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Characteristics of biochar produced from yak manure at different pyrolysis temperatures and its effects on the yield and growth of highland barley

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ABSTRACT
The yak manure based biochar was produced at different temperatures of 300, 500 and 700 □ held for 3 h, which was characterized by BET surface area, X-ray diffraction, Fourier transform infrared spectroscopy, pH measurement, analysis, scanning electron microscopy and ultimate analysis. The resultant biochar had characteristics of high surface area, high pH, porous structure and rich nutrients such as N, P, Ca, Mg, and K, inferring that the yak manure-derived biochar could be used as a soil conditioner. The field experiment was conducted to study the effect of yak manure derived biochar amendment on the yield and biological traits of highland barley, revealing that adding biochar to soil could increase the yield and growth of highland barley in short-term although the long-term benefits remain to be quantified. The present results can be useful to fill the knowledge gap regarding the potential of yak manure derived biochar to soil improvement.

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KEYWORDS
Yak manure; biochar; physicochemical property; soil amendment; barley

1. Introduction

The Napahai Plateau is located in the Southwest of China, covering a total area of nearly 34.34 km^2 with an average altitude of 3568 m. The Napahai wetland is a typical plateau wetland having unique geographical units. The wetland ecosystem in the Napahai Plateau is extremely sensitive to climate change and human disturbances. With the increasing yak feeding operations in recent years, more and more yak manure is produced. Historically, the primary use of animal manure has been fertilizers for soil, improving soil fertility and promoting the growth of crops owing to its organic and inorganic nutrient contents having properties similar to mineral fertilizers [1]. However, untreated animal manure is potentially harmful to the environment and the disposal problem cannot be neglected. Untreated manure is rich in organic pollutants and an important source of potentially dangerous pathogens that may be transported to the surface and ground water [2]. There has been an increasing concern about the effects of pathogens that are present in animal manure on human and animal health. We must concern the ability of the pathogens to survive for long periods and through treatment to remain infective in the environment until ingested by human or animal host. In addition, there are a number of environmental problems associated with these untreated manure, many agricultural fields with long-term manure applications will have higher risks of runoff and leaching of manure-derived components such as N and P, causing the deterioration of water quality, emissions of ammonia (NH_3), nitrous oxide; (N_2O), methane (CH_4), hydrogen sulfide (H_2S) and odour pollution. Besides, excessive application of manure fertilizer will cause the release of nutrient elements from agricultural fields to aquatic systems, accelerating water eutrophication [3], leading to the destruction of the ecological environment in Napahai wetland. Furthermore, if concentrations of heavy metals in livestock manure (heavy metal contaminated manure) surpassed permitted threshold the manure would have toxicity to crop. As described above, animal manure can be a valuable resource being used a fertilizer while it can be a tough problem in future development of animal industry if the impact on environment is not properly controlled and managed. Therefore, alternative strategies are needed for animal waste management to meet the stricter environmental regulations. In view of disposal of wastes, conversion of manure into biochar by pyrolysis technology is being considered as one alternative to the animal manure management.

It is well documented that biomass can be converted to various chemicals, biofuels, and solid biochar using modern processes, biomass is now increasingly perceived as a renewable resource rather than as an organic solid waste today [4,5]. Livestock manure is one of the abundant biomass sources.

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Three possible solutions to extract renewable energy from livestock manure are thermochemical, biochemical and physicochemical pathways. Thermochemical conversion represents a promising alternative due to the advantages of high temperature elimination of pathogens, drastic reduction of waste stream volume, and production of green energy or other value-added products. Pyrolysis is a thermochemical conversion process, in which the feedstock is heated in the absence of air. Three kinds of energy carriers including biochar, bio-oil and syngas are produced from biomass pyrolysis process [4–6]. In general, with a low reaction temperature, a slow heating rate, and a longer holding time, the pyrolysis produce mainly biochar [5,7,8].

Biochar is a solid carbon rich by-product (typically more that 60% carbon) of thermal stabilization of biomass or any other organic matter [9–11]. Biochar which is mainly composed of aromatic hydrocarbons, simple substance carbon, or carbon with graphene structure, exhibiting better biology stability and thermo-stability than precursor biomass. The microporous structure of the biochar and high carbon content makes it useful for several industrial applications, which have thoroughly been reviewed in literatures [9,12–25]. In agriculture fields, the biochar is used to upgrade the soil quality. The physiochemical properties of biochar are key factors for changing the soil characters such as pH, nutrient maintenance, and water retention, finally inducing heterogeneous responses in microbial species, which can lead to the changes of microbial community structure and can consequently alter soil element cycling and function [21]. It has been established that the addition of biochar in the soil will increase the rate of carbon sequestration in soil, slowing down the rate of decomposition of nutrients from soil and hence, decreasing soil acidity, finally enhancing the soil quality [12–21]. In purification industry biochar is used to remove heavy metals such as Cr, Cd, Ni, Hg and Pb. etc., and also being used in textile dye and acid gas removal [9,22–25]; and more importantly, the easily tuned surface functionality and porosity make biochar a promising platform to synthesize many carbon based functional materials [26–28], and electrochemical energy storage [29,30].

Animal manure derived biochar has received tremendous attention in recent years because its higher levels of essential plant nutrients, and higher CEC (cation exchange capacity) than plant biomass derived biochar [3,31,32]. For example, swine/pig separated-solids, paved-feedlot manure, dairy manure, poultry litter, turkey litter, and chicken manure derived biochar [3,32–44], cow manure derived biochar [44–46], cattle manure derived biochar [3,47–49], and goat-manure derived biochar [50] have been investigated, concluding that it is possible to prepare biochar with different agronomic properties depending on the feedstock and pyrolysis conditions.

