

Tuning Biochar Properties via Partial Gasification: Facilitating Inorganic Nutrients Recycling and Altering Organic Matter Leaching

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ABSTRACT: This study reports a systematic study on the potential of employing partial gasification at low conversions for tuning biochar for better properties and facilitating the recycling of inorganic nutrient species. The raw biochars were prepared from mallee wood and leaf at fast pyrolysis at 500 °C (a temperature pertinent to bio-oil production) and subsequent tuning via partial steam gasification at 725 °C and low conversions (5 and 10% on a carbon basis). The favorable structure tuning is achieved at the expense of 8–23% carbon, which would otherwise be available for sequestration during biochar application in soil. The development of the pore structure and transformation of the chemical forms of inorganic nutrient species as a result of partial gasification increase the leachability of the inorganic nutrient species in biochars via both water and Mehlich I solution. In addition, <1.5% of the organic matter in raw and tuned biochar is water-soluble. The leaching of water-soluble organic matter from the tuned biochars after re-pyrolysis and partial gasification (but absent in the same biochars after re-pyrolysis) suggests that partial gasification increases the accessibility of organic matter trapped in closed or blocked pores formed during pyrolysis. While some aromatic compounds can be leached from the raw biochar via solvent, no aromatic compounds are detected in the leachates from the tuned biochars. The tuning of biochar via partial gasification also improves the leaching kinetics of the inherent inorganic nutrient species. The overall recyclability of the inorganic nutrient species in the raw and tuned biochar shows that tuning biochar via partial gasification can be an effective strategy for facilitating the recycling of the inherent nutrient species in biochar.

1. INTRODUCTION

Mallee biomass has a unique position in Western Australia agriculture and bioenergy industries. It is planted in the Western Australia wheatbelt region to manage the serious dryland salinity issue and is considered to be a key second-generation bioenergy feedstock with a short harvesting cycle, high productivity, and small energy and carbon footprints.^{1,2} Earlier studies also demonstrated that the pyrolysis process can be used to convert mallee biomass into biochar, bio-oil, and/or bioslurry with suitable properties as a fuel.^{3–7} Growing interests have been in using fast-pyrolysis bio-oil as a substitute to liquid fuels⁸ for either direct stationary applications^{9,10} or its upgrading/refining for producing liquid transportation fuel.^{10–12} However, biomass utilization at a large scale may lead to substantial losses of plant nutrients, such as alkali and alkaline earth metallic (AAEM) species, from the soil argo-ecosystem because of continuous harvesting of biomass.¹³ Unless at least part of these plant nutrients can be returned, recycled, or compensated to the soil, continuous removal of plant nutrients from soil may lead to a biomass-based supply chain being unsustainable.

Bio-oil is typically produced from biomass fast pyrolysis at 450–550 °C for optimum yield.¹⁴ While the bio-oil is used as a fuel or further processed, the potentially vast quantity of biochar produced during commercial production of bio-oil may find important applications (e.g., soil amendment) for environmental benefits.^{15–18} During biomass pyrolysis, the majority of AAEM species are retained in biochar.^{19,20} It was shown that some of the AAEM species uptaken by biomass during its growth can be recycled to soil,^{19,21} delivering various agronomic benefits^{15,16,22–25} and achieving carbon sequestration.^{25–27} On the other hand, the structure of biochar can be

adjusted via thermochemical processing, such as gasification.²⁸ It is possible to use partial gasification for tuning biochar for desired properties and also facilitating the recycling of inherent nutrients species at a minimal carbon loss. In fact, the inherent inorganic species in biochar can be good catalysts for partial gasification of biochar,^{29,30} hence, the tuning of the biochar structure. Surprisingly, little work has been done thus far on these important aspects.

Consequently, this study carries out a systematic study on using partial gasification as a method to tune the structure of fast-pyrolysis biochar for improved biochar properties and inorganic nutrient recycling. The raw biochars were prepared from biomass fast pyrolysis at 500 °C, while the tuning process was carried out at 725 °C via partial steam gasification with minimal carbon conversions (5 and 10%).

2. EXPERIMENTAL SECTION

2.1. Biomass and Biochar Preparation. The wood and leaf components were separated from green mallee trees (*Eucalyptus loxophleba* subspecies *lissophloia*) that were harvested from Narrogin, Western Australia. Using a cutting mill (Fritsch Pulverisette 15), biomass samples of various sizes (wood, 150–250 µm and 1–2 mm; leaf, 150–250 µm) were prepared and then kept at below –9 °C prior to pyrolysis experiments. Large and small biochar particles were prepared from respective biomass samples using a quartz drop-tube/fixed-bed reactor and a fluidized-bed reactor at 500 °C, following the procedures described elsewhere.³¹ Multiple experiments were carried out to produce a sufficient amount of biochar samples required for this study.

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Table 1. Proximate and Ultimate Analyses of the Raw Biomass and Various Biochars Used in This Study

| sample ^b | moisture ^c (wt %) | proximate analysis (wt %, db) | | | ultimate analysis (wt %, daf ^a) | | | | |
|---------------------|------------------------------|-------------------------------|-----------------|-----------------|---|-----|------|------|----------------|
| | | ash | VM ^d | FC ^e | C | H | N | S | O ^f |
| Raw Biomass | | | | | | | | | |
| wood | 4.0 | 0.5 | 83.6 | 15.9 | 47.7 | 6.2 | 0.51 | 0.03 | 45.6 |
| leaf | 5.6 | 3.6 | 76.5 | 19.9 | 58.7 | 7.3 | 1.52 | 0.25 | 32.5 |
| Fine Wood Biochar | | | | | | | | | |
| FWB-500-P | 3.4 | 3.0 | 21.3 | 75.7 | 85.1 | 2.6 | 0.44 | 0.02 | 11.9 |
| FWB-725-RP | 3.8 | 3.5 | 16.9 | 79.5 | 89.6 | 0.9 | 0.44 | 0.02 | 9.1 |
| FWB-725-5%-PG | 2.9 | 3.8 | 13.7 | 82.5 | 89.2 | 1.1 | 0.35 | 0.01 | 9.3 |
| FWB-725-10%-PG | 2.8 | 4.0 | 12.5 | 83.5 | 89.2 | 1.5 | 0.16 | 0.01 | 9.2 |
| Fine Leaf Biochar | | | | | | | | | |
| FLB-500-P | 4.6 | 14.4 | 31.3 | 54.3 | 82.9 | 2.2 | 2.09 | 0.08 | 12.9 |
| FLB-725-RP | 6.7 | 16.2 | 20.0 | 63.8 | 88.7 | 0.2 | 1.93 | 0.08 | 9.1 |
| FLB-725-5%-PG | 7.5 | 16.1 | 19.9 | 64.0 | 88.0 | 0.4 | 1.47 | 0.07 | 10.1 |
| FLB-725-10%-PG | 6.9 | 16.5 | 21.4 | 62.1 | 85.7 | 0.5 | 1.30 | 0.07 | 12.5 |
| Large Wood Biochar | | | | | | | | | |
| LWB-500-P | 3.6 | 4.5 | 23.0 | 72.5 | 87.3 | 2.6 | 0.32 | 0.03 | 9.8 |
| LWB-725-RP | 3.2 | 5.1 | 13.4 | 81.5 | 87.3 | 1.3 | 0.29 | 0.03 | 11.1 |
| LWB-725-5%-PG | 4.1 | 5.2 | 13.0 | 81.8 | 89.2 | 1.3 | 0.21 | 0.02 | 9.3 |
| LWB-725-10%-PG | 3.1 | 5.5 | 13.2 | 81.3 | 88.7 | 0.9 | 0.14 | 0.02 | 10.3 |

^adaf = dry and ash free. ^bThe meaning of the sample labels are given as “XXX-DDD-YY”, in which XXX indicates the type of biochar, DDD is the processing temperature (°C), and YY indicate the conditions of biochar tuning via particle gasification. XXX can be FWB for fine wood biochar, FLB for fine leaf biochar, and LWB for biochar produced from large particle wood. DDD can be either 500 for pyrolysis at 500 °C or 725 for re-pyrolysis or partial gasification at 725 °C. YY can be P for the raw fast-pyrolysis biochars, RP for the re-pyrolyzed biochars, or 5%-PG and 10%-PG for tuned biochar after 5 and 10% partial gasification at 725 °C, respectively. ^cwt % after air dried. ^dVM = volatile matter. ^eFC = fixed carbon. ^fBy difference.

