytic carbon product that can be sequestered at the lowest costs and with large cobenefits, high biochar yields are targeted. As the sequestration of the carbon from the permanent pyrogases is the most expensive and technically challenging C-sequestration pathway, the gas production should be minimized. While pyrolysis is often optimized for the production of one product and the other two products are considered either a waste or a barely valued coproduct, in PyCCS scenarios all three pyrolysis products have to be used to optimize the transformation of the biomass carbon into pyrogenic forms for long-term C sequestration. Overall, an optimum between production costs, robustness of the process, product distribution, quality and product value, sequestration potential (half-life in the terrestrial system), and the recycling of biomass extracted nutrients should be achieved (Appendix S1).

The distribution and characteristics of the solid, liquid, and gaseous pyrolysis products depend mainly on the pyrolysis temperature, particle size, residence time of the pyrolysis volatiles in the kiln, pressure, and feedstock composition (Anca-Couce, 2016). Slow pyrolysis at low temperatures (350–450°C) has the highest solid yield, though the carbon stability of the biochar is rather low, as is the quality of the bio-oil (Camps-Arbestain et al., 2015; Fagernäs, Kuoppala, & Simell, 2012). At a given pyrolysis temperature, the biochar yield can further be increased with slow heating rates, higher residence time of the volatiles, larger particle size of the feedstock, and higher pressure (Anca-Couce, 2016).

At higher pyrolysis temperatures (700–850°C), the permanent pyrogas yield is significantly increased; consequently, lower biochar and bio-oil yields will be obtained (Anca-Couce, Sommersacher, & Scharler, 2017; Sadaka & Boateng, 2009; Tripathi, Sahu, & Ganesan, 2016). The resulting biochar contains graphite-like carbon (instead of amorphous carbon), which increases its recalcitrance, for example in soil (Budai et al., 2014; Keiluweit, Nico, Johnson, & Kleber, 2010). At these high temperatures, the pyrolytic liquids show a higher carbon content and higher aromaticity and contain a large spectrum of typical tertiary tars (Anca-Couce, 2016). Tertiary tars are molecules free of oxygen, which can be stable at high temperatures having a single aromatic ring (BTX) or several rings (PAH). Also, high-temperature pyrolysis oils have a high content of phenols. Therefore, high concentrations of BTX/PAH and phenols might pose an environmental concern for certain bio-oil use scenarios (e.g. when used in asphalt or for plant protection), but not when sequestered geologically.

Fast pyrolysis is less suited for the purpose of carbon sequestration because the overall energy expenditure is high due to the necessary drying and milling of the feedstock and very high heating rates (>500°C/s) (Lédé &

Authier, 2015). Moreover, the fast pyrolysis biochar yield and quality are rather low (Brewer et al., 2012).

To provide an example for the selection of optimal PyCCS parameters, we expose in Table 2 the results of an exemplary calculation of carbon yields, distribution, and composition for four slow and one fast pyrolysis scenarios as a function of the pyrolysis temperature according to Neves et al. (2011). Their comprehensive literature review of pyrolysis experiments includes data from more than 60 biomass samples with different reactor configurations and temperatures between 350 and 1,000°C.

Modifying pyrolysis conditions determine yield and quality of biochar, bio-oil, and permanent pyrogas. Summarizing the above considerations, we suggest the following general guidelines to optimize the pyrolysis process conditions for PyCCS scenarios:

- Produce a low portion of permanent pyrogas and high portion of biochar and bio-oil (avoid temperatures >700°C);
- Maximize the biochar yield compared to bio-oil, using rather slow than fast pyrolysis, as it is easier and less cost-intensive to sequester biochar, in soils or materials, than bio-oil;
- Achieve low H/C ratios of <0.4 and thus a high recalcitrance of biochar by using pyrolysis temperatures not lower than 450°C.

