



Article

# Pyrolysis Temperature Effects on Biochar–Water Interactions and Application for Improved Water Holding Capacity in Vineyard Soils

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**Abstract:** Grapevine cane and stalks were considered for pyrolysis at 400 to 700 °C to produce biochar for increasing the water holding capacity of vineyard soil. Feedstocks were pyrolysed using a continuous feed reactor and the resulting biochars characterized in terms of physico-chemical properties, including water retention performance. Hydrophobicity was found in biochar from both feedstocks pyrolysed at 400 °C, but not at higher temperatures. At low soil matric potential, the pyrolysis temperature was the defining variable in determining water retention whereas at higher pressures, the feedstock was the more important variable. Available water content (AWC) of biochar increased with increasing pyrolysis temperatures, with optimal results obtained from grapevine cane at a pyrolysis temperature of 700 °C, which had an AWC 23% higher than a typical clay type soil. Principal component analysis showed variability in water retention of these biochars to be closely associated with the zeta potential, as well as the carbon and ionic content, suggesting that surface charge and hydrophobicity are key properties determining water holding capacity. Pure biochars were superior in water retention performance to typical sandy soils, and so biochar amendment of these soil types may improve water holding (particularly at field capacity). Further study with pot or field trials is recommended to confirm water retention behaviour and assess the feasibility of application under different viticultural scenarios.

**Keywords:** soil water holding capacity; viticulture; biochar; pyrolysis; waste valorisation

## 1. Introduction

The application of biochar as a soil adjuvant has been suggested in numerous studies as a strategy for improving the water use efficiency of the agricultural sector [1–5], which accounts for an estimated 70% of total global freshwater use [3,6]. Whereas many such studies have found an improvement in the water holding capacity of soil following biochar addition [1–4], the result has not been consistent [6–8]. Improvements to soil hydrological functions have, in some cases, also required rates of biochar addition to soil that may be excessive for practical commercial-scale application [6], with some studies employing biochar addition rates of 90 to 135 t/ha in order to achieve beneficial effects [4].

Two common hypotheses are posited to explain the mechanism of increased hydrological function in soil following biochar addition [6]. The first is that water is stored within the pore space of the biochar [3], while the other hypothesis postulates that the increase in soil water retention is caused by the increased aggregate stability of soil after biochar application [1,4]. Some studies (e.g., [2,3]) have found a decrease in soil bulk density with biochar additions, ascribed to the low density of biochar in comparison to soil. A decrease in bulk density can result in an increase in soil porosity and aeration, potentially increasing root and microbial respiration and rainfall infiltration [3]. In either case, the extent of biochar hydrophobicity is critical to water uptake. Jeffery et al. [6] explained the absence of any improvement in soil water retention to the hydrophobicity of the biochar used, and suggested that hydrophobicity of biochars should be analysed in any assessment of biochar performance as a soil adjuvant.

Biochars produced at relatively low pyrolysis temperatures ( $\leq 400$  °C) tend to be hydrophobic due to the presence of tars containing aliphatic and aromatic compounds that clog the small pores created during pyrolysis at these temperatures, as well as the inherent hydrophobic nature of the compounds themselves [9–11]. These aliphatic and aromatic compounds are volatilized at higher pyrolysis temperatures, thereby decreasing hydrophobicity [9–12]. Polar functional groups on the surface are also removed under these high temperature conditions, resulting in few places for water molecules to form hydrogen bonds with the biochar surface. Das and Sarmah [10] state that the hydrophobic nature of low temperature biochar is not permanent, and the organic compounds contained in the tars that cause hydrophobicity could be removed by water. By water flooding (similar to the method used to displace petroleum in rocks by water), the hydrophobicity of 350 °C grapevine biochar was reduced by removing the surface aliphatics, with a corresponding reduction in the aliphatic peaks identified using Fourier transform infrared spectroscopy.

Although the majority of studies investigating the effect of biochar on water holding capacity have focused on mixed biochar-soil systems, Gray et al. [12] investigated the effect of hydrophobicity and the porosity of a biochar-only system, comparing water and ethanol uptake. Ethanol is a complete wetting agent and therefore can be used to compare hydrophobicity between samples. Biochars produced at lower pyrolysis temperatures adsorbed less water than those produced at higher temperatures. However, both biochars absorbed equivalent amounts of ethanol, supporting the hypothesis that surface hydrophobicity is modulated by pyrolysis temperature. In addition, it was also found that the biochar produced from Douglas fir chips absorbed more water than hazelnut shell biochar due to a greater porosity.

While understanding the effect of biochar on soil water holding capacity is a goal of this field of research, the variation in results from these previous mixed biochar-soil studies suggests the need for a more fundamental understanding of the effect of pyrolysis temperature on water retention in biochar before more variables are introduced. As such, the present study is focused on the effect of pyrolysis temperature on the water holding capacity of pure biochar produced from two different (but related) feedstocks: Grapevine canes and grapevine stalks. These feedstocks were chosen because viticulture is a significant horticultural activity, with grapes ranking among the top five of all fruits in terms of global production at around 70 Mt/year [13]. Vineyards require water throughout the growing season from budburst through to post-harvest [14,15] and during drier months of the year. However, water is a limiting resource for most grape growing regions, and in Australia, water cost and allocations to primary producers are of major concern in many regional communities. Vineyard-derived biochar produced onsite therefore has the benefit of improving viticultural water efficiency without the need to transport biochar long distances, thereby increasing the economic potential [16,17].

The objective of this study was to develop an understanding of the effect of pyrolysis conditions on physical properties (and water-holding capacity in particular) of vineyard derived biochars. Continuous pyrolysis equipment was employed because it is suited to mobile in-the-field use, and so would mitigate feedstock transportation, which must otherwise be considered in all biomass applications. In the study reported here, the materials and methodology are first outlined, following

which the effects of the pyrolysis temperature on the biochar physical characteristics and water retention are presented and discussed.