2.2. Biochar Tuning Experiments. Biochar tuning experiments were conducted in a fixed-bed quartz reactor (inner diameter of 60 mm), similar to the one used previously,^{28,32} via partial steam gasification at low carbon conversion (5 and 10%). Briefly, about 0.4 g of biochar was loaded to the reactor, and argon gas (ultrahigh purity) was used as a carrier gas at 3 L min⁻¹. After 15 min of purging, the reactor was then placed in a furnace that was preheated to the reaction temperature (725 °C). After the furnace was reheated to the reaction temperature, steam (adjusted to 8.2 vol % steam in argon gas) was then introduced into the reactor for commencing biochar tuning to reach 5 or 10% carbon conversion. After the completion of an experiment, the steam flow was switched off and the reactor was immediately lifted out of the furnace with continuous flowing of argon and then cooled to room temperature. The reaction time required for 5 or 10% conversion (on carbon basis) was predetermined from separate gasification experiments. To gain fundamental insights into the tuning reactions, the experimental conditions used were tested to ensure that the reactor is a differential reactor with regards to the gasification agent.³² In addition, because the temperature (500 °C) for biochar preparation was lower than the temperature (725 °C) of partial gasification for biochar tuning, separate experiments were carried out to investigate the re-pyrolysis of the raw biochars under an argon atmosphere, following the same temperature–time history. The gas products evolved during the partial steam gasification for biochar tuning and biochar re-pyrolysis were collected. The gas compositions (H₂, CO, CO₂, and CH₄) were then quantified using two gas chromatographs (PerkinElmer) equipped with dual columns (molecular sieve column and Porapak-N column).

2.3. Biochar Leaching. Three types of biochar-leaching experiments were carried out in this study. The first type is biochar leaching in a bottle with magnetic stirring under batch conditions. A total of 1 g of biochar was weighed and soaked with 1 L of ultrapure water (18.2 MΩ) in a plastic bottle, corresponding to a solid/liquid ratio of 1 g/L. A fixed amount (25 mL) of water sample was drawn from the bottle with needle and syringe at a designated time interval. The sample was then centrifuged. The supernatant was carefully decanted to a sample container, while the solid retained was mixed with an equal amount of fresh ultrapure water before adding them to the bottle. The experiment was carried out for 28 days. The leaching of inorganic

species is deemed to reach equilibrium when there is no further detectable change in the concentration in the leachate. The second type of leaching experiments is for the quantification of the total plant available AAEM species using Mehlich I solution (0.05 N HCl and 0.025 N H₂SO₄) for an extended period of 24 h, following the procedure used in a previous study.²¹ The third type of leaching experiments is the leaching of biochars using a mixed solvent of chloroform and methanol (4:1, v/v). Briefly, 0.2 g of biochar submerged in 10 mL of solvent. The samples were then shaken in an orbital shaker for 24 h and then filtered with 0.45 μm filters to yield the solution for ultraviolet (UV) fluorescence analysis. All leaching experiments were carried out at room temperature of 25 °C. Repeated experiments were carried out, and the standard errors of the data are plotted throughout the figures.

2.4. Sample Analysis. The proximate analysis was conducted according to ASTM E870-82 using thermogravimetric analysis. The contents of C, H, and N in biomass or biochar sample were carried out using an elemental analyzer (PerkinElmer CHNSO 2400 Series II). The total S and Cl in the samples were quantified following the Eschka method³³ and improved Eschka method,³⁴ respectively, using ion chromatography (IC, DIONEX ICS-1100). The content of O is calculated by difference on a dry and ash-free (daf) basis. The data are listed in Table 1. The AAEM species in biomass and biochars shown in Table 2 were quantified according to a previous procedure,³² which consists of ashing, acid digestion, and quantification using another IC (DIONEX ICS-3000). The contents of AAEM species in the leachate samples from water-leaching or Mehlich-I-leaching experiments are quantified using ICS-3000, while the contents of S, P, and Cl were separately quantified with ICS-1100. It is noted that the leaching of sulfur and phosphorus from the biochars was found to be minimal in this study and, hence, not reported. The total organic carbon (TOC) in water samples were quantified using a TOC analyzer (Shimadzu TOC-V_{CPH}).

The Brunauer–Emmett–Teller (BET) surface area of biochar was measured by N₂ adsorption using Micromeritics Tristar II model 3020 based on the BET equation.^{15,28} The micropore (<2 nm) surface area of biochar was measured by CO₂ adsorption using Micromeritics Gemini based on the Dubbin–Radushkevich (DR) equation.³⁵ The biochar samples were outgassed for at least 12 h at 120 °C. The

Table 2. Contents of Inorganic Species in Biomass and Various Biochars, Expressed as wt % on a Dry Basis^a

| sample | inorganic species (wt %, dry basis) | | | | |
|----------------|-------------------------------------|-------|-------|-------|-------|
| | Na | K | Mg | Ca | Cl |
| wood | 0.024 | 0.066 | 0.033 | 0.128 | 0.015 |
| leaf | 0.550 | 0.336 | 0.159 | 0.748 | 0.158 |
| FWB-500-P | 0.123 | 0.350 | 0.172 | 0.667 | 0.016 |
| FWB-725-RP | 0.141 | 0.380 | 0.197 | 0.749 | 0.018 |
| FWB-725-5%-PG | 0.129 | 0.412 | 0.203 | 0.806 | 0.014 |
| FWB-725-10%-PG | 0.138 | 0.440 | 0.215 | 0.827 | 0.008 |
| FLB-500-P | 2.054 | 1.187 | 0.587 | 2.794 | 0.543 |
| FLB-725-RP | 2.053 | 1.326 | 0.634 | 3.126 | 0.506 |
| FLB-725-5%-PG | 1.636 | 1.364 | 0.701 | 3.365 | 0.279 |
| FLB-725-10%-PG | 1.679 | 1.407 | 0.704 | 3.421 | 0.253 |
| LWB-500-P | 0.141 | 0.422 | 0.278 | 0.913 | 0.051 |
| LWB-725-RP | 0.154 | 0.402 | 0.271 | 0.899 | 0.048 |
| LWB-725-5%-PG | 0.131 | 0.461 | 0.315 | 1.052 | 0.036 |
| LWB-725-10%-PG | 0.144 | 0.512 | 0.333 | 1.104 | 0.024 |

^aThe meanings of the sample labels are given in footnote b of Table 1.

leachate samples were further subject to UV fluorescence spectroscopy (PerkinElmer LS55B) analysis for characterizing the aromatic compounds present in the samples. The synchronous spectra were recorded at -2800 cm^{-1} , with a slit width of 2.5 nm and scan speed of 200 nm min^{-1} .

