Consistency of biochar properties over time and production scales: A characterisation of standard materials.

Consistency of biochar properties over time and production scales: A characterisation of standard materials.

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Abstract

Users of biochar in the field require this product to reliably meet its declared specifications. For the first time, this work investigated, whether these specifications could be reproducibly obtained as a sole function of the thermal history of the biomass feedstock during slow pyrolysis, irrespective of the type and scale of the production unit. Using volatile matter content as a proxy for a wider set of biochar quality parameters, biochar from units at scales from grams to hundreds of kilograms, representing three main types of slow pyrolysis units (fixed bed, screw reactor and rotary kiln) were investigated. For the first time we showed that comparable biochar could be produced by these very different pyrolysis units, with good reproducibility within individual as well as among separate production runs.

1 Introduction

Over the past ten years, biochar research has been in a phase of a rapid growth, with over 4000 published papers as of September 2017 [1], covering an increasingly wide range of scientific and engineering disciplines. The general term “biochar” encompasses a wide range of materials with a whole spectrum of properties, depending on the feedstock used, as well as production conditions, such as highest treatment temperature (HTT), kiln residence time (RT), heating rate (HR) and biochar interaction with pyrolysis vapours [2–9]. As a result of this diversity of biochar, when applied to different soils, a whole spectrum of effects on crop responses has been reported [10–13]. Although many reported improved crop output [14–17], other studies observed no effect, or even negative effects [18–21]. A general understanding of how biochar affects the soil environment and how it interacts with soil, soil microbes and plants is still missing, although progress has been made in many directions [22].

Using or cross-referencing experimental biochar material with “standard” biochar can increase collective interpretation of data. It gives confidence in the application of standard methods and informs the relevance of measured properties to biochar function. Toward this goal the UK Biochar Research Centre (UKBRC) at the University of Edinburgh created a set of twelve Standard Biochar (https://www.biochar.ac.uk/standard_materials.php). To date (as of mid-2017), samples of these materials have been supplied to over 60 research groups around the world, for use in their research. Studies carried out using these standard biochar have since contributed extensively further data on the properties of the standard biochar and their performance in different applications [23–30]. To define these materials, the pyrolysis process used for the production has been studied in detail. This effort also enabled in-depth study of the variability of biochar properties because of changes in feedstock or process conditions.

It is well known that variations in feedstock composition, material flow rate, or in process conditions, such as HTT, lead to changes in product properties [2,31]. Therefore, biochar quality is strongly dependant on the type of pyrolysis unit, scale and its degree of control [6,32–34]. Consistency in biochar properties should presumably be embedded in the specification of bespoke, designed or engineered biochar [35–43]. Parts of the variability of biochar performance in plant trials might be attributed to variability of biochar properties related to production. To our knowledge, however, there has been no specific study of variability between repeated production runs using a range of feedstocks and at different scales.

In describing a set of standard materials already in use, our study sets a benchmark for the achievable level of consistency in biochar made from various granular feedstocks and across a range of research scales and carefully configured equipment. Through characterisation, the wider aim is to increase the cross-interpretation of future experimental works by offering a structured set of standard materials. The objectives were to assess in a comprehensive way variability in properties of biochar across a range of parameters that are relevant to its production in the field: 1) from the same pyrolysis unit but different production batches; 2) from diverse types of units; and 3) at different scales.

2 Materials and Methods

2.1 Biomass feedstocks

Five types of feedstock were selected to produce Standard Biochar (details on a sixth feedstock, sewage sludge, and resulting biochar can be found in the Supplementary Information). The feedstocks were selected to represent all major terrestrial biomass types and to cover as wide a range of physico-chemical properties as practically possible. Apart from rice husk which was imported from Sri Lanka, all the biomass was sourced from UK suppliers in spring 2013 (see Table 1). To minimise the differences in physical form, and thus remove this parameter from the already complex picture, pelleted biomass was used as feedstock for Standard Biochar. A positive side effect of this choice was improved handling and processing throughput, due to the uniform shape of pellets and their higher density. The only feedstock used in its raw form was rice husk, due to its already uniform particle size distribution. Characteristics of the five feedstocks are summarised in Table 1

Table 1 – Proximate analysis results of feedstocks for Standard Biochar production. Mean values and standard deviations for five replicate analyses are provided.

Feedstock	Source	Moisture (wt%)	Volatile Matter (wt%)	Fixed C (wt%)	Ash (wt%)
Softwood pellets (SWP)	Puffin Pellets	6.71 ± 0.03	77.92 ± 0.44	14.22 ± 0.38	1.07 ± 0.12
Wheat straw (WSP)	Agripellets	7.22 ± 0.22	70.12 ± 0.55	15.29 ± 1.08	6.44 ± 0.28
Miscanthus straw (MSP)	Agripellets	5.79 ± 0.13	72.88 ± 0.86	15.94 ± 0.40	5.10 ± 1.01
Oilseed rape straw (OSR)	Agripellets	7.98 ± 0.14	70.18 ± 0.20	15.53 ± 0.28	6.42 ± 0.15
Rice husk (RH)	Sri Lanka	6.97 ± 0.16	59.14 ± 3.27	14.84 ± 0.82	17.25 ± 4.51

2.2 Biochar

All feedstocks were pyrolysed at the HTT of 550°C and 700°C in three pyrolysis units of different scale and design, labelled Stage I, Stage II and Stage III, which are described below in sections 2.3 – 2.5. The conditions in all three units were set to ensure production conditions (thermal history) that were as comparable as possible. In the Stage I and Stage III units, multiple runs with the same feedstocks were performed resulting in different batches of biochar (only SWP and WSP feedstocks were processed in Stage I). All batches/runs analysed in this study are shown in Table 2, and production conditions are shown in Table 3.

Table 2 - Number of runs/batches analysed per biochar type and pyrolysis unit. (TGA - thermogravimetric analysis).

	550°C				700°C			
	TGA	Stage III	Stage II	Stage I	TGA	Stage III	Stage II	Stage I
MSP	4	4	1		4	2	1	
OSR	4	8	1		4	6	1	
RH	4	11	1		4	7	1	
WSP	4	8	1	4	4	5	1	4
SWP	4	11	1	5	4	9	1	5

2.3 Stage III (Pilot-scale) pyrolysis unit

2.3.1 General operation

The UKBRC Stage III Pyrolysis Unit (rotary kiln pyrolyser) as shown in Figure 1 was used to produce the UKBRC Standard Biochar set. The unit comprises a variable speed screw-feeder with attached hopper, a sealed rotating drum (inner diameter 0.244 m, heated length 2.8 m) heated by a set of electric heaters arranged in three heater banks of 16.67 kW each, a char

handling screw conveyor, a collection vessel, and an afterburner chamber. The unit can operate at temperatures of up to 850°C, and achieve mean residence times of solids between few minutes to over 40 minutes. A typical operation of the kiln consists of initial purge of the whole equipment with nitrogen, while heating to the operating temperature. This is followed by introduction of biomass into the reactor at a pre-set rate by a horizontal screw feeder. Biomass then moves along the length of the reactor, gradually undergoing drying (moisture release), devolatilisation, and charring. The residence time of material in the heated zone can be controlled by adjusting the speed of the kiln rotation and feeding rate. At the end of the rotary drum, biochar is separated from gases and vapours in an insulated discharge chamber, and transported by a screw conveyor into a sealed metal drum filled with nitrogen. The screw conveyor, with its water jacket through which cooling water was circulated, also acts as a heat exchanger, reducing the biochar temperature to well below 100°C, without directly contacting it with water. As a result, the produced biochar is dry and due to nitrogen blanketing, free of influence from air and air moisture. Gases and vapours separated in the discharge chamber are led through a heated tube into an afterburner chamber where they are combusted. Table 3 provides detailed information on the operating conditions used for all ten Standard Biochar materials.