Biochar varies widely in pH, surface area, nutrient concentration, porosity, and metal binding capacity due to the assortment of feed stock materials and thermal conversion conditions [9–11,51,52]. To the best of our knowledge, till date, there is little reported work regarding the yak manure pyrolysis [53,54], and whether the yak manure derived biochar could be amended into the soil and improve the soil quality. The objective of the present study was to investigate the characteristics of yak manure derived biochar produced at different temperatures of 300, 500, and 700 ℃ for held 3 h, and its effects on the yield and biological traits of highland barley in Napahai wetland, thereby ultimately determining the potential application of yak manure-derived biochars as a soil amendment.

2. Materials and methods

2.1. *Yak manure*

The yak manure was obtained from the Napahai Plateau in the Southwest of China. The yak manure was dried in an oven (UNB200, Mermet Germany) at 110 ℃ at least 3 h, or until getting constant weight, which was then smashed in a crushing machine and passed through a 40 mesh screen. The yak manure sample was stored in airtight containers.

2.2. *Production of biochar*

100 g dried samples of yak manure were put in a bottom-netted stainless-steel-holder and housed at the center of the tubular reactor (OTF-1200X, Hefei Kejing Ltd., China) under a nitrogen atmosphere at different target temperatures of 300, 500 and 700 ℃ for 3 h. The pyrolysis temperature was raised at a rate of 10 ℃ min^{-1}. A sweep nitrogen gas (N_2) from a cylinder regulated (using a mass flow controller) at a constant flow rate of 500 cm^3/min was precisely metered into the pyrolysis system. The resulting biochar (after power-off for about 30 min of cooling) was taken out of the sample holder to weigh its mass and finally stored in an oven for subsequent characterization.

2.3. *Characterization of yak manure derived biochar*

To observe the surface morphology pattern of yak manure after pyrolysis, the biochar samples were imaged using scanning electron microscopy (SEM) (Hitachi S-4800, Japan).

XRD analysis was carried out to identify crystallographic structure in the yak manure derived biochar samples using a computer-controlled X-ray diffractometer (X'Pert Pro MPD, Dutch) equipped with a Cu Kα radiation source operated at 65 kV and 50 mA with a scan speed of 1°/min over the 2θ range from 5° to

70°. The obtained XRD patterns were analyzed with Jade 6.0 software to remove the background radiation.

The N_2 adsorption–desorption isotherms were measured with an accelerated surface area and porosimetry system (Model No.: ASAP 2020; Micromeritics Instrument Corporation, U.S.A). Prior to the measurements, the samples were outgassed at 573 K under nitrogen flow for at least 2h. The nitrogen adsorption–desorption data were recorded at liquid nitrogen temperature (77 K). The BET surface area was calculated using the BET (Brunauer, Emmett and Teller) equation from selected N_2 adsorption data within the range of relative pressure from 0.05 to 0.35. Total pore volume was calculated by converting the amount of nitrogen gas adsorbed at a relative pressure of 0.99 to the volume of liquid adsorbed. The estimation of pore diameter or average pore size was calculated by the measured values of surface area and total pore volume based on the assumption of a straight, cylindrical and un-interconnected pore shape [55].

The pH of the biochar was measured (1:10 ratio of biochar solutions in de-ionized water following 1-h equilibrium) by a pH meter (Mettler Toledo FE-20K, Switzerland), which was calibrated with standard buffers with pH 4 and pH 7.

The possible chemical functional groups present in the biochar samples were identified by Fourier transform infrared spectroscopy (FTIR) (Thermo Scientific Nicolet iS10, US) in the range of 4000–400 $cm^{-1}$with a resolution of 0.4 cm^{-1}. To obtain the observable absorption spectra, the fine biochar sample was additionally ground to approximately 0.5 wt% with KBr (spectroscopic grade) for dilution and homogenization. Discs (12.7 mm id and approx 1 mm thick) were prepared in a manual hydraulic press (12 kPa max) at 8–9 kPa for 0.5 min.

The ultimate analysis was performed using a Vario MICRO Cube (Elementar, Germany) elemental analyzer to determine the weight fractions of non-mineral major elements such as carbon (C), hydrogen (H), nitrogen(N), and oxygen (O). Using 200 mg oven dried samples in three replications. For each analysis, the standard samples (i.e. sulfanilic acid and benzoic acid) were first analyzed for checking the experimental error within ± 0.1%.

The inorganic elemental analysis was performed using an inductively coupled plasma-atomic emission spectrometer (Perkin Elmer Optima 7000DV, USA) to determine the important nutrient elements of dried yak manure and biochar (Ca, P, K, Mg, Fe, Cu, Zn, and Mn). 0.10 g of the sample was digested by a concentrated HNO_3/H_2O_2 solution in a pressure bomb to form a homogeneous solution. The digested solution was diluted with de-ionized water, and small amount of the diluted solution was used to measure its inorganic contents.

2.4. *Effects of biochar amendment on yield and biological traits of highland barley*

The experiments were conducted from March to September in 2016. Four replicated (n = 4) trial plots (3 m × 6 m) were established, which were laid out in a randomized complete block design and with strong ridges placed around each plot for delineation to prevent biochar migration. Between row and within row distance was 60 cm and 20 cm, respectively. Prior to planting, potassium sulfate compound fertilizer was added to all of the field plots for nutrient balance at 500 kg ha^{-1}. Then biochars produced at different temperatures were applied to the topsoil of trial plots at 300 kg ha^{-1}, treatments without biochar application were set as corresponding controls. After harvesting highland barley plants on 19 September 2016, the highland barley seeds were manually separated and the whole plants were sun dried until constant weight and weighed. The growth parameters of highland barley include, yield, plant height, leaf width and leaf length were recorded.

