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**Effects of Pyrolysis Conditions and Biomass Properties on
Leachability and Recyclability of Inorganic Nutrients in Biochars
Produced from Mallee Biomass Pyrolysis**

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Master of Philosophy
of
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Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgement has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

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Abstract

Using biochar as soil amendment can recycle a majority of inherent inorganic nutrients in biomass to the soil, largely enhancing the overall sustainability of pyrolysis technology. This work investigates the effects of pyrolysis conditions (temperature and heating rate) and biomass properties (biomass component and particle size) on the leachability and recyclability of nutrients in various biochars by water leaching. Understanding these effects would contribute to research of optimising pyrolysis conditions to produce biochars with excellent leachability. Temperature and heating rate have major impacts on the leachability of nutrients in the biochar, but their effects occur in different ways. Increasing pyrolysis temperature seems to affect nutrients transformation within the biochar, where the nutrients become increasingly organically bound. Higher heating rate is likely to lead to physico-chemical changes that result in biochar with nutrients less accessible to the leaching medium. Different biomass components do not have significant influence on nutrient leachability. Particle size is shown to be an important parameter to affect nutrients leachability, mainly due to the mass transfer inhibition during pyrolysis which affects the physico-chemical properties of the resulting biochar. The application of Mehlich I nutrient extraction on a range of biochars indicates more superior nutrients availability and recyclability via dilute acid leaching. Discussion is also provided based on an overall biomass utilisation scheme encompassing biomass growth, biochar production and leaching. Apart from studying the leaching equilibrium of AAEM nutrients, leaching rate models are applied to study the leaching kinetics of the range of biochar. An extension study on the water leaching of carbon is also included in order to provide insight on biochar's potential as a soil amendment agent to achieve both nutrient recycling and carbon sequestration.

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List of Publications

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Chapter 1 Introduction

1.1 Overview

The study presents insights on the suitable production conditions of biochar from the pyrolysis of mallee biomass species in order to obtain a product suitable for enhancing nutrients recycling, soil amendment, and carbon sequestration. Since biochar soil application is a relatively new concept [1], the benefits of biochar utilisation for carbon sequestration and agricultural benefits would also need to be weighed against other options of biochar utilisation in the sustainable energy sector. Effective nutrients recycling to soils would add incentive towards the agronomic and environmental utilisation of biochar. Stable carbon fractions within biochar would also increase the confidence in the carbon sequestration ability of biochar soil applications [2, 3]. This study focuses on sustainable recycling of nutrients in biochars and the leachability (hence availability) of such elements to promote additional cycles of plant growth and harvesting. The leaching of carbon is also included to probe the potential of biochar soil applications to deliver simultaneous advantages of nutrients supply and safe long-term carbon storage.

Current research involves the quantitative and qualitative analysis of inorganic species which focus on Alkali and Alkaline Earth Metallic (AAEM) species such as Na, K, Mg, and Ca. These nutrient species in raw mallee feedstock including wood, bark, and leaf exists as a large percentage (>85%) of overall inorganics [4], and their concentrations in biochar are expected to increase by folds hence demonstrating positive attributes in terms of biochar's nutrient status. Unlike K, Na is not a crucial plant nutrient; however Na quantification allows better understanding on the occurrence and leachability of the similarly monovalent K, and other AAEM species (Mg and Ca), which are indeed essential towards plant growth [5].

A variety of factors are hypothesised to affect leaching behaviour of AAEM nutrients and carbon, including biochars produced from the pyrolysis of various biomass components of large and fine sizes at various pyrolysis temperature and both slow and fast heating rates. The main intention of the study is to identify correlations between a range of biochar types and their respective nutrient leachability, followed by providing guidelines on the overall production and valorisation of biochar from the pyrolysis of mallee biomass species. The key aim is to obtain a product suitable and optimised for simultaneously enhancing nutrients recycling, soil properties improvement, and carbon sequestration.

1.2 Objectives of This Study

This study contributes to improving understanding towards the ultimate goal of returning biochar to soil to achieve environmental and agricultural benefits. The breakdown of the overall objectives is as follows:

1. Arriving at correlations between biochar production process conditions and the nutrient properties (availability and leachability) of biochar as a soil amendment.
2. Understanding leaching equilibrium and kinetics of inherent inorganic nutrients in biochar.
3. Understanding the relative differences in leachability of carbon from biochar produced under a range of biomass components, pyrolysis conditions and particle sizes.
4. Gaining insight on optimal conditions for the pyrolysis of mallee biomass to produce valuable biochar with enhanced nutrient value.

1.3 Scope of This Study

The study investigates the effect of different biomass components and pyrolysis parameters on the leaching of mallee derived biochar. The study correlates the influences of different pyrolysis parameters to variations of biochar properties which affect overall leachability and kinetics; however the detailed mechanisms involved in biomass pyrolysis is not discussed. Furthermore, this investigation is limited to

studies of the standalone behaviour of biochar, omitting any leaching studies of soils or biochar-soil mixtures. This is mainly to avoid the heterogeneous nature of soils potentially introducing significant uncertainties to the study, making the data obtained inevitably unpredictable. The leaching kinetics is also presented by means of a lumped overall model which can satisfactorily describe the leaching process and behaviour of the current range of biochar. The leaching process and mechanisms are discussed in terms of the numerous factors and their governing effects on biochar characteristics and hence leaching rates. The investigation of geographical factors such as climate, rainfall and soil conditions are also not included in the current study, but their importance are included and acknowledged in the discussion.

Chapter 2 Literature Review

2.1 Background

Biochar application to soil is postulated to synergistically support nutrient recycling, carbon sequestration, and soil conditioning [1, 3, 6-10]. Consumption of inherent soil nutrients occurs naturally during biomass growth and these nutrients exist in various components of a biomass source. Mallee biomass and the biochar derived from this feedstock have high contents of AAEM species embedded within their structure which have the potential of being returned to the soil as essential plant nutrients. This aspect of biomass and biochar utilisation is important because it provides a fundamental scheme of recycling nutrients to the soil, as a means of improving, or at least sustaining the efficiency of land utilisation and promoting healthy growth cycles of biomass [11].

Current research embraces the relatively recent hype towards biochar's promising potential of addressing a few pressing issues in the environmental, social, and economical sense. The driving force behind such research is to arrive at numerous economic and environmental incentives from which biochar, when returned to soil, can offer towards various stakeholders. This research would serve to catalyse future research focused on different biomass feedstock or geographical locations. The leaching kinetics data over a range of pyrolysis conditions would directly contribute to the benchmarking the actual potential of mallee biomass as a nutrient provider and soil amender with a myriad of simultaneous benefits. Moreover, it would also help determine parameters with industrial significance when pyrolysis is ultimately performed on a large commercial scale. Pyrolysis of different components (wood, leaf, and bark) from mallee biomass will be conducted in a fixed-bed (FB) reactor and drop-tube fixed-bed (DTFB) reactor under a range of conditions and particle sizes, which have hypothesised influences on subsequent washing investigations. Biochar leaching will be carried out in order to determine the associated equilibrium and kinetics behaviour for the effective characterisation of biochar nutrients leaching

as affected by biomass feedstock and pyrolysis conditions. The associated leaching rates are hypothesised to adhere to exponentially or linearly decreasing patterns.

2.2 Significance of Current Study

Current research serves to offer insights to benefit the application of biochar both as a fuel and soil amender, although being more focused on the latter. For fuel applications, the equilibrium and kinetics data will demonstrate washing effectiveness and any inherent limitations of washing as a fuel pre-treatment technique. For agricultural utilisation purposes, leaching behaviours can provide guidelines on the recycling of nutrients during various soil type applications and also facilitates the benchmarking of such feasibility of the range of biochar studied. Biomass research has been conducted extensively worldwide for decades, however there remains inevitable variations between the wide assortment of biomass categories [1]. Even after narrowing down the biomass selection range to the ligno-cellulosic biomass group, the vast dissimilarities between the cellulose, hemicellulose, and lignin proportions require studying and characterising every unique feedstock source. Therefore, data describing a particular biomass source cannot be easily projected upon another. The application of biochar to soils would depend on the inherent soil properties, which is location specific. The majority of sandy soils in Western Australia are relatively unsuitable for promoting healthy plant growth, and therefore these soils are likely to require a boost in the soil properties for more effective agricultural activities. Mallee biomass has its own unique set of potential to offer the Western Australian community [12]. The perceived benefits of mallee biomass makes it an important asset for Western Australia; however such research is also deemed relevant on a global scale as enthusiasm towards diverse biomass feedstock worldwide are driven by a similar aim of curbing pressing issues of energy shortage, climate change, and widespread hunger. Although the main application from biochar research in this study is targeted at understanding biochar properties upon being returned to soil, another category of biochar application for clean energy generation may be benefited. The inorganic species present in feedstocks contribute to fouling, slagging, and corrosion issues in biomass combustion plants, which threatens the feasibility of such renewable energy

production technology [13]. Understandably, ultimate goals of simultaneous beneficial application demands concrete research findings as there exists strong correlations, which are often self-conflicting, between process conditions and subsequent effects on the product spectrum from the pyrolysis platform. The devising of optimal pyrolysis conditions that generate quality biochars which offer consistent performance largely determines its fate in both the Australian and global sustainable energy field [1]. It is also worth highlighting the overall environmental benefits from the underlying concept supporting this research. Pyrolysis-produced biochar, when applied as a fuel, offsets some fossil fuel usage, and the carbon footprint of biomass utilisation is undeniably lower. Figure 2.1 shows an overview of a sustainable biochar concept. On another note, returning biochar to the soil is a potentially marketable option that will further boost the carbon performance towards an anticipated carbon negative system. In short, this research can serve to fill the gaps of an overall big and optimistic picture, drawing correlations between pyrolysis conditions and performance tailored towards desired applications of the end products.

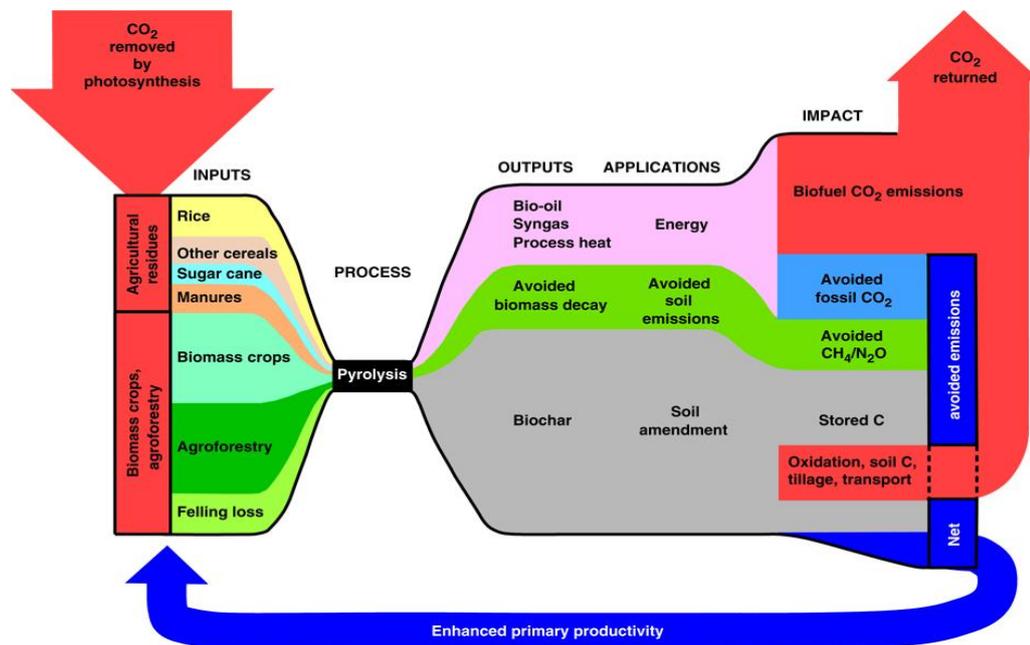


Figure 2.1. Overview of the Sustainable Biochar Concept, adapted from [138].

2.3 Biomass feedstock source for thermo-chemical transformations

There exists a wide range of biomass sources that can potentially be utilised effectively as feedstock for thermal processes that generates a spectrum of useful products and by-products. The most common ligno-cellulosic biomass supply originates from the agricultural and forestry industries. Among these choices, wood is a very common feedstock that has been studied by a myriad of research activities. In contrast, fewer studies have focused on bark and leaf as a pyrolysis feedstock although they form a very significant portion of biomass resource from the agricultural industry [14]. Moreover, the efficient component separation of whole biomass trees is economically challenging, thus large scale and industrially applied pyrolysis will very likely be carried out on majority/all of the components from an entire tree [14, 15]. Furthermore, the different components of a single biomass source leads to biochar products with very diverse characteristics [16]. Therefore, it is imperative to study the individual components of a feedstock source before the collective properties of a whole biomass feedstock and its effect on the pyrolysis process and subsequent utilisation schemes can be understood.

2.3.1 Lignocellulosic Biomass Feedstocks

The properties and internal structures of biomass have been actively researched due to the promising potential of biomass applications. The lignocellulosic biomass comprise of length scales spanning $10^{-10} - 10^1$ m, where the microstructural portions of biomass is known to play essential roles in plant growth and survival [15]. Organic C-C, C-H, C-O, and O-H bonds together with oxygenated and aromatic rings are functional groups that fundamentally form biomass. These gives rise to three biopolymers known as cellulose, hemicelluloses, and lignin. These individual portions pyrolyse and decompose of varying rates according to unique routes and mechanisms [1]. The cellulose and hemicelluloses components decompose faster within a smaller temperature window, whereas lignin appears to be more thermally stable and degrades across a larger temperature range [1, 15]. Apart from the main organic categorisation, biomass also contains relatively lower amounts of organic

extractives and inorganic groups such as AAEM species which have the potential to be recycled to the soil by means of biochar production via pyrolysis [1].

2.3.2 Mallee as a key biomass source

Properties of biochar are strongly determined by the biomass feedstock from which it was pyrolysed, and conditions at which the pyrolysis occurs [1, 17-19]. It is imperative to justify the choice of mallee biomass as biomass sources are often location specific, otherwise its inherent bulky nature [12] would impact the cost effectiveness of its utilisation. Sources of renewable energy have sparked controversy of land rivalry between food and energy production. Also, aggressive reduction proposals on fossil fuel usage would pose threats of energy price spikes; whereas diverting present food or land towards supporting biofuels would amplify the existing problem of widespread hunger, demonstrated by the biofuels boom in 2005-2007 that saw corn prices skyrocketing. Similar issues are not applicable for mallee biomass which initial purpose is as a means for combating dryland salinity [20], thus this biomass production scheme promotes food production instead of upsetting its supply chain. The abundance of mallee biomass produce in Western Australia's Wheatbelt region allows the growth, harvesting, thermo-chemical conversion process, and biochar utilisation to be focused in a relatively small radius, thus reducing problematic issues including transportation of bulky biomass or fragile biochar. Life cycle analysis further increased its value by identifying mallee biomass as carbon neutral source [20]. The utilisation of this biomass feedstock for energy production results in a biochar product which can be returned to the same land it was grown in attempt to achieve soil improvements for further cycles of tree growth and harvesting. The nutrients concentrated in the biochar due to pyrolysis originate from the soil and biomass, therefore this potentially creates a sustainable method for nutrients recycling provided a reasonable portion of the nutrients can be made available to the plant for sustained healthy growth of the mallee biomass trees [8].

2.4 Biochar for Environmental Management

Biochar discussed in this study is generally defined as carbon-rich and porous biomass-derived solid product produced under pyrolysis where there is partial or total absence of gas phase oxygen [21]. The International Biochar Initiative (IBI) defines biochar according to its purpose of being applied to the soil for achieving a range of agronomic benefits [1, 21]. This corresponds to the main purpose of biochar in this study, which is to be returned to the soil for achieving a set of simultaneous agricultural and environmental advantages. Biochar, throughout this study, is defined as the carbon-rich residue from biomass pyrolysis generated for the purpose of carbon sequestration, nutrient recycling and soil amendment. Biochar majorly consists of organic matter, but also contains mineral compounds including SiO₂, CaCO₃, KCl, and CaSO₄, nitrates, hydroxides, and oxides, to name a few [3].

Application for biochar to achieve increasingly fertile soils for improving agricultural activities is a relatively new concept that is known to be retrofitted from Terra Preta in the Amazon basin [1, 19, 22, 23]. Archaeological studies have shown that the Terra Preta soil in central Amazon is evidence of anthropogenic fertile soils. These soils have been created spanning across a millennia and are responsible for the discovery of the multiple perks of biologically and chemically stable biochar application to soils in the modern days [21, 24].

The application of biochar to soils is a research area that has sparked the interest of a myriad of studies. However, its actual implementation scheme is still raw and relatively undeveloped. However, the enthusiasm towards the concept of biochar being returned to soil is a global phenomenon that simultaneously involves climate change, renewable energy capture via pyrolysis, food security, environmental control, organic waste valorisation via soil improvement and soil nutrients recycling [21, 24]. Albeit the promising potential of biochar in this context, it is obvious that the implementation of biochar soil applications will only occur upon the assurance of adequate improvements of agricultural soil productivity and benefits towards overall environmental management [24].

2.4.1 Biochar – Applications

2.4.1.1 Biochar as a renewable fuel

Emphasis on sustainable development issues has developed greatly over the years, and undoubtedly, scrutiny on such issues will continuously intensify. Renewable energy has been in constant limelight since concern was raised over the world's energy future. Western Australia's mallee biomass offers a competitive energy ratio, when benchmarked against other energy crops such as Canola [25]. This energy ratio is the ratio of energy produced by the biomass to energy used in the production and processing of the biomass, both directly or indirectly. Biomass pyrolysis converts biomass into bio-oil and biochar while the pyrolytic gas can be used to supply energy for the pyrolysis process. While bio-oil can be further upgraded and refined for liquid biofuels production, biochar is a solid product with characteristics drastically different to the original biomass. Biochar also has significantly higher volumetric energy density than raw biomass, hence incurs lower transportation and storage expenditure [12]. The increase in energy density via pyrolysis is also more significant than the improvements achieved by optional pre-treatment methods such as pelletizing and torrefaction [26]. Grindability of biochar is also increased which makes size reduction for further utilisation such as gasification more economically feasible [12].

2.4.1.2 Biochar as a soil amendment

As mentioned above, biochar, just like its pyrolysis product counterparts (bio-oil and pyrolytic gases) possesses a reasonable energy value. However, this renewable energy potential can potentially be offset by the interest towards biochar's unprecedentedly promising potential of improving soil nutrient status, hence overriding its relatively conventional application as fuel. This is further proven via preliminary energy balance and emissions studies [25] and is of much significance because it is not often that novel and promising ideas for 'reversing' climate change is widely proposed and endorsed [1].

(a) Carbon sequestration

Although agricultural land involves a relatively low portion of the total global carbon pool; this fraction is an important proportion of the atmospheric carbon flux.

The effective management of agricultural land can serve to reduce emissions and create a more carbon-friendly agricultural system. Biochar contains carbon that has been stabilised via thermo-chemical transformation, hence can potentially be beneficial towards climate change alleviation [21, 24].

To date, the chief motivation for biochar application to soils is for addressing the global warming predicament [1]. The efforts, or lack thereof, to combat this predicament becomes intricate due to social, economical, and political constraints. Over the past decade, compromises have been drawn between industries and policy makers, which in retrospect, have all under-emphasised the urgency of more drastic actions to curb high anthropogenic greenhouse gas levels. This signals the pressing need for a climate change solution where mitigation does not come at the expense of social and economic growth, which in turn justifies the recent hype of returning biochar to soil as a mean of long-term carbon sequestration. Biochar is postulated to offer significant carbon sequestration in terms of gigatonnes per annum, and the recalcitrant nature of biochar offers delay before the carbon re-enters the overall carbon cycle [1, 27]. In particular, the synergetic benefits of biochar utilisation including clean energy generation and carbon sequestration in Western Australia is promising; however the immaturity of such technology and policies is emphasised [1, 28]. Mallee biomass earned the title as a carbon neutral fuel via lifecycle analysis [29]. It is reasonable to welcome the possibility that this characteristic, once combined with an economically feasible technology of stably adding mallee biochar to soil, would locally deliver an overall carbon negative system. This brings forth the emergence of a promising hypothesis for biochar utilisation for environmental management.

(b) Soil Productivity and Nutrients recycling

Actual field studies on the effect of biochar addition to soil have shown conflicting conclusions, which prove that the establishment of biochars performance in general is difficult due to varying geological factors such as climate and soil type. The biochar production parameters such as biomass feedstock and pyrolysis conditions [21] deviate significantly between investigations. However, the application of

biochar to soils has been shown to result in crop yield improvements through possible combinations of pathways such as the increase of nutrient use efficiency via direct nutrient supply or better retention of conventional fertiliser supplied nutrients [7, 21]. The immediate and short-term improvement of soil fertility is attributed to the direct addition of plant available inorganic nutrients, and the longer term advantages are dependent on a complex mixture of the biochar's physico-chemical properties.

Consumption of inherent soil nutrients occurs naturally during biomass growth. This study focuses on sustainable recycling of such nutrients by promoting both nutrient retention in biochars and the leachability (hence availability) of such elements to promote additional cycles of plant growth and harvesting. Apart from carbon, the inorganic fraction of biochar, in particularly AAEM species is concentrated and enriched during the process of thermal degradation. Because this corresponds to essential macro and micro nutrients for plant growth enhancement, it represents a direct benefit of biochar-amended soil [1, 19, 22]. Nutrient contents and availability in biochar are directly related to the composition and structure of biochar, which are in turn sensitive to variations in biomass properties and biochar production conditions. Such correlations are currently vague, hence posing challenges on the effort of benchmarking biochar's performance in the agricultural sector. It is imperative to understand the associated sensitivity towards variations of each factor of interest, hence further emphasizing the significance of this project.

(c) Soil conditioner

Literature has postulated that biochar improves fertiliser-use efficiency, soil structure, CEC (cation-exchange-capacity) [30], acidity levels [31], and capacity of holding water and nutrients due to its high sorption capacity [5, 19, 32-34]. Biochar is also known to display sorption properties that make them potential efficient low-cost pollutant sorbents [1, 35]. There is a very wide range of biochar properties produced under different conditions. Intricate chemical reactions during thermal degradation complicate the process of performance benchmarking. There is, however, strength in such diversity because biochar has the potential to be prepared under optimum

conditions in order to cater for a specific application and addressing specific soil conditions and/or climate.

2.4.1.3 Slow and Fast Heating Pyrolysis as an Important Thermo-chemical Conversion Process

Pyrolysis is a thermal conversion method that thermally degrades and transforms biomass under an inert, anaerobic environment into a porous carbon structure called biochar, together with condensable vapours (bio-oil) and non-condensable gases [1, 36]. The primary pyrolysis process is of endothermic nature, whereas the secondary pyrolysis process is exothermic [36]. This overall endothermic process forms an important and integral part of a sustainable integrated agronomic biomass-bioenergy scheme [1, 5, 37], and is a key thermal conversion process in biomass utilisation. Potential applications of the biochar in either the energy or agricultural sector have a common advantage of achieving a more sustainable renewable energy future. However, a myriad of available pyrolysis technology exists, each with individual time-temperature profiles, thus often resulting in considerably diverse biochar products. Slow heating pyrolysis is a relatively conventional form of pyrolysis where there is a low heating rate and long vapour residence time. Key parameters affecting slow pyrolysis are temperature, partial pressure, and vapour residence time. The prolonged vapour residence time in the pyrolysing biomass particle tends to result in a significant increase of secondary reactions, such as the decomposition of pyrolytic vapours on the biochar surface. This effect is amplified in the case where the sweeping gas rate through the particle bed is insufficiently high [21].