## 2. Materials and Methods

### 2.1. Sample Collection

Grapevine cane was sourced from Padthaway, South Australia (identified as F-C-Padthaway) on 11 July 2014 (immediately following pruning operations), transported to the University of Adelaide winery, and then stored in dry conditions at room temperature until further processing. Average moisture content of samples on receipt was 35.4% *w/w*. Grapevine stalks were collected from the same region of Padthaway (identified as F-S-Padthaway) during the subsequent 2015 vintage, with samples sourced directly following winery crushing and destemming operations. Stalks were immediately transported to the University of Adelaide and kept in refrigerated 0 °C conditions in air-tight containers until further processing to prevent microbial spoilage. The average moisture content of samples as received was 75.5% *w/w*.

### 2.2. Feedstock Preparation

The as-received grapevine canes were prepared for pyrolysis by milling using a rotary knife mill (model SK300, Retsch GmbH, Haan, Germany) with a 0.75 mm screen before being oven dried in air at 105 °C for 16 h. Due to the fibrous nature of grapevine cane, frequent blockages of the conical feed hopper were encountered during initial testing of the continuous pyrolysis unit. Several feed hopper prototypes were trialled with varying geometries. A design modification featuring an installation of a 1 mm screen with a motor-driven sweeping arm was eventually settled on to ensure feed consistency. In order to alleviate further problems, the particle size distribution following the drying of milled grapevine cane was adjusted by separating a fraction size of 212 to 500 µm by sieving to facilitate a reliable and consistent feed rate for later continuous pyrolysis processing. Sieved material was then stored in airtight containers prior to pyrolysis.

Due to the significantly higher water content, the as-received grapevine stalks were oven dried in air for 16 h at 105 °C prior to milling, in order to reduce the risk of microbial spoilage. Dried stalks were processed by the same rotary knife mill with a 0.75 mm screen and sieved to separate a fraction size of 212 and 500 µm (as per the procedure for grapevine cane) and stored in airtight containers prior to pyrolysis.

### 2.3. Thermo-Gravimetric Analysis

Thermo-gravimetric analysis (TGA) was conducted using a Setaram Labsys Thermo-gravimetric analyser (Setaram, Caluire, France) with a differential scanning calorimeter (DSC) to establish the required residence time for pyrolysis and ratios of ash to fixed carbon and volatile matters. Feedstock samples were progressively heated to the target temperature in a programmable furnace, and the total mass and mass rate change were recorded.

### 2.4. Biochar Production

The feedstocks were pyrolysed at four different temperatures (400, 500, 600, and 700 °C) (identified as 4-, 5-, 6-, 7- C- Padthaway and 4-, 5-, 6-, 7- S- Padthaway) using a lab-scale continuous tubular furnace described in Dunnigan et al. [11]. The apparatus was custom-built by the University of Adelaide with an 820 mm long stainless steel auger screw reactor (diameter of 27.3 mm, a pitch of 10 mm) and a maximum residence time of 15.5 min. A co-current carrier gas flow rate of 1.2 L/min nitrogen (NTP) was used as the dry inert atmosphere. The resulting biochar was stored in sealed air-tight containers prior to further experimentation, in order to prevent oxidation or moisture uptake that might occur due to the hygroscopic nature of the material.

### 2.5. Characterization of Feedstocks and Biochars

A CHN Elemental Analyzer (2400 Series II, Perkin Elmer, Waltham, MA, USA) was used to ascertain the carbon, hydrogen, and nitrogen contents of the feedstocks and resulting biochars. As nutrient elements are important for beneficial plant growth and understanding soil sodicity, elemental analysis of the feedstock and biochars, including calcium, potassium, and phosphorus, were determined by inductively-coupled plasma array optical emission spectroscopy (CIROS CDD Radial ICP-OES, Spectro Analytical Instruments GmbH, Kleve, Germany) applied to the product of nitric/perchloric acid digestion conducted in closed polypropylene tubes that exclude moisture uptake, according to the method of Wheal et al. [18].

The surface area and pore size distribution of each biochar was investigated via N<sub>2</sub> adsorption at 77 K and CO<sub>2</sub> adsorption at 273 K with a BELSORP-max instrument (MicrotracBEL Corp, Osaka, Japan) using the Brunauer-Emmett-Teller (BET) and non-local density functional theory (NLDFT) methods, respectively [19]. The pore size distribution for the biochars was also determined by applying non-local density functional theory (NLDFT) to the CO<sub>2</sub> adsorption/desorption isotherms. A scanning electron microscope (SEM) combined with energy dispersive X-ray spectroscopy (XL-30, Philips, Amsterdam, Netherlands) was used to determine the surface morphology of the biochars.

The zeta potential of each biochar was measured using a Nano ZS Zetasizer (Nano ZS, Malvern Panalytical Ltd., Malvern, UK) with MilliQ water as the carrier fluid. An average of 20 runs were undertaken for each sample, with a refractive index of 2.420 and an absorbance of 0.9000 used in the calculations. Sample pH was measured using the standardised conditions of Kameyama et al. [20], in which 1 g of biochar was dispersed in 25 mL of Milli Q water and mixed using an end-over-end shaker for 24 h before pH measurement of the suspension. Preliminary assessment of hydrophobicity was undertaken using a simple water drop test, where a droplet of water was dropped onto a bed of biochar and the penetration time was recorded. This was followed by quantitative assessment of the contact angle, measured by pressing each biochar into a block with approximate dimensions of a 4 mm height and 15 mm diameter using 12 ton of pressure before using the sessile drop method on an Attension Theta Optical Tensiometer (Biolin Scientific, Frölunda, Sweden) with a frame rate of 10 frames per second (FPS). Laboratory air temperature and relative humidity of approximately 21 °C and 50% RH, respectively, were maintained throughout these measurements.