2.5. Kinetic Model. It was demonstrated that a pseudo-second-order kinetic model can be used to describe the leaching of AAEM species from biochars.²¹ Therefore, the experimental data in this study was also fitted to this kinetic model for determining the pseudo-second-order leaching rate constant and initial leaching rate. The pseudo-second-order leaching model is shown in eq 1³⁶

$$\frac{dC_t}{dt} = k(C_s - C_t)^2 \quad (1)$$

where k is the second-order overall leaching rate constant ($\text{L mg}^{-1}\text{ day}^{-1}$), C_s is the equilibrium concentration (mg L^{-1}), and C_t is the concentration (mg L^{-1}) of AAEM species in water at time t .

3. RESULTS AND DISCUSSION

3.1. Carbon Loss Because of Biochar Tuning and the Characteristics of the Tuned Biochars. Previous studies investigated the effect of pyrolysis conditions on biochar nutrient availability.^{19,21,37} However, little had been done on tuning biochar structure for enhancing inherent nutrients recycling. This study considers using partial steam gasification at low conversions for tuning the structure of fast-pyrolysis biochar. Figure 1 presents the weight (panel a) and carbon retention (panel b) of the biochar (prepared from pyrolysis at $500\text{ }^\circ\text{C}$) after the re-pyrolysis and/or partial steam gasification at $725\text{ }^\circ\text{C}$. As expected, re-pyrolysis and gasification of biochar at a higher temperature cause biochar to experience additional weight loss because of the release of volatiles and conversion of some biochar into syngas. The magnitude of weight loss of these biochar is in the order of FWB-500-P > FLB-500-P > LWB-500-P derived biochar. It is clear that biochar tuning via partial gasification comes at an appreciable cost, with losses of 8–23% of carbon available for sequestration (Figure 1b). It should be noted that, for the biochar to be stable and recalcitrant from degradation when applied to soil, the H/C and O/C molar ratios of biochar need to be below 0.6 and 0.4, respectively.^{37–39} The van Krevelen diagram in Figure 2 clearly shows the tuned biochars have the O/C molar ratio (~ 0.1) and H/C molar ratio (0.05–0.2) that are well below the threshold

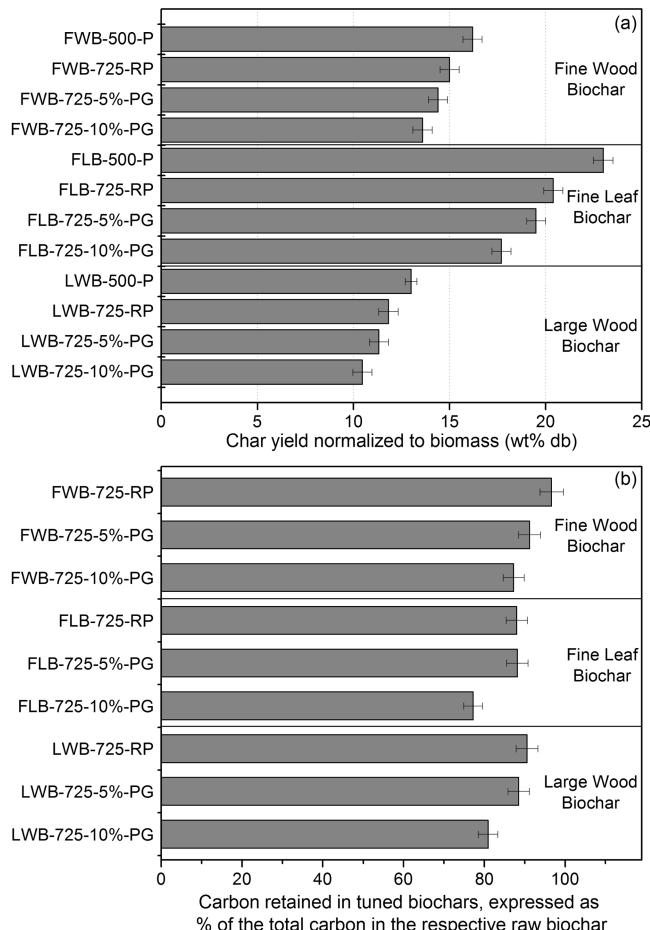


Figure 1. Weight and carbon retention of various biochars: (a) char yield from pyrolysis and partial steam gasification normalized to biomass feedstock mass (wt %, dry basis) and (b) carbon retained in the tuned biochars, expressed as a percentage of the total carbon in the respective raw biochar. The meanings of the sample labels are given in footnote b of Table 1.

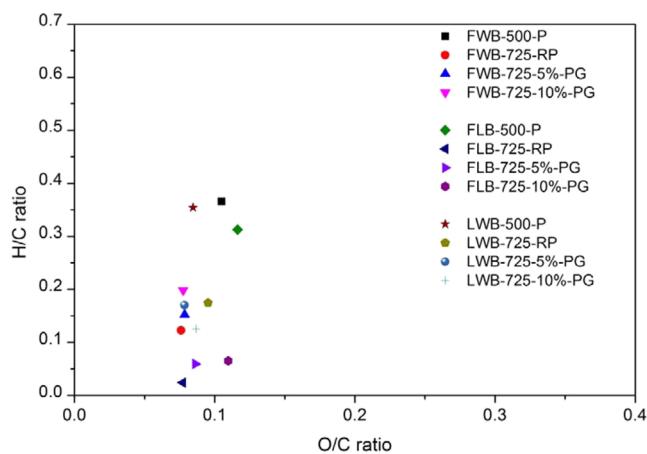


Figure 2. van Krevelen diagram for the raw, re-pyrolyzed, and tuned (via partial gasification at 5 and 10% carbon conversions, respectively) biochars. The meanings of the sample labels are given in footnote b of Table 1.

values, suggesting that carbon in the tuned biochars will be stable.

During re-pyrolysis and partial gasification, the majorities (>88%) of the inherent K, Mg, and Ca species were retained in the tuned biochars, as shown in Figure 3. However, the loss of

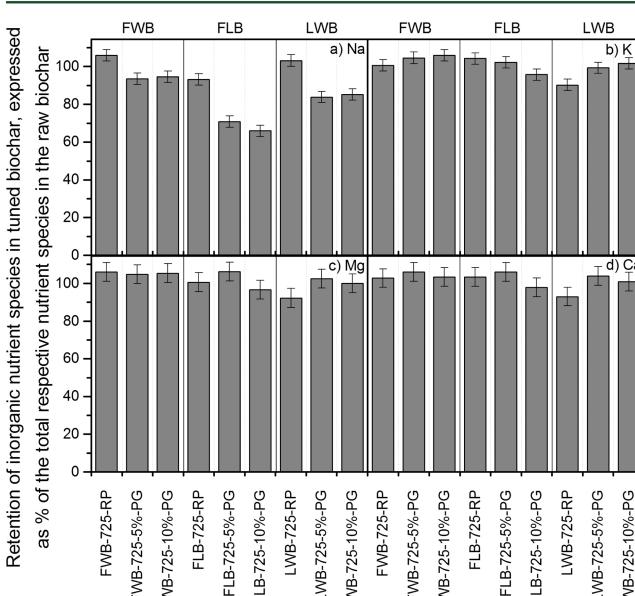


Figure 3. Retention of inorganic nutrient species in the tuned biochars, normalized to the total respective nutrient species in the raw biochars. The meanings of the sample labels are given in footnote *b* of Table 1.

Na is relatively high (up to 35%), because of Na being monovalent (in comparison to divalent Mg and Ca) and lighter (in comparison to K) and the force gas flow through the thin bed.^{40–43} For Cl, a considerable amount of Cl was also retained in biochar during fast pyrolysis (consistent with a previous report²⁰) and part of Cl was released during re-pyrolysis and partial gasification because of its volatile nature.