Fast heating rate pyrolysis is a more advanced thermal conversion process which is well-controlled to provide significantly higher heating rates ($>100\text{K min}^{-1}$) and shorter vapour residence time [15, 21]. Due to the very high heat transfer rates required during the fast heating process, the pyrolysis feedstock is limited to only fine-sized biomass. Under rapid heating conditions, the biomass degrades to form a majority of vapours and aerosols compared to solid biochar [15]. Bio-oil production demands low pyrolytic vapour residence time in order to reduce the occurrence of secondary reactions that lower the production of pyrolytic liquid. The effect of longer vapour residence time is essential in terms of inducing secondary volatiles degradation at temperatures above 500°C and possible vapour condensation at lower

temperatures [15]. The bio-oil produced from fast heating pyrolysis is a miscible compound of polar organics and water. The fast heating pyrolysis thermo-chemical conversion route can potentially offer logistical and economic benefits because the liquid-product can be stored and transported in an energy dense form to locations where it can be utilised [15]. Due to the main objective of fast heating pyrolysis being to yield maximum bio-oil, the temperatures for fast pyrolysis is commonly maintained around 500°C for the optimum production of bio-oil at the expense of the solid biochar and gaseous products [15, 21].

2.5 Key Factors during the Production of Biochar via Pyrolysis

As shown in figure 2.2, inherent biomass properties (different components of a single biomass) and pyrolysis conditions (temperature and heating rate) are factors that affect the characteristic of the produced biochars [1, 34, 38-41]. There is a very wide range of biochar properties produced under different conditions as intricate chemical reactions during thermal degradation give rise to heterogeneity which extends to the microscopic scale [1]. It is worth noting that although each key factor including pyrolysis temperature, heating rate, biomass component and particle size have various impacts on the resulting biochar and subsequent applications, these factors often overlap and are best understood as a complete intricate multi-phase thermo-chemical process.

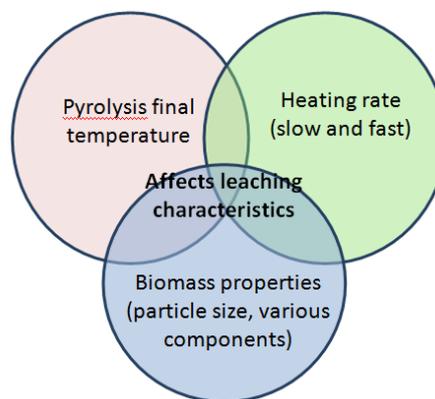


Figure 2.2. Significant pyrolysis parameters affecting biochar properties and nutrient and carbon leaching characteristics

2.5.1 Pyrolysis Temperature and Heating Rate

Pyrolysis temperature and heating rates are among the major factors influencing biochar characteristics, as these factors dictate the release of volatiles and biochar formation routes [10, 39, 44-46]. These effects from transformations during pyrolysis are expected to be extended biochar nutrient leachability/recyclability and carbon stability. There is a general observation of increased biochar surface area and pH with respect to the increase of pyrolysis temperatures. On the other hand, volatile matter, surface acidic functional groups, and cation exchange capacity are reduced [47]. The reduction in acidic functional groups on biochars surface are mainly attributed to the loss of aliphatic carboxylic acids, which has been proven by Boehm Titration data and Attenuated Total Reflection Fourier Transform Infrared Studies (ATR-FTIR) [47].

Differential Scanning Calorimetry (DCS) studies indicated the transformation of biochar into an increasingly recalcitrant and aromatic compound due to the diminishing of labile aliphatic portions [3]. The DRFIT spectroscopy method was also used to arrive at similar findings that the progression of temperature results in biochars surface acidic functional groups and aliphatic alcohol to be transformed into neutral or basic fused aromatic rings [47, 48]. The bulk chemistry modifications probed by ^{13}C MAS NMR spectroscopy also observed that higher pyrolysis temperatures promoted higher aromatic C and lower alkyl C concentration in the biochars. The pyrolysis process removes the alkyl and O-alkyl groups inherently in the raw biomass and this reduction is promoted at higher biochar production temperatures. There is also shown to be a prevailing increase of the conjugated nature of aryl groups that goes hand in hand with a more aromatic dominant compound [47].

Moreover, the observation of the loss of volatile matter from biochar had strong correlations with the increase in micropore and nanopore surface areas indicated that prior to heating those pores were filled with the volatile matter substance within the biochar framework [47]. This portion of volatile matter is also postulated to form the fraction of carbon most inclined to being leached by water, as the dissolved organic carbon had very strong correlations with acidic surface functional groups and volatile

matter content [49]. An increase in pyrolysis temperature is also shown to increase the surface area of biochar [3] which is likely due to the progressive volatilisation process that occurs as pyrolysis temperature is raised [1]. The voids formed upon the release of organic volatile compounds enhance the surface area within the biochar matrix. On the other hand, a reduced surface area can result from lower pyrolysis temperature biochar due to blockage of pores which occur more extensively from the promoted condensation of volatiles [50].

It is known that the economic feasibility of bio-oil production from pyrolysis would be greatly enhanced if the solid biochar residue is characterised as a value-adding product [1, 15, 51]. Another potential option would be to recycle the biochar product to fuel the overall endothermic pyrolysis process itself [51, 52]. Fast heating pyrolysis results in biochars with vast diversity, possibly due to the difference in extents of thermal limitations and heat transport [10]. Rapid heating production conditions introduces drastic variations from the more conventional slow pyrolysis conditions and produces a very different biochar product [53], therefore separate characterisation of leaching behaviour of each biochar type is required [1]. A significant effect of heating rate is a reduction in biochar production accompanied by an increase in tar yield [36]. Moreover, a rapid heating rate up to ~ 10,000 times higher than slow pyrolysis conditions favour rapid devolatilisation that leads to reactive biochar [1, 17]. This trend is consistent over a range of feedstock [51, 54], and is of interest towards the context of integrating bio-oil and biochar production as bio-oil is favourably produced under high heating rate conditions.

2.5.2 Inherent Biomass Properties – Different Components and Particle Size

As mentioned earlier, the wide range of biomass feedstock results in biochars with vast characteristics as the physico-chemical structures are naturally different. The impact of feedstock particle size is also an important consideration during biomass feedstock pre-treatment, mainly due to grindability issues associated with biomass feedstock which can potentially lead to significant economic constraints on biomass pyrolysis. Overall, the increase in biomass particle size leads to an increase in biochar yield. Numerous studies have reflected the effect of particle size through variations in yield, where biochar production increases with respect to particle size [1,

17, 18, 36, 55]. The pyrolytic volatiles diffusion rate is expected to be lower within larger particle size biomass, therefore this reasonably promotes the rate of secondary char formation [21].

Biomass is known to possess low thermal conductivity. This property, coupled with a larger feedstock particle size results in overall lower heating rates. This in turn induces higher biochar formation as the internal catalytically active biochar results in extensive cracking of the primary pyrolytic vapour [15]. Differences in particle size of biomass pyrolysis and biochar leaching may lead to varying behaviours due to both heat and mass transfer effects. This strong association with heat and mass transport phenomena means particle size selection is dictated by the nature of pyrolysis conducted. For example, large particle sizes applied to fast pyrolysis would impede heat and mass transfer which explains why feedstock for such pyrolysis needs to be sufficiently pulverised to achieve effective thermal conversion. Slow pyrolysis, on the other hand, is more accommodating towards larger particles. However, in both cases, the inwards transport of heat and the outward transfer of volatiles pose restrictions on the pyrolysis reactions. This effect is, however, strongly dependent on the accompanying temperature, as both factors determine the extent of thermal gradients and incomplete reactions at the particle core [56]. Experiments on thermally thick biomass samples which documented the intra-particle temperature history [57] indicated that a higher pyrolysis temperature corresponds to a steeper intra-particle thermal gradient which occurs for a shorter period. For the same sample, temperature increase at different locations within the sample occurs slower for lower reactor temperatures as the corresponding heat flux supplied is smaller. In terms of the leaching process, diffusion effects arising from larger particle size samples may lead to relatively slow and prolonged release of the nutrients compared to leaching from finer particles sizes [58].

2.6 Influence of pyrolysis on various Biochar Applications

2.6.1 Transformation of AAEM species during pyrolysis - Nutrient Content and Leaching Behaviour

Nutrient content and availability in biochar are directly related to the composition and structure of biochar, which are in turn sensitive to variations in biomass properties and biochar production conditions. Although certain nutrients are largely retained and concentrated in biochar due to pyrolysis, this does not guarantee maximum availability as they may have been transformed to a non-extractable fraction [10, 35]. Alkali and Alkaline Earth Metallic (AAEM) species act as catalysts for biomass decomposition and biochar formation. These species also influence pyrolysis chemistry and the distribution of pyrolysis products [21]. These species are also generally retained in the mallee biochar following pyrolysis. These nutrient species emanating from the mallee trees components are generally high; however, this does not have a direct relationship with the subsequent biochar's nutrient recycling ability. Therefore, the concentration of nutrients in the raw mallee biomass is unable to give insight regarding the derived biochars' nutrient value.

Under milder pyrolysis conditions including lower temperatures and heating rate, the AAEM species are largely retained within the biochar matrix after being thermally mineralised [8]. The study of X-ray Diffraction peaks from biochars of different pyrolysis temperatures indicates that the occurrences and forms of the inorganic species such as potassium and calcium undergo temperature-dependent transformations. The pattern of appearance and disappearance of peaks signifies that the mineral crystals are transformed with respect to the increasing pyrolysis temperature [34]. The extents of devolatilisation and carbon removal during pyrolysis also differs significantly between different pyrolysis methods and heating rates, thus directly contributing to a large variation of nutrient concentrations and availability within the biochar.

During pyrolysis, the original nutrient content and forms, coupled with the chemical structure undergo drastic transformations which results in a carbon rich product with a possible different distribution of inorganic species [59]. Intricate reactions that occur during pyrolysis are categorised into primary and secondary reactions; the extent of these reactions depend on inherent biomass properties and pyrolysis

conditions [44, 60-63]. Different pyrolysis conditions thus produce biochar with diverse physical and chemical structures; the biochar morphology varies and their surfaces exhibit varying extents of hydrophobic, hydrophilic, acidic, and basic properties [9, 64, 65]. Therefore, the combined effect may lead to significantly different leaching behaviours of nutrients and carbon from such biochars when returned to the soil. Correlations between these production conditions and nutrients recyclability are currently vague [35], hence posing challenges on the effort of benchmarking biochar's performance in the agricultural sector.

Liberation of alkali during pyrolysis has been studied over a range of biomass sources and proven to be strongly dependent on the natural biomass structure [13, 66]. Most of these studies [13, 62, 66] were focused on the release of alkali metals; however the release and retention of divalent alkaline earth metals are of equal importance in the context of biochars' performance as a soil amendment. Research also shows that percentage retention of the alkaline earth metals is higher as opposed to the alkali metals [62]. This agrees to K volatilisation results from wood-based biochar which occurs between 700°C - 800°C; whereas Mg and Ca has been found to volatilise above 1000°C [1]. Keown et al. [60] shows the positive effect of a continuous forced flow of gas through the char bed on the enhancement of alkali release, where any freshly formed volatiles would be diluted and swept out hence prohibiting secondary reactions. Another study investigated the consequence of large samples which promotes secondary reactions of char and volatile alkali species formed within the particle [67]. Similar conclusions are drawn with a separate investigation [60], which suggest that resistance to diffusion tends to inhibit alkali liberation – each in the inter-particle and intra-particle sense, respectively. The aforementioned secondary interactions have been postulated by another study [65] to behave as recurring adsorption and desorption of volatile alkali between char and the vapour phase. The net alkali release is thus reduced in the case where diffusion limitations prolong the escape time of each individual species. Liberation of K and Na from pyrolysis of rice straw has been studied over an extensive temperature range (400-1373°C) [68]. Vaporisation-induced lost upon 673°C resulted in a remaining fraction of K and Na of approximately half their initial values; whereas a temperature approaching 1373°C gave a slower liberation that summed to a 70% total loss. Results indicate a large proportion of K that was in plant available forms prior to

pyrolysis were lost; where the remaining consisted mainly of acid extractable or ion exchangeable forms [1].

Micro-physical characteristics of biochar are also dominant in providing access routes for solutions to access the interior of biochar. This affects the transport of soluble species and therefore the biochar nutrients availability and leachability. Although the resulting biochar physical properties are strongly dependent on the feedstock nature, the pyrolysis process may induce tar deposition or significant secondary reactions that alter the pore structure and connectivity of the biochar. These reactions are in turn directly relevant to the selection of suitable pyrolysis parameters. Moreover, high ash content biochars coupled with low production temperatures are more likely to contain surface defects and sub-grain boundaries. These provide specific locations for occurrences of liquid and gas reactions, thus enhancing dissolvability of inorganic species [1]. Porosity is an important structural effect arising from pyrolysis temperature, which has been shown to increase with respect to temperature. Postulations suggest nanopores are generated from liberation of water molecules through dehydroxylation, which promotes pore formation [69].

Similar to pyrolysis, mass transport phenomena during washing is heavily dependent on particle size where chemical reactions may dictate leaching rates for pulverised samples, whereas mass transfer are postulated to become rate limiting for similar samples of larger sizes [57, 70] . Therefore, it is also desired to extend particle size investigations on pyrolysis products towards biochar leaching characteristics.

2.7 Biochar Washing/Leaching Pertinent to Current Research

Compared to biomass/biochar washing, the washing of coal raw feedstock, char, and ash has been studied quite extensively with the aim of enhancing fuel quality such as boosting thermal values [71, 72]. Heating values generally increase with respect to decreasing ash content as a result of fuel washing [73], and occasionally, feedstock are completely de-mineralised by applying strong acids which may have damaging impacts on feedstock structure. On the other hand, there exists fewer studies on biomass washing [13, 73-77]; whereas there is a noticeable lack of research on biochar washing [70, 77, 78]. Biomass washing has been performed globally on a

range of location-specific biomass types, which is typical of biomass utilisation. Regardless of the difference in washed material, the common goal is as a pre-treatment for fuel quality improvement which relates both to thermal values or maintenance issues as biomass fuels often cause slagging, deposit formation, and catalyst deactivation during biochar combustion. The removal of inorganics from biomass also lowers the production of acidic gasses, toxic dioxin and furan generation, and corrosion during its utilisation for fuel purposes [70, 73, 74, 78, 79].

Batch leaching experiments are popular [13, 70, 73-75, 78, 80], whereas continuous washing processes in literature are limited [81]. The major factors that determine the biochar nutrient leaching properties is related to the inherent chemical nature of the species and the physical association with the biochar [49]. Leaching data offers insight regarding the association of an element with organic and/or inorganic matter; where this association can be loosely categorised into chemical bonding or mere physical attachment. Phenomena such as internal encapsulation and surface abundance of a certain compound affect both the equilibrium and kinetics of leaching. A study on straw char [70] indicated that K release exhibited a rapid primary release, followed by a secondary release of a much lower rate. This agrees to results of Fixated Flue Gas Desulphurisation Material leaching, which is described as a heterogenous non-catalytic process affected by a range of phenomena including mass transfer, dissolution, adsorption, and complexation [81]. Washing performed on straw chars by Jensen et al. [70] included the correlations between pyrolysis parameters and extraction rate of potassium. The study included the effect of two different temperatures and heating rates, where the chosen values were pertinent to the utilisation of biochar as a combustion fuel. The total release of these elements are proven to be less and also slower from chars compared to raw biomass, which indicates stronger bonding resulting from thermal degradation and biochar matrix rearrangement [70]. The release of potassium by leaching was shown to have a portion of fast release, a fraction of slow release rate, and a smaller fraction that is unresponsive to water leaching. Potassium on the surface of the biochar was also observed and possibly explains the rapidly released fraction. Another portion of potassium is dispersed within the biochar interior matrix and would lead to the secondary released fraction. The authors [70] also attributed the leaching rate to be generally diffusion limited, as experiments conducted over 24 hours indicated

continual release of potassium from the biochar studied. The initial potassium content of the leaching medium was also shown to have an effect on the maximum extractable potassium from the biochar, thus indicating the importance of a suitable solid to liquid ratio during leaching experiments. The study was also conducted using various particle sizes, however the particle size reduction and fractionation process was carried out after the biochar has been produced by pyrolysis. Therefore the particle size of biomass feedstock input into the pyrolysis process is similar for each experiment. It is also essential to identify the effect of particle size during biomass pyrolysis and its subsequent effects on the biochar product which in turns relates to the leaching characteristics. This takes into account the complex pyrolysis reactions affected by variations in sample particle size. The overall leaching kinetics is dictated by a rate limiting step which is unique in each case; plausible examples are such as pore diffusion, bulk diffusion, or surface chemical reactions [13, 70, 81]. Overall, the leaching techniques used to estimate the nutrients and carbon removal from biochar showed that water extraction could provide sufficient and effective means for making comparisons between different types of biochar, and could present reasonable estimations of carbon released on a long-term basis [49].

2.8 The Research Gap of Biochar Leaching

Research interest to date has rarely focused on biochar's nutrient status, but instead revolves around its energy potential. Moreover, studies that attempted to determine the relationship between biochar application and crop responses often lack data regarding nutrient content [1]. Thus, available literature is patchy; and more importantly no studies have specifically addressed mallee biomass as a feedstock towards the big picture of curbing global warming and generating agricultural benefits. A lack of equilibrium and kinetic studies, both in the context of biomass/biochar leaching for fuel or agronomic applications poses challenges on the effort of benchmarking biochars performance in the agricultural sector.

To date, the research on biochar application for the purpose of environmental management has been largely focused on the characterisation of physical and chemical properties including chemical composition, porosity, surface area, and surface functional groups. There also exist studies that probe the relationships

between the chemical and physical morphology [81] These attempts of effective biochar characterisation can present challenges due to the nature of biochar of being buoyant and containing high microporosity. However, these have led to a general understanding regarding the effect of the biochar production process on the properties of the derived biochar – for example, the increase in pyrolysis temperature under the absence of oxygen will result in biochar with higher porosity but lower surface acidic functional groups. The widespread research on such correlations is helpful for understanding the range of biomass pyrolysis conditions that would be suitable for specific soil amendment or stable carbon storage purposes. However, this does not dismiss the need for studies of biochar's performance as value-adding potential to a single application.

Biochar is a compound of very heterogeneous physico-chemical properties, thus characterisation by analytical parameters measurement alone is unable to serve as a representation and prediction of the nutrient release properties [49]. Moreover, results of biochar soil applications are largely dependent on the physical characteristics of the biochar including abundance of pores and internal pore networks. Therefore, this means the findings from elemental analysis and chemical based extractions are less relevant to the accurate estimation of biochar soil application behaviour.

There is a lack of methodical studies that indicate the effect of pyrolysis process parameters on the availability of mineral nutrients in the produced biochar and the effects on plant growth [21, 24]. As aforementioned, studies on biochar washing are limited, reasonably indicating that relationships between pyrolysis parameters and washability are not thoroughly understood. Due to relative recent increase in interest for the potential application of biochar as a means of soil amendment, there has been some research on washing/leaching of biochar with the main purpose of understanding biochar role as plant nutrients supplier, and makes predictions for the long term behaviour of biochar in the soil [8, 49]. Some studies avoid the incorporation of actual soil into the experiments and include the study of a range of biochar produced from various biomass feedstock and biochar production conditions. Other research have focused on actual field studies, including the incorporation of biochar to soil followed by observing and evaluating the positive effects of biochar application on crop growth and yield, as well as other factors that constitute healthy

and fertile soil [1, 82-86]. However, these studies are governed by intricate interactions between the added biochar and soil and the surroundings in general. Majority of the studies have shown improvements in plant yield, however some other studies have shown a negative effect on crop life [1, 7]. The heterogeneous nature of soils complicates the effort for obtaining consistent results to identify the behaviour of biochar as a soil fertiliser / conditioner. The combination of numerous possible effect from biological and physico-chemical factors on both the positive or negative consequences are not thoroughly understood. Therefore, studies on batches of relatively homogenous biochar in the absence of actual soil would be able to exclude the uncertainty caused by soil's heterogeneity, thus serving to provide insight upon the actual behaviour of biochar due to the effect of varying feedstock and production conditions.

The biomass/biochar leaching experiments available in literature are carried out in batch experiments, sequential washing of the solid to obtain cumulative results, and also column leaching processes. The biochar leaching investigations performed in this current study contributes to the research of biochar agricultural applications, where the nutrient release patterns can provide a broad understanding over a range of unique feedstock components and biochar production conditions. This possibly allows the initial understanding of behaviour of similar feedstock or biochars not yet studied, and simultaneously facilitates educated guesstimates during the selection of biomass sample categories and variety which in the future need to be applied for actual large-scale agronomic experiments [8]. This increases the overall efficiency and economic feasibility of future trials.

In terms of the kinetics modelling of biomass/biochar leaching, there exists a range of studies on the absorption kinetics for the purpose of contaminant removal from a solution [87-89]. Suitable kinetics models are required to accurately describe the leaching processes and be used as effective benchmarks for the leaching rates comparisons between biochar formed under a range of conditions from different feedstock species.

For the effective characterisation and benchmarking of biochars agronomic performance, a widespread amount of knowledge is required beforehand. The majority of research carried out globally since the beginning of the 'biochar

revolution' has lacked unified conclusions or benefit assurance. Biomass feedstocks and the specific needs of applications outcomes are unique to geographic locations and crop growing methods. This study is performed focusing on Western Australian mallee trees that play an essential role in managing dryland salinity in the Wheatbelt region. Specific studies on mallee biomass derived biochars are required for its advantages to be applied locally for achieving nutrient recycling and carbon sequestration objectives.

Chapter 3 Experimental Section

3.1 Biomass and Biochar Preparation

Mallee biomass (*E. loxophlebalissophloia*) were prepared via the components (wood, leaf, bark) separation, drying, milling for size reduction, and sieving for size fractionation to fine (150-250 μm for wood and leaf, <250 μm for bark with 80% in the size fraction of 150-250 μm) and large (2-4mm for wood) size fractions. The grinding of the three components (wood, leaf, and bark) were carried out in a cutting mill mounted with different sized sieves to obtained a mixture of fine biomass particle, which were later sieved separately into their individual sized fractions.

Biochars were prepared from the pyrolysis of biomass samples of different sizes under both slow and fast heating rates. For slow pyrolysis biochar preparation, a fixed-bed quartz reactor was employed, and a detailed procedure can be found elsewhere [90]. Briefly, the raw biomass was loaded into a tubular fixed-bed quartz reactor, and then heated at 10 K min⁻¹ to a desired pyrolysis temperature (300, 500, and 750 °C) and held for 15 min, under ultra-high purity UHP argon (purity >99.999%). For fast pyrolysis biochar preparation, a similar reactor was employed as a drop-tube/fixed bed reactor, following a procedure detailed elsewhere [91]. Briefly, the fine biomass samples were continuously fed into the reactor, which was preheated to a desired temperature (500 °C), at a feeding rate of around 120 mg min⁻¹ for approximately 10 minutes. During experiments, the biochar particles were retained in the reactor by a quartz frit, allowing the pyrolytic vapours and gasses to escape the reactor via the porous frit. Once the feeding was completed the reactor was immediately lifted out from the hot furnace to rapidly quench of the biochar.

3.2 Biochar Water Leaching

Approximately 1 g of biochar was immersed in 1 L of Milli-Q water (>18.2 M ohm). The bottle was covered and the mixture was stirred gently via magnetic stirrer bars. Washing parameters such as stirring rate and temperature are held constant to ensure constant leaching hydrodynamics. Stirring rate is kept sufficiently high to overcome major liquid film mass transfer resistance, yet should not lead to excessive attrition. This is due to biochar being more friable than the original biomass, following the trend of decreasing tensile strength of the pyrolysed products with respect to increasing pyrolysis temperature [1]. Stirring provided agitation to reduce mass transfer limitations resulting from liquid film diffusion and packing of the micron-sized particles. The high liquid to solid ratio eliminates the possible saturation effects that may pose limitations on maximum leachability and leaching rate. Leachate sampling was carried out at intermediate times using a syringe needle to minimize solid loss from the solution throughout the experimental period. After filtering the samples through a $0.45\mu\text{m}$ syringe filter, quantitative analysis of the biochar leachate was performed. Washing batches are carried out for sufficiently long periods until equilibrium or near-equilibrium conditions are achieved, which is identified as the maximum possible extraction under constant conditions.