### 2.6. Hydrostatic Water Retention

A water retention curve was constructed for each biochar not displaying complete hydrophobicity, as determined by the tensiometer. Volumetric water retention was measured at saturation and 1, 3, 10, 50, and 150 m matric head pressure in duplicate. Samples of each non-hydrophobic biochar were placed in 19 mm Perspex rings on wetted porous ceramic plates. Each sample was saturated with deionized water and placed in water-extraction chambers connected to pressurised nitrogen gas as described by Creswell et al. [21] and Bittelli and Flury [22]. Samples were held at these pressures for approximately 8 weeks (24 March 2015–21 May 2015) to allow hydraulic equilibrium to be established at all pressures, after which samples were weighed, oven dried overnight at 105 °C, and weighed again to determine gravimetric water content.

The bulk density of each biochar sample (measured in triplicate by weighing biochar in small cylinders of a known volume) was used to convert gravimetric water content to volumetric water content. Available water content (AWC) was determined from the hydrostatic water retention data by subtraction of the volumetric water content at a matric potential of 150 m (the 'permanent wilting point') from the volumetric water content at 'field capacity' (as measured at a matric potential of 3 m). In order to determine the statistical relationships between the physico-chemical properties of each biochar and its associated water retention performance, principal component analysis (PCA) was conducted using Scilab 6.0.2 (Scilab Enterprises, Versailles, France) and the 'Free Access Chemometric Toolbox v0.10' for Scilab (INRA/IRSTEA, Montpellier, France). Water retention data was analysed

using the methods of van Genuchten [23] and Grant et al. [24] and compared with standard soil water retention profiles to evaluate hydrostatic water retention performance.

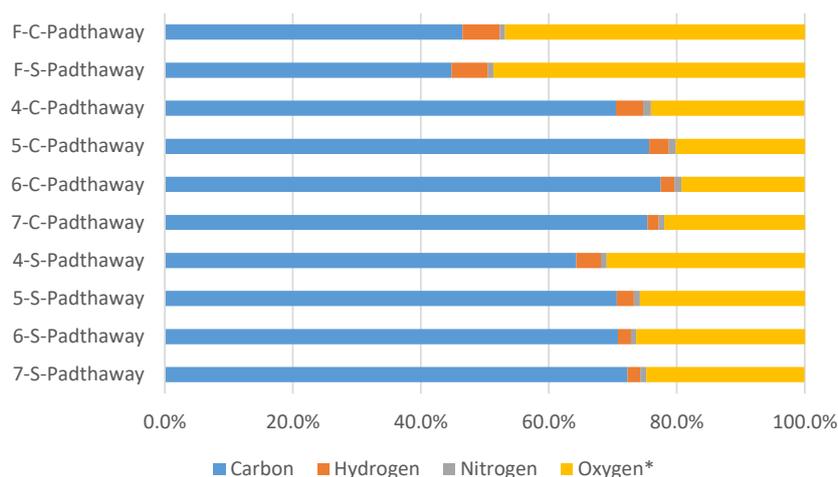
### 3. Results and Discussion

#### 3.1. Thermo-Gravimetric Analysis

During preliminary TGA testing, the derivative weight was observed to stabilise after approximately 12 min as shown in Supplementary Figure S1, indicating pyrolysis was complete. Based on these preliminary TGA results of grape feedstock samples and to provide a contingency buffer period, a constant fixed feed rate corresponding to a residence time of 15.5 min (the maximum permitted with this apparatus) was used for all subsequent runs.

#### 3.2. Biochar Physico-Chemical Characterisation

Elemental analysis showed feedstocks to be carbon rich with carbon contents ranging from 44 to 46% *w/w*. Carbon content was increased following pyrolysis in all biochar samples as expected (64–77%), with a corresponding decrease in hydrogen and oxygen following pyrolysis. Despite the similar initial carbon content of the two waste biomasses, grapevine cane consistently had a higher carbon content than the stalks at the same pyrolysis temperature. In both feedstock types, carbon content increased as pyrolysis temperature increased (Figure 1 and Supplementary Table S1).

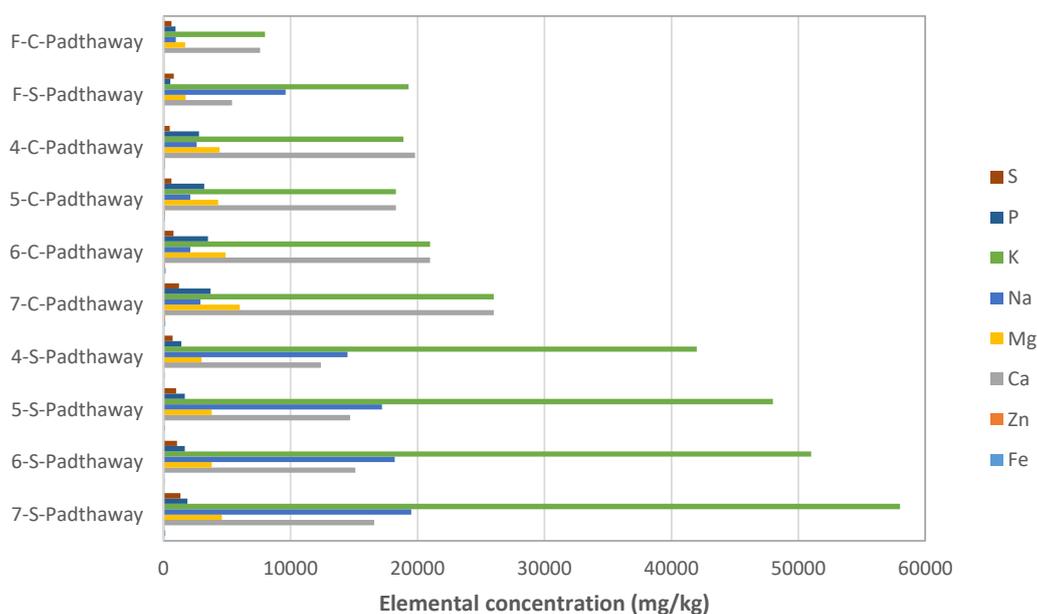


**Figure 1.** Elemental analysis by CHN. Sample Identification: F = Feedstock sample, C = Grapevine Cane, S = Stalks, 4 = 400 °C Biochar, 5 = 500 °C Biochar, 6 = 600 °C Biochar, 7 = 700 °C Biochar \* Oxygen by difference.