Based on these guidelines, we suggest using slow pyrolysis with a highest treatment temperature between 500 and 650°C for PyCCS-based CDR. In this temperature range, a compromise between high biochar yield and its recalcitrance is achieved for a large spectrum of diverse biomass feedstocks (Brassard et al., 2016; Weber & Quicker, 2018). At these temperatures, the gas yield is low, and only few minerals end up in the bio-oil. When the resulting biochar is applied to soil, either directly or via cascading use in animal husbandry or prior material use (Schmidt, 2012), most of the minerals (but only reduced portions of nitrogen) can be recycled within the biosphere.

However, the suggested temperature range does not exclude the application of higher or lower pyrolysis temperatures in individual cases. Depending on the economic scenarios and intended uses of the pyrolysis products, the production parameters can and sometimes should be adapted, for example, lower temperatures are recommended to produce biochar for peat replacement (Kern et al., 2017) or for soilless media to enhance plant growth and/or disease suppression (Jaiswal et al., 2018). Higher temperatures are necessary to produce activated biochar for remediation of contaminated soils or for electric capacitors (Frackowiak, 2007; Hagemann et al., 2018). The latter pyrolysis conditions will increase the yield of gas, but if the CO₂

after the oxidation of these gases is captured and stored, the overall carbon efficiency can still be high.

To pyrolyze biomass, the feedstock has to be harvested, transported, chipped, or milled. All these processes are currently executed by fossil fuel-driven machinery though it could equally be powered by carbon-neutral electricity. Except for the proposed concept of E-pyrolysis for CLR, pyrolysis itself has low electric consumption and the necessary thermal energy is provided by the permanent pyrogas oxidation (Crombie & Mašek, 2014). The postpyrolysis processing of the products like quenching and milling of biochar or the pumping of bio-oil to geological storages can be done electrically. The application of biochar to soil necessitates land management machinery, although the carbon footprint of an estimated one liter of diesel per ton of biochar is negligible and could in the near future be executed by electric tractors (Lünenbürger, 2012; Tubiello et al., 2013). Liquefaction and pumping of CO₂ after CLC or CLR are equally a process that could be powered by carbon-neutral electricity (Kerr, 2005). The carbon footprint for the production and maintenance of the machinery dedicated to the preparation, pyrolysis, and postproduction processes is compared to the amount of treated carbon negligible, although detailed calculations are missing in the literature. Based on these assumptions, we do not include further C-expenditures beside the C-leakages of the applied PyCCS products as considered in the chapters above (10%–20%, 2%, and 5% over 80 years for soil-applied biochar, geological bio-oil storage, and geological CO₂-storage, respectively).

11 | IMPLEMENTATION POTENTIAL AND ADVANTAGES OF PYCCS IN COMPARISON WITH BECCS

Biochar is suggested as a material for long-term carbon sequestration since the late 1990 s (Ogawa, 1991; Okimori, Ogawa, & Takahashi, 2003). However, burning pyrolysis liquids and gases and sequestering only the biochar result in C-sequestration efficiencies that are too low for making it a competitive NET (Werner et al., 2018). This is especially the case when biochar is produced at higher temperatures (>500°C), which is necessary to produce a recalcitrant product well suited for most material uses.

In earlier studies, the potential of PyCCS was calculated for harvest residues under the assumption that only the biochar is sequestered (Smith, 2016; Woolf et al., 2010, 2016). Compared to the current practice of burning or decomposition of these residues, pyrolysis would clearly be an improvement, even if only 40% of the biomass-C is eventually sequestered. However, the calculated NET potential of 0.7 Gt C_{eq}/year (Smith, 2016) would, even when doubled

under a complete PyCCS-scenario, not be sufficient to fulfill current climate change mitigation targets (Fajardy & Mac Dowell, 2017; Smith et al., 2015). Specific new and complementary global biomass production would thus be needed. When biomass production is undertaken for the purpose of NET, the carbon sequestration efficiency is the crucial factor that determines the size of the land area needed for biomass production (Werner et al., 2018). Increasing the carbon sequestration efficiency of a technology will thus decrease the land requirements substantially (Beringer, Lucht, & Schaphoff, 2011; Boysen, Lucht, Gersten, et al., 2016).