3.3 Mehlich I Extraction of Plant Available Nutrients

In order to identify the portion of plant available nutrients in the range of biochars studied, Mehlich I extraction (0.05N HCl and $0.025\text{N H}_2\text{SO}_4$), also known as dilute double acid (DDA) extraction, was performed. This method is well established in the field of soil science where the nutrients availability in soils are determined and used to benchmark soil productivity [19]. The same conditions for water leaching were applied to the leaching experiments of biochar in the Mehlich I dilute acidic medium. Due to the inherent variations between both physical and chemical properties of biochar and soil, a slightly modified dilute double acid extraction (Mehlich I) method [19, 33, 65] was carried out on the set of biochar samples. Mehlich I extraction in practice is usually carried out on soils for a shorter time-frame within minutes. However, the total leaching period was extended to 24 hours [49] to eliminate time-

controlled mass transport factors possibly arising from biochars porous structures compared to soils, and to ensure leaching approaches equilibrium. This allows a direct comparison of the respective leachable fractions of nutrients in water based and dilute acid based leaching mediums, hence providing insight upon the fraction of water leachable nutrients in relation to the dilute acid extractable fraction.

3.4 Instrumental and Analytical Techniques

Proximate and Ultimate Analysis

The proximate analysis of the biomass and biochar samples was carried out with a METTLER Thermogravimetric Analyser (TGA) according to ASTM E870-82 [137]. Approximately 10 mg of sample was placed into a TGA μ L crucible and purged with Argon for 15 minutes. The sample was then heated to 110 °C for 20 minutes until no further weight loss was observed. This weight loss represents the moisture content of the sample. After that, the sample was further heated to 950 °C at a heating rate of 50 K/min in Argon and held at the temperature for 20 min. The temperature was then decreased to 600 °C. This weight loss represents volatile matter, and the remaining sample represents char. This remaining char was then oxidised in air for 30 minutes until no weight loss was observed. The ash content of the sample is calculated based on the remaining ash in the crucible. The difference in weights between the char and residual ash represents the fixed carbon of the sample.

The content of carbon (C), hydrogen (H) and nitrogen (N) of all the samples were determined with an elemental analyser (Model: Perkin–Elmer CHNSO 2400 Series II), whereas the oxygen (O) content in the samples was determined by difference on a dry and ash-free (daf) basis.

Fourier Transform Infrared Spectroscopy

The raw biomass and raw biochars were analyzed using a Perkin-Elmer Spectrum 100 ATR-FTIR spectrometer. Briefly, a sample was ground into powder using an agate mortar and then air-dried overnight in an oven at 40 °C before each analysis. Scanning of each sample was conducted at a resolution of 2 cm^{-1} . The relative

intensities of the spectra allow semi-quantitative analysis on the functional groups, as each run was conducted with a comparable amount of sample in contact with the diamond, coupled with a constant force of 80N being applied on the sample. Basic data processing included ATR correction, baseline correction, and automatic data smoothing.

Quantification of Inorganic Species

The AAEM species in the biomass and biochar samples were quantified via ashing, acid digestion and analysis by ion chromatography an (IC) Model (Dionex ICS-3000). Firstly, approximately 20 mg of sample was placed inside Pt crucibles. AAEM species were analysed by firstly ashing the sample in a muffle furnace. The flow rate of air into the furnace was 2 L min^{-1} and the ashing program was designed to minimise losses of the species to be quantified. The ash samples in the Pt crucibles were then digested in the mixture of HF acid and HNO_3 acid, which is a solution of $\text{HNO}_3 : \text{HF}$ (1:1) at 120°C for 12 hours. The digested samples were dissolved in 0.02 M methane sulphonic acid (MSA).

The AAEM species in the digested samples were quantified by an ion chromatography system. In order to calibrate the instrument, a six-cation (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) standard solution purchased from Dionex was used. This solution was diluted with 0.02 M MSA to a range of concentrations that are suitable for the actual samples analysed. These standard samples were used to generate linear calibration curves which in turn were used for identifying the concentration of AAEM in the studied samples. The separation in the ion chromatography system is achieved via IonPac CS12A 4 x 250mm column and IonPac CG12A 4 x 50mm guard column with 0.02 M MSA as the eluent. The IC system was equipped with electrolytic suppression and conductivity detector. The leaching experiments were performed at least twice and analysed using the above procedure. The relative standard error for AAEM leaching and recyclability is $\pm 5 \%$.

3.5 Quantification of Dissolved Carbon in Leachates

The total amount of organic matter leached from biochars is quantified as total organic carbon (TOC). The TOC content in biochar leachates was analysed using TOC analyser (Shimadzu TOC-V_{CPH}). HCl was used for the acidification of biochar leachates to pH 2-3, followed by the sparging of each leachate in order to remove any inorganic carbon before the quantification of carbon is performed. Similar to the analysis of inorganic ions using Ion Chromatography, standards are run and calibration curves are obtained prior to the detection and quantification of carbon in biochar leachates. The relative standard error for carbon leaching is $\pm 6\%$.

Chapter 4 Effects of Pyrolysis Conditions and Biomass Properties on Leachability and Recyclability of Inorganic Nutrients in Biochars Produced from Mallee Biomass Pyrolysis

4.1. Introduction

In the current carbon-constrained world, biomass is considered as one of the important resources that can make substantial contributions to future energy supply, due to its abundant availability worldwide [92]. Direct use of biomass as a fuel is largely hindered by its poor fuel properties, i.e., high moisture content, bulky nature, poor grindability, etc [93]. Among the current technology for biomass utilization, pyrolysis is a cost-effective and energy-efficient process to convert biomass into biochar and bio-oil, while bio-oil can be further upgraded into drop-in transport fuels [94]. Biochar, as a major product from biomass pyrolysis, has also attracted significant attentions, because it can be directly used as a fuel as a result of its excellent fuel properties [91, 93, 95]. However, biomass extracts a large amount of inorganic nutrient species from soil during its growth. Sustainable recycling of those nutrients to the soil has become an important issue which may affect the overall sustainability of biomass production during its full life cycle. As most of inorganic nutrients are retained in biochar after pyrolysis, it was proposed that biochar can be returned to the field as a soil amendment [1], to achieve the benefits of both carbon sequestration and effective nutrients recycling. This strategy not only largely addresses the issue of nutrient recycling, but also makes biomass pyrolysis a carbon-negative process.

However, the success of such strategy is largely dependent on the leachability and overall recyclability of those inorganic nutrients in biochar. There is a lack of long-term leachability studies in the context of biochar leaching for agronomic applications [5], which poses challenges on the effort of benchmarking biochars performance in the agricultural sector as no clear linkage exists between pyrolysis

engineering and the biochars performance in agricultural science. The pyrolysis conditions seem to exhibit strong influence on the leachability of nutrient species of biochar, as different pyrolysis conditions introduce a series of intricate processes that mineralises, volatilises, and/or co-stabilises the original nutrients form in the biomass by different extents [8].

In order to simulate the time-frame of actual application of biochar in a soil environment, a series of long term leachability experiments were carried out in this study to investigate the leaching behaviour of nutrient species in a range of biochars produced from various biomass components (e.g., wood, leaf and bark) of different particle sizes under various conditions (e.g., pyrolysis temperature, heating rate). This study focuses on sustainable recycling of such nutrients in biochars and the leachability of such elements to promote additional cycles of plant growth and harvesting. The study will provide important guidelines on the pyrolysis of mallee biomass to obtain a biochar suitable for enhancing nutrients recycling as soil amendment. This study mainly focuses on the leaching of alkali and alkaline earth metallic (AAEM) species (i.e., Na, K, Mg and Ca), which are essential nutrients towards biomass growth.

4.2 Leachability and Recyclability of Inorganic Nutrients in Biochars Produced from Slow Pyrolysis of Mallee Biomass at Various Temperatures

4.2.1 Pyrolysis Biochar Yield, and C, H, O Contents in Biochars

From Figure 1, the biochar yield decreases with an increase in the pyrolysis temperature, as expected, due to increasing volatile release with pyrolysis temperature. The bio-char yield (dry basis) appears to start levelling off at temperature above 500 °C. The char yields of different mallee biomass components are in the order of bark > leaf > wood, which is consistent with the reverse order of volatile matter contents and the order of ash contents of these samples (see Table 4.1). Figure 4.2 presents the carbon, hydrogen and oxygen contents in the biochars produced from pyrolysis of the various raw biomass components. Biomass is a low-rank fuel with high oxygen content (at least ~35% in each of the mallee biomass components). It is clear in Figure 4.2 that the carbon content increases with pyrolysis

temperature, whereas the hydrogen and oxygen contents decrease with pyrolysis temperature. This is consistent with the fact that various oxygen functional groups are released as volatiles during pyrolysis. The evolution of functional groups with pyrolysis temperature will be investigated using FTIR analysis later.

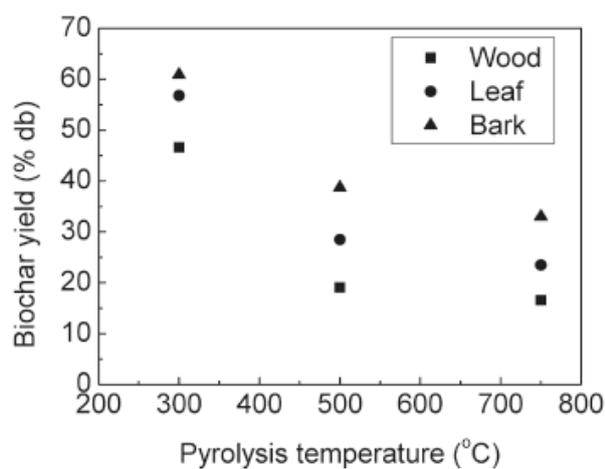


Figure 4.1. Biochar yield as a function of pyrolysis temperature.

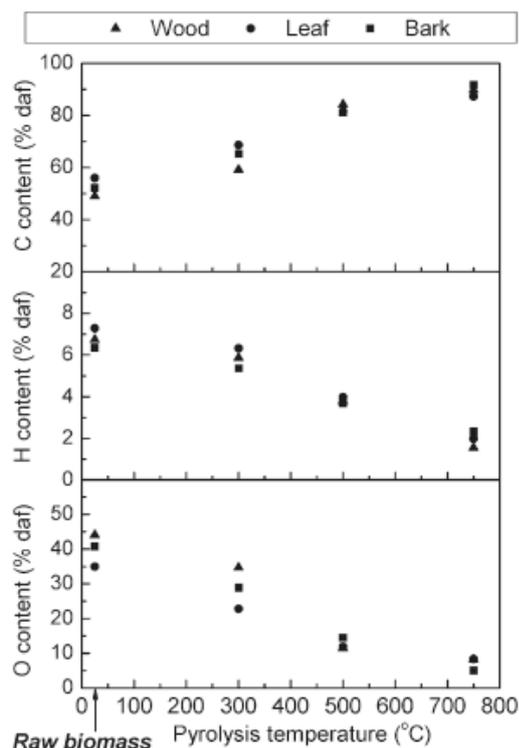


Figure 4.2. Carbon (C), hydrogen (H), and oxygen (O) contents (% daf) in the raw biomass and raw biochars from different pyrolysis temperatures. Data at 25 °C, as labeled in the figure, represent results for the raw biomass.

4.2.2 Inorganic Species in Raw Biomass and Their Retentions in Biochars

The contents of inorganic species in the biomass samples are presented in Table 4.2. Consistent with proximate analysis, the data in Table 4.2 show that bark has the highest inorganic content, followed by leaf and wood. The alkali and alkaline earth metallic (AAEM) species (particularly, Na, K, Mg, and Ca) are dominant metallic species in all the biomass samples, with Ca being the most abundant. The transition metal Fe is of very low level in the biomass samples. The contents of Si and Al are also low. The biomass samples contain various amounts of other inherent species, namely S, Cl, P, and N, which are important nutrients in biomass. Therefore, the results and discussion that follow will hence focus on Na, K, Mg, Ca, S, Cl, P, and N.

From the biochar yield (see Figure 4.1), as well as the inorganic species content in the biomass and biochars, the retention of inorganic species in the biochars was calculated. Figure 4.3 shows the retention of the various inorganic species in the

biochars after pyrolysis. It is clear that under the current conditions for biochar preparation at low pyrolysis temperatures and slow-heating rates, the majorities of the AAEM species are retained in the biochars. Under such pyrolysis conditions, the interactions between volatiles and pyrolysis biomass particles are minimal, therefore the effect of volatile biochar interactions is small [96].

Table 4.1. Proximate and Ultimate Analysis of Raw and Leached Biomass and Biochars, for Wood, Leaf and Bark

Sample ^a	Moisture, wt% (after air-dried)	Proximate analysis, wt% db			Ultimate analysis, wt% daf				
		Ash	VM ^b	FC ^c	C	H	N	S	O*
Wood									
Raw	5.3	0.4	80.7	18.9	49.0	6.7	0.19	0.02	44.1
Leached	5.9	0.2	85.4	14.5	49.1	5.9	0.38	0.01	44.6
Fine Wood-SH-Char (300°C)	4.9	1.2	65.2	33.5	59.1	5.9	0.28	0.01	34.7
Leached Fine Wood-SH-Char (300°C)	4.1	0.7	65.4	33.9	59.6	5.8	0.27	0.01	34.3
Fine Wood-SH-Char	3.3	2.6	21.5	75.9	84.2	3.8	0.46	0.03	11.5
Leached Fine Wood-SH-Char	4.2	1.8	20.6	77.6	85.1	3.9	0.44	0.02	10.5
Fine Wood-SH-Char (750°C)	5.6	3.1	10.1	86.8	89.7	1.5	0.51	0.03	8.2
Leached Fine Wood-SH-Char (750°C)	4.0	2.0	8.6	89.4	92.3	2.1	0.42	0.03	5.1
Leaf									
Raw	8.3	3.8	74.6	21.6	56.0	7.3	1.46	0.12	34.9
Leached	4.4	2.2	80.7	16.6	56.7	7.5	1.96	0.09	33.7
Fine Leaf-SH-Char (300°C)	3.7	7.3	58.6	34.1	68.6	6.3	2.01	0.12	22.8
Leached Fine Leaf-SH-Char (300°C)	5.7	4.8	57.6	37.6	68.5	6.3	2.03	0.10	23.0
Fine Leaf-SH-Char	5.1	13.2	23.9	62.9	81.6	4.0	2.42	0.10	11.8
Leached Fine Leaf-SH-Char	4.2	9.5	23.1	67.4	81.3	3.9	2.38	0.10	12.3
Fine leaf-SH-Char (750°C)	6.2	14.2	17.6	68.2	87.3	2.0	2.17	0.12	8.3
Leached Fine leaf-SH-Char (750°C)	3.6	6.7	14.7	78.6	90.7	2.0	2.37	0.08	4.7
Bark									
Raw	4.9	5.5	67.7	26.8	52.0	6.4	0.39	0.05	40.9
Leached	7.1	6.3	80.4	13.3	49.3	7.0	0.80	0.83	42.1
Fine Bark-SH-Char (300°C)	4.9	8.8	51.0	40.2	62.3	4.8	0.91	0.54	31.4
Leached Fine Bark-SH-Char (300°C)	5.7	7.2	49.1	43.7	63.9	5.2	1.07	0.60	29.3
Fine Bark-SH-Char	4.2	12.1	25.1	62.8	88.5	3.4	1.45	0.35	6.3
Leached Fine Bark-SH-Char	4.2	10.2	19.4	70.4	82.2	3.4	1.29	0.36	12.7
Fine Bark-SH-Char (750°C)	3.6	17.7	17.1	65.1	84.4	1.7	0.79	0.15	12.9
Leached Fine Bark-SH-Char (750°C)	3.6	12.8	14.7	72.5	87.0	2.0	0.88	0.22	9.9

^aPyrolysis temperature is 500°C unless otherwise stated. ^bVolatile Matter. ^cFixed Carbon.

The marginal loss/volatilization of AAEM observed here is most probably due to the release of AAEM as carboxylates during pyrolysis [97]. In contrast, P is likely to exist in some phosphate forms or some complex mineral compounds [98, 99], therefore it is not easily released during pyrolysis under such conditions. On the other hand, N and S are released to a relatively greater extent. Their volatilization increases with pyrolysis temperature. Via pyrolysis, N in solid fuels may be released as HCN, NH₃, and/or other gaseous products (e.g., N₂) whereas S is probably volatilized as H₂S [100, 101]. Cl is generally known to be released significantly during solid fuels pyrolysis [102], particularly volatilized as organic chloride and HCl during low-rank fuel pyrolysis [97]. Note that in Figure 4.3, for wood and bark biochars, due to the low Cl contents and the detection limit of the method used for Cl analysis, the retention shown is only the maximum possible retention.

Table 4.2. Inorganic Species Contents (wt % db for Na, K, Mg, Ca, Fe, Si, Al, and P; wt % daf for S, Cl, and N) in the Raw Biomass Samples

Element (wt %)	raw wood	raw leaf	raw bark
Na	0.021	0.554	0.209
K	0.074	0.380	0.111
Mg	0.036	0.145	0.080
Ca	0.124	0.765	2.659
Si	0.003	0.055	0.010
Al	0.003	0.019	0.003
Fe	0.000	0.014	0.002
P	0.018	0.108	0.024
S	0.018	0.118	0.051
Na	0.191	1.457	0.392
Cl	0.032	0.184	0.260

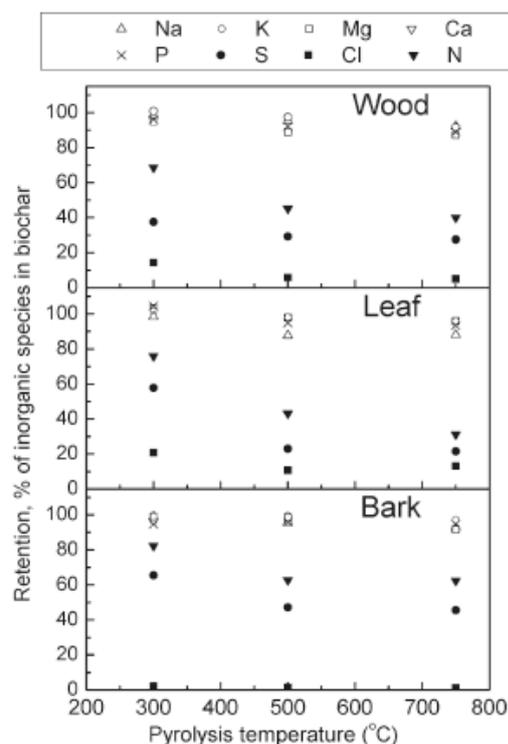


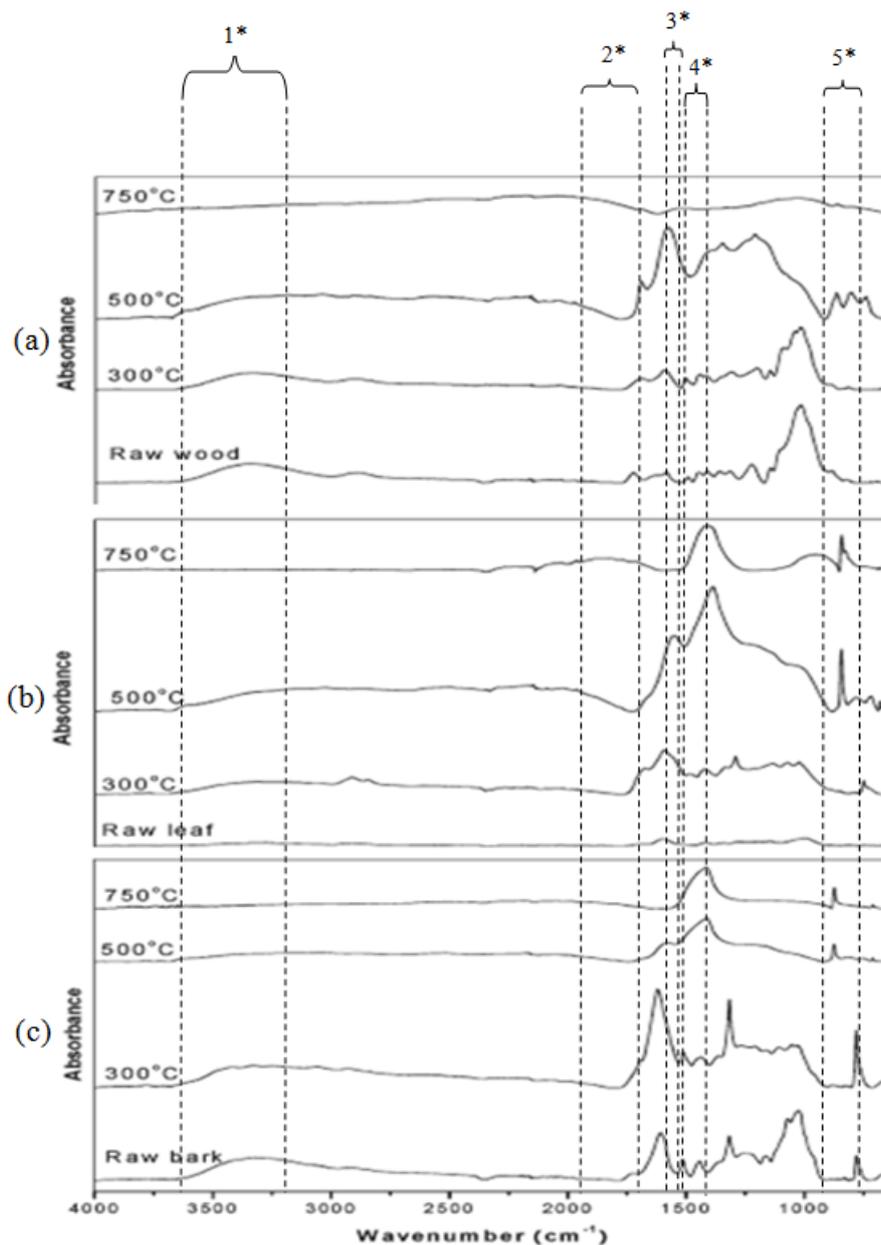
Figure 4.3. Retention of inorganic species (Na, K, Mg, Ca, P, S, Cl, and N) in the raw biochars at different pyrolysis temperatures. For Cl in wood and bark samples, the retention shown is the maximum possible retention.

4.2.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Figure 4.4 shows the FTIR spectra of raw wood, leaf, and bark and their respective biochars prepared at low (300 °C), intermediate (500 °C), and high (750 °C) temperatures. Generally, for all cases, in the raw biomass and biochars at the low temperature, oxygen functional groups are abundant. OH groups are apparent in the broad absorption range within 3600-3200 cm^{-1} , possibly due to overlapping hydroxyl bands. This indicates the possible presence of phenols and carboxylic acids, where the significant band broadening effect and shift toward lower wavenumbers is characteristic of the strong hydrogen bonding of carboxylic acids [103]. The 1800-1700 cm^{-1} region can be attributed to carbonyl structures such as carboxylic acids, lactones, anhydrides, esters, and other acetyl derivative groups [103-105]. Possible olefinic C=C stretching bands are found in the region of 1680-1620 cm^{-1} , whereas a peak at 1600 cm^{-1} is likely to be due to the presence of conjugated C=C bonds. A

general trend toward the intermediate temperature is the increasingly conjugated nature of the C=O functional groups, as explained by the shift of the bands toward lower wavenumbers, which overlaps the region of olefinic C=C stretching absorptions mentioned above [103]. This is also a spectral feature of aromatization, which leads to more conjugated bonds of the C=O with an aromatic nucleus or another C=C bond [104, 106, 107]. The 1600 cm⁻¹ peak assigned to conjugated C=C bonds [103] increases from the low to intermediate temperature and diminishes approaching the high temperature, for all biochars. The initial increase is most probably due to the increasingly conjugated nature of C=O bonds at the intermediate temperature as aforementioned. At a high temperature, this peak is no longer observable, due to loss of oxygen and the increasing dominance of aromatic rings structures in the high temperature biochar spectra.

Progressive aromatization is obvious for biochars starting from the intermediate temperature, as evidenced from the general trend of increasing bands in the 1615-1450 cm⁻¹ region [103, 104] attributed to aromatic C=C-C stretching. The ratios between the C=O and aromatic C=C—C stretching bands noticeably decreases with increasing pyrolysis temperature. Approaching the high temperature, the clearly visible bands that remain for the bark and leaf chars are those attributed to C=C—C aromatic ring stretching (1615-1450 cm⁻¹) and aromatic C—H out-of-plane bending (900-760 cm⁻¹) [103, 107, 108]. This indicates that the remaining biochar structure at high temperatures is predominantly aromatic rings with a certain degree of substitution [107, 109]. The absence of obvious bands for the high temperature wood char is probably due to the higher extent of turbostratic crystallinity in wood biochars [1], which induces a negligible change in dipole moment hence rendering IR inactive behaviour [104, 110]. Approaching a high temperature, much of the oxygen has been removed, and the remaining oxygen is expected to exist as aromatic ether [107]. Overall, common to all biochars, with increasing temperature, a reduction of all the assigned oxygen functional groups as well as an increase of aromaticity can be observed. These results from FTIR are also in accordance with the decreasing O and H contents observed earlier (Figure 4.2).