The hydrogen fraction decreased with increasing pyrolysis temperature, especially when the temperature was increased from 400 °C to 500 °C. Previous work on the same biochar production apparatus by Dunnigan et al. [25] observed that elevated pyrolysis temperatures resulted in greater net energy output than at lower temperatures. This was due to increased CH<sub>4</sub> and H<sub>2</sub> concentrations at elevated temperatures due to secondary reactions of volatiles. Grapevine cane had a larger hydrogen fraction at all temperatures except 700 °C compared to stalks. All biochars contain a higher nitrogen fraction than the respective feedstocks. The nitrogen fraction of biochar pyrolysed from grapevine cane decreased with increasing pyrolysis temperature, whereas the nitrogen fraction of biochar from stalks remained relatively consistent across the temperatures used in this study.

As described by Atkinson et al. [26], a benefit of biochar application to soil can occur through the release of nutrients directly from the biochar, making the measurement of trace elements useful. ICP-AES analysis (Figure 2 and Supplementary Table S2) showed all samples to be extremely high in calcium, magnesium, potassium, sodium, and (to a lesser extent) phosphorus, with levels two

to five times higher in the biochars compared with the raw feedstocks. It is notable that these Padthaway samples are particularly high in calcium, possibly owing to the limestone rich subsoils in that geographic region. Magnesium is similar in concentration within both feedstocks, as is sulphur. Grapevine cane has 41% more calcium and 74% more phosphorus when compared to the stalks, with a similar difference at each pyrolysis temperature as the concentration of both elements increase with increasing pyrolysis temperature. Potassium, an essential nutrient for agriculture, is initially more than twice as high in stalks than canes, and has a threefold increase in concentration from pyrolysis temperatures between 400 °C and 700 °C for both stalks and canes, to a concentration of 5.8% wt. and 2.6% wt., respectively. The largest initial elemental difference between the feedstocks is sodium, with an order of magnitude more present in the stalks versus the canes; with a similar trend observed in the derived biochars.



**Figure 2.** Elemental analysis by ICP-AES. Sample Identification: F = Feedstock sample, C = Grapevine Cane, S = Stalks, 4 = 400 °C Biochar, 5 = 500 °C Biochar, 6 = 600 °C Biochar, 7 = 700 °C Biochar. Co, Mo, Cd, Pb, As, and Se all below detection limit.

Measured zeta potentials (Table 1) of grapevine stalk-derived biochars were found to be lower in magnitude than the corresponding grapevine cane-derived biochars in all cases. All biochars were negatively charged and alkaline under test conditions; this is typical of charcoal surfaces, such as biochar and activated carbon, and consistent with the observations of Yao et al. [27] and Jung et al. [28] for various biochars derived from agricultural residues.

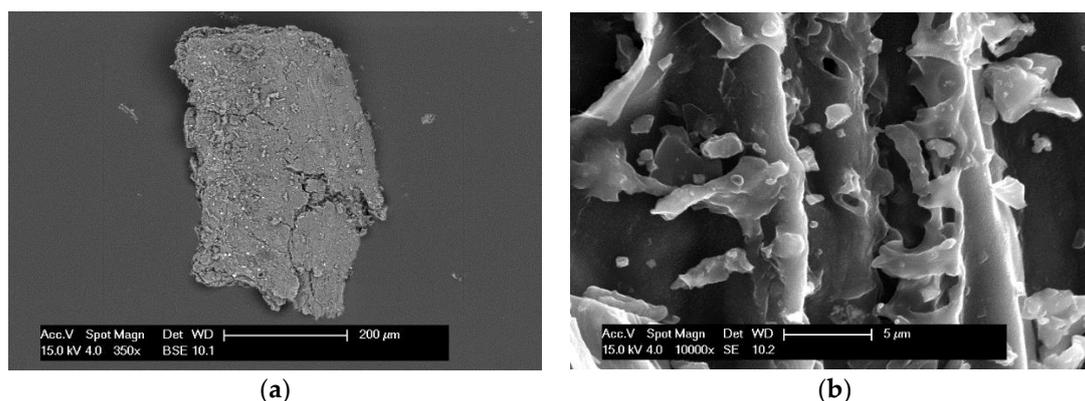
**Table 1.** Grapevine biochar physical properties.

Sample Identification	Zeta Potential (mV ± SE *)	pH (±SE *)	Surface Area (m <sup>2</sup> /g)	Pore Volume (mL/g)
4-C-Padthaway	−33.4 ± 0.13	8.17 ± 0.066	183	0.053
5-C-Padthaway	−32.5 ± 0.34	10.03 ± 0.023	281	0.077
6-C-Padthaway	−33.2 ± 0.29	9.35 ± 0.006	399	0.106
7-C-Padthaway	−29.0 ± 0.44	9.82 ± 0.024	516	0.135
4-S-Padthaway	−41.2 ± 0.95	9.17 ± 0.143	200	0.057
5-S-Padthaway	−43.5 ± 1.02	10.31 ± 0.025	302	0.082
6-S-Padthaway	−41.1 ± 0.88	9.95 ± 0.031	445	0.114
7-S-Padthaway	−41.2 ± 0.58	10.69 ± 0.012	560	0.147

Sample Identification: C = Grapevine canes, S = Stalks, 4 = 400 °C Biochar, 5 = 500 °C Biochar, 6 = 600 °C Biochar, 7 = 700 °C Biochar, \* SE = standard error.

