Department of Chemical Engineering

Leaching of Inorganic and Organic Matter from Biomass and Biochars under Various Conditions: Equilibrium, Kinetics and Implications

Sui Boon Liaw

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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 acknowledgment has been made.

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To my beloved family
and my late grandparents

Abstract

Fossil fuels such as coal remain as the major fuels for supplying energy in Australia, resulting in significant carbon emissions. In Australia, the introduction of Renewable Energy Target Scheme provides the industry with the much needed incentives to shift toward renewable energy such as biomass. Mallee tree, which is a by-product of managing dryland salinity issue in the wheatbelt region of south Western Australia, is a promising second generation biomass (lignocellulosic) feedstock. The production of mallee biomass is at a large scale, economical and achieving a relatively higher energy ratio compared to other energy crops.

Biomass can be utilised for energy production through various thermochemical processes. For example, biomass can be burnt directly or co-fired in coal power plants to generate energy. It can be converted into syngas via gasification. In addition, biomass can also be converted into biochar and bio-oil via pyrolysis, which can be used as fuels. Furthermore, lignocellulosic biomass can be hydrothermally treated to convert the hemicellulose and cellulose in biomass into fermentable sugars for bio-ethanol production.

Leaching process plays an important role in utilisation and thermochemical processes of biomass. For sample, water washing of biomass has been extensively studied as a strategy to remove the inherent ash-forming species in biomass that lead to notorious ash-related issues during biomass combustion or gasification. Batch leaching of biomass with water was also employed as the first step of sequential leaching to investigate the occurrence of inorganic species in biomass. Leaching of biochar, on the other hand, is employed to assess the recyclability of inorganic species in biochar and leachability of organic matter from biochar when it is applied to soil. Even during hydrothermal processing of biomass in hot-compressed water (HCW), the inherent inorganic species in biomass may be leached from biomass via HCW. The leaching of these elements can have a significant implication on the yield of fermentable sugar from hydrothermal processing of biomass in HCW. Despite continued research on the leaching of inorganic and organic matter from biomass and biochar, there are still a number of research gaps that are yet to be addressed.

The current study aims to provide better understanding on the leaching of inorganic and organic species from biomass and biochar under various conditions with emphasis on equilibriums, kinetics and their implications. The main objectives of this research are: (1) to study the leaching characteristics of inorganic and organic matter from biomass and the influence of the leaching of organic matter on the leaching of inorganic matter from biomass; then, a method to accurately quantify the water-soluble inorganic species in biomass is proposed; (2) to investigate the potential of partial steam gasification of fast pyrolysis biochar as a method to tune biochar properties and reduce the leaching of harmful organic matter from biochar; (3) to examine the suitability of partial steam gasification as a method to enhance the recyclability of nutrients from fast pyrolysis biochars; and (4) to provide better understanding on the leaching characteristics of alkali and alkaline earth metallic (AAEM) species in biomass under HCW condition and the occurrence of water-insoluble AAEM species in biomass.

Firstly, the results of this study show that over 30% and ~2% (on carbon basis) organic matter can be leached from mallee leaf and wood by water, respectively, producing acidic leachates containing organic acids. As a result, there are significant differences in the leaching characteristics of both organic and inorganic species in biomass between batch and semi-continuous leaching operations. Under conventional batch leaching, the acidic leachate continuously contact with the biomass for a prolonged period, resulting in the leaching of at least some water-insoluble inorganic species (e.g. organically-bound) from biomass. Therefore, the batch leaching method clearly overestimates the amount of water-soluble inorganic species in biomass. The leaching of inorganic species in biomass under batch condition exhibits two-step leaching kinetics, i.e. a rapid leaching step for an initial short period followed up a slow leaching step for a relatively long period. This study further develops a semi-continuous leaching method to address this issue via minimising the contact between the leachate and the biomass sample. The semi-continuous leaching quantifies the true water-soluble inorganic species in biomass. Its leaching kinetics include only the first rapid leaching step, with the disappearance of the second slow-leaching step due to the absence of the interaction between acidic leachate and biomass. The results suggest that in the sequential extraction scheme used in chemical fractionation, semi-continuous (instead of batch) water leaching method should be used for quantifying water-soluble inorganic species in biomass. Attention should also be paid to the potentially substantial loss of fuel materials when utilising water leaching as a pretreatment method to remove inherent inorganic species in biomass for fuel quality improvement. As result of overestimating water-soluble inorganic species and loss of organic matter, care must be taken in using water batch washing as a method for studying the effect of the inherent water-soluble inorganic species on thermochemical reactions of biomass.

Secondly, the results in this PhD thesis suggest that it is a good strategy to tune the properties of fast pyrolysis mallee biochar (fine particle wood and leaf biochar and large particle wood biochar) properties via partial steam gasification at low carbon conversions (5 – 10%) and mild temperature (725°C). Such a tuning process resulted in a small expense (can be as low as ~10%) in the amount of carbon that can be sequestrated. The pores in fast pyrolysis biochar are mainly micropores. Partial steam gasification only leads to a small increase in micropore surface area while increase of BET N_2 surface area from <100 m^2/g to between 450 and 675 m^2/g is observed, owing to the enlargement of micropores and opening of the partially blocked pores in biochar. Less than 1.5% of organic matter on carbon basis can be leached from raw and tuned biochar via water. Secondary pyrolysis generally leads to the reduction of water leachable organic matter to below detectable amount. However, small amount of organic matter is leachable from tuned biochar due to the opening of blocked pores and increase in accessibility of these leachable compounds within biochar due to development of porous structure following gasification. Analysis of water leachates shows no detectable aromatic compound. However, aromatic compound with up to 5 fused rings can be leached from raw biochar via chloroform–methanol mixture. Tuning of biochar via partial gasification produced biochar with no solvent leachable aromatic compound, reducing the risk of possible soil contamination due to leaching harmful organic species. The results further demonstrate that tuning of biochar via partial steam gasification is able to produce biochar with desired properties for soil amendments (such as promoting soil microbial activity and improving soil water holding capacity).