The production process for Standard Biochar was optimised to achieve the highest reproducibility and consistency possible. The operation was started by purging the whole unit with nitrogen for 20-30 minutes, while the electric heaters brought the unit to the pre-set operating temperature. When the reactor temperature was close to the desired temperature, biomass was introduced at a pre-set rate (see Table 3). The reactor was allowed to reach a steady state with biomass flowing through, then a further 30 minutes was allowed for the material to flow through the kiln and screw conveyor. After this time, an empty collection drum (purged with N_2) was fitted, and the target biochar started to be collected. The biochar

produced before steady state operation was reached was not included in the Standard Biochar set.

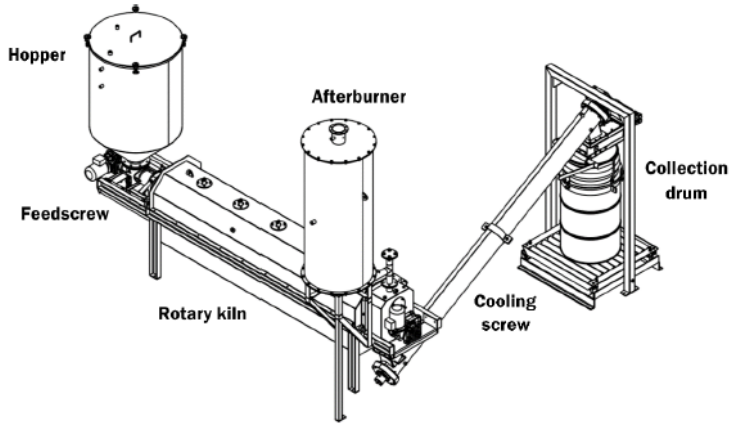

Figure 1- Rotary kiln pilot-scale pyrolysis unit (Stage III) at the UKBRC, University of Edinburgh (source: Ansac Ltd.).

2.3.2 Heating, temperature control and monitoring

The Stage III unit at UKBRC is equipped with an advanced system for monitoring and control of process temperatures. This allows careful adjustments of the reactor temperatures and monitoring of temperatures of the reactor, as well as material within the reactor.

Heating is provided by three independent heater banks with length of approx. 0.9 m each, distributed on one side, along the length of the kiln. The control of the heaters is achieved using a PID controller for each bank, with input provided by thermocouples (T1a, T3a, and T5a in Figure 2) situated in the centre of each heating zone (lengthwise) at the top of the kiln, i.e. 90° against the kiln rotation from the position of the heater banks. Besides these control thermocouples, there are a further two thermocouples (T2a and T4a) situated between the heating zones for additional monitoring of the reactor wall temperature.

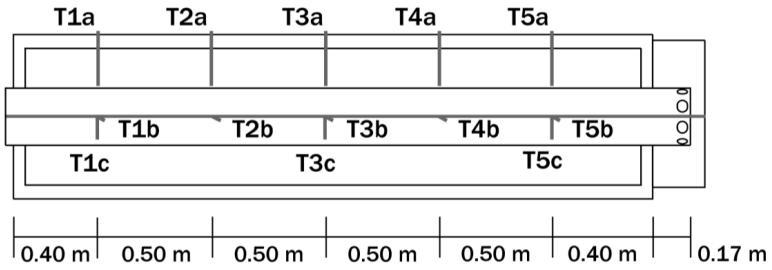

Figure 2 - Position of thermocouples: external (T1a-5a), kiln centreline (T1b-T5b) and kiln bed depth (T1c-T5c) [44].

To obtain data on temperature of the solids and gases within the reactor, we developed a specially designed system for inserting thermocouples into the rotary kiln. As a thermocouple system accessing the internal volume through the wall of the rotating drum would be very complex, access through the hollow shafts of the screw feeder and the rotary kiln was used. Eight thermocouples were inserted into various parts of the kiln, four from each end, as shown in Figure 2. The thermocouples were supported, and held in place by a stainless-steel cable, stretched through the axis of the kiln. To compensate for thermal expansion and prevent sagging of the wire and thermocouples, a counter weight continuously tensioned the wire. This array of thermocouples was distributed along the length of the kiln in such a way that temperatures of both the solids and gases could be continuously monitored. This proved critical when assessing the operating conditions under which different Standard Biochar were produced. The longitudinal positions of these thermocouples were selected to match those of the external thermocouples measuring the reactor wall temperatures (T1a – T5a), allowing the temperature profile inside the reactor to be established and compared to the reactor wall temperature profile.

2.3.3 Particle residence time distribution

In pyrolysis systems, the residence time of particles in the heated section of the reactor, and at the peak temperature, determines the particle temperature history; this is one of the most

important parameters controlling the product yield and distribution (solid/gas ratio), and in the case of biochar, its properties [4,5,45]. Experimental determination of residence time distribution of biomass particles undergoing pyrolysis in a rotary kiln is not straightforward. Therefore, several approximations were adopted in this work. Firstly, preliminary tests in a model rotary drum at room temperature suggested that there were only slight differences in flow rate through the unit between the raw biomass (pellets) and the charred pellets (which had kept their cylindrical shape). This assumption allowed the use of wood pellets of three colours (natural + two painted in blue and red colours) to study the residence time distribution, while running the rotary kiln at room temperature. To do this, a small amount (approx. 500 g) of each colour of wood pellets was fed in sequence directly into the screw feeder, and the time at which these exited the rotary kiln was observed. Pellets were collected every 30 seconds directly from the exit of the rotary drum, to avoid any mixing in the char outlet screw conveyor. Collected pellets were then spread onto a black tray forming a monolayer, avoiding individual particles covering each other, and photographed (Nikon D7000). Acquired images were analysed using image-processing software (ImageJ, National Institutes of Health), and the areas (numbers of pixels) corresponding to each of the three pellet colours used were determined. This provided information on how many pellets of which colour were collected in each of the 30s intervals. From this information it was possible to reconstruct a typical residence time distribution curve and derive mean residence times. Given the comparable size and density of pellets for all the feedstock used, with the exception of rice husk, the residence time distribution for all four pelleted feedstocks was assumed to be the same, which is considered a sufficient first approximation.

2.3.4 Biochar sampling

Representative sampling is critical in any research and analytical work, and even more so when developing standard materials [46]. To obtain representative samples from a large

number of runs, with each run typically producing a full drum worth of biochar (150-200 L), a sampling protocol was established and followed throughout the project. The objectives of the protocol were to eliminate bias during sampling, to take samples representative of the whole run of biochar for analysis, and to allow run-to-run comparison of biochar composition. The sampling method was designed to collect biochar samples to determine the average value of parameters that characterise the biochar.