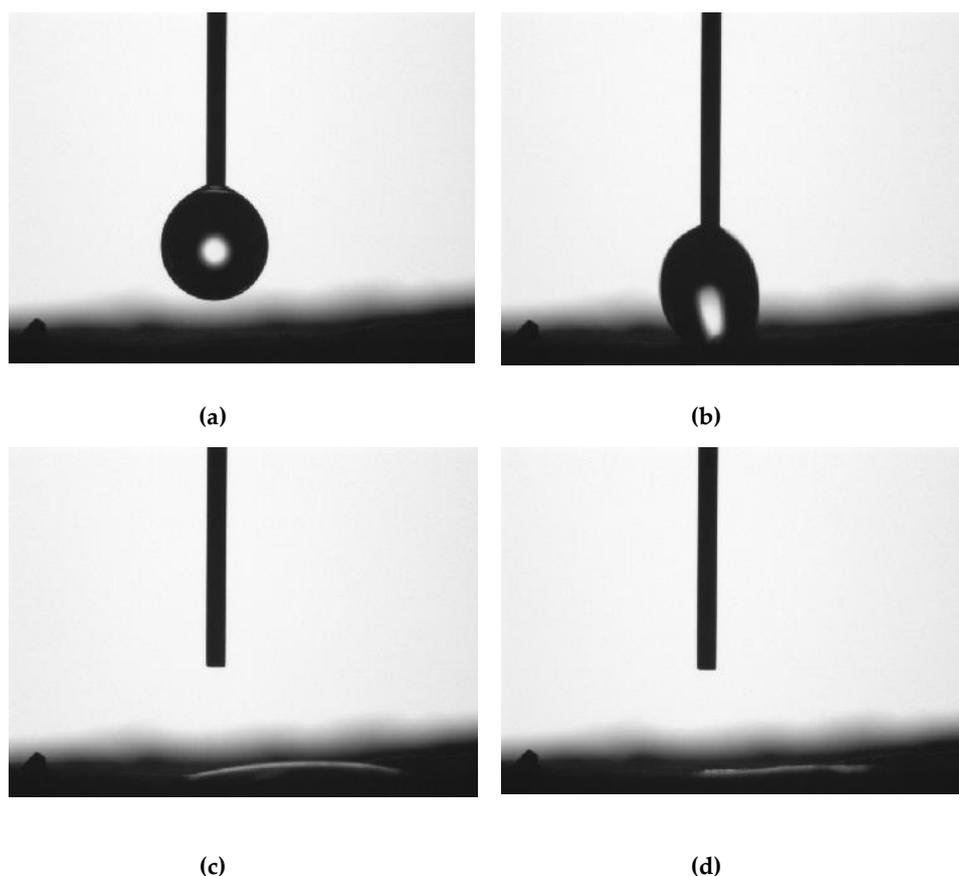
The pH (which provides an indication of potential liming ability), appears to be similar for most of the biochars pyrolysed above 400 °C, in the range of 9 to 10.7, whereas it is noticeably lower for biochars pyrolysed at 400 °C when using grapevine cane as the precursor (Table 1). The lower pH observed for biochar pyrolysed at 400 °C is potentially due to the higher amounts of carboxyl surface functional groups for those samples, which are otherwise removed during pyrolysis at higher temperature conditions [29]. An alternative explanation for the lower pH of low temperature chars is the presence of tar/bio-oil on the surface that, whilst also being hydrophobic, is known to be quite acidic [30]. Furthermore, the biochar produced from grapevine cane contains higher levels of alkali metals (Figure 2) than the stalks' biochar, which may also contribute to the difference in pH.

Pore size and surface area determination with N<sub>2</sub> using the BET method was unsuccessful for all samples because pressure equilibrium could not be established, suggesting that these biochars do not have large macro- and mesopores that would typically be associated with superior plant-available water retention. As such, no results were obtained using this method. Yao et al. [27] reported that this method is often inaccurate for materials containing micropores less than 1.5 nm, given that nitrogen is kinetically limited in its diffusion into pore cavities. Accordingly, various studies (e.g., [27,31,32]) report CO<sub>2</sub> adsorption as the preferred method to determine the pore surface area, and as such, this method was instead used for this study in place of BET analysis, with the results shown in Table 1. Subsequent SEM imaging (Figure 3a,b) also did not reveal the presence of large mesopores, confirming the pore size distribution findings from CO<sub>2</sub> adsorption (Supplementary Figure S3) that micropores dominate the biochar surface.



**Figure 3.** (a) SEM widefield image illustrating discrete biochar particle; (b) SEM close-up image (10,000×) does not reveal the presence of mesopores.

Preliminary water drop penetration tests indicated complete hydrophobicity of the 400 °C biochar samples, with water droplets remaining on the bed surface in excess of 24 h. Preliminary water drop penetration tests for biochars produced with a pyrolysis temperature of 500 °C and above suggested negligible hydrophobicity, with a droplet penetration times of less than one second. Contact angle measurements were taken to assess sample hydrophobicity, however, the results could not be obtained using the apparatus available for any biochar produced with a pyrolysis temperature of 500 °C or above. In these instances, water droplets were rapidly absorbed into the biochar, confirming the observation of negligible hydrophobicity, as shown in Figure 4.