Thirdly, tuning of biochar via partial steam gasification to enhance the recyclability of nutrients from fast pyrolysis biochars is studied. Partial steam gasification of biochar resulted in minimal volatilisation of AAEM species in biochar. However, the retention of Na in leaf biochar can be as low as ~66% owing to the more intense volatile-char interaction and forced flow of Argon gas through a thin layer of char bed. Most of the Na and K in fast pyrolysis leaf and wood char prepared at 500 °C are leachable by water or Mehlich-1 solution (plant available nutrient). However, ≤30% of Mg and Ca in wood biochar is water leachable or plant available nutrient, resulting in low recyclability of Mg and Ca. Partial steam gasification (1) promotes the development of pore structure in biochar and (2) transforms part of the AAEM species that is in the form that is not water nor dilute acid soluble into the form that is leachable by water and Mehlich-1 solution. This effectively enhanced the recyclability of AAEM in wood and leaf biochar to 85% and 96%, respectively. Further effort had been taken to fit the experimental data from water leaching of AAEM species to pseudo-second order kinetic model. It is found that partial steam gasification increases the overall kinetic rate constant and initial leaching rate, due to the same two factors aforementioned. The overall recycling of AAEM species from tuned and raw biochar is calculated by normalising the amount of plant available nutrient to the total AAEM species available in biomass. The result shows tuning of biochar via partial steam gasification greatly enhanced the overall recyclability of Mg and Ca in biochar. The result further demonstrates that biochar produced from pyrolysis of large particle feedstock can be ground and tuned to enhance the overall recyclability and leaching kinetics of the nutrient species.

Lastly, the leaching of water-insoluble alkaline earth metallic species in mallee wood under HCW conditions at 150 – 270 °C using semi-continuous reactor system is studied. The biomass sample is leached at room temperature before hydrolysis in HCW. ~90% Mg and ~96% Ca in mallee wood can be leached under HCW conditions. The leaching of Mg and Ca took 70 min to reach equilibrium at 150 °C but 90% of leachable Mg and Ca was released in <15 min at temperature ≥180 °C. The leaching kinetics of Mg and Ca remained unchanged at temperature ≥180 °C. To better understand the correlation of the leaching of water-insoluble Mg and Ca and the conversion of organic matter, the organic compound in the liquid product is analysed. The biomass conversion at 150 °C with reaction time of 70 min is ~34% and increases to ~88% at 270 °C. The hemicellulose and lignin begin to decompose at 150 °C and are completely decomposed at 180 °C. Cellulose begins to decompose at 230 °C with the reaction becoming more intense at 270 °C. It is found that the leaching of water-insoluble alkaline earth metals in mallee wood is well correlated with the recovery of arabinose during mallee wood conversion in HCW. This suggests that water-insoluble Mg and Ca are bound to organic acid functional groups on hemicellulose bunches.

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2. Mingming Zhang, **Sui Boon Liaw** and Hongwei Wu. Bioslurry as a Fuel. 5. Fuel Properties Evolution and Aging during Bioslurry Storage, *Energy & Fuel* **2013**, 27: 7560–7568.
3. Zhaoying Kong, **Sui Boon Liaw**, Xiangpeng Gao, Yun Yu and Hongwei Wu. Leaching characteristics of inherent inorganic nutrient in biochars from the slow and fast pyrolysis of mallee biomass, *Fuel* **2014**, 128: 433-441.
4. **Sui Boon Liaw** and Hongwei Wu. Tuning Biochar Properties via Partial Gasification: Facilitating Inorganic Nutrients Recycling and Altering Organic Matter Leaching, *Energy & Fuel* **2015**, 29: 4407-4417
5. **Sui Boon Liaw**, Yun Yu and Hongwei Wu. Association of Inorganic Species Release with Sugar Recovery during Wood Hydrothermal Processing, *Fuel* (Accepted)

Table of Contents

Chapter 4: Leaching of Organic and Inorganic Matter from Biomass by water: Differences between Batch and Semi-continuous Operations 59

Chapter 5: Tuning Biochar Properties via Partial Gasification: Biochar Characteristics and Leaching of Organic Matter 79

List of Figures

List of Tables

Chapter 1: Introduction

1.1 Background and Motives

To date, the Australian economy is dominantly powered by fossil fuels. Coal remains as the major fuel for electricity generation and accounted for 64% of electricity generated in Australia.[1, 2] Heavy reliance on fossil fuels results in significant carbon emission which is known to contribute to climate change and global warming. The introduction of Renewable Energy Target Scheme[3-6] in 2000 provides the essential incentive for investment toward renewable energy such as biomass. Since then, there had been substantial growth in the share of electricity generated from renewable sources.[1] Australia is targeted to generate 20 % of its electricity from renewable energy sources by 2020.[7]

In Western Australia, mallee tree is planted in the wheatbelt region to prevent the degradation of agricultural land. It is a short rotation crop regenerated as coppices with the potential for large scale production.[8-10] Unlike other energy crops, the production of mallee biomass has a high energy ratio and it does not compete with food crop for agriculture land. Therefore, mallee biomass can be a promising second-generation bioenergy feedstock.[10]

Biomass such as mallee can be used as an energy source through combustion or gasification,[7, 11] converting it to higher energy density fuels such as biochar or bioslurry through pyrolysis[12-15] or processing biomass into biofuels such as bio-ethanol through hydrolysis then fermentation.[16, 17] However, combustion or gasification of biomass is often accompanied by notorious ash related issues.[18-20] Water leaching of biomass is often employed for removal of ash forming inorganic species[20-22] or for studying the occurrence of inorganic species in biomass.[18, 23] Organic matter can also be leached from biomass[24] and can potentially lead to overestimation of water-soluble inorganic species in biomass but it is often overlooked.

In addition to their application as a fuel, biochar from pyrolysis of biomass can also be used to sequestrate carbon to soil and recycle part of the nutrients uptake by biomass during its growth. The nutrient retained in biochar can potentially return back to the soil to prevent degradation of soil from continuous removal of soil nutrient resulted from continuous harvesting of biomass.[25, 26] Leaching of biochar produced under various conditions was carried out to access the recyclability of nutrient species in biochar and leaching of potential harmful organic matter.[24, 27] However, there is potential that harmful aromatic compound can be leached from biochar[28] and the water-solubility of some plant important nutrients such as Mg and Ca is low.[27] A method has to be developed to maximise the leachability and leaching kinetic of inorganic species and minimise the leaching of harmful organic matter from biochar.

Furthermore, inorganic matter was reportedly leached from biomass during hydrolysis of biomass in hot-compressed water (HCW).[29, 30] The leaching of inorganic matter can potentially lower the yield of oligosaccharide from hydrolysis[31] for ethanol fermentation. However, the leaching characteristics of inorganic matter in HCW and its implication are not well understood. Better understanding of this process will help to improve the yield of fermentable sugar from hydrolysis of biomass in HCW, and provide useful information on the occurrence of water-insoluble alkali and alkaline earth metallic (AAEM) species in biomass.