2.5. *Soil collection and analysis*

The field experiment was conducted in Shangri-La (27.08°N, 99.70°E; 3200 m elevation) on the Napahai Plateau, China. The soil at the site was classified as sandy loam, which was flat and had middle lever fertilizer, the pre-planted crop was highland barley.

Soil samples were taken from the 0–20 cm soil layer of each plot after highland barley harvested. The samples were sealed in plastic bags and shipped to the laboratory within 1 day after sampling. After air-drying, the samples were sieved into 40 mesh. Soil pH was measured using a pH meter (Mettler Toledo FE-20K, Switzerland). The TOC was measured on an elemental analyzer(TOC-V-CPN Analyzer，Shimadzu, Japan).

2.6. *Statistical analysis*

All data were reported as means and standard deviation (SD) of the means. Analysis of variance was used to determine the statistical significance of the biochar treatment effects on barley yields and growth. Post hoc comparisons were made using least significant difference (LSD) test, with the criterion for statistical significance being set at $P < 0.05$. Data analyses were run using the SPSS software package.

3. Results and discussion

3.1. *Thermochemical properties of dried yak manure and yak manure derived biochar at different temperatures*

It has been already identified that the soil fertility and productivity are directly linked with the nutrient availability [52]. Tables 1 and 2 listed the results of ultimate and inorganic element analyses for the dried yak manure and yak manure derived biochar produced at different temperatures, respectively.

The high contents of carbon (41.1 wt%) and oxygen (39.7wt%) in the dried yak manure (Table 1) indicated that the yak manure biomass can be used as a feedstock for the biochar production. The ash-forming elements in the dried yak manure included Ca, P, Mg, Fe, K, Cu, Mn, and Zn, being present in the oxide or carbonate forms, suggesting that yak manure can be directly used as a soil fertilizer with high macronutrients in N, P, Ca, K and Mg, and micronutrients in Mn, Zn and Cu [13,32].

Table 2 illustrated that the carbon content of yak manure derived biochar was slightly above than that of the yak manure (Table 1), and the carbon content of yak manure derived biochar slightly tended to decrease with increasing temperature, but this decrease was not significant. However, H, O and N highly significantly decreased with increasing pyrolysis temperature, the contents of O, N and H were reduced from 27.4, 3.2 and 1.9 wt%, respectively at 300 ℃ to 20.7, 2.7 and 1.4 wt% at 700 ℃. The lack of increases in C content maybe possibly due to the high content of volatile materials in the feedstock, that are rapidly lost at the initial stage of the pyrolysis process [5]. The decrease of C, H, O and N contents should result from the decomposition volatilization and lignocellulose and protein present in the yak manure.

Furthermore, heat treatment reduced biomass, correspondingly increasing concentrations of major and minor nutrient elements (Ca, P, K, Mg, and Fe) and trace amounts of heavy metals (Cu, Mn, and Zn) as compared to its precursor. For example, the contents of Ca, P and K were significantly increased from 5.67, 4.52 and 2.78 wt%, respectively at 300 ℃ to 6.71, 5.65 and 3.08 wt% at 700 ℃. These results suggested that the yak manure derived biochar may be used as a potential fertilizer and amendment through nutrient additions to crops in the soil environment [13,32,56]. However, influence of biochar on the release of additional elements (e.g. Cu, Zn) should be carefully considered when used as a soil amendment due to their chronic toxicity in the liver and kidney [36,56].

Table 1. Ultimate and inorganic element analyses of the dried yak manure.

Properties	Value[a]
Ultimate analysis (wt%)[b]	
Carbon (C)	41.1 ± 0.1
Oxygen (O)	39.7 ± 0.1
Nitrogen (N)	3.6 ± 0.1
Hydrogen (H)	6.1 ± 0.1
Inorganic element analysis (wt%)[b]	
Calcium (Ca)	4.12 ± 0.02
Phosphorus (P)	3.24 ± 0.02
Potassium (K)	1.16 ± 0.01
Magnesium (Mg)	0.89 ± 0.01
Silicon (Si)	0.80 ± 0.02
Iron (Fe)	0.33 ± 0.01
Cupper (Cu)	0.09 ± 0.001
Manganese (Mn)	0.06 ± 0.001
Zinc (Zn)	0.06 ± 0.001

[a] Mean of three yak manure samples with standard deviation.
[b] Dry basis (by heating at 110 ℃ for 24 h).

Table 2. Ultimate and inorganic element analyses of the yak manure derived biochar produced at different temperatures.

