Gasification biochar as a valuable by-product for carbon sequestration and soil amendment

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Abstract: Thermal gasification of various biomass residues is a promising technology for combining bioenergy production with soil fertility management through the application of the resulting biochar as soil amendment. In this study, we investigated gasification biochar (GB) materials originating from two major global biomass fuels: straw gasification biochar (SGB) and wood gasification biochar (WGB), produced by a Low Temperature Circulating Fluidized Bed gasifier (LT-CFB) and a TwoStage gasifier, respectively, optimized to energy conversion. Stability of carbon in GB against microbial degradation was assessed in a short-term soil incubation study and compared to the traditional practice of direct incorporation of cereal straw. The GBs were chemically and physically characterized to evaluate their potential to improve soil quality parameters. After 110 days of incubation, about 3 % of the added GB carbon was respired as CO2, compared to 80 % of the straw carbon added. The stability of GB was also confirmed by low H/C and O/C ratios with lowest values for WGB (H/C 0.01 and O/C 0.14). The soil application of GBs exhibited a liming effect increasing the soil pH from ca 8 to 9. Results from scanning electron microscopy and BET analyses showed high porosity and specific surface area of both GBs, indicating a high potential to increase important soil quality parameters such as soil structure, nutrient and water retention especially for WGB. These results seem promising regarding the possibility to combine an efficient bioenergy production with various soil aspects such as carbon sequestration and soil quality improvements.

Response to Reviewers: Response to Reviewers' comments:
The units and ratios were corrected (L 143, L184).
Treatments description were also improved (L159-64)
The references have been corrected.

Thank you for your comments.
Best regards,
Veronika Hansen

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This manuscript demonstrates the potential for combining of bioenergy production and residual biochar application as soil improving and carbon sequestration agent. This study shows that carbon in gasification biochar is stable against microbial degradation. Furthermore, the liming effect, high porosity and specific surface area of the gasification biochar indicate the ability of the biochar to improve important soil quality parameters such as structure, water and nutrient retention.

Therefore, gasification of crop residues and wood waste is a promising way of producing sustainable bioenergy and reaching the political goals of fossil fuel free society, and at the same time sustaining or even improving of the soil quality, which is crucial for meeting the increasing demand for producing food and energy crops.

We hope that our experimental study might be interesting and relevant for publication in Biomass and Bioenergy. We are looking forward to receive the reviewer's comments and evaluation.

Best regards,

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***Detailed Response to Reviewers**

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Thank you for your comments.

Best regards,

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Highlights

- Biomass gasification has a potential to combine the efficient production of bioenergy with valuable biochar residuals for soil quality improvements.
- The two investigated gasification biochars are recalcitrant indicating soil carbon sequestration potential.
- Gasification biochars have a potential as soil improvers due to high specific surface area, porosity, liming effect and low PAH content.

Gasification biochar as a valuable by-product for carbon sequestration and soil amendment

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Abstract

Thermal gasification of various biomass residues is a promising technology for combining bioenergy production with soil fertility management through the application of the resulting biochar as soil amendment. In this study, we investigated gasification biochar (GB) materials originating from two major global biomass fuels: straw gasification biochar (SGB) and wood gasification biochar (WGB), produced by a Low Temperature Circulating Fluidized Bed gasifier (LT-CFB) and a TwoStage gasifier, respectively, optimized to energy conversion. Stability of carbon in GB against microbial degradation was assessed in a short-term soil incubation study and compared to the traditional practice of direct incorporation of cereal straw. The GBs were chemically and physically characterized to evaluate their potential to improve soil quality parameters. After 110 days of incubation, about 3 % of the added GB carbon was respired as CO_2, compared to 80 % of the straw carbon added. The stability of GB was also confirmed by low H/C and O/C atomic ratios with lowest values for WGB (H/C 0.01 and O/C 0.14). The soil application of GBs exhibited a liming effect increasing the soil pH from ca 8 to 9. Results from scanning electron microscopy and BET analyses showed high porosity and specific surface area of both GBs, indicating a high potential to increase important soil quality parameters such as soil structure, nutrient and water retention especially for WGB. These results seem promising regarding the possibility to combine an efficient bioenergy production with various soil aspects such as carbon sequestration and soil quality improvements.

Keywords

Gasification, Bioenergy efficiency, Biochar soil amendment, Carbon sequestration, Soil quality improvement

1. Introduction

Biomass gasification for combined heat and power (CHP) production has the potential to become an efficient and flexible way to generate bioenergy, as a broad variety of biomass residues and other organic resources can be utilized [1, 2]. In Denmark effective gasification platforms for the two major global biomass fuels, wood chips and cereal straw, are currently scaled up and close to commercial application: (1) Low Temperature Circulating Fluidized Bed gasifier (LT-CFB), specifically designed to produce energy from biomasses with high ash contents (such as straw) and (2) TwoStage gasifier, designed for converting woody biomass. The LT-CFB technology has been demonstrated in continuous operation, as a 6 MW demonstration plant, and the first 2 MW commercial plant for continues CHP production with the TwoStage process is about to produce power and district heating for a local community, Hilleroed Municipality, Denmark. This plant will produce approximately 64 tons of biochar residues annually, while the planned 60 MW full scale commercial LT-CFB plant is going to generate approximately 10 000 tons of carbon-rich residues per year. The potential further upscaling and expanding of those processes requires a strategy for the sustainable utilization of a growing amount of biochar residues produced. Recirculation and utilization of those residues to agricultural land, instead of costly disposing as a waste, would improve the sustainability and economy of the bioenergy production. Gasification biochar generally contains a considerable amount of minerals and recalcitrant carbon and is considered an attractive product for soil amendment due to its fertilizer and carbon sequestration potential [3, 4].

Carbon sequestration in soil mitigates the effect of climate change [5], and may furthermore help to maintain or even improve the soil fertility. This is of key importance to be able to fulfil the increasing global demand for producing crops for both food and energy [6]. Soil organic carbon (SOC) influences the physical, chemical and biological properties of the soil, and is essential for good soil quality [7]. Increasing SOC has been shown to improve soil aggregation, water infiltration, and water and nutrient retention [8, 9]. Traditional annual incorporation of crop residues such as cereal straw can increase soil organic matter content [10], therefore there is a concern that the removal of residues from the field for energy production may lead to soil degradation [11]. Gasification of biomass and returning the residual biochar-carbon to the field is regarded as a promising strategy combining effective bioenergy generation with the maintenance of soil carbon stocks [2]. Utilizing low quality wood and residues from timber harvesting for bioenergy production and subsequent addition of wood biochar to agricultural soils may be another strategy to increase SOC and improve arable soils' productivity, creating novel synergies between the agricultural and forestry sectors. Nevertheless, since there are qualitative differences in the molecular structure of pyrogenic carbon compared to the stable carbon derived from microbial/enzymatic soil processes [12], the impacts of substituting crop residue incorporation with the addition of gasification biochar (GB) on soil services are largely unknown and should be thoroughly investigated before implementing this into practice [8].