1.2 Scope and Objectives

The current study aims to provide better understanding on the leaching of inorganic and organic species from biomass and biochar under various conditions with emphasis on equilibrium, kinetic and implication. The detailed objectives of this study are as follows:

- To study the leaching characteristics of inorganic and organic matter from biomass and the influence of the leaching of organic matter on the leaching of inorganic matter from biomass.
- To investigate the potential of partial steam gasification of fast pyrolysis biochar as a method to tune biochar properties and reduce the leaching of harmful organic matter from biochar.
- To examine the suitability of partial steam gasification as a method to enhance the recycling of nutrients from fast pyrolysis biochars.
- To provide better understanding on the leaching characteristics of AAEM species in biomass under HCW condition and the occurrence of water-insoluble AAEM species in biomass.

1.3 Thesis Outline

This thesis consists of 8 chapters including the current chapter. The thesis structure is schematically shown in the thesis map presented as Figure 1.1. Each chapter in this thesis is outlined below:

- Chapter 1 introduces the background and objectives of the current research

- Chapter 2 provides an up-to-date literature review on leaching of inorganic and organic matter from biomass and biochar. This chapter will conclude identified research gaps and specific objectives for the current study.

- Chapter 3 provides an overview on the methodology employed to achieve the research objectives and detailed description on the sample preparation, experimental setup and analytical methods involved.

- Chapter 4 studies the leaching characteristics of inorganic and organic matter from biomass and the influence of leaching of organic matter on the leaching of inorganic matter from biomass.

- Chapter 5 investigates the potential of partial steam gasification of fast pyrolysis biochar as a method to tune biochar properties and reduce the leaching of harmful organic matter from biochar

- Chapter 6 examines the suitability of partial steam gasification as a method to enhance the recycling of nutrients from fast pyrolysis biochars. The leaching kinetic of nutrient species from biochars is also discussed in this chapter.

- Chapter 7 studies the leaching characteristics of AAEM species in biomass under HCW condition and the occurrence of water-insoluble AAEM species in biomass.

- Chapter 8 concludes the current study and lists out recommendations for future work.

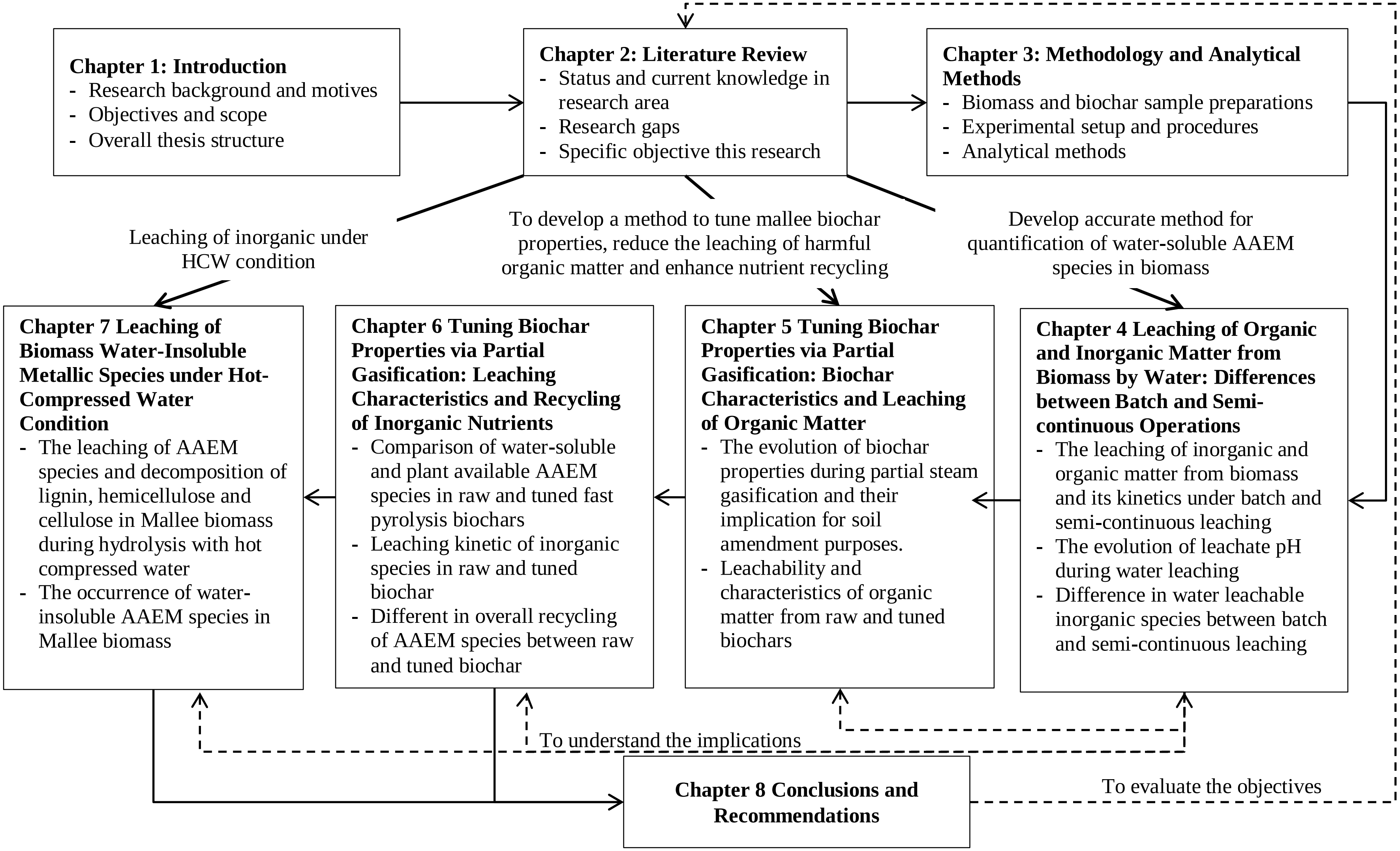


Figure 1.1: Thesis Map

Chapter 2: Literature Review

2.1 Introduction

Over the past few decades, significant amount of studies had been devoted to the thermochemical conversion for energy production. Leaching of biomass and biochar has an important role in thermochemical processes of biomass. Combustion and gasification of biomass are often accompanied by notorious ash related issue.[18, 20, 32] Significant research had been carried out to study water leaching as a method to remove ash forming species from biomass.[20, 32, 33] Biochar co-produced during fast pyrolysis for bio-oil product can be applied to soil to recycle nutrient uptake during plant growth to soil and potentially improve the sustainability of biomass pyrolysis scheme.[25, 26] Biochar leaching was carried out to study the recycling of inorganic nutrients[24, 27] and potential leaching of harmful organic matter[24] from biochars. As hydrolysis of biomass in hot-compressed water (HCW) is a promising method to convert polysaccharide in lignocellulosic biomass into oligosaccharide,[17] it is important to understand the leaching of inorganic species under HCW condition.