Properties	Biochar (300°C)[a]	Biochar (500 °C)	Biochar (70 °C)
Ultimate analysis (wt%)[b]			
Carbon (C)	41.6 ± 0.1[c]	41.3 ± 0.1	41.2 ± 0.1
Oxygen (O)	27.4 ± 0.1	24.4 ± 0.1	20.7 ± 0.1
Nitrogen (N)	3.2 ± 0.1	3.0 ± 0.1	2.7 ± 0.1
Hydrogen (H)	1.9 ± 0.1	1.7 ± 0.1	1.4 ± 0.1
Inorganic element analysis (wt%)[b]			
Calcium (Ca)	5.67 ± 0.02	6.13 ± 0.02	6.71 ± 0.02
Phosphorus (P)	4.52 ± 0.02	5.41 ± 0.02	5.65 ± 0.02
Potassium (K)	2.78 ± 0.01	2.85 ± 0.01	3.08 ± 0.01
Magnesium (Mg)	1.98 ± 0.01	2.34 ± 0.01	2.55 ± 0.01
Silicon (Si)	1.70 ± 0.02	1.90 ± 0.02	2.15 ± 0.02
Iron (Fe)	0.82 ± 0.01	0.85 ± 0.01	0.85 ± 0.01
Cupper (Cu)	0.11 ± 0.001	0.11 ± 0.001	0.12 ± 0.001
Manganese (Mn)	0.08 ± 0.001	0.08 ± 0.001	0.08 ± 0.001
Zinc (Zn)	0.14 ± 0.001	0.16 ± 0.001	0.16 ± 0.001

[a] Biochar produced at 300°C, etc.
[b] Dry basis.
[c] Mean of three biochars samples with standard deviation.

3.2. *Ph of of yak manure derived biochar*

Acid–base properties exert important influences on biochar's practical application as a soil amendment or contaminant sorbent. Because changes of pH have great impacts on many soil processes, such as nitrogen mineralization, mineral precipitation, ion exchange, and greenhouse gas emissions [13,16,57]. The histogram in Figure 1 shows the pH values of the yak manure derived biochar produced at different temperatures of 300, 400 and 700 ℃, all the resulting biochar was alkaline, demonstrating that the most of acidic groups were lost during the pyrolysis process, and the presence of alkaline metal ions, Ca, Mg, and K (Table 2) which are stable and does not volatile in the yak manure during the production of biochar. The alkaline biochar is beneficial to improving soil pH, especially for acidic soils [16,21,32]. In the present study, it is clear that the pyrolysis temperature has a significant positive effect on the pH values of biochar, the pH value significantly increased as pyrolysis temperature increased from 300 ℃ to 700 ℃ passing from a value of 7.6 to almost 11.8. The present results were closely in consistent with the findings reported by Wang and Liu [53,54], the pH value of yak manure biochar produced at 350 ℃ and 550 ℃ was 8.88 and 10.53, respectively. Generally, it is established that pH increases with pyrolysis temperature, but the magnitude of this increment depends on the raw material characteristics [3,33,57]. The pH values were lower for biochar produced at the lower pyrolysis temperatures. Substantial increase in pH occurred at the higher temperatures because of the increased relative

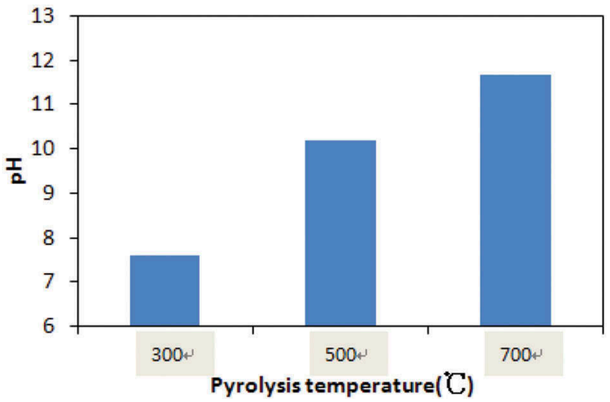

Figure 1. pH of yak manure derived biochar produced at different temperatures of 300, 400 and 700 °C.

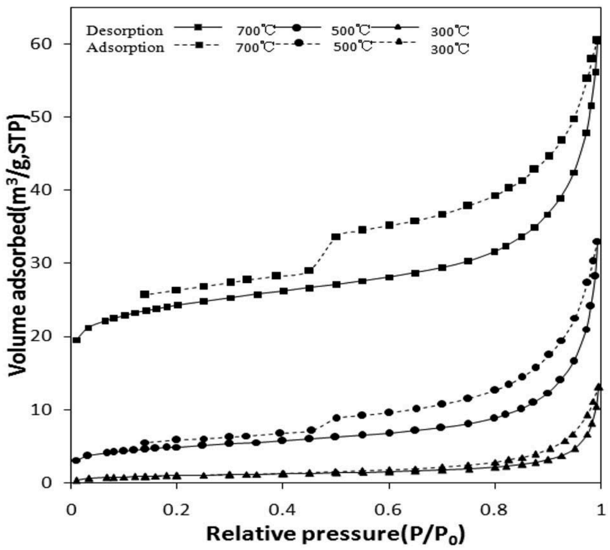

Figure 2. N_2 adsorption–desorption isotherms of yak manure derived biochar produced at different temperatures of 300, 500 and 700°C.

concentration of non-pyrolyzed inorganic elements in the feedstocks and the formation of basic surface oxides under the high pyrolysis temperature [3,35]. It is reported that inorganic carbonates were the major alkaline components of the biochar generated at high temperature, and that organic anions contributed to the alkalinity of biochar generated at low temperature [56]. Biochar from complete pyrolysis typically has a pH greater than 7.5. For example, dairy, poultry manure derived biochar through > 300°C pyrolysis had a pH range of 9.3 to above 10.0, while the plant-biomass derived biochar, such as corn stover and switchgrass, having a pH value of 11.4 and 10.4 [41,53,54]. After all the volatile matters were leached from the pyrolytic structure, the pH became constant. In the case of pH, the produced biochar may be used as soil amendments to reduce soil acidity and adsorb positively charge ions [10,21,35,36,53,54].