Figure 4 presents the data on the surface area of the raw and tuned biochars. It is noted that the BET surface area was measured by N₂ adsorption based on the BET equation, while the micropore surface area was measured by CO₂ adsorption based on the DR equation.³⁵ It can be seen in Figure 3 that the raw biochars have a micropore surface area in the range of 120–180 m²/g and BET surface area of <50 m²/g. The micropore surface area increases by ~100 m²/g during re-pyrolysis, and no significant change in the micropore surface area is observed during partial gasification. However, partial gasification leads to a significant increase in the BET surface area.²⁸ There are two possible explanations. One is that, during gasification, there appears to be a balance between the formation of new micropores and the enlargement of the existing micropores to meso- and macropores because of gas-solid reactions (with similar observations also reported previously⁴⁴). The other is that biochars contain existing closed pores. The primary and secondary pyrolysis reactions may also result in carbon deposition in the micropore,^{45,46} hence, the blockage of the micropore. Partial gasification at a low conversion gasifies the carbon materials to make these closed or blocked pores accessible.⁴⁷ However, under the current experimental conditions, while gasification leads to the opening of the closed or partially blocked pores, the formation of larger pores during partial gasification at 5 and 10% conversions appears to be the dominant process. The BET surface area of

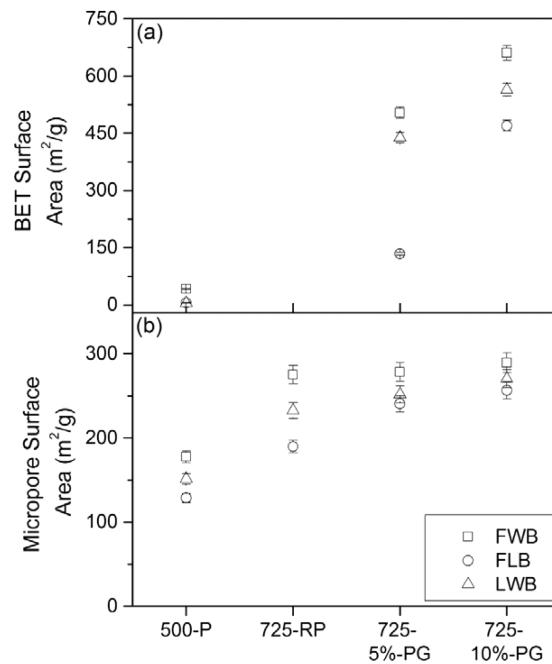


Figure 4. Surface area of various biochars: (a) BET surface area, determined via N₂ adsorption at 77 K using the BET method, and (b) micropore surface area, determined via CO₂ adsorption at 273 K using the DR method. FWB, FLB, and LWB stand for fine wood biochar, fine leaf biochar, and large wood biochar, respectively. “500-P” indicates raw biochars, and “725-RP” indicates re-pyrolyzed biochar, while “725-5%-PG” or “725-10%-PG” indicate tuned biochars via partial gasification at 5 and 10% conversions, respectively.

partially gasified biochar increases substantially as opposed to the micropore surface area. Such an increase in surface area and development of larger pores may facilitate the leaching of inorganic and organic matter from biochar (see the discussion in subsequent sections).

In addition, the data also show that the surface area of biochar produced from large biomass particles (LWB-500-P) is lower compared to the biochar produced from small biomass particles (FWB-500-P). This suggests the effect of the feedstock particle size on the structure of the resultant biochars. This is because the heat- and mass-transfer limitations arising from the fast pyrolysis of large biomass particles might lead to slowed devolatilization of the biomass core⁴⁸ and, thus, a reduction in the surface area.

3.2. Leachability of Inorganic Nutrient Species in the Raw and Tuned Biochars. Figure 5 presents the data on the leachability of inorganic nutrient species by water or Mehlich I medium. It can be seen that over 70% of Na and K in the raw biochars is water-leachable and a similar amount of Na and K is observed to be leached by Mehlich I medium. This suggests that, in the raw biochar, water leaching can recycle close to 100% of the total plant-available Na and K in the raw biochar. However, less than 30% of Mg and Ca is water-leachable from the raw biochar, while close to 50 and 90% of Mg and Ca in the raw char can be leached by Mehlich I medium, respectively. Therefore, water leaching can only recycle less than 60 and 30% of the total plant-available Mg and Ca in the raw biochars, respectively.

The most important finding in Figure 5 is that partial gasification at low carbon conversions (5 and 10%) can have a significant effect on the leachability of inorganic nutrients in the

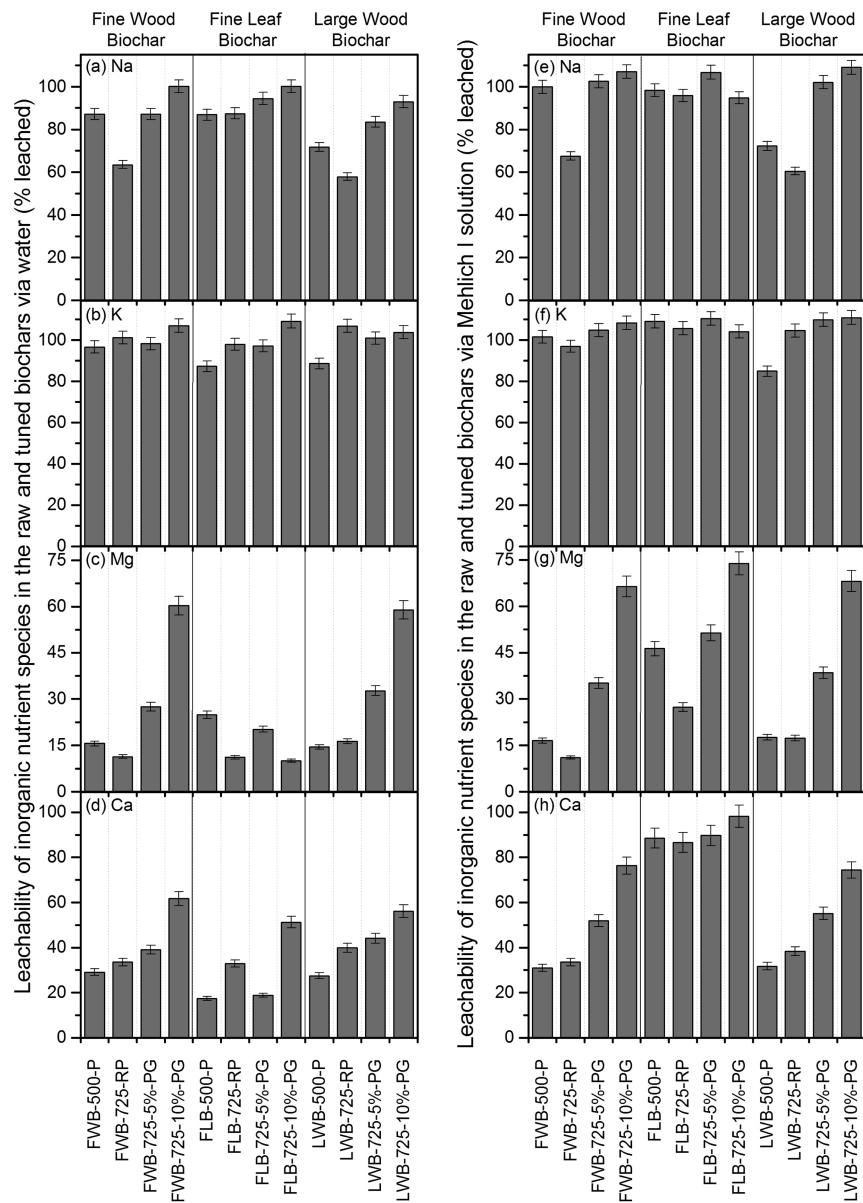


Figure 5. Leachability of inorganic nutrient species in the raw and tuned biochars via (a–d) water and (e–h) Mehlich I solution. The meanings of the sample labels are given in footnote *b* of Table 1.