The objectives of this chapter are to review the current literatures concerning the leaching of biomass and its derived biochar under various conditions, identify the research gaps and present the aims of this study. The literature review will first discuss the significance of mallee biomass in Western Australia and its significance as a bioenergy source. Next, a brief overview on biomass organic and inorganic composition will be provided. Then, the thermochemical processing of biomass is discussed. Later, a review on the importance of leaching to thermochemical processing of biomass will be given. Lastly, this chapter will conclude the research gaps identified and objectives of this study.

2.2 The significance of Mallee Biomass in Western Australia and Its Roles as a Bioenergy Source

As increasing number of countries are moving towards renewable energy, the utilisation of biomass plays a more significant role in global energy mix. However, the large scale utilisation of first-generation biofuel leads to several drawbacks. Although, the conversion technologies and market for this biofuel is well established, it has low energy efficiency and large carbon footprint.[9, 34] Large scale plantation of this feedstock such as canola for bioenergy can potentially threaten global food security due to conversion of significant agriculture land for biofuel production.[34-36]

Mallee eucalyptus is a short-rotation croppies planted in Western Australia wheatbelt region to combat the dryland salinity issue which leads to degradation of agriculture lands in the region.[8, 9, 37] To date, approximately 15,000 hectare of mallee trees have been planted by 1,000 farmers in Western Australia.[7] An estimated biomass yield of 10 – 20 green tonnes a hectare per year is achievable when growing in alley system and in the region with sufficient rainfall and appropriate soil type. In addition, there is a small traditional market for eucalyptus oil extracted from the leaves and may have a potential for industrial use,[38, 39] providing additional cost benefits for the production of mallee biomass. Moreover, the leaf oil deter the livestock from grazing the tree and therefore, no additional effort is required to fence the plantation from livestock.[7]

Unlike the first-generation feedstock, the utilisation of mallee biomass for bioenergy does not compete with food crop for agriculture land but serve to complement the use of agriculture land.[9] Various studies demonstrate the potential of mallee biomass as second-generation feedstock (lignocellulosic biomass) for bioenergy.[9, 10] Wu and co-workers demonstrate that the production of mallee biomass has significantly higher energy ratio and energy productivity compared to other energy crops used in the region such as canola used for biodiesel production.[10] Study carried out by Yu and co-workers also shows that the supply of mallee biomass can be economical with strategic implantation.[40]

2.3 Inorganic and Organic Composition of Mallee Biomass

2.3.1 Biomass Organic Composition

Lignocellulosic biomass such as mallee can be considered as a composite of structural organic components (lignin, hemicellulose and cellulose) and matrices organic and inorganic compounds. The proportion or composition of structural organic component and bulk extractive varies depending on the type of biomass and its components (wood, bark, leaf).[41] Roughly 40% of mallee biomass is made up of wood, 25% of it is bark or twig and the remaining 35% is leaf.[8] An example of the composition of mallee biomass (*Eucalyptus loxophleba*, subspecies *lissophloia*)[42] used in this work is presented in Table 2.1. The major component in wood is cellulose while extractive is dominant in bark and leaf component of mallee.

Table 2.1: The composition of mallee biomass[42]

Composition	Wood	Leaf	bark
Lignin	24.7	25.2	24.1
Cellulose	42.4	15.4	26.3
Hemicellulose	23.8	18.6	17.3
Extractive[a]	9.1	40.8	32.3
Arabinan	1.1	7.5	4.5
Xylan	18	5.5	10
Mannan	0.59	0.67	0.55
Galactan	2.1	2.4	2.2
Glucan	44.5	16.7	27.6

[a] Extractive is calculated by difference from lignin, cellulose and hemicellulose

Cellulose

Cellulose is the polymer of glucose, linked by β-1,4 glycoside linkage[43] and it is the most abundant organic compound on earth.[16] Depending on the degree of polymerisation (DP) of cellulose, its molecular weight (MW) ranges between 300,000 and 500,000. As an example, the DP of cellulose in cotton ranges from 7,000 to 10,000 while it is around 15,000 for wood.[16] The long cellulose chains are bonded to adjacent chains by a long network of hydrogen bonds,[41] forming cellulose fibril.[44] However, not all of the cellulose occurs as crystalline structure.[44] Part of it occurs in amorphous phase and its proportion varies with the biomass type. 70% of cellulose in cotton is crystalline while only 40% for wood cellulose.[16]

Hemicellulose

Unlike cellulose, hemicellulose is the polymer of pentose (mainly xylose and arabinose), hexose (glucose, galactose and mannose), and 4-O-methyl glucuronic acid and galacturonic acid residues.[16] The dominant component in hemicellulose for hardwood such as mallee is xylan (refer to Table 2.1). Typically, the structure of the hemicellulose comprises of a xylan main chain as the backbone substituted with other saccharides sidechain.[45] Compare to cellulose, the MW of hemicellulose is <30,000.[43] It has an amorphous structure owing to its heterogeneous group of bunched polysaccharides.[41, 46] Hemicellulose exists in association with cellulose in cell wall,[16] surrounded by lignin which acts as a protective sheath for the hemicellulose-cellulose structure.[46] An example of hemicellulose structure is presented in Figure 2.1.