Several studies have shown positive impacts of pyrolysis biochar, produced at relatively low temperatures (400 – 600°C), on soil properties [13, 14], which are, however, highly dependent on biochar feedstock and thermal processing conditions [15]. The physical properties of biochars, such as high porosity and specific surface area (BET), may result in an increase of not only soil water retention [16], water infiltration, and cation exchange capacity [5, 13], but also soil microbial activity [14]. Chemical properties, such as low hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios, result in high stability of biochar against microbial degradation in soil [17]. Compared to pyrolysis biochar, GB is produced at higher temperatures (around 700 – 1100°C), using low amounts of oxygen. Gasification results in higher energy yields compared to pyrolysis and leaves biochar with less, but more stable carbon, compared to pyrolysis biochar [15, 18]. Chemical characterization of GB, showing its stable structure, is well reported [4, 15, 17, 19], however studies on the effect of GB on soil and microbial processes are scarce. Concerns about the use of GB as a soil amendment include its possible content of Polycyclic Aromatic Hydrocarbons (PAH) [20], which proved to be highly variable, as e.g. in the studies of Wiedner [4] and Kloss [20], who measured values up to 15 and 33 mg kg^{-1}, respectively. Especially the wood gasification biochars showed high PAH contents [4, 17].

The aim of this study was to evaluate the potential of the biochar residues from two gasification processes to exert a beneficial effect on soil carbon sequestration and soil quality. Through a short-term soil incubation study and physical and chemical analyses, the objectives were to investigate if the gasification biochars: (1) contain carbon recalcitrant to microbial degradation; (2) have a potential to improve soil physical and chemical properties; (3) have any negative effects on microbial biomass and (4) have a potential for higher carbon sequestration rates than those achieved with traditional direct soil incorporation of the feedstock (i.e. straw).

2. Materials and methods

2.1. Biochar production

The two gasification biochars (GB) used for this study originated from continuously operated pre-commercial gasification demonstration plants. Straw gasification biochar (SGB) was produced in a Low Temperature Circulating Fluidized Bed gasifier (LT-CFB). The straw originated from winter wheat (*Triticum aestivum* L.) grown in Zealand, Denmark, but is of unknown provenance, date of harvest and chain of custody. Commercially produced wheat straw pellets were crushed prior to LT-CFB gasification for optimal gasifier operation. Wood gasification biochar (WGB) was produced from pine wood (*Pinus spp.*) chips in a TwoStage gasifier. The wood chips were commercially produced with an average chip size of 50 mm, which is the optimal size for the TwoStage process, and originated from Zealand, Denmark.

The LT-CFB gasifier (Fig. 1), developed at the Technical University of Denmark in cooperation with Danish Fluid Bed Technology, is designed to gasify biomass resources with high contents of low melting ash compounds (e.g. straw, manure or sewage sludge), that have proven difficult to convert in other processes [1]. The process is based on separate pyrolysis and gasification fluid bed reactors with a suitable circulating heating medium to transfer the heat from the gasification process to the pyrolysis. The temperature is kept below the melting point of the ash components, i.e. max process temperatures around 700 - 750^{o}C. In this way, sintering of the ash and subsequent fouling (from e.g. potassium) or corrosion (from e.g. chlorine) of the plant unit operations are avoided, as these compounds will leave the process in solid form as ash particles.

Fig. 1 here.

The char conversion in the LT-CFB gasifier is a combination of sub stoichiometric oxidation of the char and steam gasification. The retention time (few seconds) in the char reactor is relatively short. The char-ash particles are though circulated in the process until they are too small/light to be separated by the primary cyclone, subsequently most of the ash and unconverted biochar is separated out of the hot gas by the secondary cyclone. The LT-CFB technology is now owned by the company Dong Energy and is being commercialized under the name Pyroneer [21].

The TwoStage fixed bed process (Fig. 2) was invented and developed at the Technical University of Denmark and has been designed for gasification of woody biomass with low ash content [1]. The TwoStage process is characterized by having pyrolysis and gasification in separate reactors with an intermediate high temperature tar-cracking zone with temperatures of 1000 - 1200^{o}C. This allows a very fine control of the process temperatures, resulting in extremely low tar concentrations in the produced gas, making it suitable for gas engine operation or synthesis of biofuels. Due to the high temperatures, the process is only applicable for woody biomass. The char conversion is predominantly a gasification reaction between carbon and steam. The char is exposed to steam at high temperature, 800 - 1000^{o}C, for a relatively long period (30+ minutes), resulting in an activated char with a high surface area.

Fig. 2 here.

2.2. Biochar characterization

The total content of organic C, H and O in feedstock and gasification biochar was measured on an elemental analyzer (FLASH 2000 Organic Elemental Analyzer, Thermo Scientific, Cambridge UK). The WGB and wood chips were ball milled, while the straw was ground prior to this analysis. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method by nitrogen gas sorption at 77 K (Quantachrome instruments, Boynton Beach, USA). Pore size distribution was obtained by Barret-Joyner-Halenda (BJH) desorption analysis after degassing the samples for 2 hours at 160°C. The WGB was hand sieved in two fractions (0-0.5 and 0.5-1 mm) prior to this analysis. Carbon-coated biochar samples were examined by scanning electron microscope (SEM) JEOL JSM-5900 (Oxford instruments, Japan). The pH of biochar was measured in a 1:5 (w/v) biochar/Milli-Q water suspension. The ash fraction was determined by heating dried biochar at 550°C for 5 hours in a muffle furnace. Nine Polycyclic Aromatic Hydrocarbons (PAHs) were quantified after a soxhlet extraction of 2 g sample with toluene for 48 hours by Eurofins GfA (Hamburg, Germany). The measured PAHs comprised Acenaphthene, Fluorene, Phenanthrene, Fluoranthene, Pyrene, Benzo(bjk)fluoranthene, Benzo(a)pyrene, Indeno(1,2,3-cd)pyrene and Benzo(ghi)perylene. The particle size distribution of the biochars was determined by a vibrating screen method using sieves (Retsch, Germany).

2.3. Incubation study

2.3.1. Soil

A sandy loam soil from a conventional agricultural field at Bregentved estate, Zealand, Denmark (55° 22’ N, 12° 05’ E) was collected from the plough layer (0-25 cm), air dried and sieved to obtain a fraction ≤ 6 mm. The soil contained 14 % clay, 14% silt, 47 % fine sand and 24 % coarse sand. The total C content was 1.98 % and total N 0.18 %.

2.3.2. Experimental design

We conducted an incubation experiment including 7 treatments with 4 replicates each. In 280 ml PVC containers, 200 g soil (dry weight) were mixed thoroughly with either 2 g (1 %) or 10 g (5 %) straw or wood GB (dry weight). The treatments were: (1) Control soil without addition of organic material (Control), (2) soil amended with 1 % straw (Straw1), (3) soil amended with 5 % straw (Straw5), (4) soil amended with 1 % straw gasification biochar (SGB1) , (5) soil amended with 5 % straw gasification biochar (SGB5), (6) soil amended with 1 % wood gasification biochar (WGB1), (7) soil amended with 5 % wood gasification biochar (WGB5). The straw used for this experiment was from winter wheat (*Triticum aestivum* L.) produced in Zealand, Denmark. After harvest, it was bailed and kept dry. The straw material was ground to a particle size of ≤ 5 mm prior the incubation. The water content of the soil mixtures was adjusted to 50 % of the water holding capacity (determined separately for each respective mixture), and kept constant by regular weighing and watering. The containers were sealed with plastic lids with five holes (5 mm) to allow gas exchange while minimizing moisture loss, and incubated in the dark at 22°C for 110 days. The whole experiment was set up in 5 sets, enabling 5 destructive samplings. Soil respiration was measured on the same set each time, which was then used for the last destructive sampling.