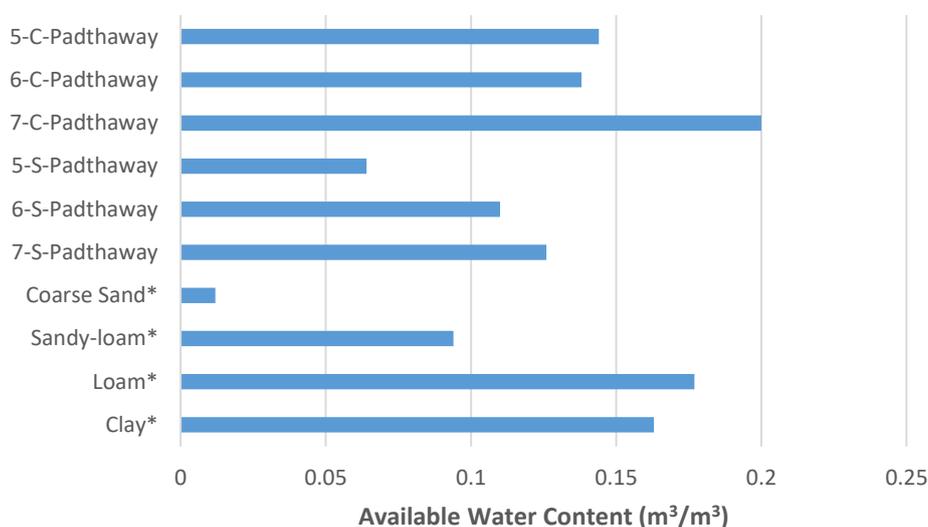
**Figure 4.** Consecutive video image frames [a to d respectively] captured during tensiometer contact angle test demonstrates rapid water adsorption and indicating negligible hydrophobicity of the biochar sample.

In contrast, the biochar feedstocks pyrolysed at 400 °C displayed clear hydrophobicity (Supplementary Figure S2), a result in line with observations by Kinney et al. [9], who observed decreasing hydrophobicity with increasing pyrolysis temperature. The grapevine cane biochar exhibited a constant contact angle of 84° over the 10 s measurement time, showing no signs of adsorption. Grapevine stalks, however, adsorbed water with an initial measurement of 114° reducing to 39° in 6 s: Results that suggest biochar from stalks are less hydrophobic than cane at the same pyrolysis temperature. The hydrophobic nature of the low temperature biochars is likely due to the presence of organic compounds present in tars on the lower temperature biochars [9,10]. The concentration of these organic compounds diminished at pyrolysis temperatures above 400 °C [33,34], explaining the clear transition between biochars across the temperature range. While Jeffery et al. [6] showed hydrophobicity in a biochar pyrolysed at 600 °C, the low residence time of 5 min would not have allowed for the complete removal of organic compounds. Given the relatively short pyrolysis residence time of 15.5 min in this study, it is possible that the hydrophobicity of the biochars pyrolysed at 400 °C could in future be decreased (or eliminated altogether) by increasing the residence time to remove more organic compounds [12].

### 3.3. Hydrostatic Water Retention

As the usefulness of a high water holding capacity is dependent on the ability of plants to extract water from the soil, the available water content (AWC) of each biochar sample was determined (Figure 5). In general, stalk biochars exhibited superior water retention compared with grapevine cane biochars, while AWC was found to increase with increasing pyrolysis temperature for each feedstock. Due to the higher water retention at the permanent wilting point of 500 °C grapevine stalks' biochar,

the AWC was half that of cane biochar at the same pyrolysis temperature, although still five times higher than that of coarse sand. Similarly, 600 °C and 700 °C grapevine stalks' biochar were also lower than the biochar from the cane biochar at the same pyrolysis temperatures.



**Figure 5.** Available water content of biochar samples. Sample Identification: C = Grapevine canes, S = Stalks, 5 = 500 °C Biochar, 6 = 600 °C Biochar, 7 = 700 °C Biochar. \* Parameters for coarse sand, sandy-loam, loam, and clay taken from Grant et al. [24].

As both feedstock and pyrolysis temperatures have an impact on water retention, the biochar with the highest AWC was 700 °C grapevine cane biochar with an AWC 23% higher than a clay-type soil [24]. Whereas AWC was observed to increase with increasing pyrolysis temperature, surface area, and pore volume, principal component analysis (PCA) suggests that (for these biochars) other factors are more significant in determining water retention performance. Principal component analysis is a form of factor analysis, which transforms original sets of variables into a smaller set of linear combinations that account for most of the variance of the original set [35]. Each principal component is extracted as a linear combination of the observed variables, where weightings are chosen to maximise the ratio of the variance of the principal component to the total variation, subject to the constraint that the sum of all weightings for each principal component is equal to one [36]. Principal components are orthogonal (uncorrelated) to one another [35]. Variables with a higher absolute weighting have a greater contribution to observed variability (either positively or negatively), whilst weightings close to zero indicate the factor has a more negligible impact. Therefore, a PCA correlation map is a visual tool that may be used to identify factors which have a significant contribution to observed variability, as well as to indicate potential groupings (or clusters) of variables which contribute in a similar way. The percentage values given on each axis label indicate the percentage variation explained by that principal component. In this study, a PCA correlation map (Supplementary Figure S4) shows the AWC is clustered together and is positively correlated with calcium, phosphorus, zinc, carbon content, and zeta potential, and negatively correlated with sodium, potassium, oxygen content, and pH. This suggests that the ionic content, surface charge, and extent of hydrophobicity are critical in determining water retention performance and—for the biochars examined in this study—more important than the surface area and pore volume.