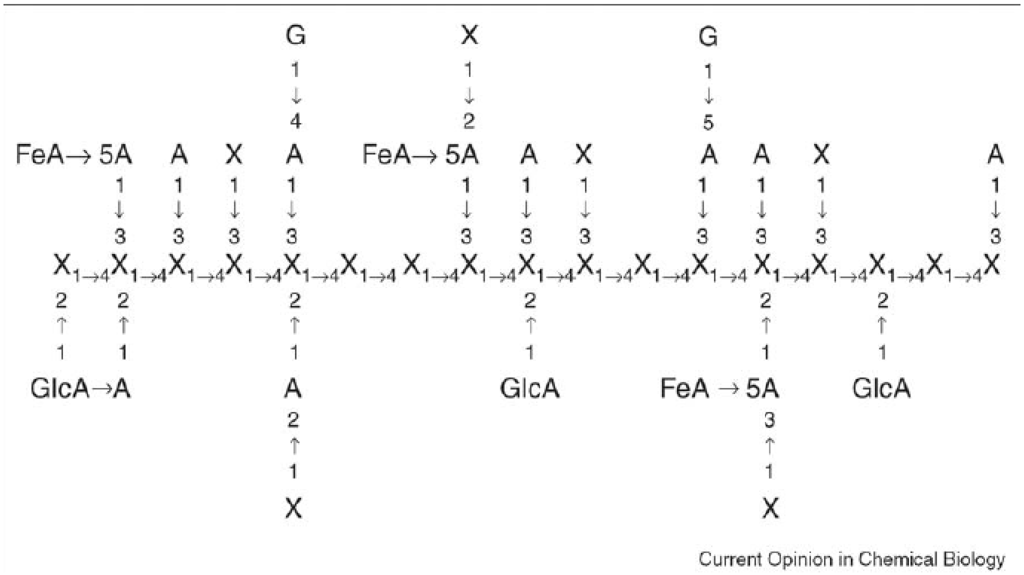


Figure 2.1: A schematic of the basic structure of hemicellulose. A as arabinose, FeA as ferulic acid, G as galactose, Glc as glucuronic acid and X as xylose.[45]

Lignin

About 25% of mallee wood, leaf and bark is lignin. It is an amorphous heteropolymer containing three different phenylpropane units, p-coumaryl alcohol, conifereryl alcohol and sinapyl alcohol (Figure 2.2), which were covalently bonded via various cross-links.[44] As aforementioned, lignin is often associated with hemicellulose and cellulose. It covers the cell walls, binds the cells together, ties and agglomerates the cellulosic fibres and holds the microfibrils with relatively high structural rigidity in a lignocellulosic complex.[41] This provides the plant with structural support,[47] impermeability and resistance to microbial attack and oxidative stress.[44] Such complex has to be broken down before the cellulose and hemicellulose is accessible, rendering the decomposition or hydrolysis of lignocellulosic biomass a challenging task.[46]

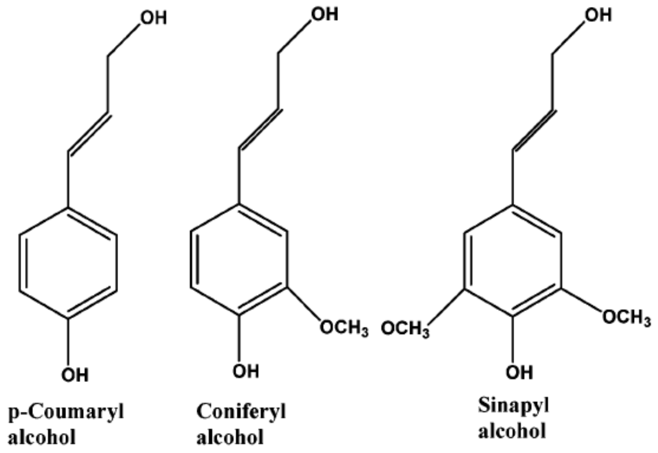


Figure 2.2: The structure of p-coumaryl alcohol, conifereryl alcohol and sinapyl alcohol.[48]

Organic Extractives

A portion of biomass is comprised of organic extractive which can be extracted via polar or non-polar solvent.[47, 48] They are 9% in the case for mallee wood and about 41% and 32% for leaf and bark, respectively (Table 2.1). These extractives may include fats, fatty acids, waxes, alkaloids, proteins, phenolics, simple sugars, pectins, mucilages, gums, resins, terpenes, starches, glycosides, saponins, and essential oils.[16, 47, 48] The amount of extractives in wood can be as low as a few percent but it can be higher at specific parts of the tree. In the case of mallee, the extractive in bark and leaf sections is higher compared to wood section (See Table 2.1). The content and composition of extractive can be different depending on location and season.[47]

2.3.2 Biomass Inorganic Species

Biomass may contain small amount of inorganic species[48] due to nutrient uptake during biomass growth.[16] These inorganic species mainly include AAEM species (Na, K, Mg and Ca), Si, Fe, Al, Cl, P, Ti and other elements where each element has its role in plant nutrition activity. For example, K and N are directly related to plant development, Ca is important for plant cellular tissues and Mg is crucial for plant vital function. The concentration of these elements varies depending on species and environmental conditions.[22] An example of inorganic elements contents in mallee biomass[24] used in this study is presented in Table 2.2.

Table 2.2: Inorganic species content in different biomass component. (Na, K, Mg, Ca, Fe, Si, Al, and P in wt% db; wt % daf for S, Cl, and N)

Element (wt%)	Wood	Leaf	bark
Na	0.0212	0.5537	0.2094
K	0.0744	0.3797	0.1105
Mg	0.0364	0.1447	0.0796
Ca	0.1236	0.7652	2.6591
Si	0.0026	0.0550	0.0099
Al	0.0025	0.0192	0.0028
Fe	0.0001	0.0142	0.0019
P	0.0182	0.1075	0.0235
S	0.0183	0.1181	0.0509
N	0.1910	1.4574	0.3918
Cl	0.0323	0.1839	0.2601

The amount of inorganic elements in wood is relatively little when compared to those in leaf and bark. Mallee biomass contains high amount of AAEM species especially Ca. The concentration of Al, Si and Fe in mallee biomass is small comparatively. In addition, mallee biomass also contains various amounts of S, Cl, P and N. The ash content in wood is ~0.4% while it is ~3.8% and ~5.5% for leaf and bark, respectively.[24] Recent study by Wu and co-workers[24] demonstrates that nearly all of Na, K and Cl in mallee biomass is water soluble while the amount of water-soluble Mg, P and S varies at 40-80%, 60-80% and 30-50% respectively. Although there is an abundant amount of Ca in mallee biomass, these are hardly water soluble. Only 5-30% of them are water soluble.

Part of these water-soluble AAEM species can be in the form of water-soluble salt associated with Cl^-, SO_4^{2-} and PO_4^{3-}. They also can occur as cations of water-soluble organic compounds such as carboxylates.[18, 24] However, the occurrence of these water-soluble Mg and Ca in the form of carboxylate is less likely as the carboxylate of these species are hardly water soluble.[24] The small amount of water-insoluble Na and K are likely to be organically bounded Na and K that are ion-exchangeable by ammonium acetate.[18, 23] The majority of water-insoluble Mg is likely to be in organically bounded and ion-exchangeable forms with a small amount of them only soluble in acid. Ca, on the other hand, varies from wood to leaf and bark. The majority of this water-insoluble Ca in wood is likely to be ion-exchangeable via ammonium acetate while the majority of it is likely to be in various forms of oxalates that are only leachable by acids.[18, 23]

As nearly all the chlorine is water soluble, the chlorine presents in biomass in the form of chlorides of AAEM species, such as NaCl and KCl.[18] The water-soluble P and S mainly present in the form of sulphate and phosphate associated with AAEM species as aforementioned. However, part of these P can also originate from organic compound which contain phosphorous such as phytic acids.[18] The remaining P and S were also reported to be in the form of sulphate and phosphate leachable via ammonium acetate and acid.[23].