- 1* OH Groups - possibly phenols and carboxylic acids
- 2* Carbonyl structures such as carboxylic acids, lactones, anhydrides, esters, and other acetyl derivative groups
- 3* Olefinic C=C stretching bands
- 4* C=C—C aromatic ring stretching
- 5* C—H aromatic out-of-plane bending

Figure 4.4. FTIR spectra for raw biomass and raw biochars from different pyrolysis temperatures (300, 500, and 750 °C): (a) wood, (b) leaf, and (c) bark.

4.2.4 Removal of Inorganic Nutrient Species in Biomass and Biochars via Water Leaching

The proximate analysis data in Table 4.1 indicate that generally the ash yield of the various samples is reduced by water leaching. Quantification of individual inorganic nutrient species in the biomass and biochar samples before and after water leaching were also carried out and the data are presented in Table 4.3. It is clear that various extents of removal of inherent inorganic nutrient species from biomass and biochar samples were achieved via water leaching, depending on biomass components, inorganic species, and pyrolysis conditions. It is noted in Table 4.3 that in some cases for the biomass, the contents of some inorganic species (such as Ca) in the water leached biomass sample are slightly higher than that of the raw biomass sample, due to the substantial removal of organic matter (see Chapter 6) during the water leaching process.

Considering part of the inherent nutrients may be released during pyrolysis, the actual amount of an inherent nutrient species in a biochar available for removal and recycling via water leaching may be less than that originally in the biomass. Therefore, the removal/recycling of each nutrient species in a biomass or biochar is then normalized as % of total amount of that nutrient species originally available in the biomass. The data are presented in Figure 4.5, and directly shows the proportions of inorganic nutrient species originally present in biomass (i.e., extracted from the soil during biomass growth) which can be ultimately recycled by biochar production from biomass pyrolysis followed by biochar water leaching. The inherent inorganic matter in the biomass or biochars can be present in one or more of the following forms: (1) salts that are ionically bound, (2) inorganic materials bound organically to the carbonaceous material, and/or (3) included and excluded mineral matter [111]. The extent of leaching of various inorganic species by water depends dominantly on the forms/mode of occurrence of the inorganic species in the biomass or biochar.

As shown in Table 4.3 and Figure 4.5a, water leaching of biomass can remove and recycle almost all Na, K, and Cl in all biomass components (wood, leaf, and bark). Figure 4.5a also indicates that 40-80% of Mg, 30-50% of S, and 60-80% of P can be leached out by water from the raw biomass, depending on the biomass component.

However, only 5-30% Ca, which is the most abundant species in these biomass samples, can be leached. Therefore, in the biomass samples, at least part of these water-soluble alkali and alkaline earth metallic species (Na, K, Mg, and Ca) are likely to exist in the form of water-soluble salts including chlorides, sulfates, and phosphates. The molar ratios of $(\text{Na} + \text{K} + 2\text{Mg} + 2\text{Ca})/(\text{Cl} + 2\text{S} + 3\text{P})$ in the leached solutions obtained from water leaching of wood, leaf, and bark are 2.1, 2.8, and 3.3, respectively. The ratios well exceed 1, suggesting that at least some of these inorganic species may also exist in other water-soluble forms besides water-soluble salts. The most likely forms are alkali (Na and K) ion-exchangeable carboxylates (an acidic/oxygen functional group and humic acid material) because the alkaline earth metal (Mg and Ca) carboxylates are hardly water-soluble. Additionally, the limited leaching of Ca that is the dominant inorganic species in these biomass samples especially bark and leaf also suggests that Ca is largely in water-insoluble forms such as carboxylates. This is consistent with the apparent carbonyl bands observed from FTIR (Figure 4.4) for the raw biomass which indicates the presence of functional groups providing capacity for ion-exchange of metal cations. Figure 4.5a also indicates that N removal and recycling of N from water leaching of biomass is little. This is consistent with the fact that N occurs largely as organically bound nutrients in biomass and is generally unavailable to plants as suggested previously [1, 112, 113].

For water leaching of biochars, the results are presented in Figure 4.5b-d for the overall recycling of inherent nutrient species in biochars. The data indicate that via biochar production from pyrolysis followed by biochar water leaching, the overall removal and recycling of most nutrients species are substantially reduced. Approximately 40-90% of Na and K in the biochars can be removed via water leaching (less than those in biomass water leaching), depending on biomass component, nutrients species, and pyrolysis conditions. The majority of Na and K are retained as nutrients in biochars (see Figure 4.3), whereas most of Cl in biomass is released during pyrolysis. Therefore, the overall recycling of Cl is close to zero via biochar applications. Clearly, Cl is released separately from the Na or K, instead of as Na or K chloride molecules, consistent with previous data on brown coal pyrolysis [97]. The reductions in Na and K recycling in the case of biochars are most likely due to the change in the chemical forms of Na and K in the biochars after pyrolysis. Na or K originally associated to Cl may be transformed into the organically bound

forms in biochar following the release of Cl during pyrolysis, either ion-exchanged to the oxygen functional groups (likely for the low- and intermediate-temperature biochars) or directly bonded to the biochar matrix (especially for the high-temperature biochars). This is supported by, as seen from FTIR (Figure 4.4), the presence of possible carboxylic acid bands for the low- and intermediate-temperature biochars. Yet, as pyrolysis temperature increases, the progressively decreasing oxygen functional groups (Figure 4.4), hence the decreasing O and H contents (see Figure 4.2), dictate a higher susceptibility of direct bonding of the species to the biochar matrix. Excess metallic species may also be transformed into other forms such as carbonates or oxides [114]. The above could account for the variation of leaching extent of Na and K with respect to pyrolysis temperature: part of the Na and K that exists in chlorides, carboxylates, or carbonates in the biochars can still be leached out by water, while Na and K that have been directly bound to the biochar matrix or that have been transformed into oxides thus cannot be leached out.

The data further indicate that S is only marginally removed from biochars through water leaching. Considering also the substantial release of S during biomass pyrolysis (see Figure 4.3), the overall recycling of S is small, as shown in Figures 4.5b-d. The dependence of leaching and recycling of S in biochars on different pyrolysis temperatures may be attributed to two reasons. One is the different retentions of S in biochars during biomass pyrolysis (see Figure 4.3). The other is the transformations of sulfur between water-soluble (such as alkali sulfates) and water-insoluble (such as organic sulfur) forms during pyrolysis [115]. For P, it is mostly retained in biochars during biomass pyrolysis at various pyrolysis temperatures (see Figure 4.3). It is noted that P can still be leached from the biochars prepared at 300 °C, suggesting this fraction possibly still exists as some water-soluble phosphates. As the pyrolysis temperature increases, these water-soluble P appear to be transformed into some water-insoluble minerals, e.g., apatite and/or other complex phosphorus-containing compounds [98, 99]. The data in Table 4.3 show that little N can be leached from the biochars for all cases, suggesting that the N retained in biochars still exist as organically bound form and hence are not leachable by water. As the retention of N following pyrolysis is also comparatively low (see Figure 4.3), the overall recycling of N via the leaching of the remaining N in the

biochar is low, further reducing the prospect of directly supplying N to soils via biochars. The relative unavailability of macronutrients N and P may be a downfall in terms of direct nutrient benefits of these biochars. Therefore, mitigation strategy such as the application of biochar in conjunction with conventional N, S, and P fertilization can potentially increase the efficiency and plant response of such supplements, as shown in previous studies [86, 116] because of enhanced ammonium and phosphate retention due to reversible adsorption effects [1]. The findings on different leachability that can be achieved with different biomass components at different pyrolysis temperatures may also provide guidelines for developing optimum strategy for such applications. Particularly, because Ca is the dominant inorganic nutrient species in biomass and biochar samples, the substantial leaching of Ca in biochar prepared at 750 °C suggests that simple heat treatment may be employed to tune biochars to facilitate the recycling of Ca in these biochars.

Following pyrolysis, it is important to note that the leaching and recycling of Mg becomes almost zero, suggesting that the originally water-soluble Mg has been transformed into organically bound forms or compounds such as carbonate and/or oxide [114] which are hardly water-soluble. These transformations stem from the decreasing oxygen functional groups and the increasing aromaticity as pyrolysis progresses to higher temperatures, as evidenced from FTIR (Figure 4.4). As alkaline earth metal (Mg and Ca) carboxylates and carbonates are hardly water-soluble, partly explaining the lower leachability of Mg and Ca compared to Na and K from the biochars. It is also interesting to note that a somewhat reverse trend, compared to that of Mg, is observed for the leaching of Ca with pyrolysis temperature. The leaching of Ca increases substantially at 750 °C. The data suggest that following pyrolysis, Ca most probably still exists in organically bound forms or exists as carbonate and oxide [114], which are not soluble or only sparingly soluble in water. Hence, the high leaching of Ca at the high pyrolysis temperature is most likely to be due to emergence of calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$), a salt existing in aqueous solution which has much higher solubility than CaCO_3 during water leaching.

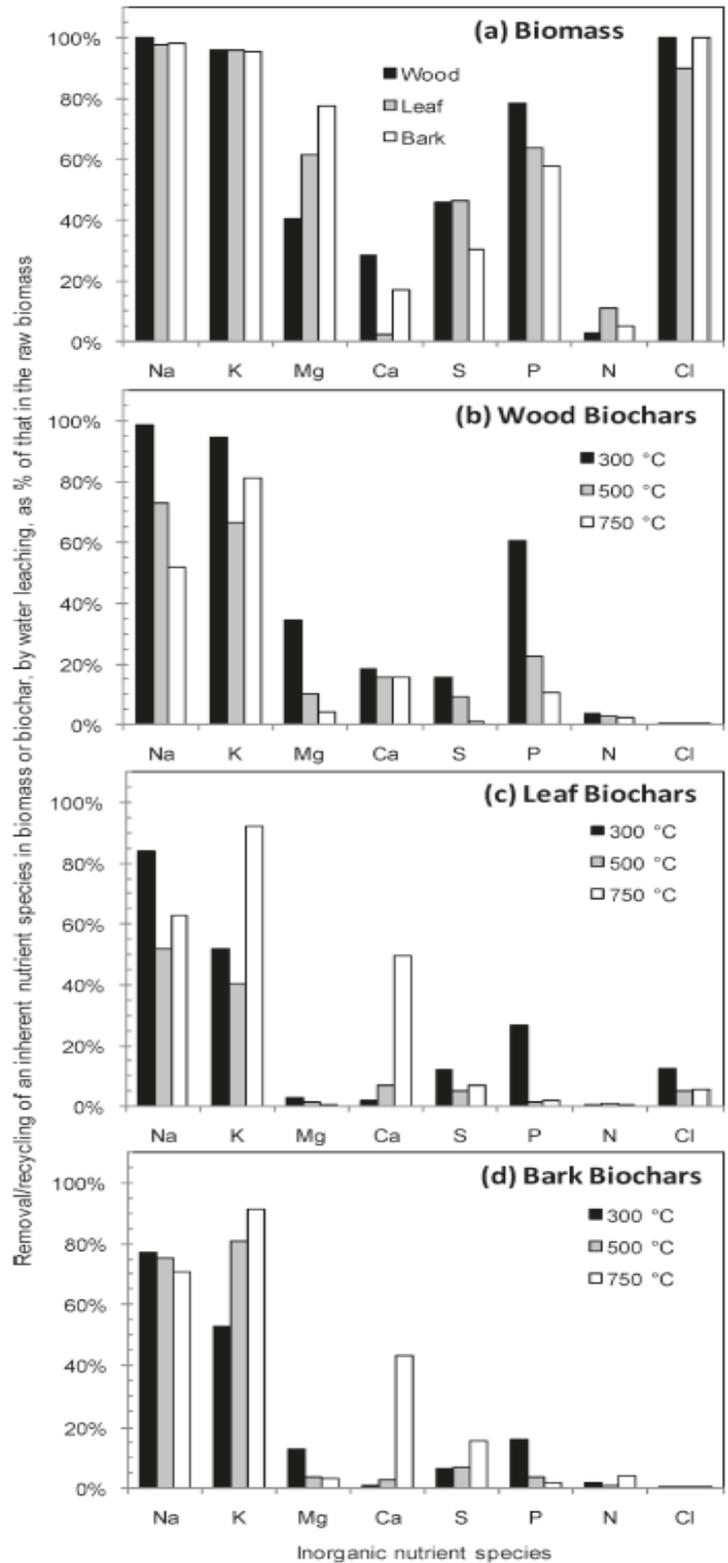


Figure 4.5. Overall removal (or recycling) of various inherent nutrients in biomass and biochar samples via water leaching, normalized to the total nutrients originally present in biomass.

Table 4.3. Inorganic Species Contents (wt % db for Na, K, Mg, Ca, and P; wt % daf for S, Cl and N) in Raw and Leached Biomass and Biochars, for Wood, Leaf and Bark

Element (wt%)	Wood							
	Biomass		Fine Wood-SH-Char (300°C)		Fine Wood-SH-Char ^a		Fine Wood-SH-Char (750°C)	
	Raw	Leached	Unleached	Leached	Unleached	Leached	Unleached	Leached
Na	0.021	<0.01	0.045	<0.01	0.106	0.025	0.118	0.052
K	0.074	0.002	0.161	0.010	0.379	0.120	0.411	0.047
Mg	0.036	0.020	0.074	0.048	0.169	0.151	0.191	0.183
Ca	0.124	0.084	0.267	0.222	0.583	0.485	0.669	0.556
Cl	0.032	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
S	0.018	0.010	0.015	0.009	0.029	0.020	0.031	0.031
P	0.018	0.003	0.037	0.014	0.088	0.067	0.097	0.086
N	0.191	0.203	0.283	0.272	0.462	0.437	0.515	0.418
Element (wt%)	Leaf							
	Biomass		Fine Leaf-SH-Char (300°C)		Fine Leaf-SH-Char ^a		Fine Leaf-SH-Char (750°C)	
	Raw	Leached	Unleached	Leached	Unleached	Leached	Unleached	Leached
Na	0.554	0.019	1.009	0.192	1.902	0.895	2.258	0.774
K	0.380	0.021	0.679	0.336	1.306	0.773	1.550	0.057
Mg	0.145	0.077	0.251	0.248	0.445	0.452	0.543	0.543
Ca	0.765	1.142	1.333	1.395	2.556	2.388	3.022	1.403
Cl	0.184	0.026	0.069	0.028	0.075	0.038	0.116	0.066
S	0.118	0.088	0.124	0.100	0.104	0.097	0.121	0.081
P	0.108	0.054	0.198	0.150	0.357	0.354	0.428	0.442
N	1.457	1.800	2.005	2.027	2.415	2.383	2.173	2.367
Element (wt%)	Bark							
	Biomass		Fine Bark-SH-Char (300°C)		Fine Bark-SH-Char ^a		Fine Bark-SH-Char (750°C)	
	Raw	Leached	Unleached	Leached	Unleached	Leached	Unleached	Leached
Na	0.209	0.006	0.340	0.075	0.517	0.110	0.587	0.139
K	0.111	0.007	0.175	0.080	0.284	0.054	0.326	0.020
Mg	0.080	0.026	0.129	0.113	0.202	0.195	0.221	0.215
Ca	2.659	3.162	3.977	4.182	6.356	6.198	6.967	3.518
Cl	0.260	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
S	0.051	0.051	0.056	0.051	0.068	0.058	0.077	0.051
P	0.023	0.014	0.037	0.031	0.058	0.061	0.067	0.068
N	0.392	0.533	0.547	0.539	0.692	0.684	0.817	0.704

^a Pyrolysis temperature is 500°C unless otherwise stated.

4.3 Leachability and Recyclability of Inorganic Nutrients in Biochars Produced from the Slow and Fast Pyrolysis of Mallee Biomass at 500 °C

4.3.1 Yields and properties of biochars from slow and fast pyrolysis

Figure 4.6 shows the yields of biochars produced from the slow and fast pyrolysis of different biomass components (wood, leaf and bark) and wood of two different particle sizes. It is well known that fast pyrolysis condition promotes the release of volatiles, leading to a lower char yield [15, 117, 118]. Indeed, lower char yields are obtained from fast pyrolysis (~19%, ~26% and ~35% for wood, leaf, and bark, respectively) compared to those from slow pyrolysis (~21%, ~32%, and ~41% for wood, leaf, and bark, respectively) across all biomass samples. It can also be seen that the effect of heating rate on biomass pyrolysis seems to be different for different biomass components. For example, the difference between the char yields of slow and fast pyrolysis is large for leaf and bark (with a difference of ~6%), but low for wood (with a difference of ~2%). Obviously, such different effect of heating rate on char yield for different biomass is mainly attributed to the different feedstock properties, particularly the content of volatile matter. A high content of volatile matter seems to reduce the effect of heating rate on char yield. Moreover, the biomass particle size seems to also reduce the effect of heating rate on char formation, because the char yield prepared from large wood is similar with those produced from fine wood for both slow and fast pyrolysis. This is reasonable since large particle size largely reduces the heating rate, particularly under fast heating conditions.

Regardless the slow or fast heating condition, biochars produced from the bark have much higher yields, followed by those produced from the leaf and wood. This is also due to the different feedstock properties for bark, leaf and wood. For example, a high content of AAEM species in the feedstock is reported to largely promote the char formation during pyrolysis [119-121]. The results in this study agree with this finding, since the char yields of different biomass components exactly follow the

order of the content of AAEM species in the feedstock, i.e., bark > leaf > wood (see Figure 4.6 and Table 4.5).

The properties of the biochars are also different under slow and fast pyrolysis. As shown in Table 4.4, a higher C content and a lower O content are observed for the biochars produced from the slow pyrolysis of all biomass samples compared those from fast pyrolysis. This indicates that slow pyrolysis produces biochars with higher degree of carbonisation and less oxygen functional groups, probably due to prolonged pyrolysis time during slow pyrolysis. In addition, slow pyrolysis also results in biochar with a lower volatile matter content compared to fast pyrolysis. This might due to the slower release of volatile during slow pyrolysis and/or more volatile being adsorbed on biochar surface during fast pyrolysis [122]. On the contrary, the biochars produced from the slow pyrolysis of the large wood have similar content of volatile matter, C, H, N and O compared to the biochar from the fast pyrolysis. The results above clearly indicate the dissimilarity of the property of biochar produced from slow and fast pyrolysis. This can potentially affect the leachability and nutrient availability of these biochars, which will be discussed in the following sections.

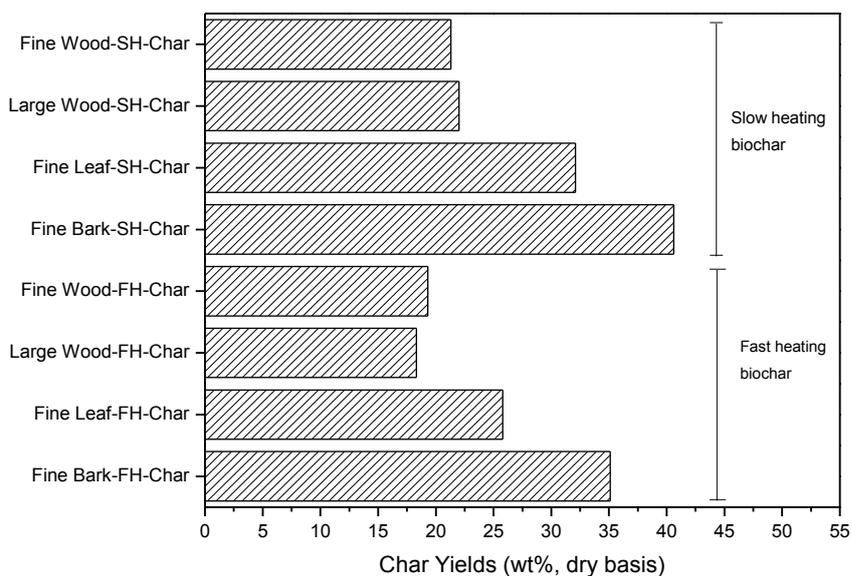


Figure 4.6. The Yield of Biochar Produced Slow Heating (SH) and Fast Heating (FH) Pyrolysis of Wood, Leaf and Bark at 500 °C.

Table 4.4. Properties of Wood, Leaf, Bark and Their Derived Biochars Produced from Slow Heating (SH) and Fast Heating (FH) Pyrolysis at 500 °C (Fine Wood, Leaf, Particles with a Size Fraction of 150–250 µm; Fine bark, Particles with a Size Fraction of <250 µm; Large Wood, Particles with a Size Fraction of 2–4 mm)

Samples	Moisture ^a (wt%)	Proximate (wt %, db)			Ultimate (wt%, daf ^d)			
		Ash	VM ^b	FC ^c	C	H	N	O ^e
Wood	5.1	0.4	80.0	19.6	48.7	6.5	0.2	44.6
Leaf	8.0	3.7	75.0	21.3	55.8	7.0	1.4	35.8
Bark	4.7	5.3	68.0	26.7	51.0	6.2	0.4	42.4
Fine Wood-SH-Char	3.1	2.4	21.0	76.6	83.1	3.7	0.4	12.8
Large Wood-SH-Char	2.4	2.4	16.4	81.2	86.4	2.8	0.3	10.6
Fine Leaf-SH-Char	5.3	13.0	23.5	63.5	82.0	3.9	2.4	11.7
Fine Bark-SH-Char	4.5	11.8	24.9	63.3	85.1	2.9	0.7	11.3
Fine Wood-FH-Char	2.0	4.3	29.7	66.0	78.7	3.3	0.3	17.6
Large Wood-FH-Char	2.9	3.3	19.8	76.9	83.6	3.0	0.5	12.9
Fine Leaf-FH-Char	5.9	16.2	34.3	49.5	75.6	3.1	2.2	19.1
Fine Bark-FH-Char	4.6	13.7	31.9	54.4	80.2	3.2	0.7	15.9

^a wt% after air dried; ^b VM–volatile matter; ^c FC–fixed carbon; ^d daf–dry ash free; ^e by difference

Sample calculations for Proximate and Ultimate Analyses in Table 4.4 are shown below for Fine Wood-SH Char.

Proximate Analysis Sample Calculations

Note: subscript 'ar' = as received

$$\begin{aligned}
 \text{ash (wt\% db)} &= \frac{\text{ash}_{ar} * 100}{100 - \text{wt\% moisture}} \\
 &= \frac{2.3 * 100}{100 - 3.1} \\
 &= 2.4\%
 \end{aligned}$$

$$\begin{aligned}
 \text{VM (wt\% db)} &= \frac{\text{VM}_{ar} * 100}{100 - \text{wt\% moisture}} \\
 &= \frac{20.3 * 100}{100 - 3.1} \\
 &= 21.0\%
 \end{aligned}$$

$$\begin{aligned}
 FC \text{ (wt\% db)} &= \frac{FC_{ar} * 100}{100 - \text{wt\% moisture}} \\
 &= \frac{74.2 * 100}{100 - 3.1} \\
 &= 76.6\%
 \end{aligned}$$

Ultimate Analysis Sample Calculations

$$\begin{aligned}
 C_{daf} &= \frac{C_{ar}}{100 - \text{wt\% ash} - \text{wt\% moisture}} \\
 &= \frac{78.56 * 100}{100 - 2.4 - 3.1} \\
 &= 83.1\%
 \end{aligned}$$

$$\begin{aligned}
 H_{daf} &= \frac{H_{ar}}{100 - \text{wt\% ash} - \text{wt\% moisture}} \\
 &= \frac{3.51 * 100}{100 - 2.4 - 3.1} \\
 &= 3.7\%
 \end{aligned}$$

$$\begin{aligned}
 N_{daf} &= \frac{N_{ar}}{100 - \text{wt\% ash} - \text{wt\% moisture}} \\
 &= \frac{0.42 * 100}{100 - 2.4 - 3.1} \\
 &= 0.4\%
 \end{aligned}$$

$$\begin{aligned}
 O_{daf} &= 100 - C_{daf} - H_{daf} - N_{daf} \\
 &= 100 - 83.1 - 3.7 - 0.4 \\
 &= 12.8\%
 \end{aligned}$$

Table 4.5. Contents of AAEM Species in Wood, Leaf, Bark and Their Derived Biochars Produced from Slow Heating (SH) and Fast Heating (FH) Pyrolysis at 500 °C. (Fine Wood and Leaf, Particles with a Size Fraction of 150–250 µm; Fine Bark, Particles with a Size Fraction of <250 µm; Large Wood, Particles with a Size Fraction of 2–4 mm)

Samples	Inorganic Species (wt% db)*			
	Na	K	Mg	Ca
Wood	0.022	0.071	0.033	0.140
Leaf	0.554	0.383	0.146	0.765
Bark	0.209	0.111	0.085	2.659
Fine Wood-SH-Char	0.113	0.357	0.167	0.751
Large Wood-SH-Char	0.114	0.444	0.219	0.713
Fine Leaf-SH-Char	1.536	1.038	0.346	2.238
Fine Bark-SH-Char	0.453	0.218	0.165	5.983
Fine Wood-FH-Char	0.178	0.498	0.262	1.346
Large Wood-FH-Char	0.110	0.404	0.214	0.768
Fine Leaf-FH-Char	2.435	1.278	0.556	3.227
Fine Bark-FH-Char	0.632	0.595	0.353	6.248

*The microbalance used for this study is accurate to 0.001 mg.