Sampling from a 205 L drum was carried out using a stainless steel 600 mm long concentric tube slot sampler. This type of sampler is suitable for collecting large volume cross sectional samples from free-flowing granular solids in drums. The sampler used has three sampling slots that are integrated along the length of the inner section. These are exposed after the sampler is inserted into the solid by rotating the inner section. Using this approach, a depth profile composite sample of the biochar is collected from the drum. The sampling process is repeated until five or more composite sample increments have been collected and combined in a 500 mL glass jar. Secondary sub-sampling from the combined sample for analysis is then carried out as required. A schematic illustrating the sampling method is shown in Figure 3.

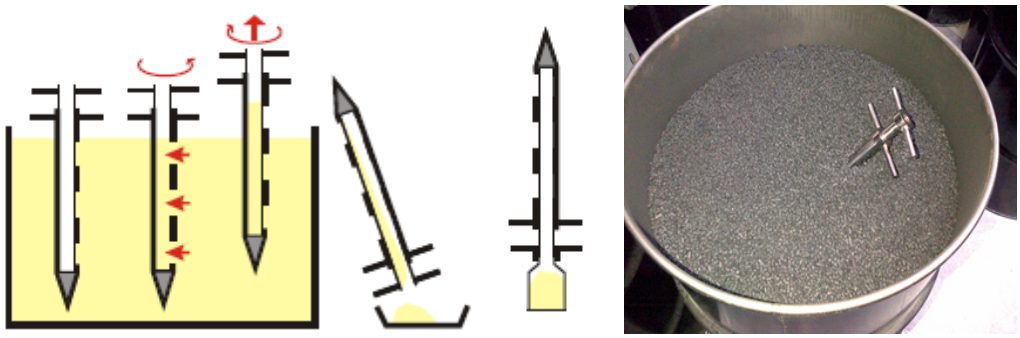

Figure 3 - Sampling from biochar drums using a concentric tube slot sample (source of image on the left: www.samplingsystems.com).

2.4 Laboratory auger pyrolysis unit

The Stage II pyrolysis unit is a continuous-screw pyrolysis unit (auger reactor) which uses an electrically heated split-tube furnace with an inner diameter of 100 mm. After an initial nitrogen purge of the unit (through feed hopper, start of screw reactor and discharge shoot) using a combined flow of 20 L min^{-1}, flowrates are reduced to a carrier purge of 1 L min^{-1} and a purge supplying nitrogen to the char vessel at 4 L min^{-1}. The feed hopper transports the feedstock (typical feeding rate 500 g h^{-1}) to a rotary valve where it drops onto the furnace screw.

The screw transports the material through two heated areas with a combined length of around 0.75 m. The discharge chamber, which separates pyrolysis vapours and solids (biochar), was actively heated up with heating elements set to 500°C and 400°C, respectively. A third heating element (heating tape) set to 400°C heated the pipes that connect the discharge chamber with the afterburner, where the pyrolysis vapours are combusted using a propane burner.

At various parts of the pyrolysis unit, pressure and temperature were measured. Figure 4 shows a schematic of the unit and more details on the unit can be found in Buss et al., (2016b) [3].

The ten biochar produced in the auger reactor used the same residence times and HTT as for the Stage III pyrolysis unit described above.

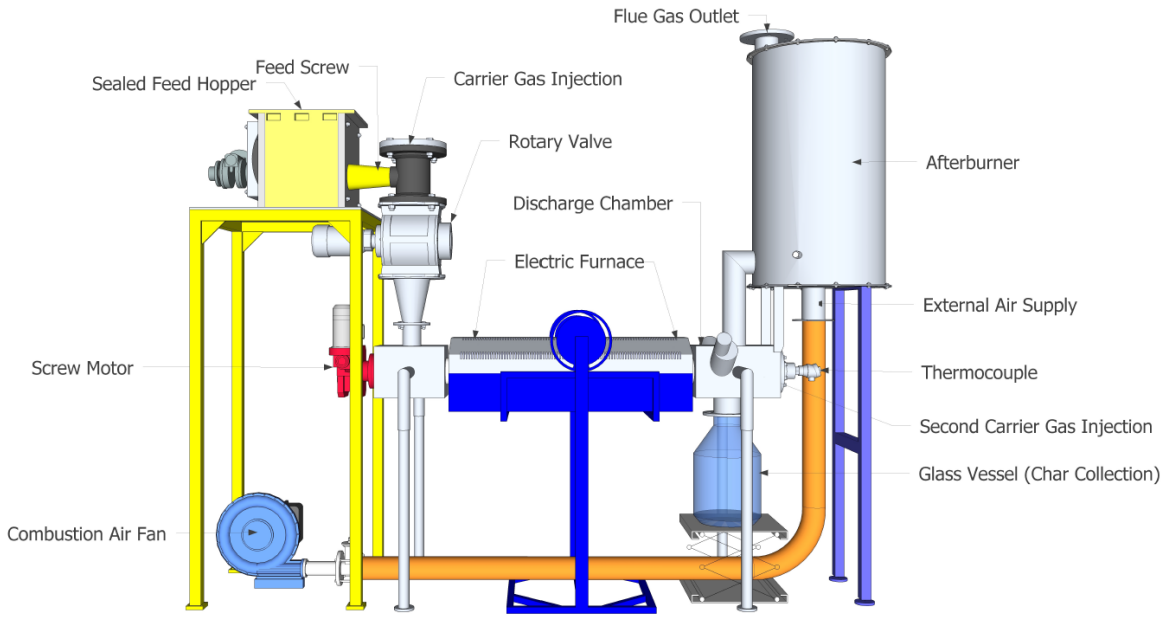

Figure 4 - Auger reactor (Stage II) at the UKBRC, University of Edinburgh [3].

2.5 Laboratory batch pyrolysis unit

The Stage I pyrolysis unit is a small-scale, batch pyrolysis reactor with a vertical quartz tube (inner diameter 50 mm) which has a sample bed depth of around 200 mm and is heated up by a 12 kW infra-red gold image furnace (P610C; ULVACRIKO, Yokohama, Japan). A condensation system was assembled to collect different fractions of condensable gases in cold traps, while non-condensable gases were collected in a gas bag for further analysis. More details about the pyrolysis unit set-up and use can be found elsewhere [31] and a schematic is shown in Figure 5.

In the Stage I unit, the pyrolysis parameters (HTT, heating rate and RT at HTT) were setup in such a way as to replicate the conditions experienced by WSP and SWP biomass particles in the Stage III unit, see Table 3. These parameters were determined based on in-depth investigations of the temperature profiles and residence times of the feedstock particles in the Stage III rotary kiln unit.