2.4 Thermochemical Processing of Biomass

Biomass can be used as fuel or energy production via various thermochemical processes. Biomass can be directly burnt or co-fired to generate energy or turned into syngas via gasification process. In addition, biomass can also be converted into biochar or bio-oil via pyrolysis process which then can be used as fuels. Biomass can also be hydrothermally treated to break down its hemicellulose and cellulose into oligosaccharides, which can be subsequently fermented to bio-ethanol.

2.4.1 Combustion and Gasification of Biomass

Combustion and Gasification of Biomass: Ash Related Issues

Biomass can be burnt to generate heat and power. One of such example is the large amount of wood residues generated by wood production industry are typically used to generate power.[11] In Queensland, Australia, sugarcane bagasse from its sugarcane industry had been widely used to generate power with the excess power being fed back to the power grid.[7] Furthermore, biomass can also co-fired with fossil fuels such as coal in existing coal fired power plants[49-51] to reduce the greenhouse gases emission.[7] However, the amount of biomass co-fired is usually kept below 10% in order to avoid adverse effect on the operation of the plants.[7, 52] In addition, biomass can be used to produce syngas via gasification[7] in fixed or fluidised bed gasifier.[53] The syngas can be used as fuel in boilers, engines and combustion turbine[7] or upgraded to transportation fuels.[54]

However, the high alkali metals and chlorine content in biomass lead to several ash related issues during combustion and gasification of biomass. These include formation of slags and fouling deposits, corrosion,[18-20, 32, 55-57] sintering and agglomeration of bed material.[18, 22, 57-62] Na and K in biomass mostly present in the form of water-soluble or organic bound K^+ as aforementioned. As opposed to the insoluble forms of K, these forms of K can vaporise[55] and release to flue gas during combustion and can actively participate in further reaction.[18] High chlorine content in biomass may result in formation of highly corrosive KCl. The presence of KCl lowers the first melting temperature of the fly ash, resulting in sticky ash at lower temperatures. Water-soluble Mg and Ca in biomass on the other hand, can lead to sintering and formation of hard deposits from their carbonates.[18] In addition, Na and K have high mobility and might react with inert bed material to form a sticky surface which promotes the agglomeration of these particles and eventually result in defluidisation.[20, 58, 59] Alkali metals are also likely to react with silica in residue ash at temperatures well below 900 °C which can lead to formation of deposits on the bed surface.[20, 63]

2.4.2 Pyrolysis of Biomass

Overview of Biomass Pyrolysis Technology

Although biomass can be directly used as a fuel, the bulky nature of biomass, its low energy density and high moisture content[12] and in the case of mallee, high cost associated with long distance transportation[40] limits the utilisation of biomass as a fuel. In addition, the poor grindability of biomass such as mallee also leads to significant cost for size reduction, limiting the amount of biomass that can be co-fired in conventional coal based power plant. However, these undesirable characteristics can be eliminated though pyrolysis.[12]

Through pyrolysis, the energy density increase from ~10 MJ/kg for green mallee wood to ~32 MJ/kg for biochar and ~17 MJ/kg for bio-oil which were prepared at 500 °C.[12, 14] However, due to the low bulk density of biochar, there is no significant improvement in term of its volumetric energy density (~5 GJ/m^3 for green biomass to ~9 GJ/m^3 for biochar).[12] Pyrolysis of biomass is a thermal degradation process where the biomass is heated under oxygen depleted environment to produce biochar (solid), bio-oil (liquid) and fuel gas products.[64] The pyrolysis process can be categorised into conventional pyrolysis (slow pyrolysis), fast pyrolysis and flash pyrolysis. The range of operating conditions for these three pyrolysis processes is listed in Table 2.3. Each of these pyrolysis processes result in different distribution of pyrolysis products.

Table 2.3: Typical main operation conditions for pyrolysis processes[64]

	Slow Pyrolysis	Fast Pyrolysis	Flash Pyrolysis
Pyrolysis Temperature (K)	550 – 950	850 – 1250	1050 – 1300
Heating rate (K/s)	0.1 – 1	10–200	> 1000
Particle Size (mm)	5 – 50	< 1	< 0.2
Solid residence time (s)	450 – 550	0.5 – 1.0	< 0.5

Slow pyrolysis produces significant portion of biochar (35%), bio-oil (30%) and fuel gas (35%),[26] thus is typically employed when biochar is the desired product.[64] For production of bio-oil, fast pyrolysis is generally employed.[26, 64] The high heating rate experienced by biomass in this reactor system causes biomass to undergo thermal decomposition to form vapours, aerosols and light gases. The short vapour residence (<1 s) time and rapid cooling of vapour product in fast pyrolyser lead to higher bio-oil yield (50-70% bio-oil, 10-30% biochar and 15-20% noncondensable gas by mass).[26, 65] Compared to slow and fast pyrolysis, flash pyrolysis requires fine biomass particle and high heating rate. Under this pyrolysis condition, the major product is gaseous compound.[64, 66]

Biochar as a Fuel

Biochar can be used as a solid fuel. In fact, several properties of biochar make it a good candidate for co-combustion in coal based power stations. Its good grindability drastically improves the size reduction efficiency with existing ball mills in the coal power plant compared to biomass, addressing the issues such as incomplete burn out and blockage or bridging in the feeding system due to coarse biomass particle.[12] Low sulphur content in biochar and its relatively similar NO_x emission compared to coal means that biochar can be co-fired with coal without additional effort for SO_x and NO_x emission control.[26] Recent study on particulate matter (PM) emission from combustion of biochar demonstrates a reduced PM_1 emission compared to direct combustion of biomass,[67] resulting in reduced pollution due to emission of PM.