3.3. *BET surface area of yak manure derived biochar*

The BET surface area and pore structure of biochar have an important influence on its physical chemical properties [24]. In accordance to the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC), adsorbent pores are classified into three groups: micropores (size < 2nm), mesopores (2–50 nm), and macropores (>50 nm). Micropores can be divided into ultramicropores (width less than 0.7nm) and supermicropores (width from 0.7 to 2nm). Figure 2 shows the adsorption and desorption isotherms of N_2 for the yak manure derived biochar produced at different temperatures of 300, 500 and 700 ℃. As the curve intensity in the adsorption isotherms increased, a larger BET surface area was observed. The isotherms corresponding to the biochar after 300 °C exhibit of type III [55], indicating that the biochar has a small amount of micropore and mesoporous and weak sorption. The shapes of the isotherms for the samples produced at 500 and 700 ℃ were similar, showing the presence of desorption hysteresis, it is clear that these isotherms are type IV which should be the characteristic of the mesoporous materials due to the nitrogen condensation [55].

Table 3 lists the BET surface area and total pore volume of all the biochar samples. The results revealed that the porous characteristics were largely dependent on the pyrolysis temperature. An increase in the pyrolysis temperature from 300 to 700 ℃ resulted in a significant increase in the BET surface area, total pore volume, microporous surface area and microporous pore volume, the BET surface areas were 3.6, 17.3 and 82.9 $m^2\ g^{-1}$ at 300, 500 and 700 ℃, respectively. The findings were in close agreement with the previous studies regarding swine manure derived biochar [36] and goat manure derived biochar [50]. The BET surface area of swine manure derived biochar obtained at 500 ℃ was 3.9 $m^2\ g^{-1}$, and obtained at 700 ℃ was 59 $m^2\ g^{-1}$, the BET surface area of goat manure derived biochar obtained at 700 ℃ was 39.1 $m^2\ g^{-1}$, and obtained at 800 ℃ was 93.5 $m^2\ g^{-1}$. The increase in surface area with increasing pyrolysis temperature is due to the significant increase with the release of volatiles [4,5,26]. The increase in pyrolysis

Table 3. Porous characteristics of yak manure derived biochar produced at different temperatures.

Biochar sample	BET surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Microporous surface area ($m^2\ g^{-1}$)	Microporous pore volume ($cm^3\ g^{-1}$)	Average pore width (nm)
Biochar -300 ℃	3.6	0.010	–	–	11.3
Biochar -500 ℃	17.3	0.033	4.4	0.0019	7.5
Biochar -700 ℃	82.9	0.074	52.8	0.024	3.6

temperature increased the amount of volatile organic compounds and created more pores, which contribute to a larger surface area. The higher surface area is preferable because it helps to improve the soil structure, increases the total water retention in the soil and provides the ecological niches for soil microorganisms [9,10]. Based on data in Figure 2 and Table 3, the pyrolysis temperature at around 700 ℃ seemed to be optimal for the production of yak manure derived biochar with a comparatively higher BET surface area of 82.9 $m^2\ g^{-1}$.

3.4. *Surface morphology (SEM) analysis of yak manure derived biochar*

SEM is mostly used for characterizing biochar and effective for detecting biochar macropores [51]. The SEM images of the biochar produced at different pyrolysis temperatures are illustrated in Figure 3, showing the presence of aligned honeycomb-like groups of pores and the pores are cross-linked on the surface of biochar, most likely due to the carbonaceous skeleton from the biological capillary structure of the raw material [26]. The porous structures of biochar show a variety of shapes and sizes that cover the ranges of micropores, mesopores, and macropores. This was consistent with the findings from N_2 adsorption–desorption isotherms for surface area measurement discussed in the section 3.3.

Figure 3 clearly shows that the pyrolysis temperature has an effect on the structure of the biochar. With the onset of the pyrolysis process, porous

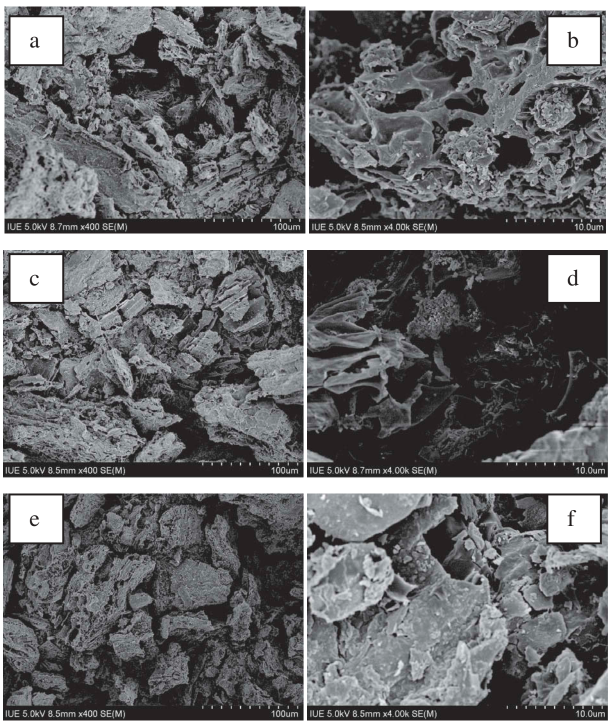

Figure 3. SEM images of yak manure derived biochar produced at different temperatures: (a and b) 300°C, (c and d) 500 °C, (e and f) 700°C.

structures were found at the surface of the biochar formed. The porous structure of the biochar is created during the pyrolysis process by the production of volatile matter. As the matter escapes, pores and cracks begin to appear on the surface of the biochar. The pictures show increased porosity from volatiles escaping during thermochemical degradation as the pyrolysis temperature increases. Generally, the surface area of biochar increases with increasing temperature at which deformation occurs. This may be an indication that the rate of pore formation exceeded that of pore destruction, due to pore enlargement and collapse at the earlier stage and then vice versa at the later stage of pyrolysis [26]. The high temperature causes micropores to widen as it destroys the walls between adjacent pores, resulting in the enlargement of pores and an increase in total pore volume, which results in the higher pore properties. The SEM image of biochar obtained at 700 ℃ showed the knaggy surface and some pore structure.