The current benchmark for BECCS-based NETs is a C-sequestration efficiency (CSE) of 90% (Klein et al., 2014), which can *theoretically* be attained, but only at high economic costs and environmental risks (Fajardy & Mac Dowell, 2017; Smith et al., 2015). PyCCS systems can equally *theoretically* attain CSEs of ~90% when the sequestration of CO₂-CCS is included and more realistically 70%–80% (Table 2) when only biochar *and* bio-oil are sequestered. Using the latter pathway avoids the high costs, environmental risks, and societal challenges of geological CO₂ storage. The technology for PyCCS is ready to be implemented across small-to-industrial scales: Networks of small production units could be installed avoiding the constraints of using massive industrial power plants only (Schmidt & Shackley, 2016). Rather than establishing vast industrial biomass plantations with their monoculture drawbacks, their trade-offs with food production, and other SDGs or their environmental side effects (Boysen, Lucht, Schellnhuber, et al., 2016), a network of smaller scale PyCCS systems would allow to establish biomass as a desired and cultivated coproduct of agriculture, for example in agroforestry, silvopasture, and perennial coppicing types of agricultures (i.e. carbon farming approaches, (Toensmeier, 2016)). However, the logistics of such farm-based PyCCS systems producing biochar for local soil applications while delivering the bio-oil to centralized processing facilities are challenging especially in tropical and subtropical countries with poor infrastructure and low degree of economic organization.

If PyCCS generates sustainable tCDR that are paid for by society (i.e. negative carbon taxes), economic incentives could be provided for farmers to optimize their land management with combined crop and biomass production. Thanks to the plant growth-enhancing properties of biochar-based fertilization, the same food and feed crop productivity per cultivation area could be maintained, while the focus on additional biomass production could increase the NPP of agricultural land and thus the terrestrial carbon accumulation. With biochar being applied back to agricultural soils, preferentially nutrient-loaded after cascading use (Schmidt et al., 2017), most of the nutrients would be

recycled back to the soil, maintaining the soil fertility in the long term. Thanks to the yield increasing value of biochar and the added value of bio-oil and biochar, once a market can be established for its material use, the C-sequestration costs of PyCCS may be expected to be significantly lower than for BECCS. However, for the moment this can only be assumed as it is not yet possible to provide a comprehensive cost-benefit assessment based on peer-reviewed literature.

The expected 25% yield increases in tropical and subtropical climates (Jeffery et al., 2017) following the amendment of biochar to soil would lead to a higher production of biomass and thus to more positive feedstock toward PyCCS. Consequentially, the 70%–80% C-sequestration efficiency of the biochar and bio-oil PyCCS pathway could effectively rise to >90%. Moreover, biochar application could reduce agricultural non-CO₂ GHG emissions (Kammann et al., 2017) and most likely increase nonbiochar soil organic matter (Tian et al., 2016; Weng et al., 2017). Considering all these secondary climate mitigation effects of PyCCS, the high C-sequestration efficiencies would translate into an even higher climate mitigation potential.

Another major argument for pursuing PyCCS instead of BECCS is the fact that the supposed massive switch from fossil fuel energy production to bioenergy production (170 EJ/year (Smith et al., 2015)) is economically unlikely at a large scale. Solar and wind energy production costs are expected to decrease to <0.03 USD/kWh (Kumar Sahu, 2015), whereas prices for bioelectricity production without CCS range from 0.06 USD with waste materials as feedstock to >0.12 USD for low-cost feedstock and can go up to 0.30 USD when pelletized biomass has to be purchased (International Renewable Energy Agency, 2012). Although the transformation of biomass into heat for, for example, district heating systems in temperate climates may remain economically viable at current prices of 0.02–0.04 USD/kWh, the global need for heating is rather small compared to the global electricity demand, particularly in tropical climates. Considering further that biomass will have to become the principal source of chemicals for C-based materials when decarbonization (i.e. the reduction in anthropogenic carbon emissions) eventually leads to phasing out of fossil carbon (Honary & Singh, 2010), prices for biomass feedstock and thus for bioenergy will increase rather than decrease in the future. Hence, the long-term economic viability of biomass-based electricity production becomes increasingly unlikely, even if carbon-offset payments would finance the extra costs for CCS. If the production of thermal energy from biomass remains an important factor for the future energy mix, at least in temperate climates, the bio-oil and permanent pyrogas of PyCCS systems hold an interesting potential as flexible energy carrier to produce heat on demand in the cold