Bio-oil as a fuel

Compared to biochar, bio-oil from biomass pyrolysis can have a wider application as a fuel. However, several unusual properties of bio-oil including but not limited to high oxygen content, low pH, presence of ash, high viscosity, instability of bio-oil and its high water content presented various challenges for its applications.[68-70] Nevertheless, bio-oil can be burnt in boilers, furnaces, engines and turbines for energy generation.[48] Substantial tests carried out at Neste Oy in a 2.5 MW Danstoker boiler equipped with a dual fuel burner shows the boiler can operate at acceptable condition with various fuel oil to bio-oil ratios. A slight modification is required to improve the combustion stability for operating with bio-oil only but this resulted in high particulate emission.[70]

The only commercial system known to generate heat from bio-oil is at the Red Arrow Products pyrolysis plant in Wisconsin, which has been running for more than ten years.[70-72]

Combustion of bio-oil in diesel engine was also tested. Studies show that bio-oil can be combusted efficiently in medium-speed diesel engine with a pilot injection system for ignition.[70, 73] However, a large variation in bio-oil composition could result in difficulty in adjusting the injection system. The acidity and particulate in bio-oil and high CO emission are also additional concerns. Despite these negative characteristics, the thermal efficiency of bio-oil is found to be similar to diesel fuel.[70] Ormrod and Webster[74] also reported their success on operating a modified dual-fuel six-cylinder 250 kWe diesel engine for more than 400 hours. Three of the cylinders were modified to feed bio-oil with 5% diesel as pilot fuels and the other three cylinders ran entirely on bio-oil. However, the NO_x emission was higher compared to that from diesel and diesel is required for engine ignition.

In addition, the application of bio-oil also has the potential to expand to turbine engine with the first test carried out can be tracked to early 1980s.[70] During 1990s, some studies were carried out with a 2.5 MWe class GT2500 engine from Mashproekt in Ukraine. It is found that the combustion with bio-oil releases less NO_x and SO_x but the emission of particulate is high compared to diesel.[70, 75] A separate study carried out by Strenziok and co-workers[76] between 1999 and 2000 on a modified 75 kWe commercial turbine shows that bio-oil can be burnt in dual fuel mode. The combustion chamber is fitted with an ignition nozzle for diesel (40%) and a main nozzle for bio-oil (60%). The turbine was started with diesel and the supply to main nozzle switched to bio-oil during operation. It was estimated that this operating condition has 73% of the power output ran on diesel. Although bio-oil is not suitable as a transportation fuel, various reviews were done to investigate the potential for upgrading bio-oil into syntactic transportation fuels. These methods include hydrotreating, hydrocracking and catalytic vapour cracking.[68, 70, 77] Hydrotreating of bio-oil is a catalytic hydrogenation process taking place under a high pressure and moderate temperature condition to remove oxygen in bio-oil as water.[68, 70]

Hydrocracking requires the bio-oil vapour to be separated into a carbohydrate-derived aqueous phase and a lignin fraction.[26, 77] The aqueous phase will be converted into hydrogen via steam reforming for hydrocracking the lignin fraction to hydrocarbons.[70] Catalytic vapour cracking on the other hand removes oxygen in bio-oil via simultaneous dehydration and decarboxylation over acidic zeolite catalyst.[70] However, compared to bio-oil application in static burners and generators, its potential as a transportation fuel is at a relatively infancy stage.

Furthermore, bio-oil can be mixed with finely ground biochar to produce bioslurry fuel. A recent study by Abdullah and Wu demonstrates that bioslurry prepared from mallee biomass at 20% biochar loading has high energy density of ~18 MJ/kg and has desirable rheological properties for combustion and gasification.[14] In addition, the high energy density also indicates that the bioslurry can be economically transported to a central processing plant where it can be gasified to syngas for liquid fuel production.[13, 70]

Biochar for Environment and Agronomic Benefits

Other than as a fuel, biochar from biomass pyrolysis can also be applied to soil to achieve various environmental and agronomic benefits.[25, 26] As the carbon in biochar is stable for a long period of time,[78] application of biochars to soil has the potential to sequestrate atmospheric carbon to the ground for millennia.[25, 26] While the bio-oil produced from a fast pyrolyser has promising applications as a fuel, application of the biochar co-produced to soil has the potential to turn bio-oil into a carbon negative energy source.[25, 79] It is estimated that ~31 kg of C can be removed from the atmosphere for every GJ of energy produced.[80] With its minimal risk of large scale release of sequestrated carbon and accountability, biochar sequestration is perceived as a near-term technology for carbon sequestration.[79]

Large scale production of renewable fuels from biomass can result in significant amount of crop residues being removed from the field.[81] Various researchers expressed their concerns on their potential negative impacts to soil and water quality[25, 26, 81] which can lead to lower crop yield and jeopardise the sustainability of bioenergy production.[25] Continuous harvesting of crop residue removes plant nutrients such as C, N, K, P, Ca and Mg uptake during biomass growth from soil thus decline in soil fertility. It can also lead to reduction in soil organic matter, cation exchange capacity and water holding capacity and restrict the air and water penetration in soil.[25, 26] Moreover, the reduction of soil organic carbon could heavily discount the carbon credit gain from utilisation of bioenergy.[26]

However, the soil quality where this biomass is harvested can be enhanced by returning the biochar[25, 26, 78-80] coproduced from fast pyrolyser and concurrently improves the overall sustainability of the pyrolysis scheme. The application of biochar in soil increases the soil ability to retain nutrients[25, 26, 82] and agriculture chemicals.[25] This reduces the leaching of nutrients and chemicals to surface and ground water. In addition, incorporating biochar to soil has the potential to return the valuable nutrient species retained in biochar during pyrolysis back to the soil.[24, 27, 78] The porous nature of biochar can help to reduce the bulk density of high clay soil, improve the drainage, aeration and root penetration. Furthermore, it also helps to increase water holding capacity of sandy soils.[25, 78] The liming effect from application of biochar also helps to balance out the acidifying effect from application of N fertilisers.[25]

2.4.3 Hydrothermal Conversion of Biomass

An Overview to Biomass Hydrolysis Process

Currently, majority of the bioethanol in countries like US and Brazil are produced from food crop containing sugar and starch such as sugarcane and corn,[45, 83, 84] resulted in competition between farm lands for energy production purposes. As human are unable to digest cellulose,[46] the production of bioethanol from lignocellulosic biomass such as mallee does not result in food or fuel dilemma and can reduce the reliance on food crops for bioethanol production. Production of bioethanol from starch is a reasonably developed process via the pathway of enzymic liquefaction, scarification and finally, fermentation. However, the production of bioethanol from lignocellulosic biomass through enzymic hydrolysis is hindered by several factors. Mainly, the sheathing effect of hemicellulose and lignin around cellulose leads to resistance of lignocellulose material against decomposition or hydrolysis.[46] The low surface area due to cellulose crystallinity in lignocellulose biomass further increases the resistivity of cellulose to biological attack.[45] In addition, the high cost and very low specific activity of cellulase enzyme result in long digestion time. Moreover, the thermal inactivation of the enzyme (thus limit the recyclability of the enzyme) and the inhibition of hydrolysis product to enzymic hydrolysis reaction limit the efficiency of the process.[16, 85] Recent development of genetically modified organism which produced large quantity of callulase enzyme that digest the cellulose efficiently,[86] brought down the cost of the cellulase enzyme and increased the efficiency of enzymic hydrolysis significantly. Nevertheless, the resistance of cellulose to enzymic hydrolysis remained as an issue.