Complete water retention behaviour was examined with the widely used water retention model of van Genuchten [23] as shown in Equation (1):

$$\frac{\theta(h) - \theta_{res}}{\theta_s - \theta_{res}} = \left[1 + (\alpha h)^N\right]^{-M}, \quad (1)$$

where  $\alpha$ ,  $N$ ,  $M$ , and  $\theta_{res}$  are freely adjustable fitting parameters;  $h$  is the matric head pressure (m);  $\theta$  corresponds to the volumetric water content; and the subscript,  $s$ , indicates the volumetric water content at the point of saturation, with the model parameters also listed in Table 2. As described by Grant et al. [24], these freely adjustable fitting parameters do not have any well-defined physical meaning. For comparison, biochar water retention performance was also modelled using the Groenevelt-Grant water retention model [24] as shown in Equation (2):

$$\theta(h) = \theta_s - k_1 \left\{ \exp \left[ - \left( \frac{k_0}{h} \right)^n \right] \right\}, \quad (2)$$

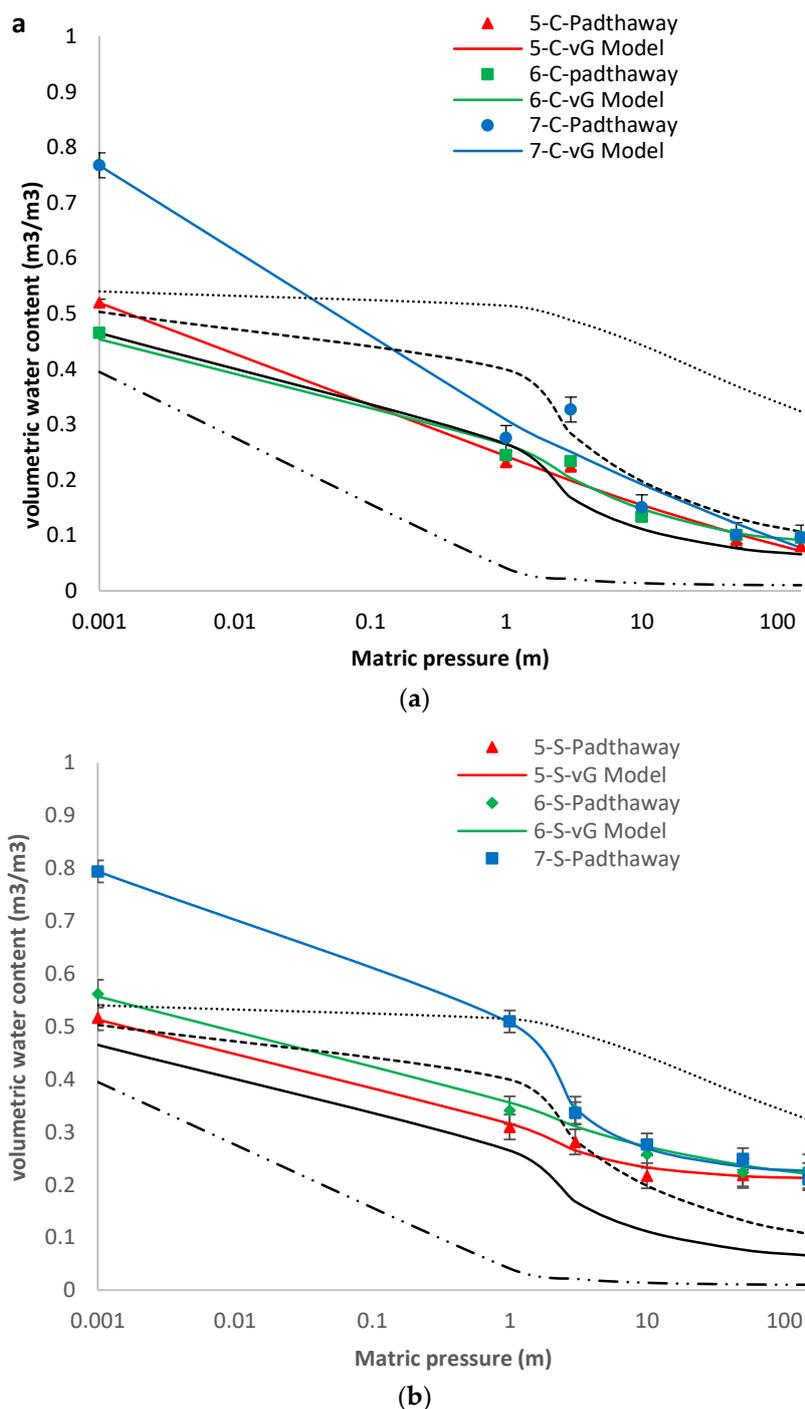
where  $k_0$ ,  $k_1$ , and  $n$  are freely adjustable fitting parameters. As per Equation (1),  $h$  is the matric head pressure (m) and  $\theta$  corresponds to the volumetric water content, while the subscript,  $s$ , indicates the volumetric water content at the point of saturation, with the model parameters also listed in Table 2. As described by Grant et al. [24], the Groenevelt-Grant model has the advantage over the van Genuchten model in that it can be infinitely integrated or differentiated (being an exponential function). According to Grant et al. [24], this feature of the Groenevelt-Grant model addresses limitations of the van Genuchten model relating to the difficulty in obtaining simple analytical (closed-form) solutions for relative hydraulic conductivity, owing to the difficulty in correctly describing the tortuosity component of the unsaturated hydraulic conductivity function.