biochars. For water leaching, there are potentially substantial increases in the amount of water-leachable Mg and/or Ca in biochars. For example, water-leachable Mg in tuned fine (FWB) and large (LWB) wood biochar almost quadrupled (from ~16 to 60%) after 10% gasification, and water-leachable Ca increases from ~30 to ~60%. However, the trend for Mg in leaf biochars (FLB) following partial gasification is not clear. The partial gasification process also brought the amount of water-soluble Na and K to ~100%. It is clear that partial gasification of the raw biochar can facilitate the recovery of inorganic nutrient species from biochars prepared from fast pyrolysis. For Mehlich I medium leaching, partial gasification can also significantly increase the total plant-available Mg and Ca. For example, the total plant-available Mg in fine and large wood biochar increases from ~15 to ~65%, while it increases from 46 to 74% for fine leaf biochar. The plant available Ca in both fine and large wood biochar increases from ~30 to ~75%. The increases in the leachability (by water or Mehlich I solution) of

inorganic nutrients as a result of partial gasification may be attributed to at least two reasons. One is that partial gasification opens the closed or blocked micropore and also enlarges the micropore because of the gas–solid reactions as aforementioned. Therefore, the inorganic nutrient species, which was encapsulated in the char structure during fast pyrolysis^{21,45} and inaccessible, would have become accessible by the leaching medium. The other is that the gasification reactions may have changed some of the inorganic nutrient species in biochars to more leachable chemical forms.³⁰

It is further noted in Figure 5 that there is a noticeable difference in water-soluble and total plant-available (Mehlich-I-extracted) Na and K between the FWB-500-P and LWB-500-P biochars. This is likely due to the differences in the conditions for biochar preparation. LWB-500-P was prepared from large wood particles in a fluidized-bed (FB) reactor, while FWB-500-P was prepared from fine wood particles in a drop-tube/fixed-bed (DTFB) reactor. During pyrolysis, the mass-transfer

resistance for the volatiles within the pyrolyzing large wood particles promotes the secondary reactions of volatiles within the particles. These result in more carbon deposition within the micropore and, hence, more encapsulation of inorganic nutrient species in the blocked pores.^{21,46} The data in Figure 5 show that grinding the large LWB-500-P biochar particles into fines, followed up by biochar tuning via partial gasification, can improve the leachability of inorganic nutrient species. It can be seen that water-soluble Na and K in LWB-500-P biochar increase from ~72 and ~88% to ~93 and ~103%, respectively, while all Na and K become leachable in the Mehlich I solution medium.

The leachability of chlorine from the raw and tuned biochars by water is presented in Figure 6. Please note that the data on

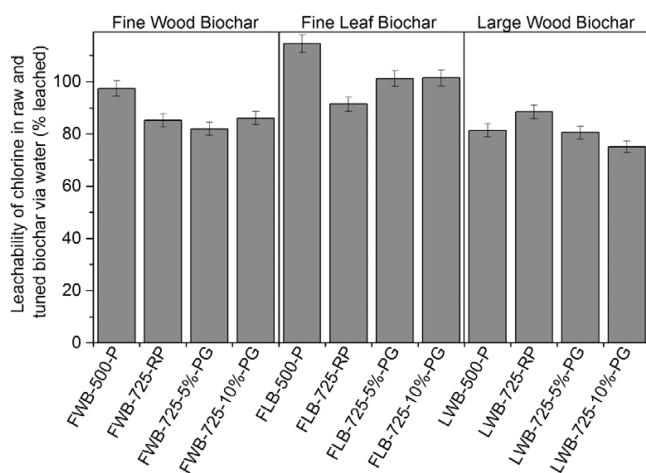


Figure 6. Leachability of chlorine in raw and tuned biochar via water. The meanings of the sample labels are given in footnote *b* of Table 1.

chlorine leaching by the Mehlich I solution medium are not available because the Mehlich I solution itself contains chlorine. It can be seen that, while all chlorine in biomass is water-soluble,⁴⁹ ~80% of chlorine in raw biochar is water-soluble. This is consistent with the previous report that, during pyrolysis, a proportion of chlorine bound to biochar is transformed into the water-insoluble form.²⁰ Furthermore, re-pyrolysis and partial gasification have an insignificant effect on the distribution of water-soluble chlorine in biochar.

3.3. Leachability of Organic Matter from the Raw and Tuned Biochars. Figure 7 shows that some organic matter was leached from the raw biochar and tuned biochars. Similar to biochar produced from slow pyrolysis,¹⁹ the amount of organic matter leachable via water in these biochars is <1.5% (on a carbon basis). It is noted that, for the raw biochars prepared from fast pyrolysis (at 500 °C), the tuned biochars (particularly for FWB-725-RP and FLB-725-RP biochars and to a lesser extent for LWB-725-RP biochar) after the re-pyrolysis of the raw biochars at 725 °C reduce the amount of leachable organic matter to below the quantification limit of our method (0.06% of C in biochar). This is plausible because re-pyrolysis at a higher temperature might result in the cracking of heavy tars in raw biochar⁵⁰ and/or the release of at least some organic matter on the biochar surface. It is interesting to note that, after partial gasification at low conversions, there are actually a significant amount of organic matter leached from the tuned biochars. The data clearly demonstrate that there are leachable organic matter locked in at least part of the pore system within the biochars

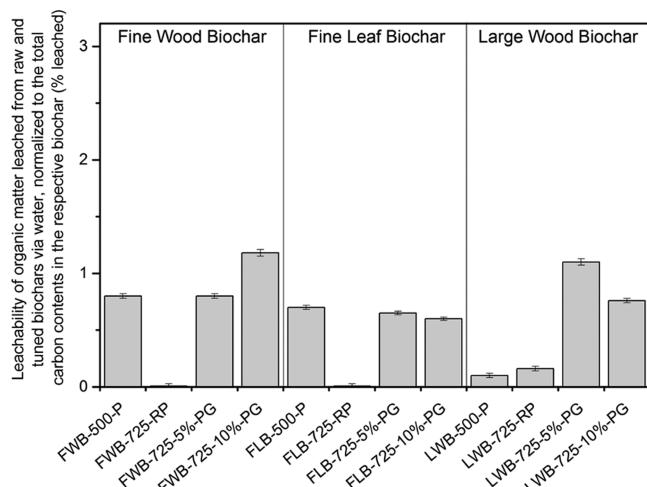


Figure 7. Leachability of organic matter leachable from the raw and tuned biochars via water, normalized to the total carbon contents in the respective biochars. The meanings of the sample labels are given in footnote *b* of Table 1.

and such organic matter is inaccessible to leaching medium because that part of the pore system is either closed or blocked (e.g., by carbon deposition during pyrolysis). Partial gasification opens these closed/blocked pore systems, so that the locked organic matter becomes accessible. In addition, partial gasification leads to the formation of larger pores, such as macro- and mesopores,⁵¹ which also act as a transport system for leaching.