AAEM (wt% db) in Biochar (Fine Wood-SH-Char) Sample Calculation

$$\begin{aligned}
 Na \text{ (wt\% db)} &= \frac{Na_{ar} \% * ash \text{ (wt\% db)}}{100} \\
 &= \frac{4.6888 * 2.4}{100} \\
 &= 0.113\%
 \end{aligned}$$

4.3.2 Leachability and nutrient availability of AAEM species in biochars from slow and fast pyrolysis

4.3.2.1 Overall leachability of AAEM species in biochars by water and Mehlich I extractions

Figure 4.7 presents the amounts of water-soluble and total plant available AAEM species in the biochars, quantified by water and Mehlich I extractions, respectively. Overall, ~58–100% of Na, ~47–100% of K, ~13–22% of Mg, and ~9–38% of Ca are

water-soluble for all the prepared biochars. On the other hand, the amount of total plant available AAEM species in the biochars are ~100%, ~93–100%, ~21–72%, and ~38–94% for Na, K, Mg, and Ca, respectively. These results clearly demonstrate that water extraction is easier to leach the alkali metals (Na and K), but not for alkaline earth metals (Mg and Ca). Mehlich I extraction leads to a significant increase in the nutrients leached from biochar, but the leached Mg is still quite low compared to other three AAEM species.

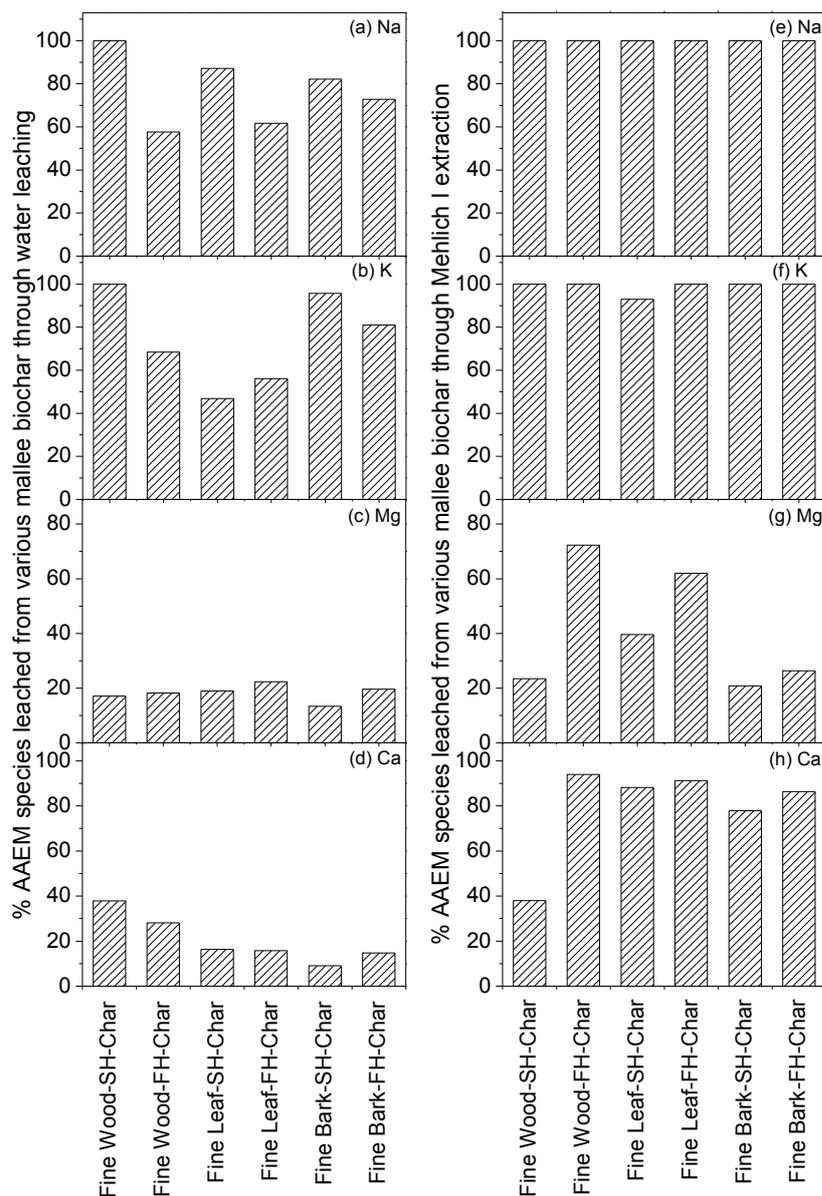


Figure 4.7. % AAEM species leached from biochars prepared mallee biomass. Panel (a-d) through water leaching, and (e-h) Mehlich I solution leachable.

4.3.2.2 A comparison of the leachability of AAEM species in biochars from slow and fast pyrolysis

As shown in Figure 4.7, there are significant differences in the water-soluble and total plant available AAEM species in the biochars between slow and fast pyrolysis for all biomass components. Overall, a smaller amount of water-soluble AAEM species, especially for Na and K, can be observed for the biochars produced from fast pyrolysis, compare to those from slow pyrolysis. The main reasons responsible for the reduction in the amount of water-soluble AAEM species in the biochar from fast pyrolysis remain unclear, as a result of the complicated pyrolysis mechanism of slow and fast pyrolysis.

However, the leachability of AAEM species in biochar is at least determined by the following two important factors. One is the occurrence forms and distribution of AAEM species in biochar. It is known that almost all the Na and K and small amounts of Mg and Ca are water-soluble for raw biomass [123]. However, during pyrolysis, at least a portion of water-soluble AAEM species are transformed into other forms with reduced leachability in water, i.e., organically-bound forms that are water-insoluble but soluble in dilute acid. According to our results, the water leachable Na and K were found to decrease for biochars produced from fast pyrolysis, but almost all of the Na and K in both slow and fast pyrolysis biochars are leachable by dilute acid, supporting that fast pyrolysis produces a biochar with a higher fraction of organically-bound AAEM species. In addition, fast pyrolysis also increases the amount of dilute acid soluble Mg and Ca. A lower dilute acid leachable Mg and Ca from slow pyrolysis biochar may due to a higher degree of carbonisation as indicated by higher carbon content (Table 4.4), resulting in Mg and Ca being bonded to biochar structures, i.e., as $C-M^{2+}-C$ [124, 125]. A higher oxygen content in fast pyrolysis biochar also indicates that Mg and Ca are more likely to attach to carboxyl group which are ion-exchangeable, hence becoming dilute acid leachable.

Another important factor which affects the leachability of AAEM species in biochar is the morphological structure of biochar, because part of water-soluble AAEM species in biochar may become inaccessible to water resulting from possible pore blockage, i.e., due to promoted secondary reactions and melting of biochar structure

[1, 43]. This could be due to several reasons. First of all, the drop-tube/fixed bed reactor used for fast pyrolysis experiments in this study favours the secondary reactions between volatile and char, thus promoting the soot deposits on char surface. Whereas in the slow pyrolysis experiments, the volatile released is quickly diluted and swept away by the carrier gas thus minimising the contact between volatile and char surface. Second, the pyrolysis temperature (500 °C) chosen for pyrolysis experiments seems to favour the soot formation as well. Such temperature is good for bio-oil production, but not sufficiently high to encourage the secondary char thermal cracking reactions [126]. These reactions, if severe, will offset the amount of soot production by transforming the soot into non-condensable gases. Third, fast pyrolysis also results in a significant change of biochar morphological structures due to melting and plastic deformation phenomena [43]. This leads to more significant alteration of biochar cell structure during fast pyrolysis, particularly for samples of higher volatiles matter content such as wood and leaf species [1]. This changes the flow characteristics of volatiles within the pyrolysing particle, affecting the convective transfer of volatiles to the sample surface. This may also prolong the residence time of volatiles within the particle and also leads to inhibited mass transfer effects during both fast pyrolysis and biochar leaching.

Therefore, the combined effects of less water-soluble AAEM species in biochar and the biochar structure with physical morphology less favourable for water leaching are more likely to explain the considerably lower nutrients leachability from a range of biochars from fast pyrolysis of all three biomass components.

4.3.2.3 Effect of biomass component on the leachability of AAEM species in biochars from slow and fast pyrolysis

The difference in the leaching behaviour of AAEM species between slow and fast pyrolysis biochars is found to vary with biomass component. Fast pyrolysis greatly decreases the leachability of AAEM species in the biochar for wood and leaf, but not for bark. For example, the leached Na reduces from ~100% to ~58% for wood biochar, from ~88% to 62% for leaf biochar, and from ~82% to ~73% for bark biochar, when the pyrolysis condition changes from slow to fast pyrolysis. Such a significant reduction of the leachability of AAEM species for fast pyrolysis of wood and leaf can be also explained by the above two factors. On one hand, more water-

soluble AAEM species are transformed into water-insoluble but acid soluble forms during fast pyrolysis of wood and leaf, compared to that for bark, as reflected by the difference of leached AAEM species between water and dilute acid leaching (see Figure 4.7). On the other hand, the wood and leaf contain a larger fractions of volatile matter (see Table 4.4) which has a higher soot-forming tendency on biochar surface [1]. This speculation can be supported by the results in Figure 4.7 for wood and leaf, as fast pyrolysis leads to an apparent reduction in the water-soluble AAEM species, but significantly increases the water-insoluble but acid-soluble AAEM species.

When comparing the leachability of AAEM species in biochars from slow or fast pyrolysis of three biomass components, it is interesting to see the trend for slow pyrolysis are contrary to that for fast pyrolysis. For example, the leachability of AAEM species in slow pyrolysis biochar generally follows the order of wood > leaf > bark, while that for fast pyrolysis biochar is in the order of bark > leaf > wood. Obviously, such contrary trends are due to the different properties (i.e., the occurrence forms and distribution of the AAEM species in biomass and the volatile content) of biomass component, resulting in their different pyrolysis behaviours thus producing biochars of different physical and chemical structures.

4.3.2.4 Effect of biomass particle size on the leachability of biochars from slow and fast pyrolysis

Since the pyrolysis of fine biomass particle is impractical in industrial practice due to the poor grindability of biomass [12], the leaching behaviour of the AAEM species in biochar prepared from large wood particle is also studied. Figure 4.8 shows the leachability of AAEM species in biochars from slow and fast pyrolysis of small and large particle wood. Interestingly, an increase in particle size reduces the leachability of AAEM species for slow pyrolysis biochar, but an opposite trend is observed for fast pyrolysis biochar. Due to the intra-particle mass transfer resistance, one key difference in the pyrolysis of large biomass is the presence of extensive intra-particle physical and chemical reactions within large biomass particles during pyrolysis. The poor biomass thermal conductivity results in non-uniform heating, making the primary reactions unable to be carried out swiftly in sequential manner [15]. A large particle size can also lead to more extensive secondary reactions between volatile

and hot char surface, as volatile from colder inner surface diffuses and contacts with thicker layer of hot char, resulting in partial encapsulation of these AAEM species. An increase in particle size increases the volatile residence time, causing prolonged desorption and reabsorption of the AAEM species in char matrix [127]. This transforms some water-soluble AAEM species into water-insoluble or even acid-insoluble forms, as supported by our results in Figure 4.8.

The increased intra-particle secondary reactions seem to explain the effect of particle size for slow pyrolysis biochar, but not for fast pyrolysis biochar. The detailed reason for the increased leachability of AAEM species in the biochar from fast pyrolysis of large wood is still not clear. It might be due to the heat transfer limitation arising from the increase in particle size as aforementioned, resulting in different biochar characteristics. An increase in particle size reduces the overall heating rate experienced by the biomass particles in drop-tube/fixed-bed reactor, i.e., from ~400 to ~50 °C/s. It also causes significant temperature gradient within the particles [39]. It is possible that fast pyrolysis may take place dominantly at the outer layer of the biomass while the core of biomass particle still experiences pyrolysis at a significantly lower heating rate. An increase in the char formation observed in Figure 4.6 also suggests that part of the large biomass particle underwent slow pyrolysis rather than fast pyrolysis throughout the particle. This is also supported by a significant reduction of water-insoluble but acid-soluble (as ion exchangeable) Mg and Ca in the biochars.

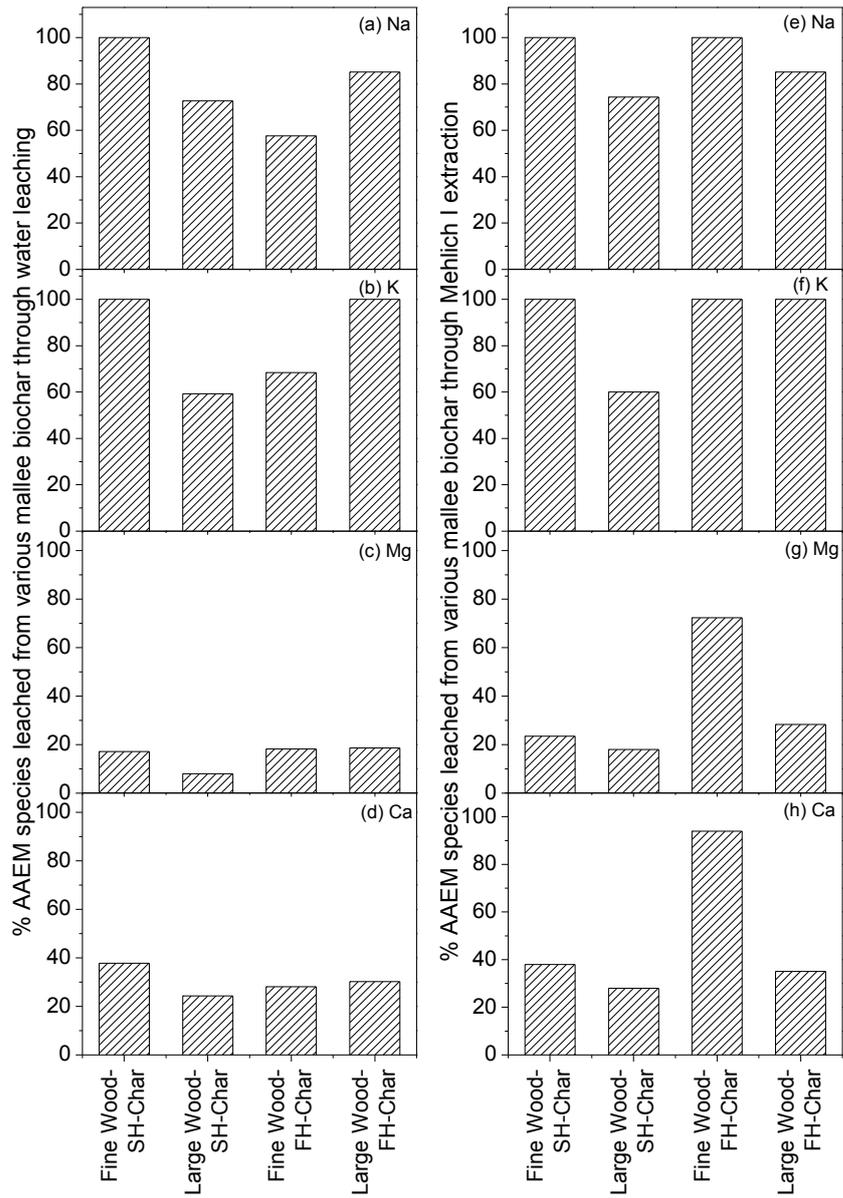


Figure 4.8. % AAEM species leached from biochars prepared from fine and large mallee wood. Panels (a-d) through water and panels (e-h) through Mehlich I extraction.

4.3.3 Overall nutrients recycling

In order to understand the potential of biochar soil application on nutrient utilisation efficiency, it is essential to consider the nutrients recycling during the overall process of biomass growth and harvesting, biochar production and leaching. Figure 4.9 shows the total amount of recycled AAEM nutrient species through Mehlich I (based on total plant available nutrients) normalised as a percentage of the total original amount of that species inherently found in the raw biomass. The overall recyclability of nutrients from biomass varies with pyrolysis conditions and biomass properties as the recyclability depends on the pyrolysis thermo-chemical processes, the biochar characteristics and nutrient availability/occurrence. For example, the overall recyclability of Na ranges from ~75 – 100%, ~80 – 100% for K, ~16 – 61% for Mg and ~32 – 99% for Ca, for all the biochars studied. The recyclability of Na and K are relatively high, however still significant amounts of alkaline earth metals, especially Mg, are not leachable by dilute acid, suggesting that significant portion of alkaline earth metals exists as dilute acid insoluble forms, thus not available for plant uptake when these biochars are applied to soil. This study has shown that nutrients can potentially be recycled, to varying extents, by returning agricultural biomass derived biochar to soil. The extent of nutrients leachability and recyclability depend on the production conditions and inherent biomass properties.

The variation in biomass component results in a dissimilarity of overall recyclability of the AAEM species especially Mg and Ca in biochar due to difference in the occurrence of their inherent AAEM species. In practical, it is unlikely that mallee tree will be completely separated into individual component due to its high harvest cost. However, this data will provide crucial data to estimate the overall nutrient recycling of a whole tree when part of the tree for purposes other than soil application.

Bio-oil is typically produced from fast pyrolysis of biomass at 500°C to obtain an optimum yield. A high overall nutrient recyclability from fast pyrolysis biochar leads to possible utilisation of fast pyrolysis biochar for agronomic purposes and provides appropriate alternatives for the usage of biochar as a by-product from bio-oil production. However, it is important to note that the fast pyrolysis in this study is specifically referred to processes carried out within a drop-tube/fixed-bed pyrolysis reactor. Furthermore, a large variety of existing and under-development laboratory

scale/pilot plant fast heating reactor configurations provide significantly different fast pyrolysis mechanisms, likely resulting in a range of biochars with different physico-chemical characteristics and potentially different AAEM species leaching behaviours.

Typical commercial pyrolysis schemes involve processes that are largely mass transfer limited [39], and this consideration is essential in deciding the characteristics of resultant biochar. In industrially-relevant practices, the particle size of pyrolysis feedstock may be restricted to large due to economic constraints arising from poor biomass grindability. This study has shown that the overall recycling of nutrients from the fine and larger size biochars do not show a very large dissimilarity. However, the leaching process of larger size biochars tend to be slower and potentially more kinetically inhibited due to mass transfer considerations, hence creating a possible advantage for soil nutrient recycling objectives by promoting a time-controlled release of nutrients to the soil.

It is also worth noting that the leaching studies performed were based on very dilute solid to liquid ratios in order to prevent any result deviation caused by solubility or saturation limitations. The actual scenario of biochar soil applications would, however, differ from the current study's leaching environments as it would be governed by factors including soil quality, climate, and rainfall patterns, to name a few. Therefore, although nutrient removal and recycling behaviour in the soil are likely to differ from those in this research, this study delivers useful insights regarding the nutrient release behaviour and its relationship with biomass feedstock and biochar production condition, which surpass the effectiveness of analytical characterisation methods and the prediction of biochar nutrients behaviour by projecting the analytical values. The relatively more direct assessment in this study allows the effective understanding of possible physico-chemical differences on maximum extractability among the range of biochars studied. This aids the optimisation of the overall biochar production schemes that focus on a single most valuable product or more commonly requires a compromise of all the compounds from the pyrolysis products spectrum.

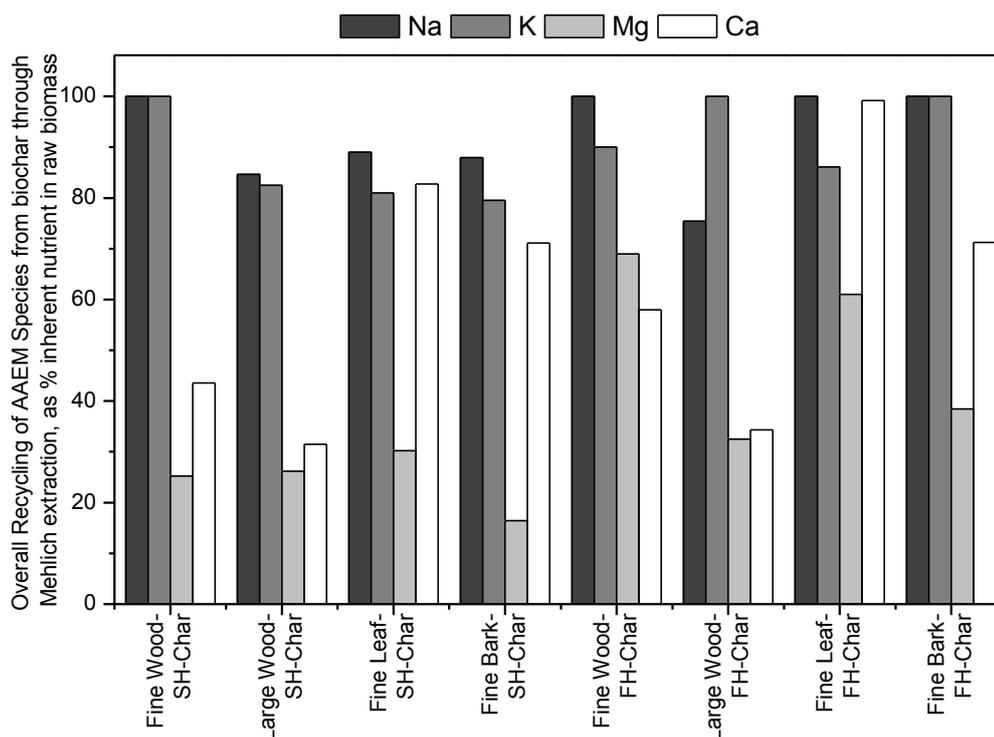


Figure 4.9. Overall recycling of AAEM species from biochar through Mehlich I extraction normalised to inherent nutrient in raw biomass.

4.4 Conclusion

This study investigated the removal of a broad range of inherent inorganic species from mallee biomass and biochars by water leaching. With increasing pyrolysis temperature, the biochar yield decreases, the biochar C content increases, while the biochar H and O contents decrease. The AAEM species and P are mostly retained in the biochars following pyrolysis. During pyrolysis, substantial amounts of N and S are volatilized, while Cl is almost all released during pyrolysis under the experimental conditions. FTIR analysis has provided evidence that the oxygen functional groups in the biochars diminish and the biochar aromaticity increases with increasing pyrolysis temperature. Water leaching can recycle almost all of K, Na, and Cl, large proportions of S, P, and Mg, but limited Ca and little N in all biomass samples. The data further show that via biomass pyrolysis followed by biochar water

leaching, the overall recycling of most of the nutrient species originally present in biomass (as results of leaching of inherent nutrients in biochars) is substantially reduced. Such reductions are due to either substantial release of nutrients (Cl, S, and N) during pyrolysis or most nutrient species (Na, K, Mg, P) in biochars being transformed into increasingly stable forms that are difficult to be leached by water. For Ca that is the dominant inorganic nutrient species in these biomass and biochar samples, the data suggest that heat treatment may be employed to tune these biochars to facilitate their recycling.