2.3.3. Soil analysis

Destructive soil samplings were taken at day 1, 8, 16, 32 and 110. All treatments were analyzed for nitrate (NO_3^-), ammonium (NH_4^+) and dissolved organic carbon (DOC) content by extracting 10 g of fresh soil with 50 mL 0.5 mol K_2SO_4 L^{-1}. The suspensions were shaken on a horizontal shaker for 1 h (2.5 Hz), filtrated through pleated filter paper with retention of 5-8 µm (Grade 202F, Frisenette Aps, Denmark) and stored at -20°C until analysis. The extracts were analyzed for concentrations of NO_3^- and NH_4^+ on an AutoAnalyzer 3 (AA3 Bran and Luebbe, Norderstedt, Germany), and for DOC on a TOC-VCPH (Shimadzu Corp., Kyoto, Japan). The soil microbial biomass carbon (SMB-C) content in each treatment was determined by vacuum incubation of 10 g soil mixture with chloroform for 24 hours, followed by K_2SO_4 extraction. The SMB-C was estimated from the relationship SMB-C = ($DOC_{fumigated}$ – $DOC_{unfumigated}$)/0.45 [22]. The soil pH was determined using soil-water suspension of 5 g soil and 25 ml of Milli-Q water.

2.4. Soil respiration

The CO_2 emission from each sample was measured with an infra-red gas analyzer (LI-COR 8100, Lincoln, Nebraska USA). The measuring frequency ranged from daily in the beginning of the experiment to once a month at the end. The emissions were measured at day 1, 2, 3, 4, 5, 8, 10, 12, 15, 18, 22, 30, 36, 46, 52, 67 and 110 of the incubation period.

2.5. Statistical analysis

Statistical analysis of the data was performed in R, version 3.0.2. The significant interaction effect between treatment and time (day) was assessed using a two-way analysis of variance (ANOVA). The differences between treatments within each day of measurement were analyzed using the Student-Newman-Keuls (SNK) test from the R-package “agricolae” at $P \leq 0.05$.

3. Results

3.1. Biochar characterization

Table 1 illustrates that 4 and 10 % of the carbon in wood and straw feedstock, respectively, were retained in the biochar fraction. The chemical characterization of soil, feedstock and biochars is given in Table 2. Gasification of straw and wood chips led to mass loss of H and O, decrease of H/C and O/C atomic ratios and increase of ash percentage. The carbon content was higher, while H/C and O/C ratios were lower for WGB compared to SGB. The total content of 9 PAHs was 5 mg kg^{-1} in SGB and 0.69 mg kg^{-1} in WGB.

The particle size distribution of biochars is shown in Table 3. Generally, the SGB was a fine powder consisting of small particles, whereas WGB was a mixture of both very small and large particles (up to 1 cm).The majority of WGB-particles were larger than 0.045 mm, while the opposite was true for SGB. Table 4 presents results from BET analysis. Specific surface area (SSA) and pore volume were higher for WGB compared to SGB. The particle size of WGB was crucial, as SSA and pore diameter were more than twice as high in particles larger than 0.5 mm compared to particles smaller than 0.5 mm. SEM images illustrated in Fig. 3 show the porous structure of both biochars and the higher proportion of internal pores in WGB compared to SGB.

Table 1 here.

Table 2 here.

Table 3 here.

Table 4 here.

Fig. 3 here.

3.2. Incubation study

3.2.1. Soil sampling

The addition of straw resulted in a decrease of soil mineral nitrogen (N_{min}) content (NO_3^- + NH_4^+) to almost zero already at the second sampling day and stayed at that level during the rest of the incubation period (Fig. 4). In contrast, the N_{min} level increased over time in the control treatment and after the addition of GB. The application of the high dosage of GB resulted in about the same N_{min} content as in the control treatment, while the low dosage of GB decreased N_{min} significantly.

Both straw and SGB amendments caused a significantly increased content of dissolved organic carbon (DOC) in soil compared to the control treatment throughout the incubation period, except the Straw1 treatment at the last sampling day (Fig. 5A). At day 1, an especially high DOC level could be observed in the treatment with 5 % straw. On the contrary, the soil amendment with WGB led to a significantly lower DOC content compared to all other treatments throughout the incubation period.

The content of soil microbial biomass carbon (SMB-C) was - in accordance with DOC - significantly increased after addition of straw compared to the rest of the treatments, especially in the beginning of the incubation (Fig. 5B). Subsequently, the SMB-C decreased until day 16 and increased again towards the end of the incubation. After 8 days of incubation, the content of SMB-C in WGB-treated soil was significantly lower than in the control treatment, and this difference became larger with time. On the contrary, there was no consistent effect of adding SGB on SMB-C: only at day 8 and 110 in the high-dosage treatment the SMB-C was lower compared to the control.

Addition of both gasification biochars increased the pH of the soil significantly, and the difference remained throughout the incubation period (Fig. 6). After 110 days, the pH increased by 1.13 and 1.36 units for SGB5 and WGB5, respectively. By contrast, soil amendment with straw significantly decreased the pH in the beginning of the incubation, whereas there was no difference anymore after 110 days.

Fig. 4 here

Fig. 5 here.

Fig. 6 here.

3.2.2. Soil respiration

The addition of straw to soil, at both 1 and 5%, resulted in significantly higher CO_2 emissions compared to control and GB treatments throughout the experimental period (Fig. 7A). The peak CO_2 emissions in the straw and control treatments were observed during the first week of measurement. Soil amendment with GB did not result in any initial emissions, and the treatment WGB5 even resulted in negative fluxes during the first week (Fig. 7B). After 110 days of incubation, the cumulative total emissions were highest for straw treatments, reaching 3.51 and 9.17 mg C g^{-1} soil emitted as CO_2 for Straw1 and Straw5, respectively. GB treatments resulted in cumulative total emissions of 1.7 – 2 mg C g^{-1} soil emitted as CO_2, slightly higher than the control (1.65 mg g^{-1} soil) (data not shown). Fig. 7C illustrates the cumulative fraction of added carbon respired within 110 days. At the end of the incubation, 78 and 41 % of straw carbon added was respired in treatments Straw1 and Straw5, respectively, while only 1-3 % of added biochar carbon was respired.

Fig. 7 here.

4. Discussion

4.1. Soil carbon sequestration potential

A markedly smaller proportion of added carbon was respired in the GB treatments compared to the straw treatments, which reflects the aromatic and recalcitrant structure of the residual carbon in these biochar materials [4] after energy production during the process of gasification (Fig. 7C). The addition of the high dosage of WGB resulted even in an initially negative CO_2 flux, probably caused by binding CO_2 through carbonation of soluble Ca and Mg contained in the biochar, forming $CaCO_3$ and $MgCO_3$ [23, 24]. The CO_2 peak after straw soil incorporation was reflected in the high initial contents of DOC and SMB-C in these treatments, confirming that the easily degradable carbon pool in the straw was rapidly decomposed by the soil microbial biomass, followed by a decrease in CO_2 emissions (Fig. 7A). The very high content of SMB-C at day 1 in the high dosage straw treatment was, however, surprising (Fig. 5B), and could be attributed to chloroform-labile substances in the straw itself, as also suggested by Duong [25] observing similar effects.