The macropores in biochar affect the soil's hydrology and microbial environment [13]. The existence of pores on the biochar suggests the potential in soil amendment because the biochar porosity can play an important role in facilitating the movement of roots through the soil, serve as habitats for a variety of microorganism, retaining soil nutrients and improving the water holding capacity [9,10]. Surface area of biochar was usually contributed by its micro pore area and it has a significant effect on water adsorption capacity. The larger the pores, the easier the penetration of water, plant roots and fungal hyphae in the soil particles. Generally, porosity of biochar which is less than 30 μm will hold water in place [10]. Shafie found the pore diameter of biochar was 5–6 μm and the membrane thickness was 2.3–2.66 μm, which have a high tendency of water retention [58].

3.5. *X-ray diffraction (XRD) of yak manure biochars*

Crystalline materials in the samples were tentatively identified by XRD using significant peaks of characterizing possible minerals present in the resulting biochar [51]. Figure 4 illustrated the XRD patterns of yak manure derived biochar produced at different temperatures of 300, 500 and700 ℃. The XRD patterns of significant peaks of resulting biochar were quite similar to each other, are broad and indicative of amorphous materials having some degree of short-range order. It can be seen that the most strong peaks at 2θ 26.8° (d = 3.33 Å) and, 29.5°(d = 3.03 Å) indicated the presence of inorganic components such as quartz (SiO_2, ASTM 46–1045), and calcite/limestone ($CaCO_3$, ASTM 05–0586) [35]. The presence of calcite

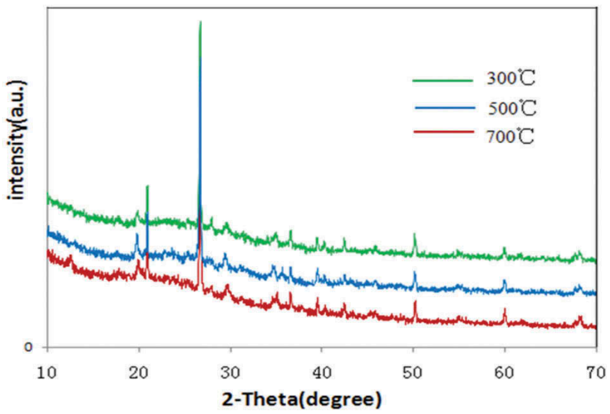

Figure 4. XRD patterns of yak manure derived biochar produced at temperatures of 300, 500 and 700°C.

is consistent with the alkalinity of the yak manure derived biochar (Figure 1). The biochar showed higher number of crystalline phases [59], it is to be noted that the higher crystallinity of the aforementioned samples are not the inherent nature of the biochar, but rather contributed by high amount of inorganic minerals present in it. These types of chars are often known as turbostratic chars, which are dominated by disordered graphitic crystallites [56].

In addition to calcite and quartz which were present for all the biochar, the sylvite (KCl, ASTM 41–1476) and the phosphate mineral whitlockite ($(Ca,Mg)_3(PO_4)_2$) was identified in biochar [35], which was also further confirmed by the ultimate and inorganic element analyses for yak manure derived biochar at different pyrolysis temperatures, containing high contents of Ca, P, Mg and K (Table 2). The present XRD patterns were quite similar to the XRD pattern of chicken litter derived biochar reported by Koutcheiko, *et al* [60].

3.6. *FTIR of of yak manure biochar*

FTIR is usually used for structural analysis and characterization of functional groups present on biochar surfaces. The FTIR spectra can demonstrate qualitative differences in the surface functional groups of the biochar due to the differences of original feedstocks as well as different pyrolysis conditions. In the present study, the physical-chemical of properties of all three biochars produced at temperatures of 300, 500 and 700 ℃ were similar (Table 2), resulting in the FTIR spectra of yak manure derived biochar being quite similar, in order to the clarity of the graph and the surface area of biochar produced at 700 ℃ being the highest among them, Figure 5 just shows the FTIR spectra of the yak manure derived biochar produced at 700 ℃. Although a simple interpretation of the spectrum is challenging, the broad band near 3400 cm^{-1} is indicative of the hydroxy O-H stretching vibration contained in cellulose and hemicelluloses structures confirming the presence of C-OH functional groups in the produced biochar. The bands below 600 cm^{-1}were probably due to M-X stretching vibrations in both inorganic halogen compounds (M-metal, X-halogen) such as KCl and $CaCl_2$ [36,60]. Aromatic and heteroaromatic compounds were also confirmed by C-H wagging vibrations in the region between 800 and 600 cm^{-1} [61]. Bands associated with PO_4^{3-}, Si-O-Si in plane vibration (asymmetric stretching) and C-O stretching vibration structures were found between 1000 and 1100 cm^{-1} [33,61]. The bands at around 1400 cm^{-1} could be attributed to CO_3^{2-} or C-H flexural vibration of Olefins [35] C = O stretching vibrations for amides was noted at 1600 cm^{-1} [33]. The bands at 2353 cm^{-1} was associated with P–H stretching bands of organo phosphorus [41]. The bands at 2935 cm^{-1} and 2885 cm^{-1} were associated with C–H stretching bands of methylene methyl, and methoxyl groups [62] C-H and O-H groups are dominant in all biochars and these functional groups have been reported to form stable complexes with heavy metals in the soils amended with biochar, thereby increasing the definite adsorption of the metals, being more effective for immobilize heavy metals [21,53,54,56,63,64]. These FTIR results were also in agreement with the results of XRD (Figure 4) and elemental analyses (Table 2).