Pyrolysis of mallee wood, leaf and bark under slow and fast pyrolysis conditions produces biochar with different physio-chemical properties and different occurrence forms and distributions of AAEM species in biochar. Compared to slow pyrolysis, fast pyrolysis of fine feedstock gives biochars with lower water-soluble Na and K possibility due to part of the water-soluble portion becomes organically bound or encapsulated within the biochar structures. However, fast pyrolysis produces biochars with higher plant available Mg and Ca and more carboxyl groups present on the surface of biochars. The biochars prepared from wood, leaf and bark, all have dissimilarity in the water-soluble Na, K and Ca, due to differences in their occurrence forms and distributions between these components. Slow pyrolysis of large wood results in a reduction in water-soluble and dilute acid-soluble Na and K due to more extensive secondary reactions, while an increase in water-soluble Na and K is observed for biochars produced from fast pyrolysis of large particle wood, probably due to a lower overall heating rate and temperature gradient resulting from heat transfer resistance. The overall nutrients recycling shows the potential of biochar being returned to soil to complete the loop of nutrient recycling and enhance the sustainability and overall efficiency of the biomass utilisation cycle.

Chapter 5 Leaching Kinetics of Inorganic Species in Biochars Derived from Mallee Biomass

5.1 Introduction

Chapter 4 presented the leaching equilibrium behaviour of AAEM species in mallee biochars produced under different pyrolysis conditions (e.g., feedstock, temperature, particle size and heating rate). The results suggested that AAEM species are released rapidly at an initial leaching stage, followed by slower residual leaching towards equilibrium. Such leaching processes are generally time-consuming. Therefore, it is important to describe the kinetic behaviour of biochar leaching using a suitable kinetic model to practically predict the short and long-term release rates of nutrients in biochar when applying it for soil amendment and to reveal fundamental mechanisms governing the nutrients release during biochar leaching.

Previous studies mainly focused on the absorption kinetics of biochar for the purpose of contaminant removal from a solution [87-89]. Studies on the leaching kinetics of biomass [128] and biochar [8, 70, 77] are fewer. Moreover, little research has been reported on the leaching kinetics of biochars produced under different pyrolysis conditions. Such linkage between pyrolysis conditions and biochar leaching kinetics can be effectively employed to tune pyrolysis conditions in order to produce biochars with outstanding leaching properties.

Thus, the objective of this chapter is to systematically investigate the leaching kinetics of selected biochars which were produced under typical pyrolysis conditions. Both first-order and second-order kinetics models were evaluated to explore suitable model(s) which can accurately describe biochar leaching kinetics. Different leaching kinetics of AAEM nutrients were also discussed, followed by discussion on the effects of pyrolysis conditions on biochar leaching kinetics.

It is worth mentioning that biochars develop their porosity during thermo-chemical reactions at pyrolysis temperatures covered in this study [1, 139]. A fraction of the

pores within a biochar particle's complex pore network can be assessed by the solvent and allow the dissolved solute to travel outwards of the particle. The exact quantification of pore sizes and volumes are complicated due to the wide range of pore sizes in biochars including macropores, mesopores, and micropores [1, 139]. The range of pores are unable to be characterised using a single method, for example BET nitrogen adsorption [139]. Furthermore, nitrogen adsorptions measurements are unable to measure macropores, therefore it is unable to provide full insight on biochar pore distribution [140]. A combined range of analytical techniques such as CO₂ adsorption, mercury porosimetry, pycnometry should be used for biochar pore characterisation [1, 139, 140]. The detailed mechanisms of leached solute transport and biochar pore characterisation are beyond the scope of this study.

5.2 Results and Discussion

5.2.1 Description of First-Order and Second-Order Kinetic Models

First-order kinetic model can be expressed as Equation 5.1 [87, 88, 128].

$$-\ln\left(\frac{C_{i,s}-C_{i,t}}{C_{i,s}}\right) = k_i t \text{ (Equation 5.1)}$$

where $C_{i,s}$ is equilibrium concentration (mg L^{-1}) of species i , $C_{i,t}$ is its concentration (mg L^{-1}) in water at a leaching time t , and k_i is the leaching rate (day^{-1}) of species i . If the leaching of species i follows first-order model, the plot of $-\ln\left(\frac{C_{i,s}-C_{i,t}}{C_{i,s}}\right)$ and time t should give a straight line. Equation 5.1 is used for generating data shown in Figure 5.1.

Second-order kinetic model is described as Equation 5.2 [87, 88, 128] below.

$$\frac{dC_{i,t}}{dt} = k(C_{i,s} - C_{i,t})^2 \text{ (Equation 5.2)}$$

where k is the second order leaching rate constant ($L \text{ mg}^{-1} \text{ day}^{-1}$); $C_{i,s}$ is equilibrium concentration (mg L^{-1}) of species i and $C_{i,t}$ is its concentration (mg L^{-1}) in water at a leaching time t . Integrated rate law (Equation 5.3) can be obtained by integrating Equation 5.2 with the boundary condition $t = 0$ to t and $C_{i,t} = 0$ to $C_{i,t}$.

Rearrangement of Equation 5.3 gives its linear form (Equation 5.4). Equation 5.4 is used for generating data shown in Figure 5.2. The initial leaching rate h can be expressed by Equation 5.5 when t approaches 0. Equation 5.3-5.5 are referenced from [87, 88, 128].

$$C_{i,t} = \frac{C_{i,s}^2 kt}{1 + C_{i,s} kt} \text{ (Equation 5.3)}$$

$$\frac{t}{C_{i,t}} = \frac{t}{C_{i,s}} + \frac{1}{kC_{i,s}^2} \text{ (Equation 5.4)}$$

$$h = kC_{i,s}^2 \text{ (Equation 5.5)}$$

By fitting the data into t/C_t versus t , leaching parameter $C_{i,s}$ can be obtained from the slope and k can be calculated from the intercept [87, 88, 128]. These kinetic parameters are shown in Table 5.1.

5.2.2 Evaluation of First-Order and Second-Order Kinetic Model

Figure 5.1 presents the fitting curves for leaching kinetics of AAEM species in biochars produced under typical pyrolysis conditions using the first-order kinetic model. It should be noted that majority of AAEM species were leached out within 3 days, as shown in Chapter 4, and accordingly only the leaching process within 3 days are considered here. Clearly, water leaching of AAEM species does not follow first-order kinetics, with two distinct leaching steps presented, i.e. a relatively fast initial leaching process followed by a slower residual leaching process towards equilibrium.

Figure 5.1 (a-d) shows that plotting the experimental data according to Equation 5.1 does not give a straight line. In general, two separate leaching stages are observed. The first stage is an initial steep slope that corresponds to the relatively rapid initial leaching process. This is possibly due to the dissolution of the AAEM species on the outer surface of the biochar. This initial steep slope is followed by a slope with less gradient that represents a slower leaching step. Therefore, the experimental data is not suitably described by the first order model in Equation 5.1, but is more suitably described by the second order model which reflects both the slow and fast leaching steps .

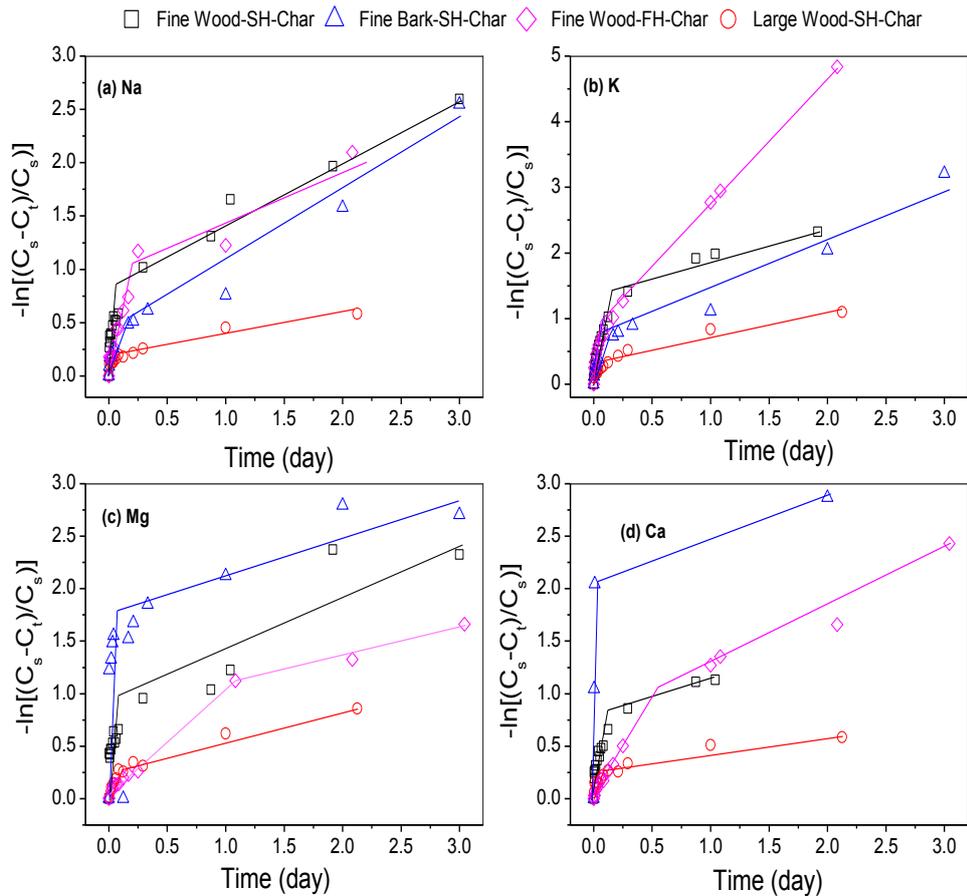


Figure 5.1. Correlation between $-\ln\left(\frac{C_{i,s}-C_{i,t}}{C_{i,s}}\right)$ and leaching time t for (a) Na, (b) K, (c) Mg and (d) Ca in biochars produced under typical pyrolysis conditions.

Figure 5.3-5.10 shows the amount of AAEM retained in biochar over time. A quick reduction followed by gradual reduction in AAEM retention in biochar is observed and consistent for all the biochars studied. Additional efforts were taken to fit experimental data from the leaching process to the pseudo-second order model, and the fitted kinetic parameters are shown in Table 5.1. A reasonably good fit was obtained, showing this model can be used to describe the leaching kinetics. It is important to note that for biochar prepared from large particle biomass, only the data points from day 1 and onwards were used for data fitting as the plot of t versus t/C_t for these biochars is not linear due to a relatively slow leaching rate within the first day. Biochar prepared at 500 °C has a relatively low molar ratio of (O+N)/C,

indicating a low biochar surface polarity resulting from the reduction of surface functional groups at a higher pyrolysis temperature, hence the biochar is relatively hydrophobic [129]. Furthermore, biomass of a larger particle has a smaller total surface area, resulting in the slow superficial wetting of hydrophobic char surface thus a relatively slower leaching rate within the first day.

The pseudo second order model kinetics parameters shown in Table 1 represent lumped parameters which include all the possible mechanisms involved in the overall leaching process. Figure 5.2 (a-d) shows a reasonably good fit of the experimental data to the pseudo second order model. This is speculated to be due to a fast primary leaching step followed by secondary time-consuming diffusion attributed to the interconnected network of multiple sized pores within the biochars [1, 87].

From the fitted parameters presented in Table 5.1, neither the variation in reactor configuration nor the variation in biomass component have a clear effect on the overall leaching rate constant and the initial leaching rate constant of nutrient species in biomass. However, overall and initial leaching rate constants are consistently lower for larger particle size biomass, likely due to a combination of the effects of less available surface area in contact with the leaching medium and the mass transfer resistance experienced by the leached species within the interior diffusion route of the particle pores as discussed earlier. A larger particle size corresponds to a longer pathway for the solvent to be transported inwards and for the dissolved solutes to travel outwards from the particle. This is also clearly demonstrated in Figure 5.3-5.10, which shows the initial leaching rate is slower and a longer leaching time is needed to reach equilibrium for large wood under slow heating. The total sample mass loading was maintained at a constant level throughout this study in order to maintain a similar ratio of sample mass to leaching medium volume thus the effective surface area per unit volume that comes in contact with the leaching medium is lower for larger biochar samples. Therefore, during the early leaching stage, there is more effective and rapid dissolving of surface soluble species for finer biochar samples. Moreover, a large particle size not only increases the time required for wetting process as aforementioned but also increases in the diffusion path length (due to porosity and connectivity of the pore in biochar) of water solubility nutrient to bulk liquid. This possibly explains the lower leaching rates exhibited by the biochars of larger particle size.

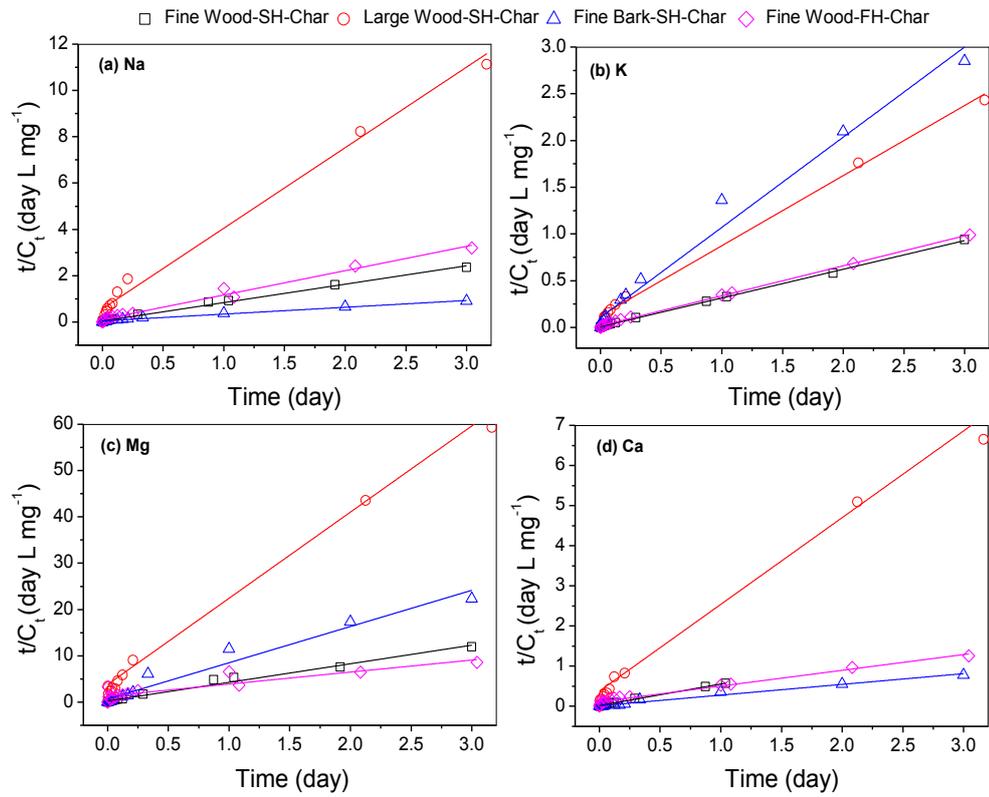


Figure 5.2. Second-order leaching kinetics of (a) Na, (b) K, (c) Mg and (d) Ca in biochars produced under typical pyrolysis conditions.

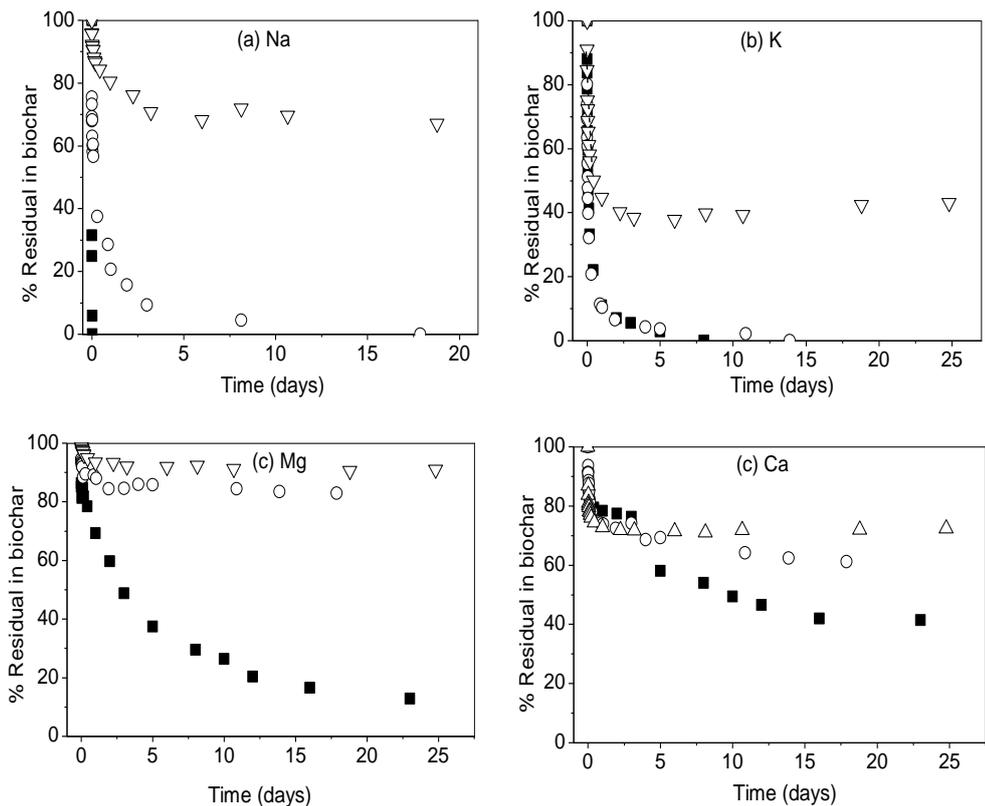


Figure 5.3. Water leaching of laboratory scale fixed-bed (FB) reactor produced wood biochar. Effect of pyrolysis temperature -% residual of AAEM species in biochar. (a) Na; (b) K; (c) Mg; and (d) Ca. Parameters: ■ - T=300°C, ○ - 500°C, ▽ - 750°C; slow heating; 150-250 μ m fine wood particle

Table 5.1. Leaching kinetic parameters for AAEM nutrient species

Sample ID ^a	Elements	Kinetic Parameters		
		k (L mg ⁻¹ day ⁻¹)	h (L mg ⁻¹ day ⁻¹)	r ²
Fine Wood-SH-Char (300°C)	Na	466.4	30.6	0.98
	K	7.6	12.4	1.00
	Mg	2.9	0.6	0.98
	Ca	2.4	0.5	0.94
Fine Wood-SH-Char	Na	6.8	12.9	1.00
	K	5.0	59.5	1.00
	Mg	27.4	1.9	1.00
	Ca	1.2	8.6	0.99
Fine Wood-SH-Char (750°C)	Na	4.9	1.1	0.99
	K	6.6	50.2	1.00
	Mg	16.4	0.4	1.00
	Ca	0.5	2.2	1.00
Large Wood-SH-Char (300°C)	Na	22.3	2.4	0.99
	K	2.7	3.6	0.99
	Mg	1.5	0.1	0.96
	Ca	1.2	0.3	0.98
Large Wood-SH-Char	Na	1.3	0.4	0.99
	K	1.2	3.9	0.99
	Mg	8.6	0.1	0.96
	Ca	0.6	0.7	0.99
Fine Leaf-SH-Char	Na	1.1	76.9	0.96
	K	2.1	41.7	0.98
	Mg	64.1	0.2	0.84
	Ca	2.2	27.9	1.00
Fine Leaf-FH-Char	Na	1.5	270.3	1.00
	K	2.9	116.3	1.00
	Mg	4.4	2.9	0.98
	Ca	2.7	44.1	1.00
Fine Bark-SH-Char	Na	1.9	21.5	0.98
	K	8.8	9.4	0.99
	Mg	46.7	0.9	0.97
	Ca	2.7	39.4	0.99
Fine Bark-FH-Char	Na	4.2	116.3	1.00
	K	47.7	250.0	1.00
	Mg	7.7	1.9	1.00
	Ca	0.4	23.4	0.99
Fine Wood-FH-Char	Na	5.8	5.8	0.99
	K	5.6	54.6	1.00
	Mg	1.0	0.2	0.98
	Ca	1.0	7.1	1.00
Large Wood-FH-Char	Na	0.5	0.4	0.99
	K	0.2	4.0	0.99
	Mg	0.8	0.1	0.98
	Ca	0.1	0.5	0.97

^aPyrolysis temperature is 500°C unless otherwise stated.

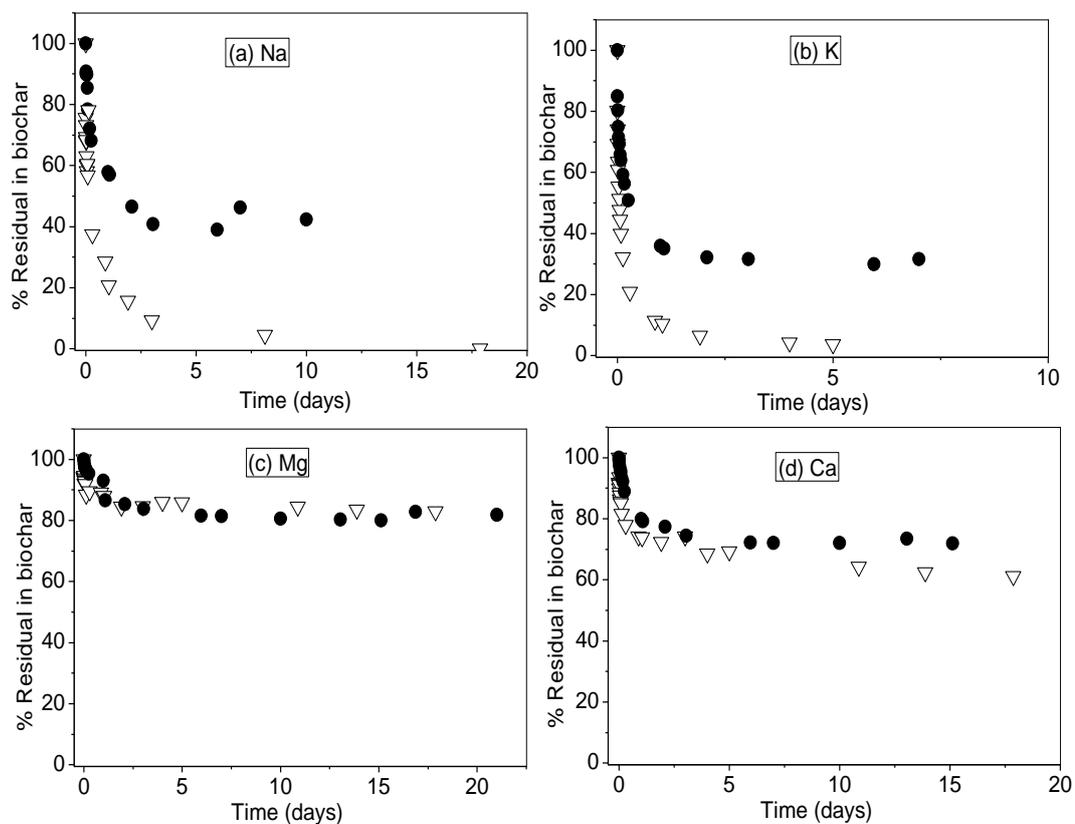


Figure 5.4. Water leaching of laboratory scale DTFB reactor produced wood biochar. Effect of heating rate -% residual of AAEM species in biochar. (a) Na; (b) K; (c) Mg; and (d) Ca. ● - biochar from fast-heating pyrolysis; ▽ - biochar from slow-heating pyrolysis. Parameters: T=500°C; 150-250µm wood particles.