The DOC level in both biochar treatments was – in accordance with their low CO_2 emissions - significantly lower than that in straw treatments (Fig. 5A). WGB-treated soils were even lower in DOC than SGB-treated soils, which could be due to a higher content of stable carbon, probably caused by higher process temperatures during the wood gasification compared to the straw gasification [26]. The DOC content of SGB was higher than that of the control treatment, but did not result in any corresponding CO_2 emissions. This might be due to CO_2-binding by carbonation occurring simultaneously with CO_2 emissions and therefore concealing soil respiration. However, the DOC value in SGB treatments might also have been overestimated due to very small particles of the biochar which were not retained by the filter during the extraction process. The DOC content in WGB treatments was even significantly lower than in the control treatment, which might be explained by a sorption of organic substances to WGB, as the SSA of wood biochar is very high [14, 27]. This was also confirmed by the clear color of WGB extracts in contrast to the brownish color of the other treatments. The DOC sorption by WGB could explain low CO_2 emissions and the low content of SMB-C, as DOC is a carbon source for the microorganisms [27, 28]. However, the adsorption of both DOC and microorganisms to biochar may potentially also result in higher substrate consumption and therefore increase microbial activity [14]. Generally, our results confirm that DOC-related parameters based on soil extraction procedures should be interpreted with caution, as e.g. also Liang et al. [29] showed that the fumigation-extraction method leads to an underestimation of SMB-C in biochar-amended soil due to sorption processes. The high N mineralization observed in the WGB treatments is another indicator that soil microbial activity was not inhibited by WGB (Fig. 4). Further studies are required to assess the effect of GB on soil microbial biomass.

The GB carbon stability was also confirmed by their H/C and O/C atomic ratios, that had been decreased compared to the original feedstock to values below 0.6 and 0.4, respectively (Table 2), which is in agreement with the recommended thresholds indicating carbon recalcitrance [17, 26]. The H/C and O/C atomic ratios of WGB were even lower in comparison with SGB.

4.2. Improvement of soil quality

Results from BET and SEM analyses illustrated a higher SSA and porosity in WGB compared to SGB (Table 4, Fig. 3). Besides the feedstock itself, the higher process temperature [19, 20, 27] in the wood gasification process could contribute to those characteristics, as WGB and SGB were produced at about 1000° and 700° C, respectively. However, both GBs in this study showed a relatively high SSA in comparison with other studies, where the SSA of GBs ranged from 5 to 62 $m^2\ g^{-1}$ [15, 19] and that of pyrolysis biochars from 1 to 320 $m^2\ g^{-1}$ [20, 27, 30]. According to

Schimmelpfennig and Glaser [17], biochar with a SSA higher than 100 m^2 g^{-1} has the potential for improvement of soil water and nutrient retention and porosity of the soil, which could benefit microbes and plants. This requirement is definitely fulfilled by the WGB with an SSA of the same magnitude as activated charcoal, which is probably due to the steam activation in the wood gasification process [31]. The lower porosity of SGB is probably also caused by the processing, as the straw fuel was pelletized and crushed, and gasified in a circulating fluidized bed (see section 2.1.). Cereal straw has about 6 times the amount of minerals (ash) compared to the wood chips used to produce WGB, which might result in mineral matter occupying the pores of biochars or being exposed at the surface of the biochar particles and blocking the pores, thereby causing the lower SSA [32].

Addition of both biochars resulted in an increase of soil pH due to their alkalinity (Fig. 6). The frequently described liming effect of biochar can improve plant nutrient availability, especially in case of phosphorus in low-pH soils [3, 9, 27], and may have a beneficial effect on soil fertility and plant growth on acidic soils [33].

Soil incorporation of straw with a wide C/N ratio often results in initial N immobilization [34, 35] and subsequent slow N release [11]. The N immobilization was also observed in this study in the straw treatments (Fig. 4). Contrarily, the soil application of GBs led to N levels similar to the control soil, which means that no initial adverse effects on plant growth - as they can occur after the application of pyrolysis biochar [36] - are to be expected after GB soil application. However, there is no obvious explanation for the decreased N_{min} levels compared to the control soils in the low dosage of both GBs.

The total PAH content of both biochars was well below the threshold limit of 12 mg kg^{-1} for bioash soil application according to the Danish Ministry of the Environment (Table 2). Eventual PAH content in GB originates from PAHs in the produced gas, where they are formed as a decomposition product of gaseous pyrolysis tars. If the GB stays in contact with the produced gas at low temperatures, PAHs may subsequently condense on the GB. Although high PAH contents are often reported for wood gasification biochars [4, 17], the WGB in this study showed a value of 0.69 mg kg^{-1}, which is far below the limit, despite the high process temperatures. This is due to the successful decomposition of PAHs during the TwoStage process, as the separation of the pyrolysis and gasification reactors allows for a controlled gas phase partial oxidation of the pyrolysis tars (Fig. 2). Consequently, the PAHs formed during the partial oxidation subsequently react with the activated char in the char bed and are decomposed [37]. As a consequence of the in-process decomposition, the concentration of PAHs in the produced gas is very low and hence no significant PAH condensation on the WGB is possible [38]. Additionally, in the process, the WGB is separated from the produced gas at high temperature (750 °C), which is significantly higher than the dew point of the low PAH concentration in the gas and thus minimizes the possible condensation of PAHs on the WGB.

4.3. Biomass for both energy and soil amendment

Biomass, such as crop residues and wood waste, is a renewable global energy source, and efficient energy conversion is required to reach the ambitious political goal in many countries to obtain a fossil fuel free society. According to an LCA analysis by Nguyen et al. [2], gasification is - in comparison with the dominating direct combustion - more environmentally friendly due to primarily three main factors: (1) a higher energy efficiency, (2) reduced emission of major air pollutants and (3) a higher carbon content in the residual fraction [2]. The LT-CFB process has some unique features compared to direct combustion, as it can operate on crop residues and biomass related waste, which are normally problematic for direct combustion. The produced gas has a low content of ash alkali and can thus be combusted at high temperatures resulting in very efficient gas utilization and energy conversion. The TwoStage gasification process allows for efficient utilization of wood at small to medium scale. By producing clean and tar free gas, which can be used in a gas engine for combined heat and power production, it is possible, even for a small scale plant, to achieve efficiencies comparable with those of large scale power plants [1].

Crop residue removal for energy production can potentially reduce the soil carbon and nutrient content and thereby the soil quality. Powlson et al. [11] concluded that removal or incorporation of straw had a small effect on soil organic carbon content; however, even a small change in SOC could have large negative impacts on soil physical properties. To date, the biochar fraction extracted from the gasification process is not considered a valuable product, though, if it can be developed into a soil amendment of high fertilizer and soil improver value, this will significantly improve the economic feasibility and sustainability of the gasification technology [39]. On future markets, such parameters have increasing importance, and the sustainability of a particular bioenergy chain will to a large extent depend on the possibilities for its by-products recycling potential [40]. Nevertheless, considering the complexity of effects of SOC on soil quality, the question, whether field application of gasification biochar may replace SOC originating from crop residues, requires further research.