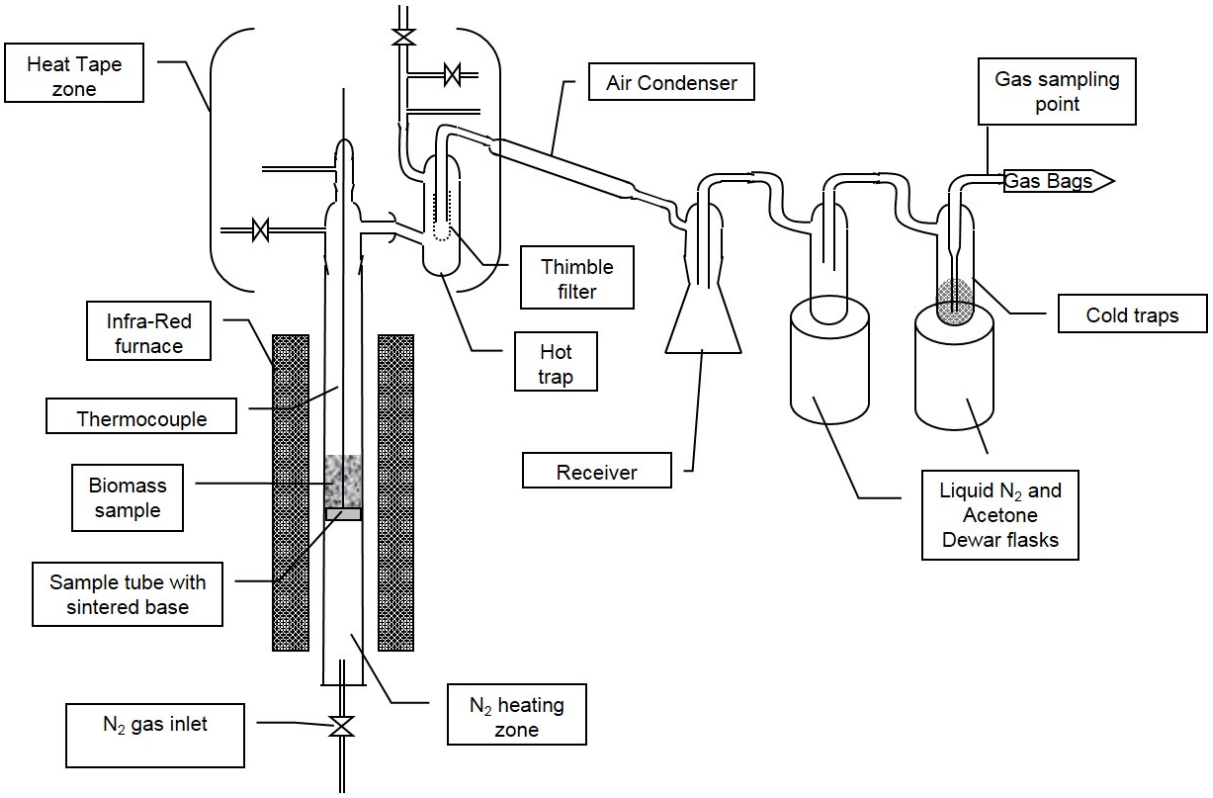

Figure 5 – Stage I pyrolysis reactor (batch) and pyrolysis vapour condensation system [31].

2.6 Micro-pyrolysis via thermogravimetric analysis (TGA)

A thermogravimetric analyser (Mettler-Toledo TGA/DSC1) was used to replicate biochar produced in the Stage III unit (as described in section 2.3). For this approx. 15 mg of finely ground feedstock was placed in 70 µl alumina crucibles and subjected to pyrolysis conditions using the pyrolysis parameters (HTT, heating rate and RT at HTT) as shown in Table 3. Pyrolysis was carried out under nitrogen with a purge gas flow rate of 150 mL min^{-1}. The TGA, possessing the highest degree of control of all the pyrolysis units utilised in this study, was used for comparison of biochar yield and volatile matter content (VMC) with the lab-/pilot-scale pyrolysis units to establish readily reproducible baseline values.

2.7 Biochar/feedstock analysis

Biochar samples collected as described in section 2.3.4 from the drums produced by the Stage III unit and corresponding representative sampling of the smaller containers of biochar

produced in Stage I and II units were sub-sampled and then crushed to a homogenous fine powder using pestle and mortar. Proximate analysis (fixed carbon content, VMC, and ash) was then used to confirm material consistency within runs (one production batch), between runs (multiple batches) and among different pyrolysis units. This measure was selected based on the fact that it has been shown to correlate with important biochar properties [47], such as stability [7,31], phytotoxicity [48,49] or degree of conversion [45].

Proximate analysis of all biochar samples and corresponding feedstock was carried out in a thermogravimetric analyser (Mettler-Toledo TGA/DSC1). For this analysis, samples in 70 µl alumina crucibles (approx. 15 mg) were first heated to 105°C under flow of N_2 at 25°C min^{-1} to determine the moisture content; the temperature was then raised at a rate of 25°C min^{-1} to 900°C where it was kept for 10 min to eliminate volatile matter. Following this period, the gas supply was switched from nitrogen to air, to determine the ash content by combusting the sample for 20 min at 900°C. Fixed carbon content and VMC are given on a dry, ash-free basis, in wt% of the original mass of the dry sample. A quality control sample was analysed with every batch of biochar (~20-30 biochar at a time).

2.8 Statistics

Statistical analysis was performed with R (Version 1.0.143, www.r-project.org) and Sigma plot (Version 13.0, Systat Software Inc.) using a statistical significance level of 0.05. Before performing one-way ANOVAs all data were tested for normality.

For comparing the variability within-batch and the between-batch variability of the Stage I biochar, a Levene-test was performed with the batches as individual groups (comparison of variances). Additionally, one-way ANOVAs were performed on all batches of each biochar to determine potential difference in the mean of the VMC, followed by Tukey's post-hoc

tests in case of WSP 700. For the within-run and between-run variability of the biochar produced with the Stage III unit, a Levene test was performed.

To compare the influence of pyrolysis and the influence of the two pyrolysis temperatures on the variability of the VMC, again a Levene-test was performed either with “pyrolysis” as one category, taking both temperature biochar together or taking the two temperatures individually.

Finally, One-way ANOVAs were performed to determine differences in VMC between the different pyrolysis units which was followed by a Tukey’s post-hoc test (suitable for unequal sample sizes). For data presented in the SI, equal variance, two-sided t-tests were performed.

3 Results and Discussion

As the aim of the standard biochar development work was to obtain materials with narrow ranges of specifications, produced under reproducible conditions, the variability in biochar quality was of paramount interest. The key parameters influencing consistency of biochar quality parameters both within a single production batch and among batches are: thermal history of biomass and biochar particles in a pyrolysis unit, the design/type of pyrolysis unit, and uniformity and consistency of feedstock properties. The effects of these parameters on biochar yield and quality parameters are discussed in this section.

3.1 Reactor temperature profiles and biochar temperature history in the rotary kiln pyrolysis unit

The thermal history of biomass/ biochar in the pilot-scale Stage III reactor, where >2 t of UKBRC Standard Biochar were produced, was of key importance, and therefore one of the focus points of this study. This parameter is significantly under-reported in the literature, due to the difficulty in obtaining necessary data. The temperature profiles measured for the reactor wall as well as the solids and gases inside the rotary kiln are presented in Figure 6. These show gradual increase in temperature of the material as it travels through the kiln. It can be seen that the profiles vary for naturally granular rice husk relative to pelleted materials, reflecting the different physical and chemical properties, affecting heat transfer and decomposition dynamics. A low between-run variation associated with these temperature profiles during steady state operation is a critical parameter for minimising variability in the degree of conversion of the char produced over the duration of a production run.