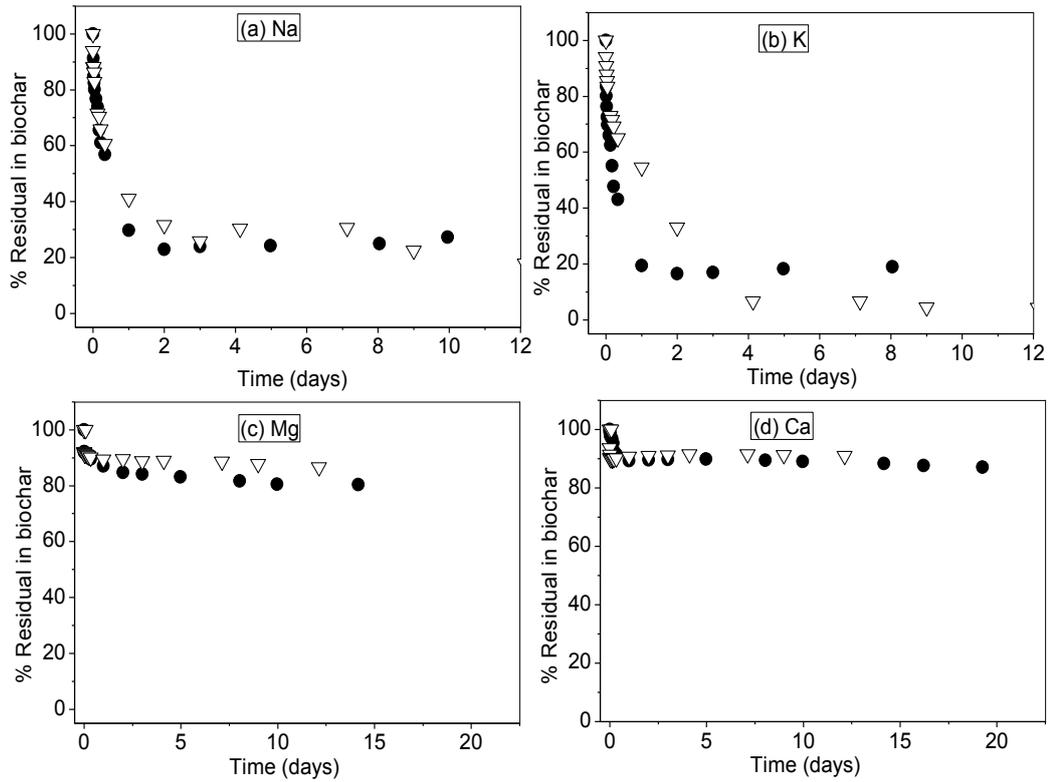


Figure 5.5. Water leaching of laboratory scale DTFB reactor produced bark biochar. Effect of heating rate -% residual of AAEM species in biochar. (a) Na; (b) K; (c) Mg; and (d) Ca. ● - biochar from fast-heating pyrolysis; ▽ - biochar from slow-heating pyrolysis. Parameters: T=500°C; <250μm bark particles.

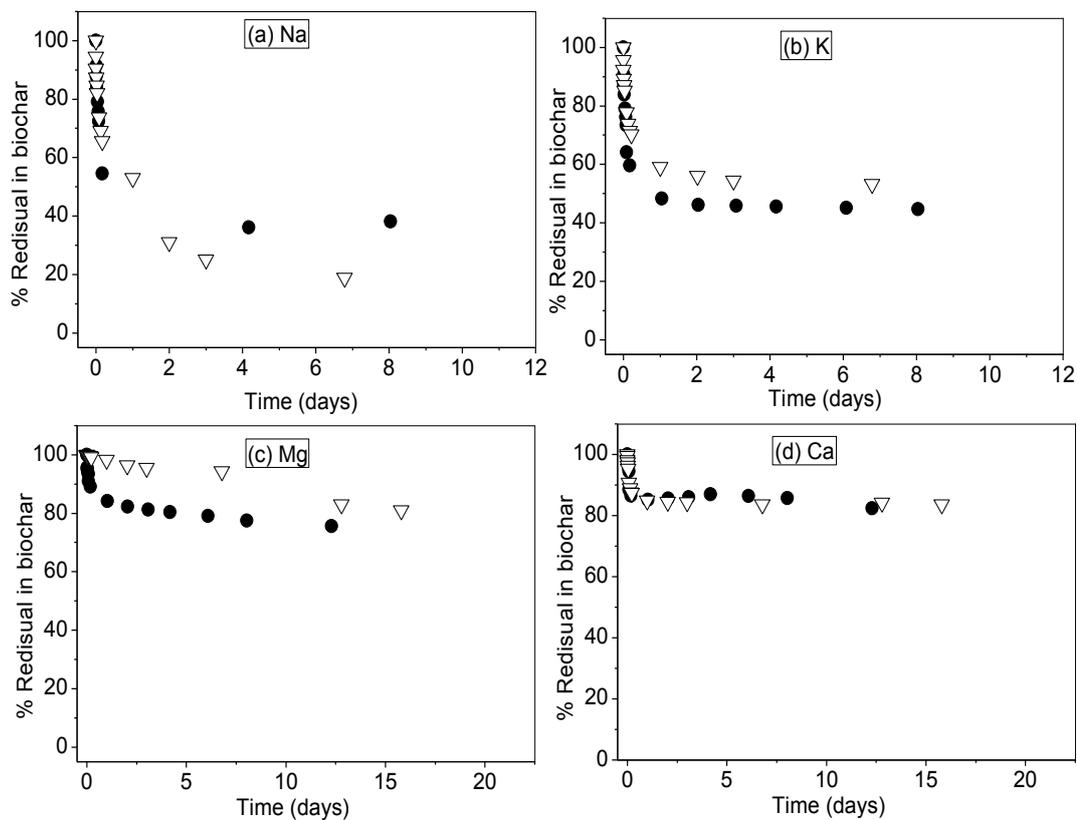


Figure 5.6. Water leaching of laboratory scale produced leaf biochar. Effect of heating rate- % residual of AAEM species in biochar. (a) Na; (b) K; (c) Mg; and (d) Ca. ● - biochar from fast-heating pyrolysis; ▽ - biochar from slow-heating pyrolysis. Parameters: T=500°C; 150-250µm leaf particles.

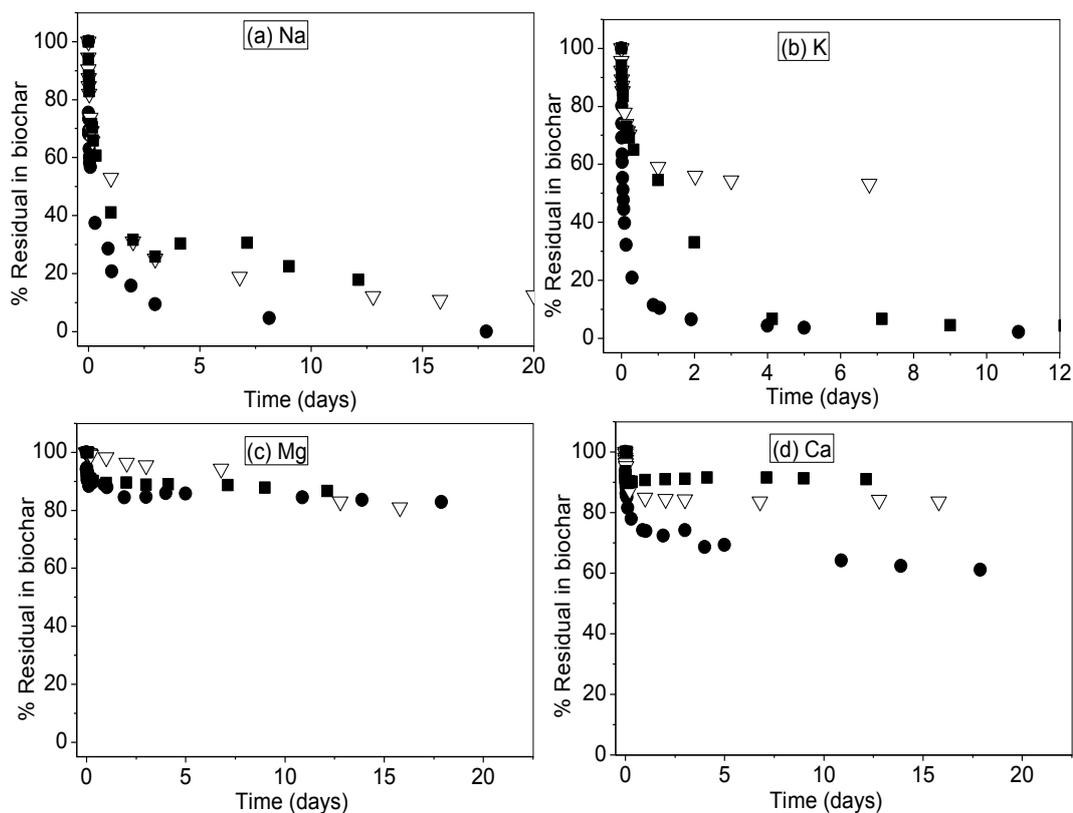


Figure 5.7. Water leaching of laboratory scale FB reactor produced biochar. Effect of biomass components as pyrolysis feedstock - % residual of AAEM species in biochar (a) Na; (b) K; (c) Mg; and (d) Ca. ● - biochar from wood; ▽ - biochar from leaf; ■ - biochar from bark. Parameters: T=500°C; slow heating; 150-250 μ m fine wood & leaf particles, <250 μ m fine bark particles.

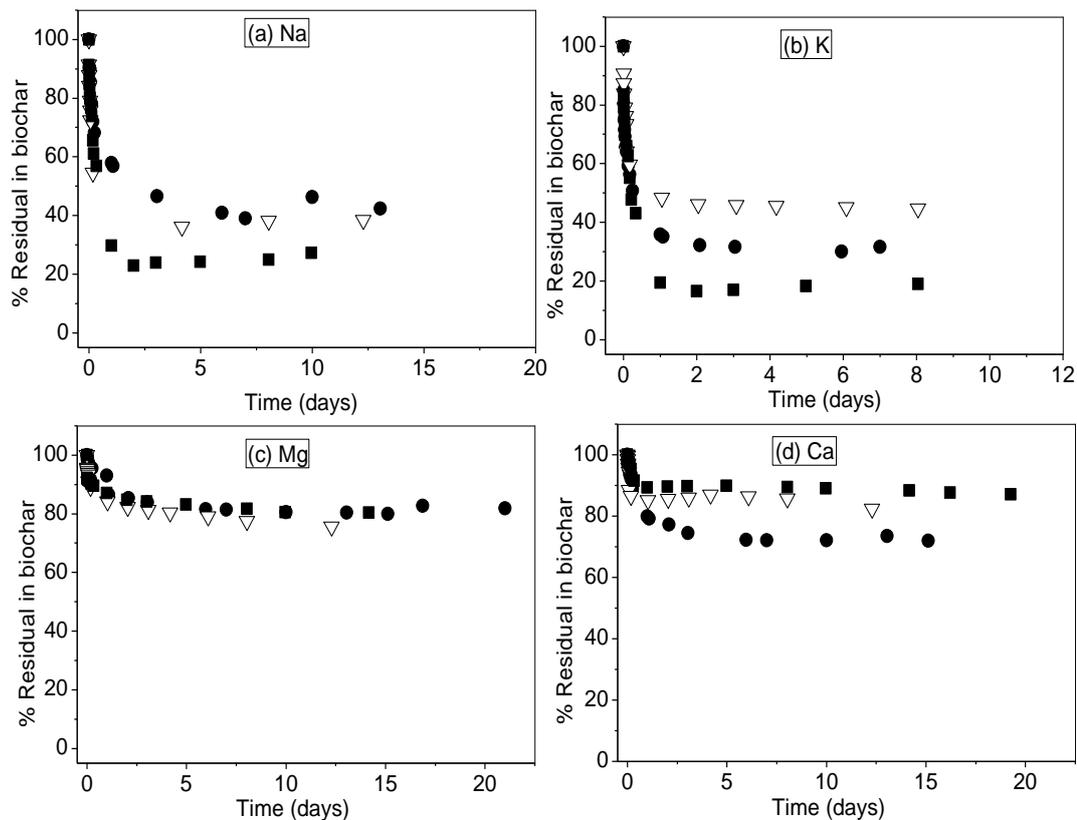


Figure 5.8. Water leaching of laboratory scale DTFB reactor produced biochar. Effect of biomass components as pyrolysis feedstock - % residual of AAEM species in biochar (a) Na; (b) K; (c) Mg; and (d) Ca. ● - biochar from wood; ▽ - biochar from leaf; ■ - biochar from bark. Parameters: T=500°C; fast heating; 150-250 μ m fine wood & leaf particles, <250 μ m fine bark particles.

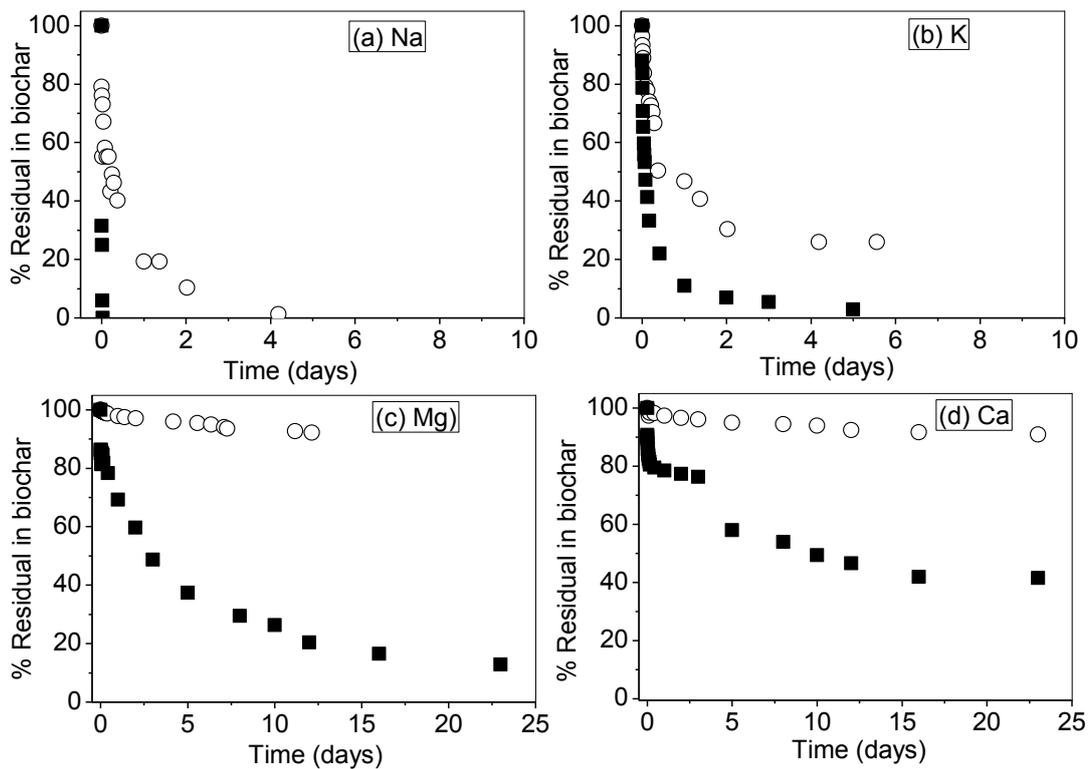


Figure 5.9. Water leaching of laboratory scale FB reactor produced wood biochar. Effect of biomass particle size -% residual of AAEM species in biochar. (a) Na; (b) K; (c) Mg; and (d) Ca. ○ - biochar from 2-4mm large wood particles; ■ - biochar from 150-250µm fine wood particles. Parameters: T=300°C; slow heating.

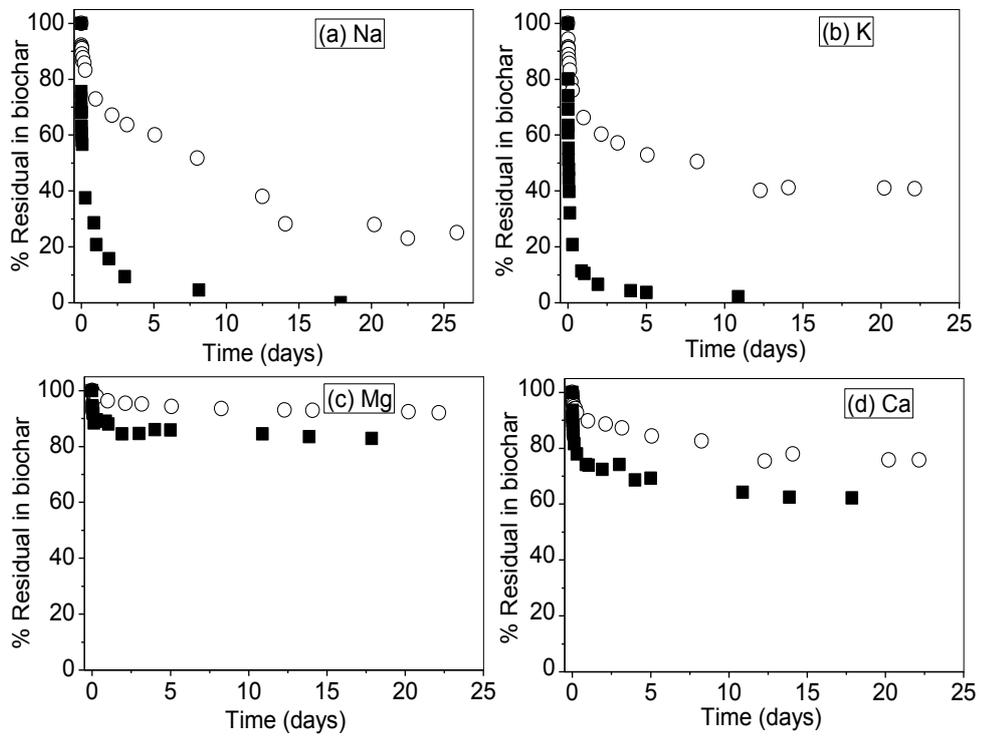


Figure 5.10. Water leaching of laboratory scale produced wood biochar. Effect of biomass particle size -% residual of AAEM species in biochar. (a) Na; (b) K; (c) Mg; and (d) Ca. ○ - biochar from 150-250µm fine wood particles; □ - biochar from 2-4mm large wood particles. Parameters: T=500°C; slow heating.

5.3 Further Discussion

Although the leaching rates for nutrients species vary across the range of different biochar in this study, the common observation is the very low leaching kinetics from the majority of the biochar. This is interesting because the leaching rate constants are low even for the fine size biochar, which indicates that the inherent biomass plant physico-chemical structures in addition to extensive rearrangement and morphological transformation throughout the biochar formation process has resulted in biochar with relatively slow leaching characteristic for the range of species studied.

Previous studies on raw biomass leaching in water has been reported to exhibit diffusion governed characteristics and less controlled by the kinetics of the solubilisation process [79]. The conversion of biomass to biochar via pyrolysis such as performed in this study is known to result in a solid product which contains fractions of less leachable compounds and also a more porous physical structure. Therefore, the biochar leaching is also expected to be similarly or even more diffusion controlled compared to biomass leaching.

Table 5.1 shows the variations of leaching rate constants with respect to the different biochar compounds produced from a range of feedstock and pyrolysis conditions. As discussed earlier, not all biochar types lead to clear variations in trends of leaching kinetics, apart from the obvious effect of larger particle size biomass and biochar on leaching kinetics inhibition. A study by Zheng et al. studied the release of K from grass derived biochar and also found that the release kinetics was agreeable with second order leaching model [35]. The leaching parameters differences in terms of magnitudes with respect to different pyrolysis conditions are similar to the current study. Moreover, an increase in the grass biochar production temperature over the range of 300°C to 600°C did not result in a consistent trend change in the magnitude of leaching constants, which is similar to this study of mallee biochar.

The studies performed by Ho. et al on the leaching of an organic compound from raw wood showed an apparent relationship of the second order data fitting slopes and leaching rates with the leaching medium temperature [128]. Their study was limited to the variations in leaching temperature, where higher leaching temperature was shown to result in an overall higher leaching rate. Furthermore, another study conducted on the leaching of and inorganic ions from raw saline irrigated biomass

showed that the water leaching rates of Na did not display consistent a trend/relationship with respect to the increase in leaching medium temperature [79]. This shows that the leaching process of AAEM ions from raw biomass itself may be governed by a complicated series of factors, therefore the transformations experienced by biochar during pyrolysis such as in this current study, has further affected the properties directly related to leaching kinetics. Apart from that, the nature of the biochar surface with varying degrees of sorption affinity can potentially affect the in situ concentration of the leached species at a particular instant, prior to reaching steady-state leached concentrations. This effect is however not expected to be significant due to the effective stirring achieved for all studies.

In contrary the outcome of this study for both nutrients leaching kinetics from biochar, studies of biochar nutrient release by Mukherjee et al. [49] indicated the lack of importance of the leaching period or mixing efficiency, and instead found strong relationships with the solid-solution dissolution based on equilibrium instead of kinetics as per this study. This conclusion was drawn based on the similar leaching behaviour based on both batch and column leaching investigations. The potential solvent/solute ratio inhibiting factor was identified as the main factor that affects the nutrient release [49], which is not agreeable to this current study. This may be due to the different biochar nutrients between the two studies, where the study by Mukherjee et al. [49] focused on nitrogen and phosphorus, compared to the AAEM species in this study. Furthermore, the different biomass feedstock (oak, pine, and grass) and production method applied in their investigation could also lead to the deviation in biochar properties and in turns affects the nutrient leaching dynamics. Mukherjee et al. [49] introduced a pyrolysis method of introducing a pre-combustion process in full atmosphere, followed by pyrolysis in a pure nitrogen environment. Their biochar sample production method focused on simulating the agricultural residue cool burning or natural forest fires, and differs significantly from the well-controlled continuous inert gas-purged pyrolysis in the current study. This once again emphasizes the significance of biochar heterogeneity from a myriad of factors and the need for individual and application-specific studies.

5.4 Conclusions

The kinetics of AAEM nutrients leaching from mallee derived biochar were applied as a second-order leaching model. The experimental data provided a reasonably good fit to the model and was able to provide insight upon the variations in leaching rates with respect to different biochar production parameters. Generally, the leaching of AAEM nutrients from biochar is slow, due to the biochar structure with internal bends and pores which lead to time-consuming travel of the leached species. The effect of larger biomass pyrolysis sample particle size on the subsequent biochar leaching rate reduction was apparent.

Chapter 6 Effects of Pyrolysis Conditions and Biomass Properties on Stability of Carbon in Biochars

6.1 Introduction

Chapter 4 presented the leaching equilibrium behaviour of AAEM species in a range of mallee biochars produced from different feedstocks under various conditions. Chapter 5 discussed the kinetics of the nutrient leaching process.

Biochar stability is the major deciding factor when benchmarking its potential benefits as a means of carbon sequestration. Studies have indicated that biochar has the potential to remain stable for hundreds to thousands of years [21]. The majority of carbon in biochar are recalcitrant aromatic fractions as opposed to less stable organic carbon in the original feedstock. Therefore, biochar will act a more stable form of carbon in the environment as opposed to the raw plant residues [34]. Therefore, upon being applied to soils, the stable carbon in biochar can act as a carbon sink which is less likely to be transformed into carbon dioxide and released back into the atmosphere as commonly seen during plant respiration [1, 21, 24]. Therefore, it is also important to describe the equilibrium and kinetic behaviour of carbon from biochar. This chapter extends the discussion towards the biochar carbon water leaching behaviour of a range of biochar upon being applied to the soil.

6.2 Leachabilities of Carbon from biochar

Table 6.1 shows the summary of leachabilities of carbon from a range of biochar samples prepared from different mallee tree components, sizes, and pyrolysis conditions. Generally, the leaching of carbon was very time consuming and the leachabilities varied across the range of biochar from different biomass source and production conditions. Although the maximum leached fractions of carbon from the biochars are significantly lower than the AAEM inorganic nutrients, the leaching of

carbon from the biochar requires much longer periods compared to the leaching of AAEM nutrients. This indicates that the release of carbon is potentially more kinetically suppressed compared to the leaching of nutrients from the biochar samples. Figures 6.1 to 6.6 shows the leaching profiles of carbon from the range of biochar studied.

Table 6.1. Summary of the data on the leachabilities of carbon from biochar samples

Sample ID^a	% Carbon	Equilibrium Time (days)
Fine Wood-SH-Char (300°C)	1.7	52
Fine Wood-SH-Char	0.6	17
Fine Wood-SH-Char (750°C)	0.6	3
Large Wood-SH-Char (300°C)	1.6	50
Large Wood-SH-Char	0.6	14
Fine Leaf-SH-Char	1.7	24
Fine Bark-SH-Char	1.1	53
Fine Wood-FH-Char	0.7	11
Fine Leaf-FH-Char	2.2	17
Fine Bark-FH-Char	1.3	4

^aPyrolysis temperature is 500°C unless otherwise stated.