In contrast to pyrolysis, which is usually engineered to produce biochar with gas and heat as co-products, the main product of gasification is energy in form of syngas, while biochar is considered a co-product. Thus, gasification produces more energy and less biochar compared to pyrolysis [18]. It is, however, important to find a balance in the amount of carbon utilized for energy generation and carbon left in the biochar for soil application. In the present study, we had a focus on both energy and biochar production. In the LT-CFB process, 90 % of the feedstock-carbon was used for energy production, while 10 % remained in the biochar (Table 1). In the TwoStage process, 96 % carbon was utilized for energy and 4 % remained in the biochar. Therefore, LT-CFB gasification of straw and biochar soil amendment could on the longer term have a comparable soil carbon sequestration potential to the TwoStage gasification of wood, despite the fact that WGB carbon showed a higher stability compared to SGB. Currently, the LT-CFB gasification processes are flexible technologies, allowing an energy output of up to 97 % of the carbon input, which would reduce the SGB's carbon content from the present ca. 50 % to 20 – 30 %.

5. Conclusion

In this study, we suggest that thermal gasification of biomass residues is able to combine the production of bioenergy and a biochar fraction that can exert a positive impact on soil quality. Our results showed that gasification biochar (GB) carbon is more resistant to microbial degradation compared to straw carbon and has a potential for soil carbon sequestration. Furthermore, the GBs in our study exhibited a potential as soil improving agents due to their high specific surface area, porosity and liming effect, with PAH contents below the threshold limit. However, the differences found between the two biochar materials will probably qualify them to benefit different soil parameters. WGB with higher SSA, lower PAH content and higher carbon stability, caused both by feedstock source but also by process conditions, could increase water holding capacity and nutrient retention on sandy soils, while SGB could be preferably used as a fertilizer or liming agent. Gasification of straw and wood chips and field application of the biochar is therefore an integrative approach combining both agriculture and forestry with the energy sector, which seems to be an attractive option to maximize both energy output and soil carbon sequestration. The results of the present study reveal that it is worthwhile to further test the potential of GB soil amendment, as it has been done for more traditional pyrolysis biochar materials [26, 27, 34]. In this regard, it will be crucial to investigate the soil application of GBs also in longer-term studies, pot and field experiments, to be able to determine the effect on plant yields, soil biota and soil quality.

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Fig. 1 – Schematic of Low Temperature Circulating Fluidized Bed gasifier (LT-CFB) [21].

Fig. 2 – Schematic of the TwoStage gasifier [1].

Fig. 3 - Scanning electron microscope (SEM) images; left: straw gasification biochar (SGF) and right: wood gasification biochar (WGB).

Fig. 4 – Content of soil mineral nitrogen (N_{min}) during the incubation period of 110 days. Straw1= soil amended with 1% straw, Straw5= soil amended with 5 % straw, SGB1= soil amended with 1 % straw gasification biochar, SGB5= soil amended with 5 % straw gasification biochar, WGB1= soil amended with 1 % wood gasification biochar, WGB5= soil amended with 5 % wood gasification biochar, Control= untreated soil. Values presented are means with standard error bars (n =4). Treatments with different letters are significantly different at the last day of the incubation ($P < 0.05$).

Fig. 5 – A) Content of dissolved organic carbon (DOC) in soil during the incubation period of 110 days. B) Content of soil microbial biomass-carbon (SMB-C) in soil during the incubation period of 110 days. For treatment abbreviations, see Fig. 4. Values presented are means with standard error bars (n =4). Treatments with different letters are significantly different at the last day of the incubation ($P < 0.05$).

Fig. 6 – Soil pH at day 1, 8, and 110 of the incubation period. For treatment abbreviations, see Fig. 4. Values presented are means with standard error bars (n =3). Treatments with different letters are significantly different ($P < 0.05$).

Fig. 7 – A) CO_2 fluxes from soil during the incubation period of 110 days. B) CO_2 fluxes during the first 8 days of incubation. C) Cumulative fraction of added carbon respired from soil during the

incubation period of 110 days. For treatment abbreviations, see Fig. 4. Values presented are means with standard error bars (*n* =4). Treatments with different letters are significantly different at the last day of the incubation ($P < 0.05$).

Table 1 – Carbon and energy balance for TwoStage gasifier and Low-temperature circulating fluidized bed gasifier (LT-FCB) reflecting the carbon loss in the GB used in this study.

	Percentage TwoStage input		Percentage LT-CFB input	
	Fractional distribution			
	Carbon (%)	Energy (%)	Carbon (%)	Energy (%)
Biomass feedstock	100	100	100	100
Product gas output	96	92	90	85-87
Biochar output	4	4	10	10
Loss	-	4	-	3-5

Table2

Table 2 - Chemical characterization of soil, feedstock and biochars (SGB = straw gasification biochar, WGB = wood gasification biochar).

	Soil	Straw	Wood chips	SGB	WGB
C (%)	1.98	45.50	52.04	46.80	65.29
H (%)	-	5.52	7	0.97	0.63
O (%)	-	36.85	41.16	13.11	8.99
H/C atomic ratio	-	1.46	1.61	0.25	0.12
O/C atomic ratio	-	0.61	0.59	0.21	0.10
pH (water)	7.9	-	-	11.6	11.1
Ash (%)	-	4.85	0.75	52	33
Σ PAH[a] (mg kg^{-1})	-	-	-	5	0.69

[a] Sum af Acenaphthene, Fluorene, Phenanthrene, Fluoranthene, Pyrene, Benzo(bjk)fluoranthene, Benzo(a)pyrene, Indeno(1,2,3-cd)pyrene and Benzo(ghi)perylene.

Table 3 - Particle size distribution of straw gasification biochar (SGB) and wood gasification biochar (WGB).

Biochar	Particle size distribution in % of dry mass		
	< 0.045 mm	0.045-0.125 mm	>0.125 mm
SGB	89.4	10.3	0.3
WGB	33.0	13.7	53.3

Table

Table 4: BET specific surface area (SSA), pore volume and diameter of straw gasification biochar (SGB) and wood gasification biochar (WGB).