Data extracted from the temperature profiles, and associated production parameters for the Standard Biochar are shown in Table 3. From the data, it can be seen that the reactor wall temperature was identical to the set point temperature, confirming a high degree of control of the reactor temperature. The table also shows the extent to which the mean maximum

temperature of the char bed moving in the reactor differed from the reactor wall temperatures. Although the differences between the reactor wall and measured char bed temperatures were relatively small (<10°C) during pyrolysis at 550°C, pyrolysis at 700°C showed considerably larger differences between the wall and char temperatures for most materials (see Table 3). Potential causes may include differences in heat transfer, endothermic and exothermic reactions, etc., for more in-depth discussion see Roy-Poirier (2014) [44].

Based on the bed temperature profiles and residence time distribution for particles passing through the reactor, it is possible to estimate the range of time for material particles maintained at the HTT as well as heating rate (Table 3). These results show that the time at HTT was dependant on feedstock and set temperature. It was generally longer for pyrolysis set at 700°C. The calculated heating rate for most of the materials and pyrolysis conditions fell within a range of approx. 70–100°C min^{-1}, and therefore the process falls into the slow/intermediate pyrolysis category. Previous work showed that heating rate variations within this range have no notable effect on biochar properties [31].

The estimated heating rates were further applied to produce comparable biochar using the TGA and Stage I pyrolysis unit (batch reactor). Although differences in heating rates can be seen as a function of pyrolysis temperature, it is not possible to discern a clear trend. This supports the view that heating rate is not only a function of the reactor wall temperature, but also of feedstock composition and physical properties and form of particles.

Table 3 - Standard Biochar production parameters in the Stage III pyrolysis unit. The kiln residence time, heating rate, and residence time at HTT were calculated based on measured temperature profiles and particle residence time distributions, and therefore represent best estimates.

Biochar	Mean kiln residence time (min)	Nominal HTT (°C)	Reactor wall temp. (°C)	Mean char bed steady state temp. (°C)	Heating rate (°C min^{-1})	Residence time at HTT (min)
SWP 550	12.0	550	550	545	78	3.9

SWP 700	12.0	700	700	681	87	5.0
WSP 550	15.0	550	550	549	80	5.0
WSP 700	15.0	700	700	668	79	6.0
MSP 550	12.0	550	550	554	65	3.9
MSP 700	12.0	700	700	-	80	5.0
OSR 550	12.0	550	550	553	78	5.0
OSR 700	12.0	700	700	696	103	5.0
RH 550	15.0	550	550	556	98	8.5
RH 700	17.0	700	700	680	92	9.0

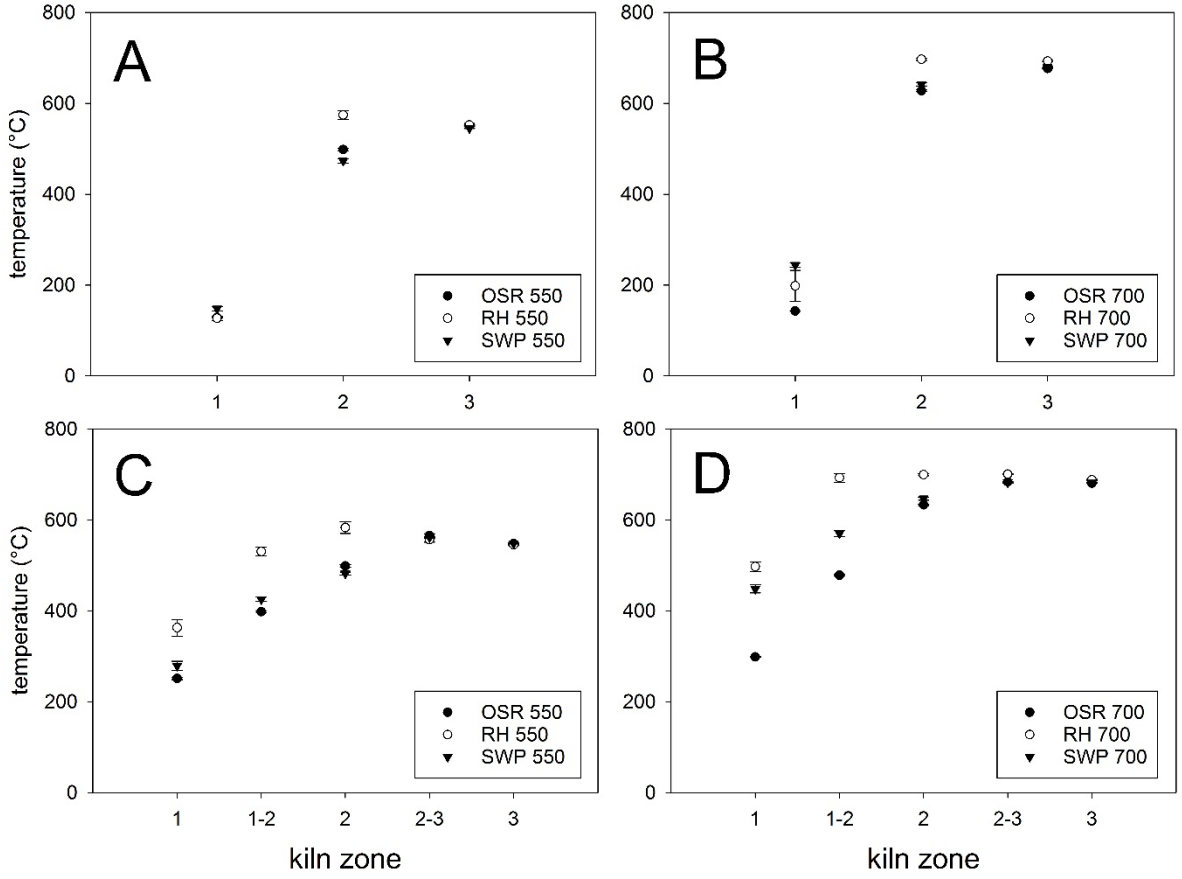

Figure 6 - Mean temperature profiles along the length of the rotary kiln pyrolysis unit (Stage III) during steady state operation. A) solid bed temperature during pyrolysis at 550°C; B) solid bed temperature during pyrolysis at 700°C; (C) head space temperature during pyrolysis at 550°C; (D) head space temperature during pyrolysis at 700°C. The kiln zone numbers indicate the position in the kiln corresponding to the different heater bands.

3.2 Char yields

The yield of the ten biochar produced from five feedstocks at two HTT (550 and 700°C) are show in Figure 7 (see also S Table 1). These results were compared to the yield of char obtained by pyrolysis of the same feedstock under the same nominal conditions in a TGA and a small fixed bed reactor (Stage I). Small losses of biochar can occur in the rotary kiln as a result of entrainment of fine particles together with pyrolysis gases into the afterburner chamber or partial combustion due to small amounts of oxygen in the unit. This can explain the lower yields observed in the Stage III unit. The fact that biochar yields in the TGA and Stage I were very similar, despite TGA using finely ground biomass particles while Stage I used whole pellets, shows that under the conditions of intermediate pyrolysis particle size did not play a strong role.