Aromatic compounds, such as polycyclic aromatic hydrocarbons (PAHs), are known to be present in biochar.⁵² The leaching of aromatic compounds from biochar during soil application may result in undesirable environmental impact. Therefore, the raw and tuned biochars were leached with a chloroform/methanol mixture (4:1, v/v) for 24 h for characterization of the leachable aromatic compound. The UV fluorescence synchronous spectra of the resultant leachate are presented in Figure 8. The spectra show that raw biochar contains solvent-leachable aromatic compounds. The maxima centered at ~350 nm for the spectra of raw fine wood (FWB-500-P) and leaf biochar (FLB-500-P) indicate the leaching of 2–3 fused ring aromatic compounds, while the maximum centered at ~390 nm for the spectrum of a large wood biochar (LWB-500-P) indicates the leaching of larger 3–5 fused ring aromatic compounds. The higher intensity in the raw fine leaf biochar and large wood biochar spectra suggests that a higher amount of aromatic compound can be leached from these biochars compared to raw fine wood biochar. However, no leaching of the aromatic compound in the re-pyrolyzed and tuned biochar is detected. It is also noted that UV fluorescence spectra of the leachates collected from the leaching of tuned biochars using both water and Mehlich I solution showed the absence of aromatic compounds. The absence of these aromatic compounds suggests that those aromatic compounds were mostly likely depolymerized or cracked during re-pyrolysis or partial gasification (as a result of more intense reactions at a higher temperature⁵⁰). In addition, it is known that steam gasification can lead to selective removal of smaller and reactive components within biochar at low conversions, resulting in the tuned biochars, which have a stable and highly aromatic structure.²⁸ Therefore, partial gasification at low conversions tunes the raw biochar to be virtually free of leachable aromatic compounds.

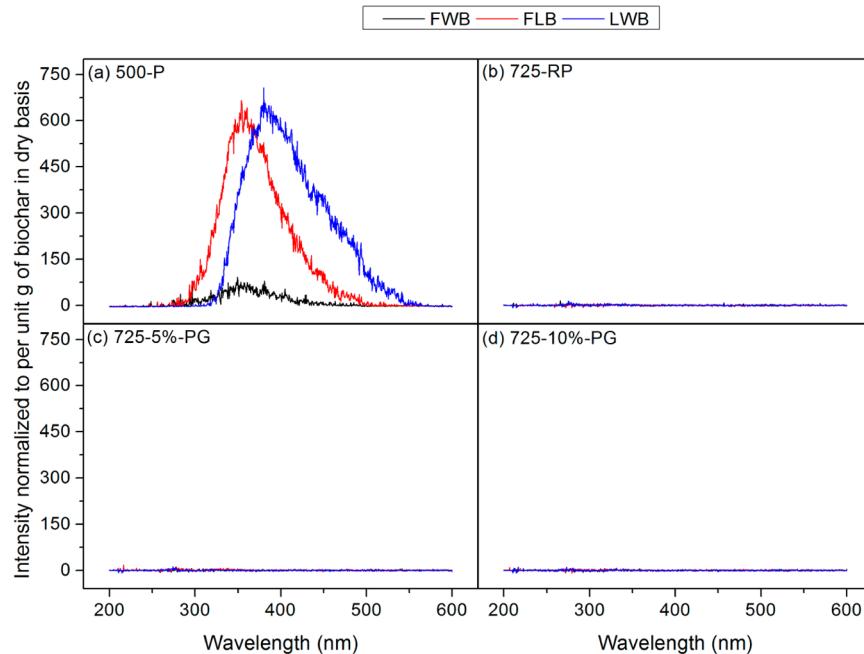


Figure 8. UV fluorescence spectra of methanol/chloroform wash solution normalized to per gram of biochar (dry basis). The wavelength of the spectra shown is the wavelength of the excitation monochromator: spectra for (a) raw biochar, (b) biochar after re-pyrolysis, (c) 5% gasification biochar, and (d) 10% gasification biochar.

3.4. Leaching Kinetics and Kinetic Model. Figures 9 and 10 show the leaching kinetics of inorganic and organic matter from the raw and tuned biochars. The experimental data were then fitted to the pseudo-second-order kinetic model, with the values of the fitted parameters tabulated in Table 3. It can be seen that the r^2 values of the data fitting are all above 0.97, suggesting that the pseudo-second-order kinetic model is suitable to describe the leaching kinetics of inorganic nutrient species and organic carbon from the raw and tuned biochars. The data in Table 3 further show that partial gasification generally increases the overall leaching rate constant and the initial leaching rate. This is reflected by the fact that, in Figure 9, there is a sharp increase in the leaching of inorganic nutrient species from tuned biochars within the first 2 days of the 28 day leaching period. Therefore, partial gasification enhances not only the recycling but also leaching kinetics of the inherent inorganic nutrients in the biochars. This is a desired but expected outcome because of at least two reasons. One reason is that partial gasification leads to the formation and enlargement of the pore system and the opening of closed/blocked pores, as discussed in previous sections. This tunes the raw biochar into a highly porous tuned biochar with a high surface area. Such a porous structure of the tuned biochar reduces the intraparticle mass-transfer resistance of the inorganic nutrient species during leaching. A higher surface area in the tuned biochar also promotes the ionization or dissolution of the inorganic nutrient species because of the increased exposure of these species to the leaching medium. The other reason is that partial gasification has changed the occurrence forms of the inorganic nutrient species within the tuned biochar. For example, at least part of Mg and Ca has been transformed from the water-insoluble form into the water-soluble form and become water-leachable.

3.5. Further Discussion. The results presented thus far show that K (and Na) in the raw biochar prepared by biomass pyrolysis at 500 °C is generally plant-available, and its recycling

can be achievable via water leaching, while the plant availability and recyclability of inherent Mg and Ca in the raw biochars are poor (see Figure 5). It can be further seen in Table 2 that Mg and Ca accounted for more than 65 and 50% of the total major inorganic nutrient species in the raw wood and leaf biochars, respectively. K, Mg, and Ca are crucial to plant growth.^{53–55} The poor plant availability of Mg and Ca translates to only ~50% of all major inorganic nutrient species (Na, K, Ca, Mg, and Cl) in the raw biochar being returned during the direct soil application of the raw biochars.

The results presented thus far also show that tuning the raw biochars via partial gasification can potentially increase the plant availability of the inorganic nutrient species in the biochars substantially. To further illustrate and evaluate the overall recyclability of the inorganic nutrient species in the raw and tuned biochars, the amounts of plant-available inorganic nutrient species (measured via Mehlich I solution leaching) in various biochars are normalized to those present in the raw biomass materials. As shown in Figure 11, partial gasification at low conversions can be a good strategy for tuning biochar because it clearly enhances the overall recyclability of inorganic nutrient species, particularly Mg and Ca. The overall recyclability of Na is low after tuning via partial gasification because of the release of Na during gasification. This is not a concern because, in Western Australia, mallee is planted in agricultural land for managing dryland salinity and there is oversupply of Na (in the form of NaCl salt⁵⁵).

Tuning biochar via partial gasification also leads to positive changes in the pore structure of biochar, with several practical implications. First, it is known that biochar porosity and surface area play important roles in amended soil water holding capacity and bioactivity,⁵⁶ and a surface area of >150 m²/g has been recommended and considered as preferable for good performance in soil.^{38,39} The results in this paper show that partial gasification at low conversions can tune the biochar structure to have a surface area significantly larger than 150 m²/