Biochar	Particle size (mm)	SSA (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (nm)
SGB	0-1	75	0.04	3.71
WGB	0-0.5	426	0.52	1.43
WGB	0.5-1	1027	0.58	3.73

Figure2

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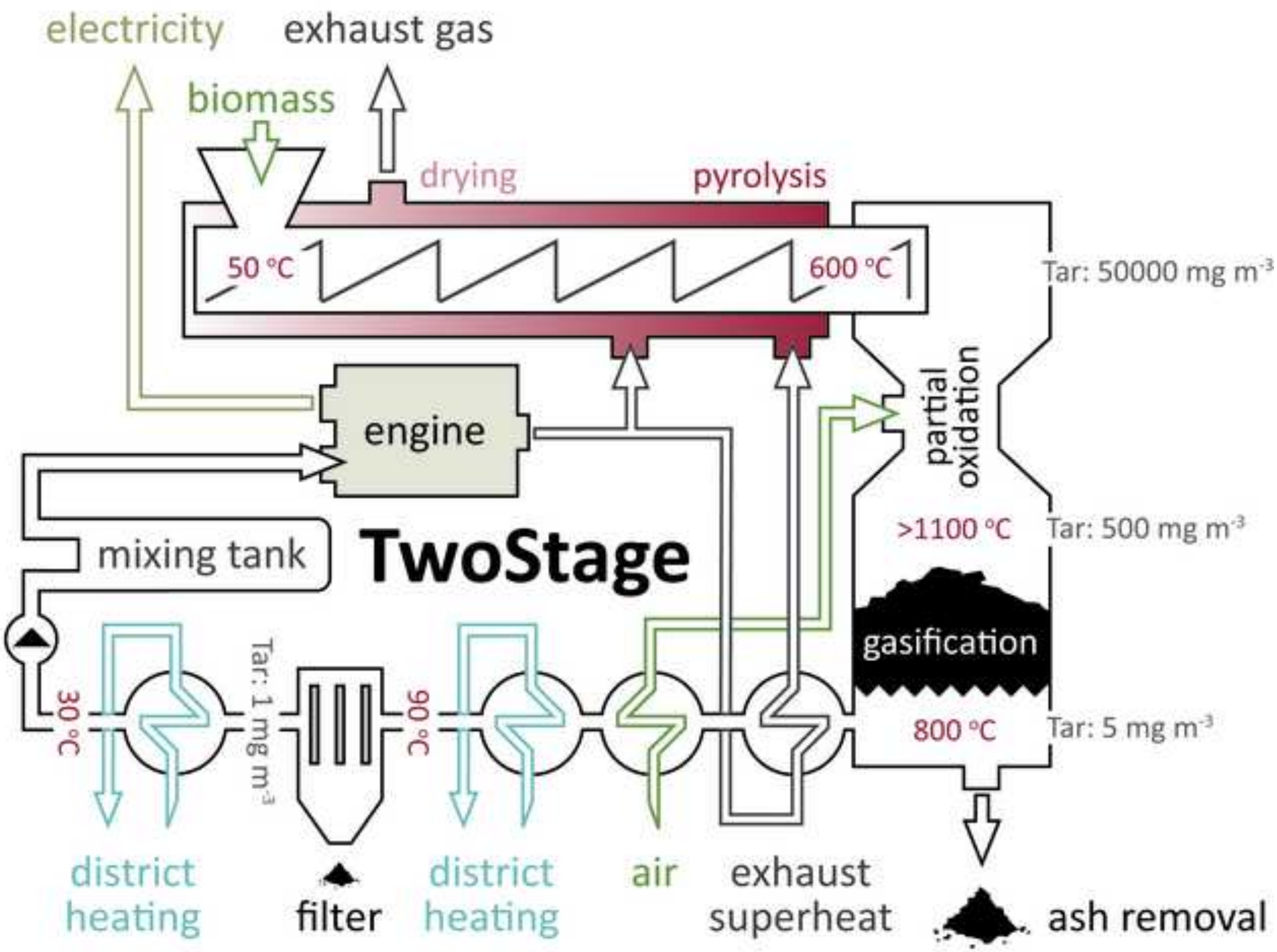

All tar concentrations measured per volume gas produced.

All gas volumes measured at Normal Temperature and Pressure i.e. 20 °C and 101325 kg m^{-1} s^{-2}

Figure4
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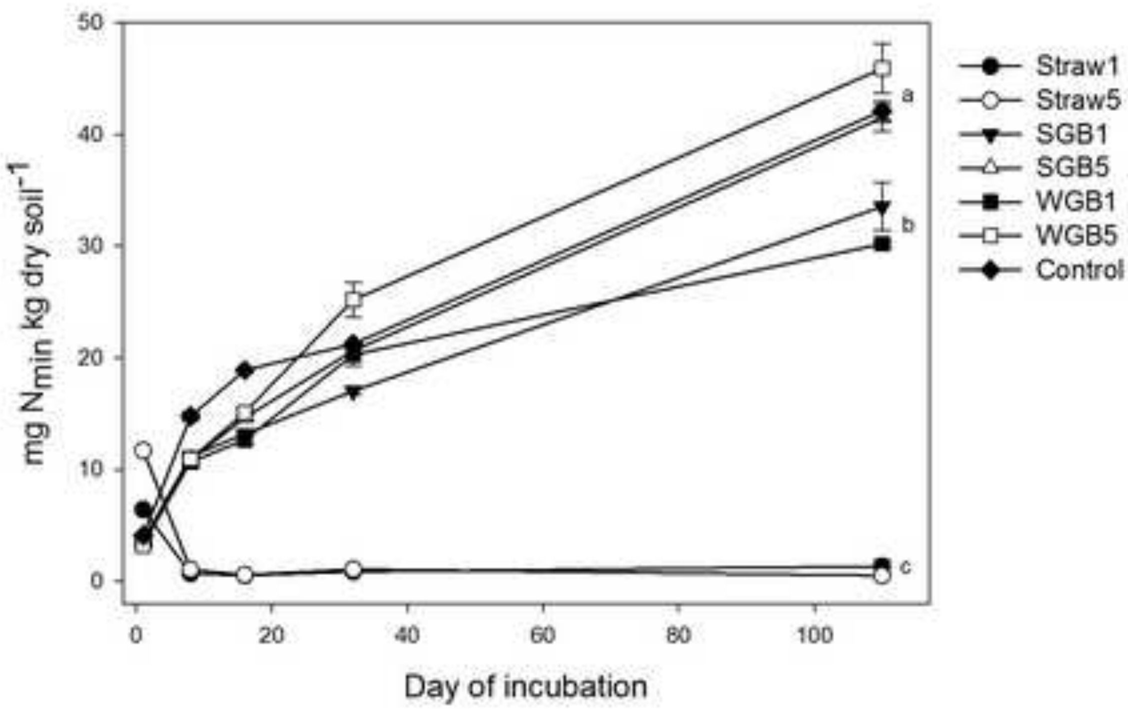