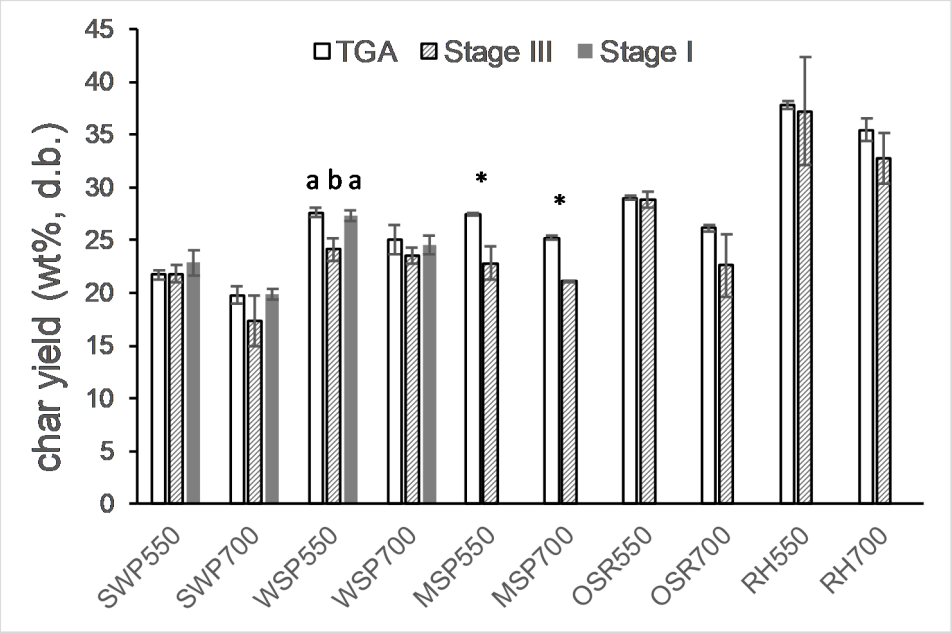

Figure 7 – Figure 7 - Yield of biochar from Stage III unit compared to yield obtained under same nominal conditions in the Stage I unit and a TGA. Error bars represent standard deviation with n = 4 for TGA, n = 3 for Stage I SWP 550 and 700, n = 4 for WSP 550 and WSP 700 and n according to S Table 1 for Stage III samples. * show significant differences between the TGA and Stage III biochar yield determined by t-tests. Different letters indicate differences determined by ANOVA, followed by Tukey post-hoc tests.

3.3 Within- and between-batch/run variation

A previous study has shown that the properties of biochar even within a single batch can be highly variable, highlighting the need for representative sampling [46]. The variability among batches/runs could potentially be even larger than within a single batch, and therefore here we compared variability of biochar within a batch (based on VMC) against the variability in-between batches/runs (representative samples).

Samples were taken from different depths of a laboratory fixed-bed batch reactor within a single batch for the four biochar produced in the batch pyrolysis unit (Stage I). The variability of VM of biochar produced within and between repeat runs of Stage I are shown in Figure 8, for each biochar type. The error associated with each mean are as follows (95% confidence interval): SWP 550 14.27% ± 1.17%; SWP 700 6.61 ± 0.30%; WSP 550 15.68% ± 1.75%; WSP 700 9.76% ± 1.02%.

A one-way ANOVA was performed to identify statistical differences between the batches. SWP 550, SWP 700 and WSP 550 do not show any statistically significant differences between the batches. Additionally, a Levene-test was performed which did not show statistical differences in variability within the batches and compared to the means of all batches (Figure 8). Hence, the within-batch variability is similar to the between-batch variability. Within the WSP 700 biochar there was a statistically significant difference ($p = 0.038$) determined by a one-way ANOVA. However, a Tukey post-hoc test did not reveal any statistical difference between the batches with the highest difference of means (PNB 1020/19 and PNB1018/155). Hence, there is some variation in the full data set which is not completely explained by chance, but none of the individual treatments is statistically different from each other. Overall, taking all four different biochar into account, the batch-to-batch variability is minimal and under well-controlled production conditions the biochar properties in the batch reactor can be ensured even when produced in different runs.

Furthermore, samples were taken from one drum of RH 550 and RH 700 produced in the Stage III pyrolysis unit and compared to the variability of different pyrolysis runs. The within-drum sampling of RH 550 and RH 700 product indicated within-run variability comparable to the variability between runs compared with a Levene-test (no significant difference, Figure 9). This is an important finding as it suggests that biochar can be produced quite consistently between runs and by units of different design, at least with the level of process control embodied in our Stage I and Stage III units.