In a summary, according to the above discussion, the produced yak manure biochar has characteristics of high surface area, high pH, pore structures, having C-H, C = O, O-H functional groups and rich nutrients such as N, P, Ca, Mg, and K, implying that the yak manure-derived biochar could be used as a soil amendment [10,13,14].

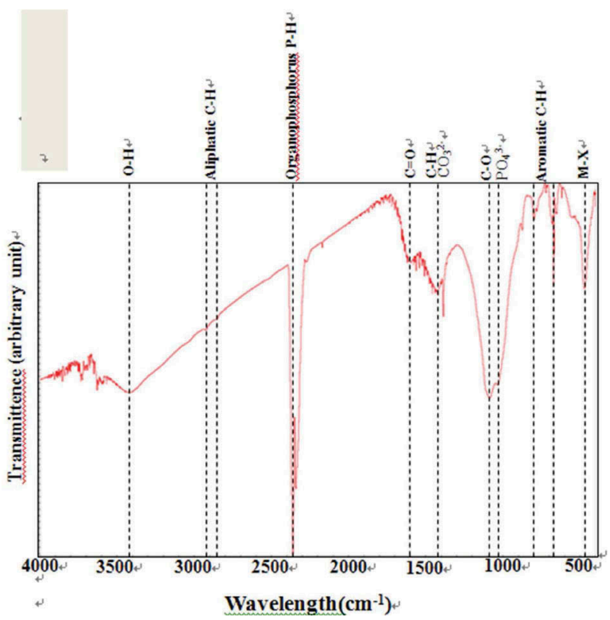

Figure 5. FTIR spectra of yak manure derived biochar produced at 700°C.

3.7. Effects of biochar amendment on soil physical and chemical properties

The effects of biochar amendment on soil physical and chemical properties for highland barley soil were illustrated in Table 4. Compared to the corresponding control, biochar amendment significantly increased soil pH from 7.32 ± 0.03 to 7.47 ± 0.07, 7.53 ± 0.06 and 7.51 ± 0.11, respectively, while soil TOC also increased from 37.72 ± 1.24 to 38.08 ± 1.58, 42.40 ± 1.79 and 43.59 ± 2.33, respectively. It can be found that yak manure derived biochar (700 ℃) application significantly increased the pH of the rhizosphere soil by 0.19 ($P < 0.05$) and soil TOC by 15.56% ($P < 0.05$) as compared to the corresponding control. Notably, although soil C increased under biochar amendment, it had no significant effects on soil N and P contents.

Soil pH and TOC were key indicators of soil quality. As expected, the addition of biochar to soils contributed to soil C. During the carbonization process, the C in biochar becomes more aromatic in form, which leaded to a higher percentage of recalcitrant C in biochar. This resulted in a much higher organic carbon content of soil amended with biochar. Addition biochars resulted in an increase of soil pH due to their alkalinity, as biochar application affected soil pH, it might indirectly alter the supply of nutrients to plants [32].

3.8. Effects of biochar amendment on the yield and growth of highland barley

In the field of agriculture, the biochar is used to upgrade the soil quality. It is proposed that possible reactions that may occur after biochar incorporation into soil include dissolution–precipitation, adsorption–desorption, acid–base and redox reactions. As a result, the biochar might increase pH, soil-water holding capacity, cation exchange capacity (CEC) and electrical conductivity, which all together significantly contribute to the overall soil fertility [9,10,13,14,21]. It must be pointed out that effects and mechanisms of biochar on soil improvement and pollution remediation are very complicated, however, it has been proposed that the feedstock types and pyrolysis temperature will determine biochar properties of surface properties, structures, elemental composition, redox capacity, conductivity, pH, CEC, and VOCs. Such properties play key roles in microbial activity and soil process. Soil improvement is achieved by addition of biochar, enhancing carbon storage, soil fertility and quality, and contaminant (organic and heavy metal) immobilization and transformation by modifying soil microbial habitats and (or) directly influencing microbial metabolisms, which together induce changes in microbial activity and microbial community structures [14,21]. According to the specific purposes, different biochar types should be considered and investigated [21]. So, in the present study, the effects of yak manure derived biochar amendment on the yield and growth of highland barley were investigated.

Figure 6 shows the experimental field located at Shangri-La (27.08°N, 99.70°E; 3200 m elevation) on the Napahai Plateau, China. The soil was sandy loam, which was flat and had middle lever fertilizer, the pre-planted crop was highland barley. Table 5 lists results of effects of biochar amendment on the yield and growth of highland barley. It can be found that in addition to leaf width, the yield, plant height and leaf length were significantly increased by all treatments as compared with the control, showing that biochar application had positive effects on the highland barley growth. The high-temperature biochar is more effective at promoting crop productivity than low-temperature biochar. In comparison with the corresponding controls, it could be seen that biochar amendment (700 ℃) increased the yield of highland barley 1944.42 ± 3.45 to 2386.27 ± 4.87 kg ha^{-1} and leaf length from 25.54 ± 1.23 to 30.23 ± 1.67 cm, respectively (Table 5), yak manure derived biochar amendment increased the highland barley yields by 22.72% ($P < 0.05$) and the leaf length 18.44% ($P < 0.05$), respectively. It showed that the yak manure derived biochar amendment had a significantly positive effects on the yield and growth of highland barley ($P < 0.05$).