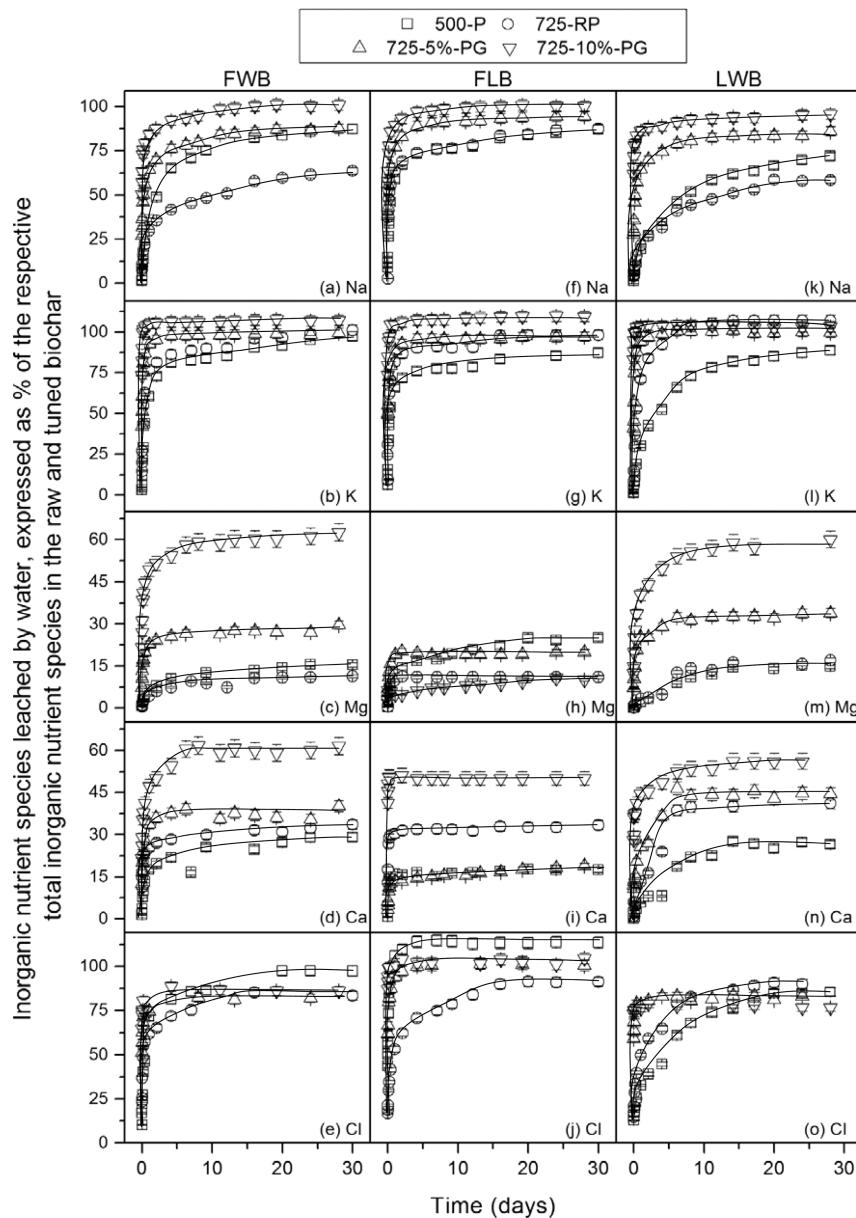


Figure 9. Leaching kinetics of inorganic nutrient species from various biochars: (a–e) fine wood biochars (FWB), (f–j) fine leaf biochars (FLB), and (k–o) large wood biochars (LWB). “500-P” indicates raw biochar, and “725-RP” indicates re-pyrolyzed biochar, while “725-5%-PG” or “725-10%-PG” indicate tuned biochars via partial gasification at 5 and 10% conversions, respectively.

g. Second, it was postulated that soil microbe activity is unlikely to benefit from the addition of biochar with micropores (<2 nm), because these pores are inaccessible by most bacteria and fungi^{57,58} (with sizes of $0.5\text{--}5 \mu\text{m}$ ⁵⁹). The results in this paper show that tuning via partial gasification leads to the formation of larger pores in tuned biochars (hence, potentially providing more habitat for soil microbes and protecting them from their gazers⁵⁶). Third, biochar with a large surface area and rich in macropores with a pore diameter of >50 nm are known to potentially have a high water holding capacity.⁶⁰ The higher surface area and formation of large pores in tuned mallee biochars (via partial gasification reported in this paper) can bring significant benefits when the tuned biochars are applied to soil. This is of great importance and highly desired to the sandy soil (abundant in the agriculture land in Western Australia⁵⁴), which suffers from a low water holding capacity because of its low surface area.⁵⁹

There are also several important considerations in choosing the process parameters of partial gasification for tuning biochar structure and facilitating inorganic nutrients recycling. There are mainly three parameters of consideration, i.e., conversion, temperature, and particle size. The first important consideration is biochar conversion during tuning via partial gasification. To make the tuning strategy meaningful and practically useful, it is critical to achieve the desired structural tuning with minimized weight loss of the biochar, which would be subsequently returned to soil for carbon sequestration, and minimized losses of inherent inorganic nutrients. Therefore, the gasification should be performed at low conversions, and the data in this paper show that 5–10% conversion is sufficient. A too low conversion may not achieve the desired objectives of tuning, while a too high conversion leads to significant loss of carbon, which would be otherwise available for sequestration. The second important parameter is the choice of a suitable

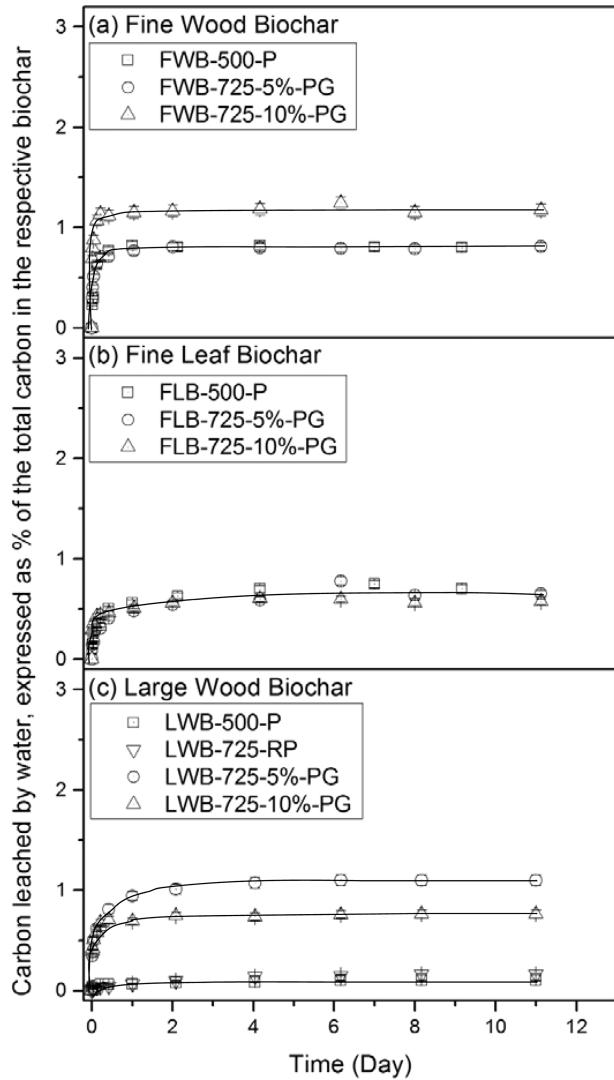


Figure 10. Leaching kinetics of organic matter (on a carbon basis) from the raw and tuned biochars: (a) fine wood biochars, (b) fine leaf biochars, and (c) large wood biochars. The meanings of the sample labels are given in footnote *b* of Table 1.

gasification temperature, considering a balance among processing time, energy consumption, and potential loss of useful inorganic nutrient species. At a too low temperature, gasification reaction is slow; the process would benefit from a low energy input, favorable retention of inorganic nutrient species in the tuned biochar, and good process controllability but suffer from a prolonged tuning time. However, at a too high temperature, gasification reaction is fast; the process benefits from a fast tuning time but becomes difficult to control, demands high energy input, and suffers from potential release of useful inorganic nutrient species during the tuning process. Therefore, the application of partial gasification for tuning biochars is recommended to be performed at low conversions (below 10%) and a suitable temperature. The third and last consideration is particle size. Gasification of small biochar particles can be significantly faster than that of large biochar particles because small particles reduce intraparticle mass-transfer limitations and provide considerably more surface area available for gasification reactions.⁶¹ It is known that, while the grindability of mallee biomass is poor, the biochar produced from biomass pyrolysis has excellent grindability, so that size