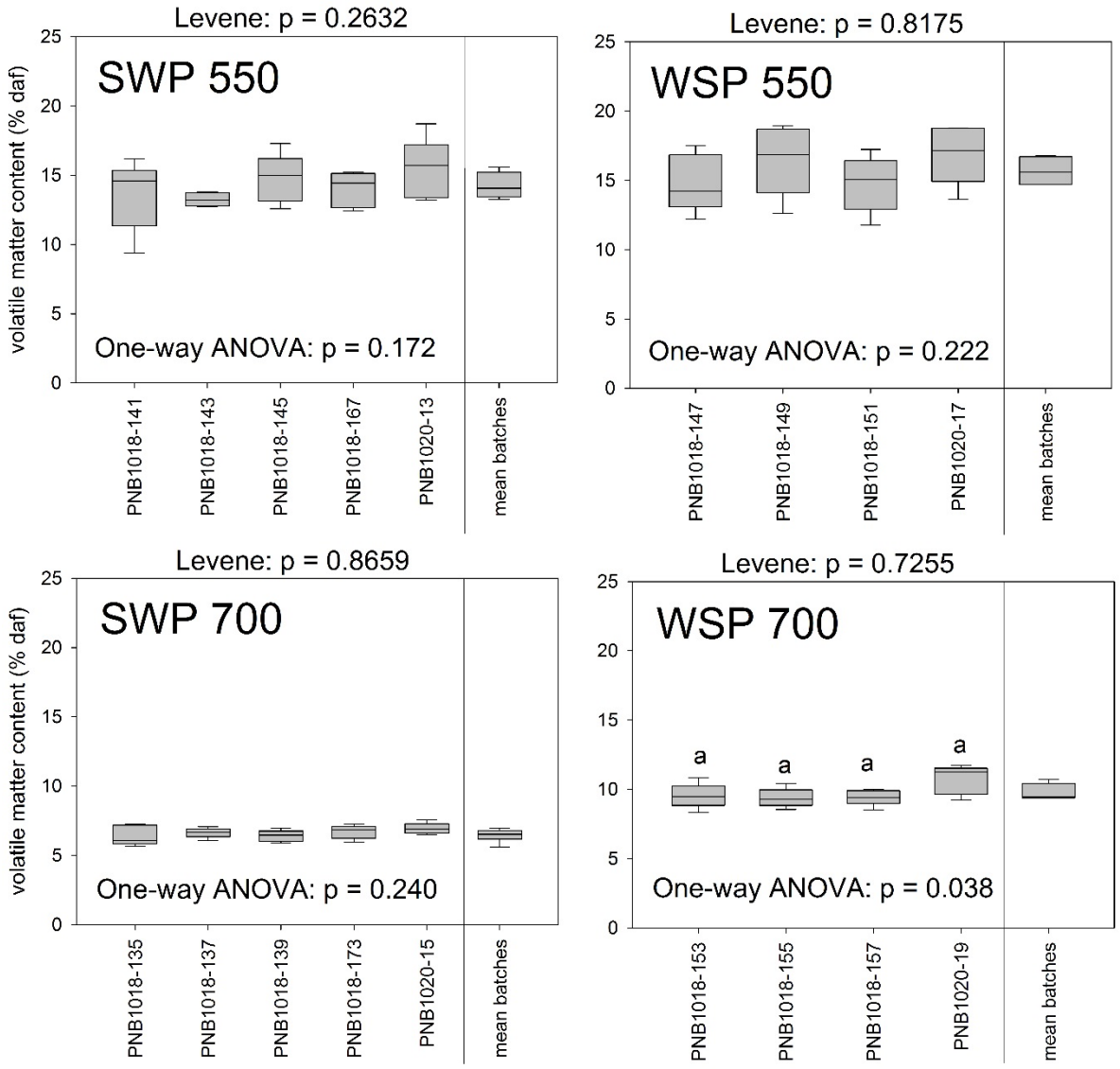

Figure 8 - Box plot of volatile matter content (% dry ash-free basis) for four biochar produced in the Stage I pyrolysis unit. The codes at the bottom of each figure signify an individual batch, produced on different days with the same feedstock and pyrolysis parameters (replicates taken from different depth of the biochar bed in the reactor (n = 6)). The box plots on the right show the mean values of each batch. The p-values are the result from Levene-tests and one-way ANOVAs performed on all batches of each biochar, followed by Tukey post-hoc tests in case of WSP 700.

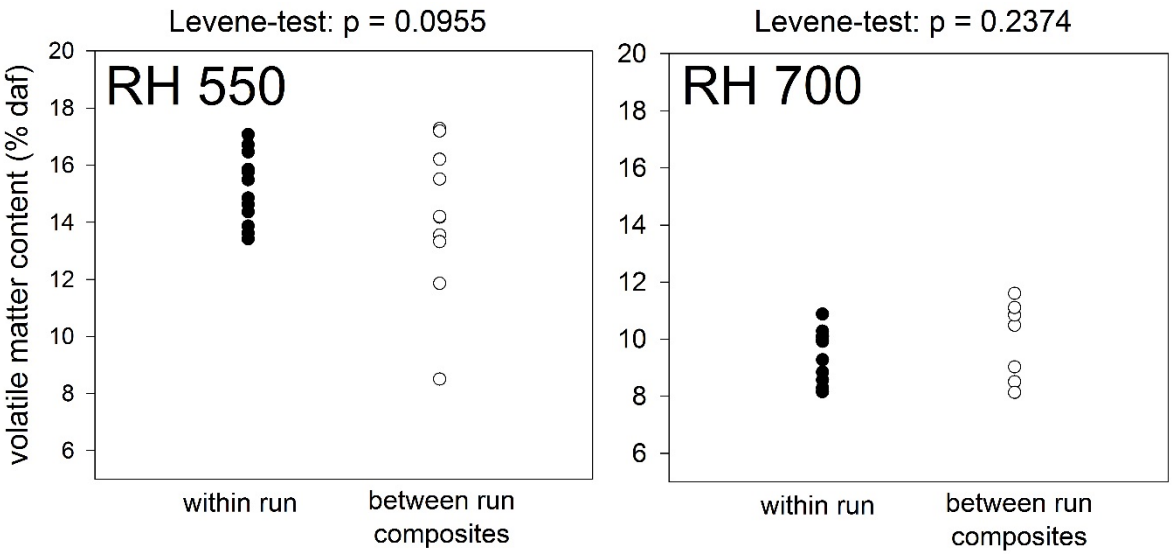

Figure 9 - Volatile matter content (% dry ash-free basis) for biochar produced with the Stage III pyrolysis unit. The black data points are individual measurements taken from one run with replicate samples taken from different parts of the storage drum (n = 12). The white data points are measurements for different runs of biochar produced on different days with the same feedstock and pyrolysis parameters. Two biochar are shown: rice husk pyrolysed at 550°C (eleven different runs) and at 700°C (seven different runs). P-values from Levene-tests are shown above the figures.

3.4 Feedstock variability vs. biochar variability

Having addressed production parameters related to the pyrolysis process, we focussed on finding out the extent to which the variability in biochar quality parameters (again VMC as a proxy) originates from the feedstock used for the pyrolysis process.

As seen in Table 4, there were only significantly greater variances in VMC of biochar OSR 550 and RH 550 compared to their respective feedstocks as determined by Levene's tests ($p = 0.0455$ and 0.0462). This means the variance in these two materials increased due to pyrolysis. In all the other materials, and when taking both temperatures for OSR and RH into account, there was no significant difference in the variances.

Biochar produced at higher HTT have lower standard deviations than the biochar produced at lower HTT in both feedstocks and pyrolysis units, as shown in Figure 8 and Figure 9, and supported in most cases by Table 4 (apart from RH). It indicates that more severe carbonisation conditions result in a more homogenous biochar material. Hence, higher pyrolysis temperatures can be used to reduce variability in biochar. Similar effect could possibly be achieved by extended thermal treatment even under lower temperatures, but this was not tested in this work.

We can therefore conclude from this that most of the variance in the VMC (and by approximation biochar quality parameters) originates from the feedstock and has not been introduced by the pyrolysis process. Hence, under highly controlled pyrolysis conditions in well-designed pyrolysis reactors at steady state, the variability in biochar quality parameters is not significantly greater than the variability already present in the biomass feedstock.

Table 4 - Comparison of variability (variance) in five feedstocks compared to ten resulting biochar produced with the Stage III pyrolysis unit. Volatile matter content is shown in % as mean with standard deviation. n signifies the number of different biochar production runs analysed for each type of biochar. The variance in the feedstock was compared to the variance in the biochar produced from the respective feedstock, at one temperature individually ("temperature" in table) and taking both temperatures into account as individual groups ("pyrolysis" in table") using the Levene's test. Bold p-values mean that there is a significant difference ($p < 0.05$).

type	volatile matter content (% daf)				p-value	
	AV	±	SD	n	temperature	pyrolysis
MSP feed	82.66	±	0.41	5		0.3878
MSP 550	13.22	±	1.59	4	0.2967	
MSP 700	8.72	±	0.13	2	0.2479	
OSR feed	82.80	±	0.29	5		0.1053
OSR 550	20.35	±	3.22	8	**0.0455**	
OSR 700	16.87	±	4.42	6	0.0562	
RH feed	80.87	±	0.39	5		0.0686

RH 550	13.97	±	2.61	11	**0.0462**	
RH 700	9.95	±	1.38	7	0.0602	
WSP feed	83.05	±	1.14	5		0.3834
WSP 550	15.16	±	1.55	8	0.3823	
WSP 700	11.06	±	0.98	5	0.7515	
SWP feed	85.33	±	0.41	5		0.2727
SWP 550	14.83	±	1.03	11	0.1015	
SWP 700	7.47	±	1.02	9	0.1682	

3.5 Comparison of different pyrolysis technologies

While small-scale (batch) pyrolysis units are often preferred to produce biochar for research purposes, larger, often continuous processing will be necessary to produce biochar on an industrial scale. Hence, it is important to investigate whether biochar resulting from different pyrolysis technologies (different scale and set-up) differ in terms of their quality parameters (VMC) when operated under the same nominal conditions.

As discussed in Section 3.3, there were minimal differences in VMC within runs/batches and between runs/batches, and therefore, representative samples from different batches (Stage I and III) and within-run samples (Stage II) were equally treated as replicates representing the particular pyrolysis technology for the purpose of this comparison (Figure 10).