Figure5
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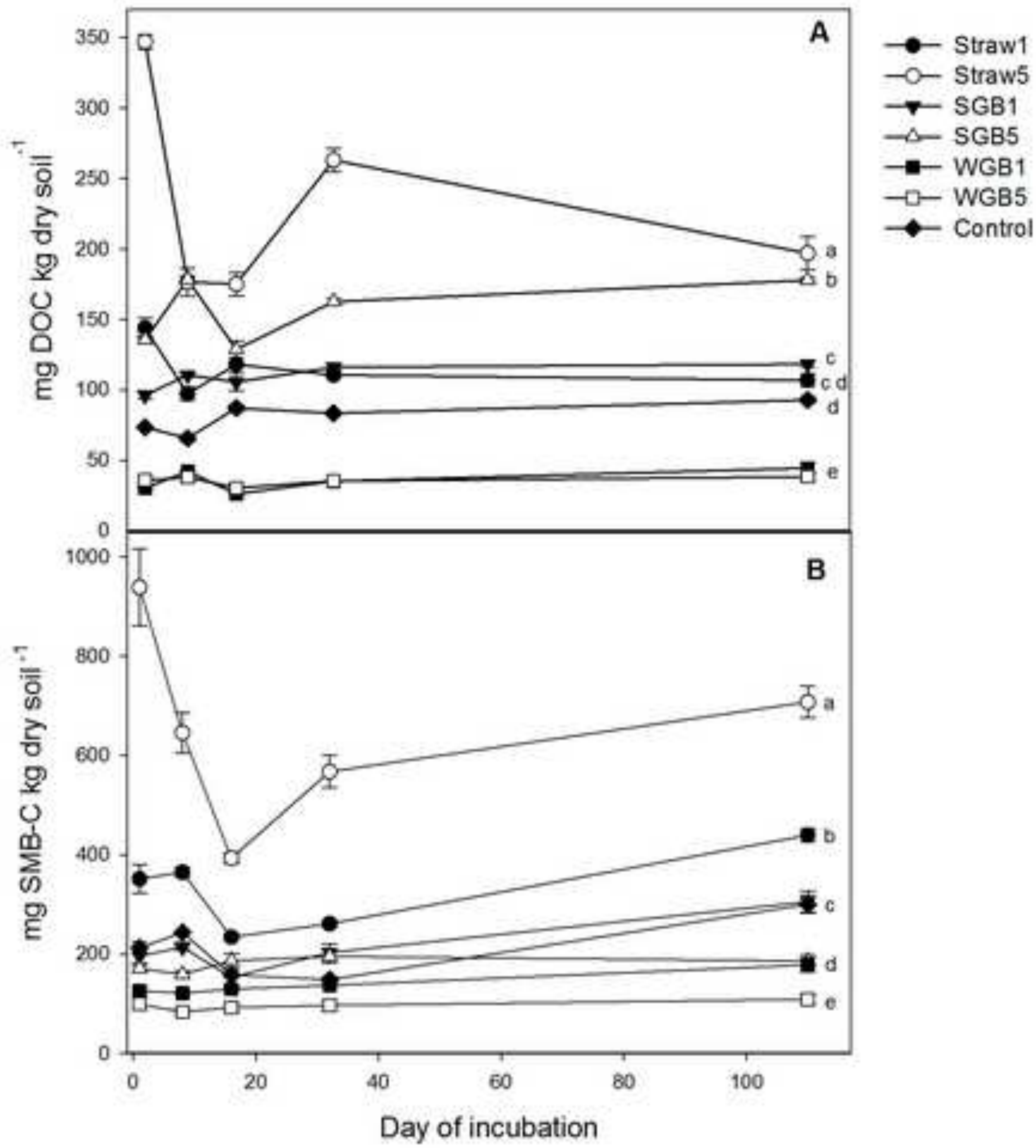

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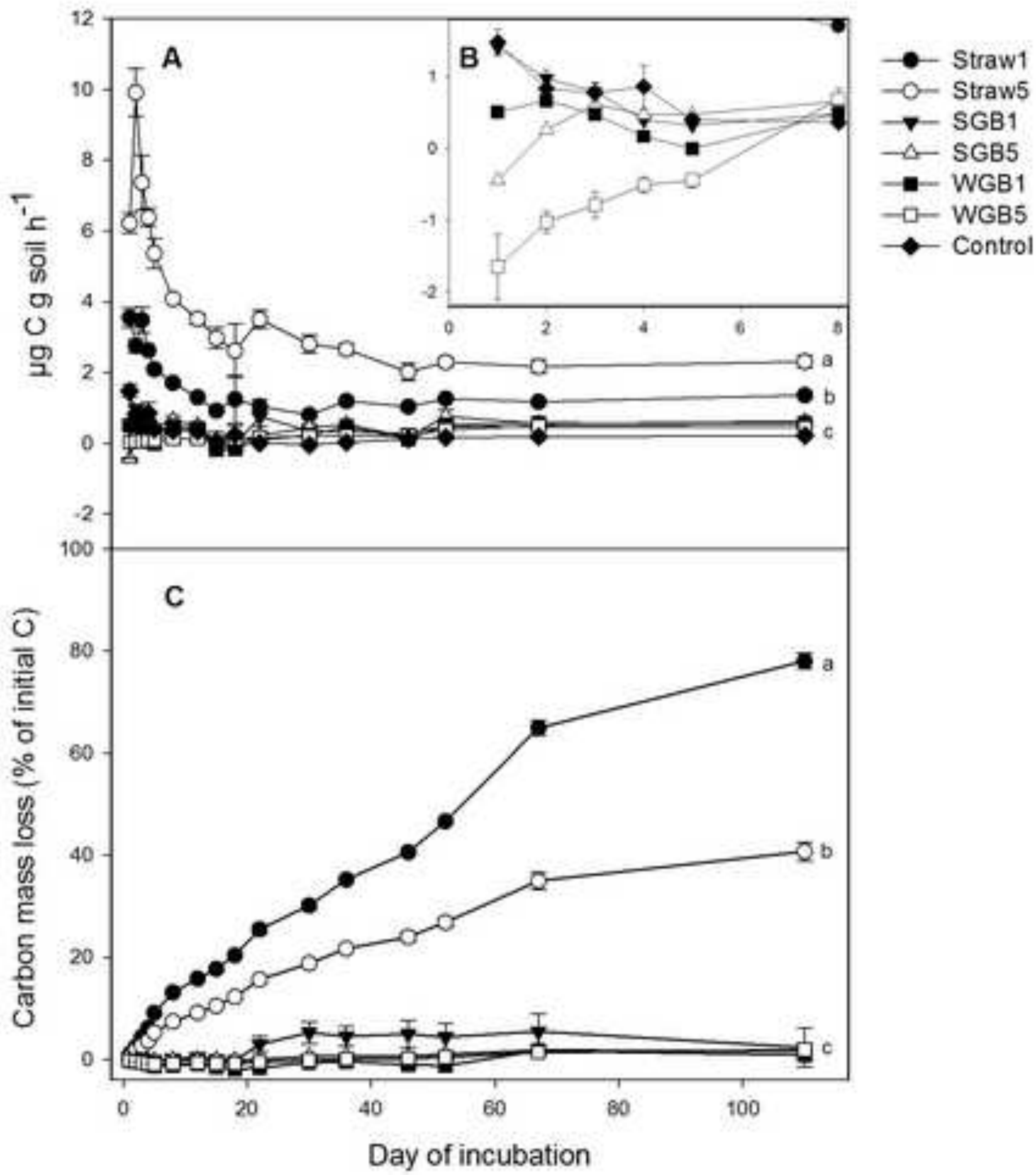