**Table 2.** Van Genuchten and Groenevelt-Grant soil water retention model parameters for grapevine biochar samples.

Sample Identification	Van Genuchten Parameters					Groenevelt-Grant Model Parameters					
	$\theta_{res}$	$\alpha$	$N$	$M$	$R^2$	SSE	$K_0$	$K_1$	$n$	$R^2$	SSE
5-C-Padthaway	-0.240	178.832	2.324	0.038	0.992	$1.1 \times 10^{-3}$	0.140	0.510	0.298	0.982	$2.3 \times 10^{-3}$
6-C-Padthaway	0.820	0.198	0.494	2.008	0.982	$1.7 \times 10^{-3}$	0.394	0.426	0.358	0.982	$1.7 \times 10^{-3}$
7-C-Padthaway	-0.485	768.4	10.263	0.007	0.971	$9.4 \times 10^{-3}$	0.213	0.673	0.521	0.960	$1.3 \times 10^{-2}$
5-S-Padthaway	0.211	1.419	0.707	1.297	0.991	$5.9 \times 10^{-4}$	0.265	0.310	0.648	0.991	$6.4 \times 10^{-4}$
6-S-Padthaway	0.177	10.982	0.750	0.394	0.980	$1.6 \times 10^{-3}$	0.232	0.387	0.325	0.980	$1.6 \times 10^{-3}$
7-S-Padthaway	0.220	2.388	3.017	0.257	0.998	$6.0 \times 10^{-4}$	0.674	0.569	0.958	0.997	$7.4 \times 10^{-4}$
Coarse Sand *	0.010	16.746	1.897	0.470	-	-	0.074	0.386	0.921	-	-
Sandy-loam *	0.053	3.244	2.95	0.190	-	-	0.674	0.398	0.847	-	-
Loam *	0.061	1.782	2.542	0.160	-	-	1.57	0.413	0.666	-	-
Clay *	0.178	0.142	0.774	0.371	-	-	51.8	0.460	0.269	-	-

Sample Identification: C = Grapevine canes, S = Stalks, 5 = 500 °C Biochar, 6 = 600 °C Biochar, 7 = 700 °C Biochar. \* Parameters for coarse sand, loam, and clay taken from Grant et al. [24].

Figure 6a,b show the water retention curve for each of the biochar samples for grapevine cane and stalk biochars, respectively. The van Genuchten water retention model parameters from Grant et al. [24] were used to generate water retention profiles for four contrasting soil types (coarse sand, sandy-loam, loam, and clay), which were also included in these figures to provide a comparison with the results obtained for the pure biochar samples (similar water retention profiles are also obtained when using the Groenevelt-Grant model and the associated parameters listed in Table 2). From Figure 6, there appears to be three distinct zones relating to the influence of feedstock, pyrolysis temperature, or a combination of both. As the matric head potential is increased (from 50 to 150 m), there is a clear difference between the grapevine cane and grapevine stalk based biochars, with the volumetric water content of stalk biochars holding approximately double the amount of water than biochar from grapevine cane at the same matric pressure.



**Figure 6.** Water retention curve of biochars with van Genuchten models fitted from (a) grapevine cane biochar, (b) grapevine stalk biochar. Error bars denote standard error.

Within this range of matric pressure (50–150 m), the pyrolysis temperature appears to have had little effect on water holding capacity. At lower matric pressures (<50 m), the changes in biochar properties associated with the pyrolysis temperature appear to exert a greater effect, with the difference between biochars pyrolysed at different temperatures becoming more marked as matric pressures approach field capacity and then saturation. The higher pyrolysis temperature, especially for the grapevine stalk biochars, enables a higher volumetric water content at the 10 m pressure. The dependence on the biochar pyrolysis temperature increases until the 0 m pressure, where the

700 °C biochar from both grapevine stalks and cane have a 25–30% higher volumetric water content than the other biochar samples.

Based on the water retention data presented by Grant et al. [24], the volumetric water content of pure biochars is similar to that of a soil with a sandy-loam to loam texture over the matric pressure range examined. These results in isolation would suggest that over the matric pressure range tested (which represents typical vineyard soil water management from field capacity to beyond the normal limits of vineyard regulated deficit irrigation [15]), biochar is unlikely to have a significant additional effect on water retention when applied to vineyards with soils of a loam texture. A study by Kameyama et al. [20] examined the water retention of clay soil amended with biochar derived from sugar cane bagasse, with similar results observed to those of the present study for matric pressures in excess of 10 kPa (1 m). However, water content was increased in biochar-amended soils compared with the control at matric pressures between 0 and 10 kPa (<1 m); i.e., from saturation to field capacity. Kameyama et al. [20] reported that volumetric water content at saturation was increased significantly, (from 0.57 to 0.60 for the soil control compared with 0.76 to 0.80 for a 10% w/w addition of biochar) with studies [37,38] showing similar findings in biochar-amended sandy soils. Biochar application to vineyard soils of a sand to sandy loam texture may result in an improvement in soil water retention. However, the matric pressures investigated by Karhu et al. [37] and Novak et al. [38] are not typically seen in conventional vineyard irrigation management over the growing season (particularly if management practices, such as partial root-zone drying or regulated deficit irrigation, are employed). Further field study would be required to confirm this water retention behaviour under commercial scale viticultural conditions.

Given that high addition rates may be necessary for agriculturally relevant results [6], banding could potentially be explored to increase water holding efficiency in the root zone without ineffective application in the midrows [39]. Clearly, this is more challenging to implement in a viticultural environment compared with application to broad-acre annual crops (such as vegetable or grains), and further study involving pot trials or field application is required to ascertain the feasibility of this approach. Additional benefits accrue from the direct supply of nutrients to the soil, pH adjustment from the liming effect, and increased fertilizer efficiency [26]. These effects would increase the economic potential of biochar application, in addition to the increased water holding capacity explored in the present study.

#### 4. Conclusions

Grapevine cane and stalks were successfully pyrolysed using a continuous feed reactor to produce biochars with varying physico-chemical properties, including water retention performance. Hydrophobicity was found in biochar from both feedstocks pyrolysed at 400 °C, but not at higher temperatures, likely due to the removal of aliphatic and aromatic compounds. The available water content (AWC) of biochar increased with increasing pyrolysis temperatures, with optimal results obtained from grapevine cane at a pyrolysis temperature of 700 °C. Amelioration of sandy soils using this biochar amendment may improve water holding (particularly at field capacity); however, pot or field trials are recommended to confirm water retention behaviour and commercial feasibility.

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