Results of the comparison in Figure 10 show some differences between the pyrolysis technologies. However, only the biochar produced in the TGA showed statistically significant differences in VMC when compared to biochar from lab-/ pilot-scale units. No statistically significant differences were observed among the lab-/ pilot-scale units. As the microscale pyrolysis in the TGA is very different in its nature from that in the lab-/ pilot-scale pyrolysis units (as for the char yield in 3.2), e.g., sample in form of a thin layer of fine powder, volatiles immediately swept away by purge gas, it is not surprising that it yields biochar with different properties even when the nominal processing conditions are set to replicate the temperature history experienced by particles in the larger units.

We also compared the VMC between the pyrolysis unit excluding the TGA data via t-tests and one-way ANOVAs as appropriate (S Figure 1). There was no statistically significant difference between the units for nine out of ten biochar, only SWP 550 produced in the Stage II unit showed a slightly, but statistically significant, lower VMC than corresponding biochar produced in the Stage III unit ($p = 0.035$; Stage II: 13.12 ± 0.16; Stage III: 14.81 ± 0.97).

The finding that VMC was mostly independent of the type and scale of pyrolysis processing is important in the context of biochar development and deployment, as it shows for the first time that biochar production can be scaled-up using different types of technologies without negatively affecting biochar properties. However, the equipment used in our work has a high degree of process control, particularly to avoid condensation of pyrolysis vapours beyond the heated zone. Condensation of tars was shown to result in elevated concentrations of VOC, PAHs (in particular higher-molecular weight PAHs) and increased VMC in biochar [6,32,49]. This would not only diminish its quality but also increase the potential for toxic effect. To produce biochar of comparable properties in different types of pyrolysis technologies such as those tested here (batch, auger-reactor, and rotary kiln), the feedstock/biochar needs to experience the same thermal history (heating rate, HTT, residence time at HTT).

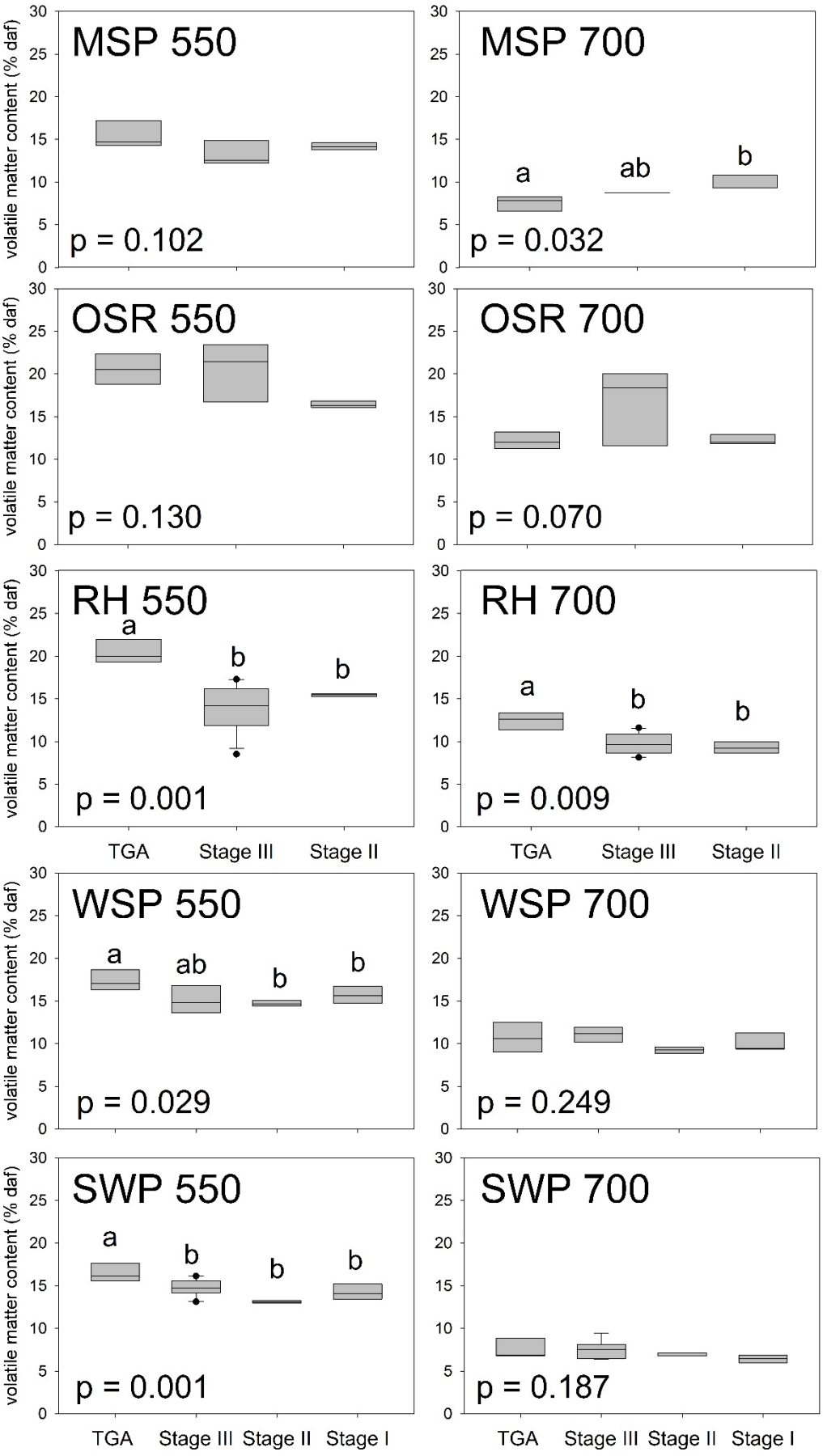
MSP 550
p = 0.102
MSP 700
a
ab
b
p = 0.032
OSR 550
p = 0.130
OSR 700
p = 0.070
RH 550
a
b
b
p = 0.001
RH 700
a
b
b
p = 0.009
WSP 550
a
ab
b
b
p = 0.029
WSP 700
p = 0.249
SWP 550
a
b
b
b
p = 0.001
SWP 700
p = 0.187
volatile matter content (% daf)
0
5
10
15
20
25
30
TGA
Stage III
Stage II
Stage I

Figure 10 - Effect of pyrolysis technology on volatile matter content (% daf) in ten biochar produced from five different materials. Thermogravimetric analysis (TGA), Stage I, II and III units stand for the three different pyrolysis technologies. One-way ANOVAs were performed and the p-values are given in the figures. Different number of replicates were analysed for the different materials. The samples for the Stage II unit reflect within run replicates while the replicates for Stage I and III show average of different runs/batches. Letters in the figures show groups with statistically significant differences determined by Tukey's post-hoc test.

4 Conclusions

Volatile matter content as a proxy for a wider set of biochar properties was found to be consistent among biochar samples produced in grams to 100 kg quantities, and also among runs. If the level of process control in our laboratory and pilot-scale experimental facilities can be applied at industrial scale, this has important implications for biochar development and deployment. For the first time, we showed that it is possible for biochar production to be scaled-up using different technologies without changes in key biochar quality parameters.

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