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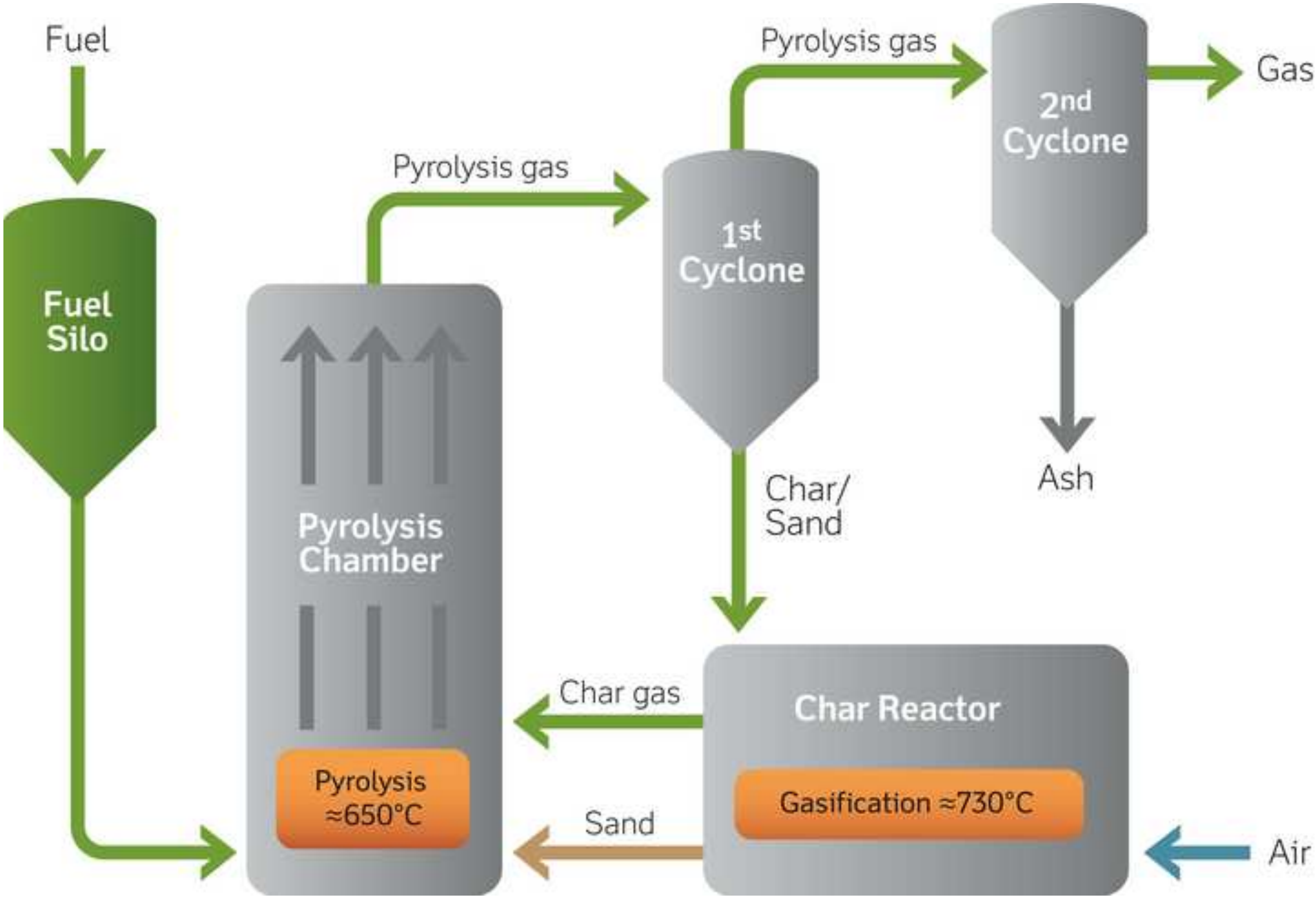

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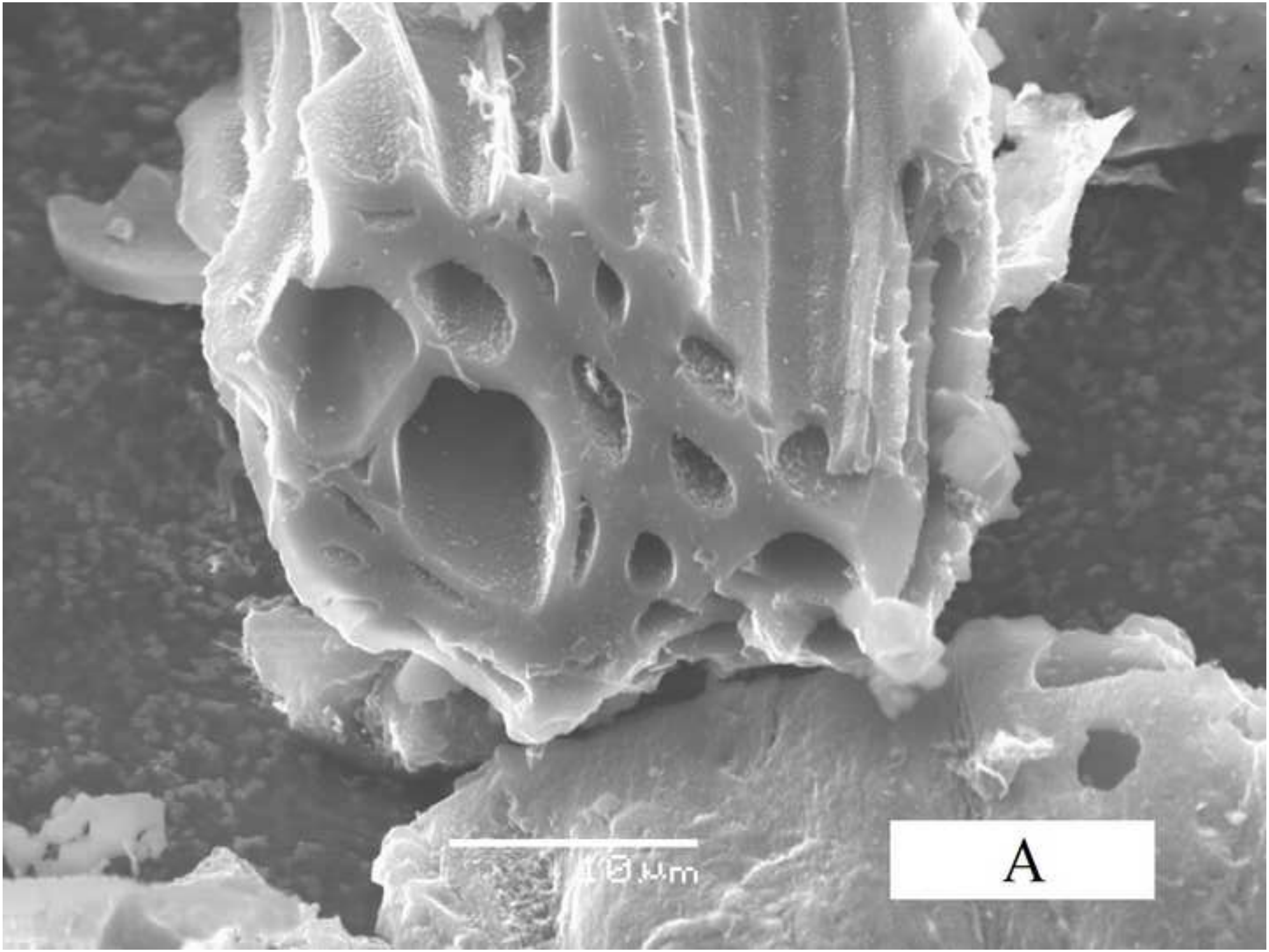

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