season while it could be sequestered in the warm season or when market prices for heat are low. Biomass pyrolysis could also produce fuel, especially methane and hydrogen, to replace fossil fuel though the carbon sequestration efficiency of the system would be lowered.

Pyrolytic carbon capture and storage is mainly designed to produce biomaterials that have multiple industrial and agronomic uses *besides* sequestering carbon. This does, however, not exclude that in some scenarios biofuels may remain for a more or less long transitional period a valuable coproduct of PyCCS. While all pyrolytic products already have an industrial value with a current market price, the large-scale adaptation of the technology will certainly depend on the price that the global community is willing to pay per sequestered ton of carbon. The current price paid by the market for biochar (300–600 Eur/t (Schmidt & Shackley, 2016)) and bio-oil (150–400 Eur/t (Alibaba, 2018)) exceeds by far its energetic value, which is about 135 and 33 Eur, respectively (based on a caloric value of 29 GJ/t = 8.1 MWh/t for biochar and 6.8 GJ/t = 1.9 MWh/t for bio-oil; an average price of 60 Eur/MWh electricity (Kost et al., 2013); the average energy efficiency of 32% for coal-fired power plants with CCS (Goto, Yogo, & Higashii, 2013); and a 10% for investment and operational costs). It is difficult to foresee how these market prices for pyrolytic products may develop, once a massive global expansion of the technology would occur, although it can be assumed that a quickly increasing offer would exert pricing pressure before new bio-carbon-based markets develop. The evolution of PyCCS pricing will mainly depend on the timing of phasing-out fossil fuels where (pyrolytic) biomass carbon will have to replace fossil carbon as a base material for the chemical industry. Substantial carbon taxes, paying for carbon sequestration, would have at least to pay for the economic contingencies and assure that the pyrogenic carbon is sequestered in the long term without (for economic reasons) being oxidized to atmospheric CO₂.

12 | CONCLUSION

This review demonstrates that PyCCS holds the prospect, when mediated by a substantial increase in sustainable biomass production, to mitigate global climate change and to curb the concentration of atmospheric carbon. In contrast to BECCS, PyCCS is expected to provide additional ecosystem services, to recycle biomass nutrients within the biosphere, to be ready for implementation within a shorter time frame, to be scalable also at the village and farm levels, to provide advanced products for the bioeconomy, and to avoid the high costs and risks of liquid CO₂ sequestration. The C-sequestering use of bio-oil and biochar as raw materials for the chemical and construction industry

could increasingly replace fossil oil during the expected phasing out of fossil fuels. Given the current economic and political situation, it seems extremely unlikely that, anytime soon, global governance may decide to set the incentives to pump bio-oil into geological storages. However, it may become an option of last resort if the combustion of fossil fuels will not be reduced quickly enough within the next 30 years. In the meantime, a mix of PyCCS and BECCS, where pyrogas is used for methane and hydrogen fuel production, and where biochar is applied to soil or used in biomaterials, could evolve into a way forward to early adoption of scalable, SDG-supporting CDR technologies.

ACKNOWLEDGEMENTS

This study was conducted within the BMBF-funded project BioCAP-CCS, grants no. 01LS1620A and 01LS1620B.

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SUPPORTING INFORMATION

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How to cite this article: Schmidt H-P, Anca-Couce A, Hagemann N, et al. Pyrogenic carbon capture and storage. *GCB Bioenergy*. 2019;11:573–591. <https://doi.org/10.1111/gcbb.12553>