6.2.1 Effect of Pyrolysis Temperature

Figure 6.1 shows the effect of pyrolysis temperature on carbon leachability of wood biochars. The release profiles of carbon from the biochar species over an extended period are indicative of the long term release of the carbon towards equilibrium. However, the percentage of carbon leached from the biochars across the wide range of pyrolysis temperatures is generally low and limited to <2%. The percentage carbon leached from wood biochar produced at 300°C is shown to be considerably higher than that of biochar produced at intermediate and high pyrolysis temperatures. This is likely due to the low pyrolysis temperature of 300°C which produced less recalcitrant biochar, therefore the carbon leaching behaviour of such samples is more pronounced. The percent carbon leached from 500°C and 750°C biochars is lower, and there is negligible difference between the leachability of the two biochars. This indicates that upon a pyrolysis temperature of 500°C, the thermal process has

transformed the organic structure of the raw biomass into an increasingly aromatic and stable form unresponsive towards water leaching but more favourable for carbon sequestration purposes [21]. A range of other studies have found that leaching of organics from biochar is dependent on pyrolysis temperature [34, 49, 52, 130-132]. As discussed in section 4.2, leaching of inorganic nutrients is more favoured from biochars of lower production temperature; this section shows that leaching of organics follow similar trends. Studies have shown that the dissolved organic carbon and biochar acidic content are possibly related, where it is postulated that biochars produced at lower pyrolysis temperatures have higher water leachability of organic carbon due to its higher acid content [34, 133]. Increasing pyrolysis temperature results in biochar which is more carbonised as the thermo-chemical transformations during pyrolysis such as devolatilisation reduces aliphatic functional groups and volatiles. Mukherjee et al. correlated the water soluble organic carbon with the volatile matter and acid functional groups content [49]; earlier studies correlated the portion of labile carbon in biochars with aliphaticity and richness in volatile species [134]. Judging from the consistent decrease in acidic functional groups content between low and high temperature biochars which is also found for the current mallee biochar studied [52], the leaching of organics is likely to decrease with respect to increasing biochar production temperature. The low pyrolysis temperature of 300°C is also sufficiently low to produce biochar with substantial residual content of leachable humic compounds and low molecular weight neutrals such as alcohols, aldehydes, ketones, sugars, and protein building blocks [131]. As observed in Figure 6.1, the difference in carbon leachability is quite significant between the 300°C and 500°C temperatures, however the further increase in temperature to 750°C did not have notable effects on carbon leachability. A study by Al-Wabel et al. [34] showed similar results where the temperature increase from 200°C to 400°C resulted in a lower portion of dissolved organic carbon from the derived biochar. However, temperatures higher than 400°C did not lead to significant variations in the biochar's labile or dissolvable organic carbon [34]. Furthermore, the degradation of cellulose which is mostly complete before 400°C [131] may explain the relatively insignificant differences between carbon leachability among the 500°C and 750°C biochars, due to extensive carbonisation and aromatisation of original leachable carbohydrate carbon upon reaching the final temperature of 500°C.

Although the increase in pyrolysis temperature resulted in biochar with less dissolvable carbon and becoming decreasingly labile, the formation of undesirable toxic compounds also increases at higher temperatures, as pyrolysis temperature has a significant effect on the toxicity level of biochar [3]. Therefore, the higher temperature biochars may be more favourable for carbon sequestration but can potentially pose eco-toxicological risks upon being added to soils. However, the overall low leachability of carbon from the mallee biomass derived biochars in the present study is an indication that the issue of dangerous PAH levels is relatively unlikely to occur. The total amount of Polycyclic Aromatic Hydrocarbon (PAH) levels released in studies of wood biochar by Singh et al. also showed a value below the safety limit [135]. However, if different biomass feedstock are used for pyrolysis, apart from those mentioned in Singh et al. and this current study, the potential exceeding of PAH safety levels should be given further consideration.

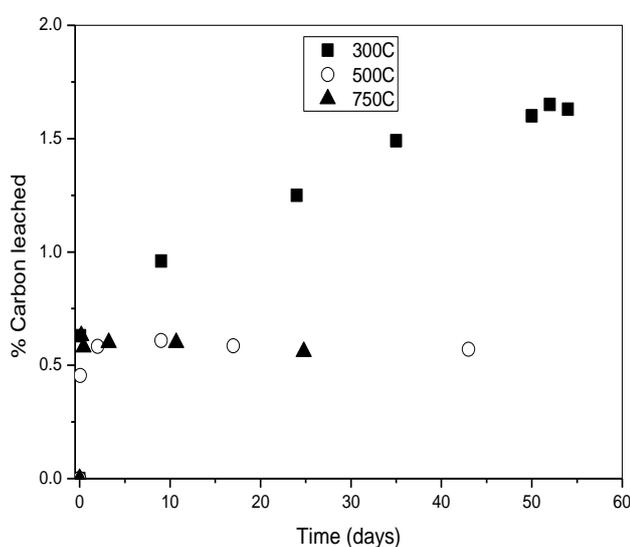


Figure 6.1. Water leaching of laboratory scale FB reactor produced biochar. Effect of pyrolysis temperature- % Leaching of carbon in biochar. ■ - 300°C; ○ -500°C;- ▲ 750°C; Parameters: slow heating; 150-250 μm fine wood particles.

6.2.2 Effect of biomass components

Figure 6.2 and 6.3 shows the effect of biomass components as pyrolysis feedstocks on the difference in carbon leachability from the derived biochars of both slow and fast heating rates, respectively. Biochar from both heating rates show similar trends of percent carbon leached (leaf>bark>wood), where the highest amount of carbon leached was below 2.5%. Studies of biochar mineralisation rates by Singh et al. also indicated carbon mineralisation rates were higher in leaf biochars compared to wood derived biochars [132]. The difference between carbon leachability from the biochars derived from different biomass components is possibly due to the variations in the chemical structures of both the raw biomass and the post-pyrolysis biochar. The higher mineral content in the leaf biochar may have partially contributed to the lower carbon stability by causing imperfections in the makeup of carbon and reducing the fraction of directly-linked recalcitrant carbon lattice structure [132].

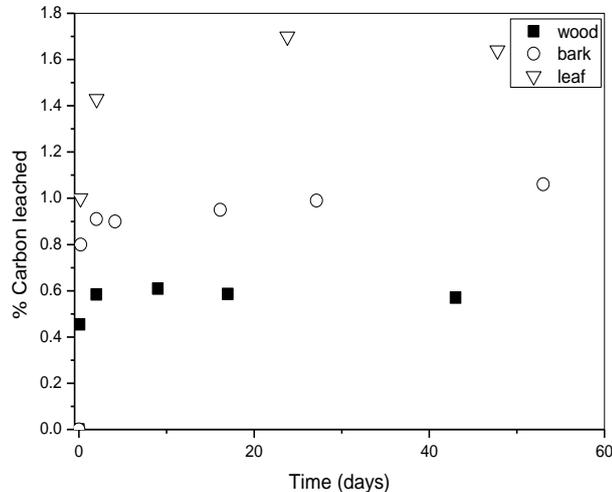


Figure 6.2. Water leaching of laboratory scale FB reactor produced biochar. Effect of Biomass Components- % Leaching of carbon in biochar. ■ - biochar from wood; ○ - biochar from bark; ▽- biochar from leaf. Parameters: slow heating; 150-250µm fine particles.

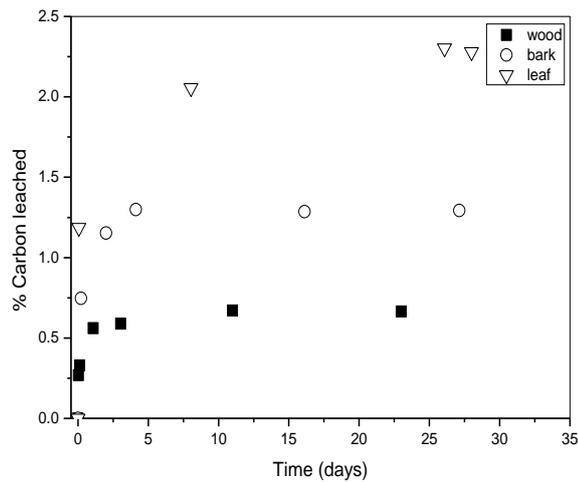


Figure 6.3. Water leaching of laboratory scale DTFB reactor produced biochar. Effect of Biomass Components- % Leaching of carbon in biochar. ■ - biochar from wood; ○ - biochar from bark; ▽ - biochar from leaf. Parameters: fast heating; 150-250µm fine particles.

6.2.3 Effect of heating rate

Figure 6.4 shows the effect of heating rate on the water leaching of carbon. Generally, more carbon is leached from the fast heating-rate biochars prepared under similar conditions, where a consistent trend can be seen for all the biochar (wood, bark, and leaf). As mentioned earlier, higher pyrolysis temperatures result in more carbonised biochar with lower oxygen functional groups content and lower carbohydrate properties compared to the lower temperature biochar. Under fast heating pyrolysis conditions, the thermal limitations is higher [10, 52] and effective residence time is lower and less time is available for micro-structural rearrangement of the biochar to form stable carbon structures, therefore the extent of carbonisation may be lower hence resulting in a biochar with richer contents of carbohydrate groups [52]. Fast heating pyrolysis is known to produce biochar with more labile aliphatic groups which are more susceptible to leaching [52], similar to the effect of lower pyrolysis temperatures. This in turns results in higher carbon leachability compared to their

slow heating counterparts. Therefore, both lower pyrolysis temperatures and faster heating rates have the effect of producing biochar with higher fractions of leachable carbon. On the other hand, the more extensive secondary reactions and possible sorption of volatile organic matter to the biochar surface [136] possibly explains the higher carbon leachability for these range of biochars due to a fraction of these volatile compounds being water soluble.

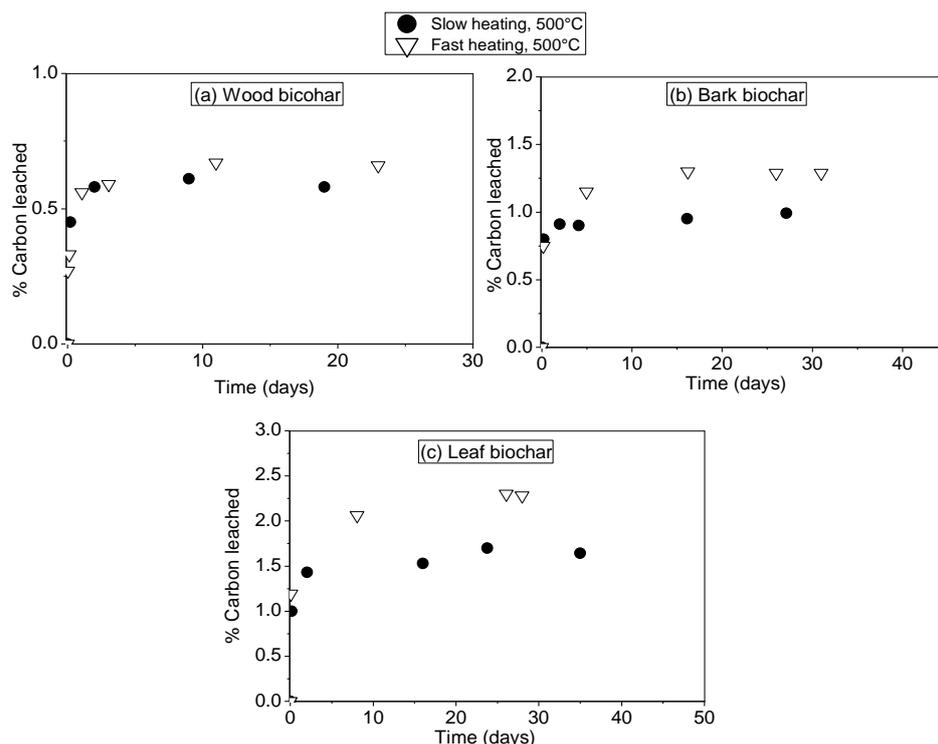


Figure 6.4. Water leaching of laboratory scale slow and fast heating rate pyrolysis produced biochar. Effect of heating rate -% Leaching of Carbon in biochar. (a) Biochar from wood; (b) Biochar from bark; (c) Biochar from leaf; ● - biochar from slow-heating pyrolysis in FB reactor; ▽ - biochar from fast-heating pyrolysis in DT-FB reactor. Parameters: T=500°C; 150-250µm fine particles.

6.2.4 Effect of Particle Size

Figure 6.5 and 6.6 depicts relatively similar leachability of carbon from biochars produced from different particle size wood biomass at the same temperature. The slow heating condition in this case provides adequate heating time for biomass particles of both size ranges to undergo relatively similar progression of the carbonisation process, thus resulting in biochar of similar labile and soluble carbon content.

In terms of the ability of biochar as a safe means of sequestering carbon, the potential of large extents of carbon leachability is not expected, as shown from the low carbon leachability in this study. Although biomass properties and pyrolysis conditions have certain effects on carbon leachability, the overall leaching of carbon over prolonged periods from the biochars in this study are relatively low. This works in favour of biochar application to soil for stable carbon storage purposes.

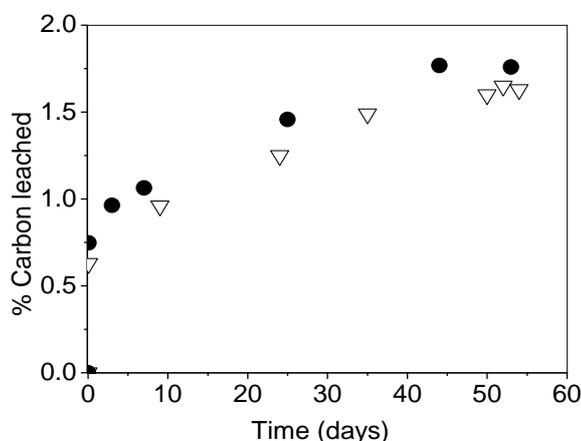


Figure 6.5. Water leaching of laboratory scale FB reactor produced biochar. Effect of Particle Size-% Leaching of Carbon in biochar; ▽- biochar from 150-250µm wood; ●- biochar from 2-4mm wood. Parameters: T=300°C; slow heating.

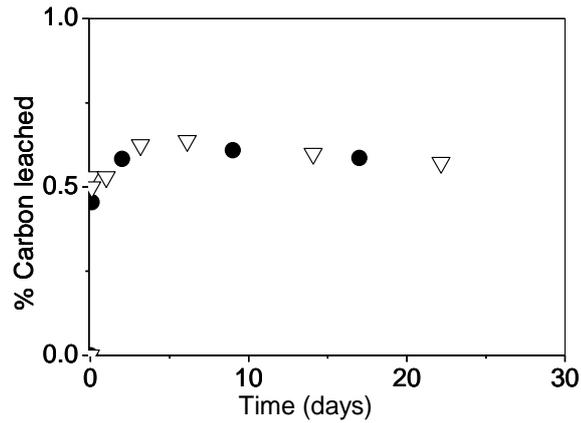


Figure 6.6. Water leaching of laboratory scale FB reactor produced biochar. Effect of Particle Size-% Leaching of Carbon in biochar; ∇ - biochar from 150-250 μ m wood; \bullet - biochar from 2-4mm wood. Parameters: T=500°C; slow heating.

6.3 Pseudo Second Order Leaching Kinetics of Carbon

The kinetics of AAEM nutrients leaching from mallee derived biochar were applied to a second-order leaching model. In Chapter 6, the experimental data for Carbon leaching is applied to the same model. The kinetic parameters represent lumped parameters which include all the possible mechanisms involved in the overall leaching process. Table 6.2 and Figure 6.7 show that the experimental data provided a reasonably good fit to the model and was able to provide insight upon the variations in leaching rates with respect to different biochar production parameters. Although wood biochar (slow and fast heating) display the lowest carbon maximum extractability among the biomass components, its leaching of carbon is the fastest for the same biochar. The increase in pyrolysis temperature from 300°C to 500°C results in a higher carbon leaching rate, most possibly due to the increased carbon concentration in the increasingly carbonaceous biochar produced at 500°C which increases the concentration driving force during leaching. Pyrolysis temperature beyond 500°C did not lead to further increase in carbon leaching rates for wood biochar. There is only a slight reduction in overall carbon leaching rate for biochars produced under fast heating conditions across all components (wood, bark, leaf). The

carbon leached from the biochars likely consist of a complex combination of organic acids, water soluble carbohydrates and phenolics. The organic compounds are of larger molecular structures compared to the alkali and alkaline earth metallic ions, thus the leaching of organics would be expected to be easily hindered by the biochar structure. The larger sample particle size leads to a slightly lower leaching rate of carbon which is likely due to the inhibiting mass transport effects of the larger particle size, similar to the discussion for AAEM nutrients leaching in Chapter 5. Similar to the leaching of AAEM species, the leaching of carbon may likely have a rapid initial leaching process followed by a slower diffusion inhibited leaching process. A larger particle size means that the dissolved solute needs to travel a longer distance out of the particle.

This study shows that both the overall maximum fraction of carbon released and the carbon leaching rate from the biochar samples in this study is low, thus resulting in the promising potential for a stable carbon storage method by returning biochar to soils with the purpose of climate change mitigation.

Table 6.2. Second order Leaching kinetic parameters for carbon leaching from biochar

Sample ID ^a	Leaching Kinetic Parameters for Carbon		
	k	h	r ²
Fine Wood-SH-Char (300°C)	0.1	9.0	1.00
Fine Wood-SH-Char	5.7	133.3	1.00
Fine Wood-SH-Char (750°C)	5.2	250.0	1.00
Large Wood-SH-Char (300°C)	0.03	5.8	0.99
Large Wood-SH-Char	4.0	100.0	1.00
Fine Leaf-SH-Char	2.3	416.7	1.00
Fine Bark-SH-Char	0.6	50.0	1.00
Fine Wood-FH-Char	1.4	38.9	1.00
Fine Leaf-FH-Char	0.4	103.9	1.00
Fine Bark-FH-Char	0.4	55.6	1.00

^aPyrolysis temperature is 500°C unless otherwise stated.

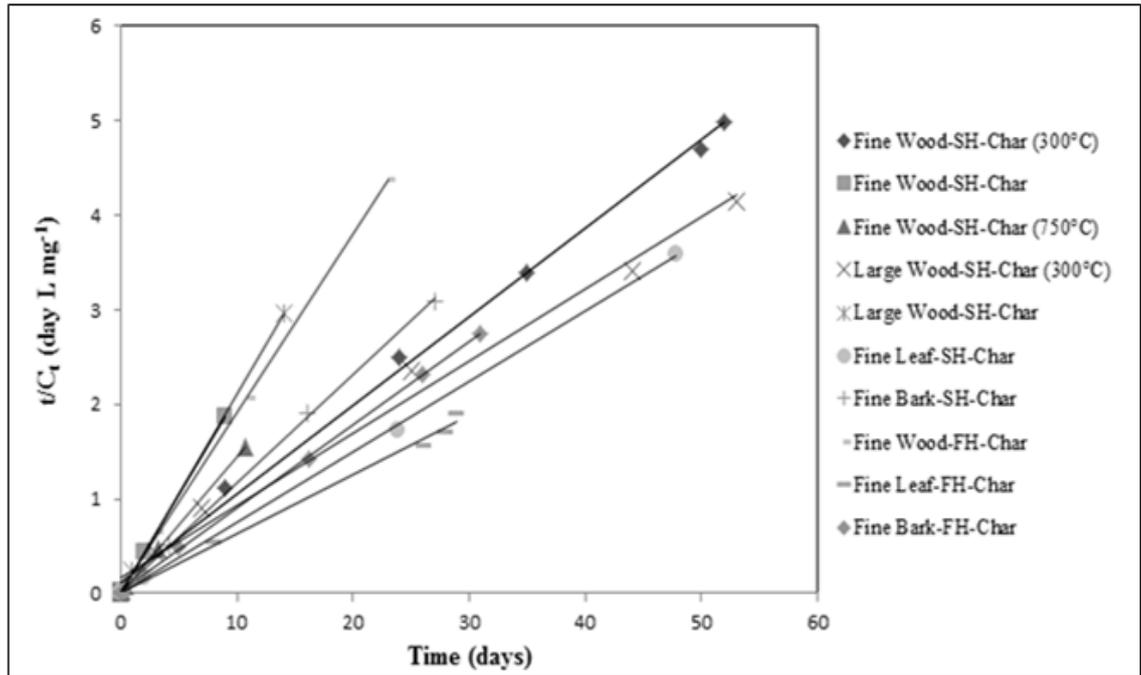


Figure 6.7. Second-order leaching kinetics of Carbon in biochars produced under typical pyrolysis conditions. (Pyrolysis temperature is 500°C unless otherwise stated).

6.4 Conclusions

Overall, the leaching of carbon from the entire range of biochar is low, hence indicating a potential benefit for long-term biochar application to soils for simultaneous nutrient recycling and carbon sequestration purposes. The kinetics of carbon leaching from mallee derived biochar were described by a second-order leaching model. The experimental data was able to be fitted well to the model. Generally, the leaching of carbon from biochar is slow, due to the biochar structure which reduces the mass transport rate of the leached species. Similar to the leaching kinetics study of AAEM species in Chapter 5, the effect of larger biomass pyrolysis sample particle size reduces the leaching rate of carbon.

Chapter 7 Conclusions and Recommendations

7.1 Introduction

Chapter 7 summarises the findings from this entire study and provides recommendations for future research. This study has focused on research of mallee biochar and its potential as a soil amendment agent. The effect of pyrolysis conditions used to produce the biochar, such as temperature and heating rate, were studied to identify the conditions in favour of production of high quality biochar in the context of nutrient recycling. Mallee tree components (wood, leaf, and bark) and different sample particle size were also among the variables included in the study. Apart from that, a pseudo second order kinetics model was proven to represent the leaching behaviour reasonably well. Lastly, an extension study of the leaching of carbon from the range of mallee biochar was performed. The following sections summarise the conclusions of the various chapters in this thesis.

7.2 Conclusions

7.2.1 Effects of Pyrolysis Conditions and Biomass Properties on Leachability and Recyclability of Inorganic Nutrients in Biochars Produced from Mallee Biomass Pyrolysis

- Temperature and heating rate has significant effects on leaching of AAEM from mallee biochars.
- Biochars produced from lower pyrolysis temperatures and under slow heating rate conditions are more favourable in terms of their nutrient availability.
- Different biomass components did not show significant effects on the nutrients leachabilities; any differences were attributed to the differences in inherent physico-chemical structures of the biomass and/or biochar.
- An increase in particle size has profound impacts on the pyrolysis thermo-chemical reactions and hence biochar nutrient leaching.

7.2.2 Leaching Kinetics of Inorganic Species in Biochars Derived from Mallee Biomass

- The pseudo second order model provides a reasonable fit for describing the release of AAEM nutrients from the biochar in this study.
- There is no significant impact on biomass components and pyrolysis conditions on biochar leaching kinetics.
- Larger biomass particles results in reduced AAEM leaching rates from biochars.

7.2.3 Effects of Pyrolysis Conditions and Biomass Properties on Leachability and Recyclability of Carbon in Biochars

- The preliminary study shows that the overall leaching of carbon from the range of biochar studied was low (below 2.5%). The leaching kinetics were also low.
- The effect of temperature, heating rate, and biomass components do not have major impacts on carbon leachability.
- An increase in particle size of biomass particles results in reduced carbon leaching rates from biochars.
- The pseudo second order model is suitable for describing the leaching of carbon from the biochar in this study.

7.3 Recommendations for Future Research

Based on the research outcome of this study, recommendations for future research is summarised as follows:

1. Identify the relationship between biomass plant structure and leaching.
2. Identify the long-term nutrients release from biochar and soil mixtures, taking into account the different soil types.
3. Study the effect of leaching medium temperature on equilibrium and kinetics of biochar leaching.
4. Develop a multi-step mathematical model for simulating leaching.
5. Obtain diffusion coefficients for the leaching process.
6. Identify separate stages and phenomena that occur during leaching and the kinetics for each step.

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