It is well known that the effect of the biochar amendment on crop systems partly depends on pyrolysis conditions [65]. Biochars produced at high temperature tend to be alkaline and contain relatively few biologically active volatile compounds that can effective at promoting crop productivity [52,66]. The The porous

Figure 6. Photos of the experimental fields.

Table 4. Effects of biochar on soil physical and chemical properties.

Treatments	pH	TOC(mg/g)	C (mg/g)	N (mg/g)	P (mg/g)
Control	7.32 ± 0.03 c	37.72 ± 1.24 b	31.35 ± 0.85 b	3.14 ± 0.04 b	1.91 ± 0.05 b
Biochar (300 ℃)	7.47 ± 0.07 a	38.08 ± 1.58 a	32.85 ± 1.02 b	3.05 ± 0.04 a	1.89 ± 0.06 a
Biochar(500 ℃)	7.53 ± 0.06 b	42.40 ± 1.79 a	33.78 ± 1.46 b	3.12 ± 0.05 b	1.99 ± 0.06 a
Biochar(700 ℃)	7.51 ± 0.11 b	43.59 ± 2.33 a	32.46 ± 1.87 a	3.23 ± 0.06 b	1.94 ± 0.07 b

All values represent means±SD; values within a column followed by the same letter do not differ significantly (LSD test, $p = 0.05$; $n = 4$)

Table 5. Effects of yak manure derived biochar produced at different temperatures on the yield and growth characteristics of the highland barley.

Treatments	Yield(kg ha^{-1})	Plant height(cm)	Leaf width(cm)	Leaf length(cm)
Control	1944.42 ± 3.45 b	98.52 ± 2.44 b	2.24 ± 0.15 c	25.54 ± 1.23 b
Biochar (300℃)	2056.18. ± 5.74 a	101.54 ± 1.65 c	2.23 ± 0.07 b	26.76 ± 2.04 b
Biochar(500℃)	2070.36 ± 2.75 a	102.14 ± 3.04 ab	2.35 ± 0.08 b	27.17 ± 0.88 a
Biochar(700℃)	2386.27 ± 4.87 b	102.22 ± 2.36 a	2.41 ± 0.04 a	30.23 ± 1.67 a

All values represent means±SD; values within a column followed by the same letter do not differ significantly (LSD test, p = 0.05; n = 4)

structure of biochar can result in enhanced nutrient availability through water retention and improved water balance, finally improving plant nutrient use efficiency when added as a soil conditioner [9,10]. The main roles of biochar for enhancing plant growth are directly through its nutrient contents, and indirectly through its effects on nutrients use efficiency. The improvement of soil water holding capacity by biochar addition was considered a key factor to obtain a good grains yield. In a word, the biochar can be used a slow-releasing nutrient material due to the unique biochar structures and the adsorption–desorption process. The porous network within biochars can hinder the release of the nutrients. The strong adsorption behavior of biochar makes it a perfect naturally formed soil additive to concentrate nutrients in soil and thus allow for slow desorption into the aqueous phase for plant uptake [9,10,14,21].

In the present study, the produced yak manure derived biochar is of an alkaline nature, thus applying biochar to soils is associated with increases in soil pH. The mechanism of immobilization might be a result of precipitation due to the rise in soil pH due to the application of the basic biochar or even by the electrostatic interaction on the carboxyl groups of the biochar or through coordination byπelectrons (C-C) of carbon [55,63]. The yak manure derived biochar has characteristics of porous structure, high pH, and rich nutrients such as N, P, Ca, Mg, and K, resulting in the highland barley growth and high yield [10,21]. Our results suggest that yak manure derived biochar may significantly influence soil physicochemical properties, which is a promising amendment to increase soil nutrient level.

However, it must be concerned that manure biochar may not be a suitable choice for every soil. Up to now, the knowledge of biochar's impact on soil physical, chemical and biological properties is still lacking [9,21,32]. Future efforts should be focused on the interaction mechanism of biochar with soil nutrients and microbiota, facilitating the application of biochar as a soil amendment. With a better understanding of manure biochar's influence upon soil properties, a systematic guidance for the design and production of biochar can be applied to achieve the purposes of enhancing soil nutrients' levels.

4. Conclusions

In this study, biochar was produced using yak manure under various pyrolysis temperatures and its physicochemical properties were investigated. Based on the physical and chemical properties of the resulting biochar, the temperature of around 700 ℃ was found to be the optimal condition for producing mesoporous carbon-like material with BET surface area of 82.9 m^2 g^{-1}, demonstrating that the yak manure can be used as a feedstock for the biochar production. The presence of nutrients such as N, P, Ca, Mg, and K in the resultant biochar implied that the biochar may be used as a soil amendment. The field experiment was conducted to study the effect of the yak manure biochar amendment on yield and biological traits of highland barley. The results revealed that adding biochar to the soil could increase the yield and improve the growth of highland barley in the short-term although the long-term benefits remain to be quantified. The present study provides necessary information in filling the present technology gap on the pyrolysis of the yak manure and application of yak manure derived biochar as a soil amendment for improving the soil physical, chemical and biological properties. Further investigations should be urged to verify the proposed interactions mechanisms between biochar and microbiota for soil remediation and improvement.

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Disclosure statement

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