Table 3. Kinetic Parameters for Water Leaching of Various Biochars^a

| sample | Na | | | Mg | | | Ca | | | C | | |
|----------------|----------|----------|-----------------------|----------|----------|-----------------------|----------|----------|-----------------------|----------|----------|-----------------------|
| | <i>k</i> | <i>h</i> | <i>r</i> ² |
| FWB-500-P | 0.711 | 0.864 | 0.998 | 0.523 | 6.022 | 0.999 | 3.470 | 0.239 | 0.991 | 0.757 | 2.803 | 0.995 |
| FWB-725-RP | 1.073 | 0.783 | 0.990 | 0.694 | 9.248 | 0.998 | 4.098 | 0.194 | 0.994 | 1.502 | 8.372 | 0.998 |
| FWB-725-5%-PG | 3.418 | 3.948 | 0.998 | 6.494 | 98.230 | 0.999 | 14.702 | 4.111 | 0.999 | 3.339 | 30.613 | 0.999 |
| FWB-725-10%-PG | 5.601 | 8.550 | 0.999 | 16.856 | 29.100 | 0.999 | 5.183 | 7.201 | 0.999 | 1.390 | 30.681 | 0.999 |
| FLB-500-P | 0.113 | 32.482 | 0.998 | 0.241 | 23.242 | 0.998 | 0.512 | 1.043 | 0.990 | 0.824 | 17.709 | 0.998 |
| FLB-725-RP | 0.112 | 30.687 | 0.998 | 0.280 | 40.782 | 0.999 | 5.843 | 3.065 | 0.997 | 0.745 | 67.241 | 0.999 |
| FLB-725-5%-PG | 0.396 | 80.421 | 0.999 | 1.107 | 163.950 | 1.000 | 39.997 | 57.570 | 0.998 | 0.284 | 9.004 | 0.993 |
| FLB-725-10%-PG | 0.836 | 200.360 | 1.000 | 2.032 | 404.510 | 1.000 | 1.482 | 0.5881 | 0.971 | 26.163 | 6775.501 | 0.999 |
| LWB-500-P | 0.397 | 0.391 | 0.984 | 0.161 | 2.161 | 0.995 | 0.488 | 0.104 | 0.990 | 0.095 | 0.717 | 0.986 |
| LWB-725-RP | 0.296 | 0.283 | 0.990 | 0.574 | 10.366 | 0.999 | 1.408 | 0.268 | 0.993 | 0.443 | 5.185 | 0.994 |
| LWB-725-5%-PG | 3.255 | 3.786 | 0.999 | 4.398 | 87.680 | 0.999 | 4.028 | 3.989 | 0.999 | 0.646 | 13.275 | 0.998 |
| LWB-725-10%-PG | 14.287 | 24.479 | 0.999 | 38.902 | 105.90 | 0.999 | 1.7313 | 6.343 | 0.999 | 0.930 | 33.231 | 0.999 |

^a*k* is the overall leaching rate ($L \text{ mg}^{-1} \text{ day}^{-1}$), and *h* is the initial leaching rate ($L \text{ mg}^{-1} \text{ day}^{-1}$), at time close to 0, while *r*² is the goodness of fit from kinetic parameter fitting. The meanings of the sample labels are given in footnote *b* of Table 1. ^bN/A = not available because the amount of carbon leached is below the detection limit.

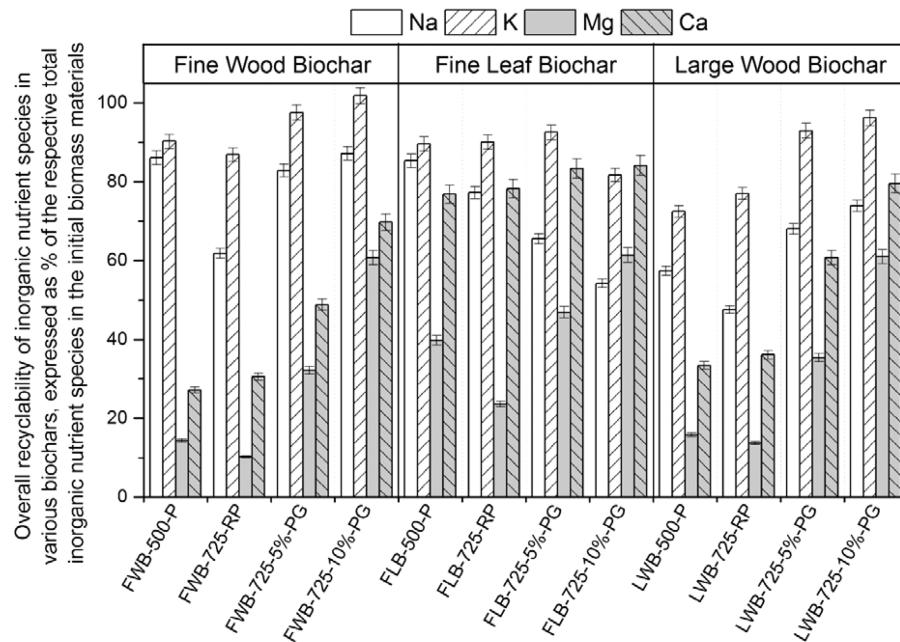


Figure 11. Overall recyclability of inorganic nutrient species in the raw and tuned biochars (measured via leaching by Mehlich I solution), normalized to the respective total inorganic nutrient species in the initial biomass materials. The meanings of the sample labels are given in footnote b of Table 1.

reduction of biochar (instead of biomass) is favored.⁶ It was also reported that direct leaching of inorganic nutrient species from large biochar particles is slow because of intraparticle mass-transfer limitations.²¹ Therefore, the results in this study show that, for tuning purposes, the biochar produced from the pyrolysis of large biomass particles can be first ground into small particles, followed by partial gasification for tuning. This leads to not only a fast process for biochar tuning but also improved leaching kinetics of tuned biochar. Of course, care should be taken during biochar size reduction because extensive grinding leads to the ground biochar containing increased contents of fine particulate matter, which can remain airborne for a significant period of time during soil application and poses a potential health risk to workers and the neighboring environment.⁶²

4. CONCLUSION

Tuning of fast-pyrolysis biochars via partial gasification at low conversion (5 and 10% on a carbon basis) produced highly porous tuned biochars, which are of not only increased accessibility of the inorganic nutrient species encapsulated in the pores during pyrolysis but also with more inorganic species in their more leachable forms. Both lead to enhanced leachability and leaching kinetics of the inherent inorganic nutrient species in fast-pyrolysis biochar but at the loss of 8–23% of carbon in biochar available for sequestration (because of gasification). In addition, the leaching study shows that <1.5% of organic matter (on a carbon basis) in tuned biochar is leachable by water possibly because of the increased accessibility of organic matter trapped within the pore during pyrolysis. Furthermore, tuning biochar via partial gasification also leads to the re-polymerization and/or cracking of aromatic compounds, so that little aromatic compounds can be leached out from the tuned biochar by solvent. A comparison on the overall recycling of inorganic nutrient species in raw and tuned biochars demonstrates that partial gasification at low con-

versions can be employed to tune biochars for enhanced recycling of inherent nutrient species. The results from this study also indicate large particle biochar can be ground and tuned via partial gasification for better nutrient-leaching performance.

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Notes

The authors declare no competing financial interest.

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