Other than enzymic hydrolysis, various processes such as acid hydrolysis, alkaline hydrolysis and hydrolysis in hot-compressed water (HCW) can be used to decompose cellulose into its monomer or oligomers or served as pre-treatment prior to enzymic hydrolysis.[16] High glucose yield is achievable with dilute acid hydrolysis but this process can suffer from extensive glucose degradation and heat transfer limitation at higher temperatures.[16, 87] Although hydrolysis in concentrated acid has a glucose yield close to 100% and minimal glucose degradation, the cost, environmental and corrosion issues associated with the utilisation of acid and lack of reliable methods to recover the acid render this process economically unviable.[16, 85] Similarly, alkaline hydrolysis also results in low sugar yield due to degradation of sugar at temperatures lower than 100 °C. In addition, the formation of organic acids during hydrolysis also leads to consumption of alkali.[16, 88]

Unlike acid and alkaline hydrolysis, hydrolysis of lignocellulose biomass in HCW does not involve catalyst or chemical thus the environmental and corrosion issues resulted from the use of acid and alkaline can be avoided.[16] Even though the glucose yield from hydrolysis in HCW is low compared to acid hydrolysis,[16] the recovery of glucose oligomers and their derivative are about 80% in semi-continuous reactor.[17] These oligomers can be further decomposed into glucose via enzymic hydrolysis for bioethanol fermentation.

The hydrolysis of biomass or cellulose in HCW can be carried out either in batch,[29, 89-91] semi-continuous,[17, 30, 90, 92-95] or continuous[96-99] reactor systems. For batch system,[29, 89-91] the raw material and water are charged into the reactor before the reactor is sealed, pressurised then heated to and hold at the designated temperature and time. The reactor content is quenched at the end of the process. In semi-continuous reactor system, [61, 63, 66-70] the raw material is charged into and retained in the reactor. A stream of HCW at the desired temperature is fed to the reactor and passed through the bed of raw material. As for continuous reactor system,[96-99] both raw material and liquid is fed to the reactor in the form of slurry. The reactor effluent in semi-continuous and continuous reactor system is immediately cooled. The short liquid product residence time in these systems results in less degradation of liquid product thus higher sugar yield compared to batch system.[98, 99] The long liquid product residence time in batch system can lead to significant degradation of sugar into oil and char.[16] The difference in cellulose decomposition behaviour is also observed between different reactor systems. For instance, Lü and Saka[90] reported that the cellulose of Japanese beech started to decompose at 170 °C in batch system but it was not observed at temperature below 210 °C in semi-continuous system.

Decomposition of Hemicellulose, Lignin and Cellulose in HCW

Hemicellulose, cellulose and lignin component of biomass solubilise in HCW at different temperature due to their occurrence in biomass. As discussed in section 2.3.1, hemicellulose and lignin has an amorphous structure. They are solubilised in HCW at temperature as low as 180 °C in semi-continuous system.[30, 100-102] At 230 °C, most of the hemicellulose is hydrolysed within 15 minutes. However, the recovery of hemicellulose drops at higher HCW temperature due to the decomposition of hemicellulose saccharides such as xylose, into secondary products.[90] Cellulose which has a crystalline structure in biomass starts to decompose between 210 °C – 230 °C in HCW.[30, 90, 100] In study carried out by Lü and Saka,[90] the recovery of glucose oligomers (C1-C5) peaks at 270 °C with recovery rate of 16.1%. However, a separate study carried out by Yu and Wu[17] with a smaller sample size shows that the recovery of C1-C5 glucose oligomers at 270 °C is in the range of 31% - 34% and the glucose yield via post-hydrolysis is close to 80%. This shows that glucose oligomers resulted from hydrolysis at higher temperature is ready to undergo further decomposition reactions, which decreases the recovery of glucose oligomers from cellulose.

The decomposition of saccharides in hydrolysis liquid product can take place via dehydration or fragmentation. Examples of these dehydration compounds are furfural, hydroxymethylfurfural and levoglucose. The decomposition of monosaccharides via fragmentation produces compounds such as methylglyoxal, glycolaldehyde and erythose. The resultant compounds can undergo further decomposition to form low molecular weight compounds such as organic acids.[90, 103-105]

2.5 The Importance of Leaching Process to Thermochemical Processes of biomass

Leaching process plays an important role in thermochemical process of biomass. Water washing of biomass is the key for addressing the ash related issues associated with biomass combustion and gasification. Leaching of biochar is important for studies of the recyclability of nutrient species and leaching of organic matter from biochar used for soil amendment purposes. This can have a huge implication on sustainability of bioenergy production via pyrolysis. During hydrothermal treatment of biomass, the biomass is essentially immerged in hot water under high pressure condition where the inorganic species in biomass can be leached out under this condition. This process along with the implications of inorganic species leaching to hydrothermal conversion will be reviewed in this section.

2.5.1 Water Leaching of Biomass

Table 2.4 lists down examples of water leaching of biomass and their purposes. Mostly, waster washing of biomass is employed as a pre-treatment method for the removal of alkali metals and other inorganic species such as Cl, S and P.[20, 22, 32, 33, 53, 63, 106-110] Water washing is also used as the first step in sequential leaching of biomass for quantification of water-soluble compound in biomass[18, 23]. Some researchers also use water washing to remove AAEM species from biomass to study their effect on pyrolysis[111, 112] and gasification behaviour[113] or their influence on the yield and composition of bio-oil[114]. Wu and co-workers on the other hand, used water leaching of biomass as a mean to quantify the recycling of biomass inherent nutrient species.[24] In the literatures studied, most of the water leaching implemented are batch leaching. Only exceptional few was carried out in a semi-batch manner.[106, 108]

Batch Leaching of Biomass in Sequential Leaching Scheme

Chemical fractionation provides important information on fuel mineral chemistry and ash forming species to predict the fuel ash behaviour for possible corrosion risks in combustion devices. Sequential leaching employed provides an insight to the occurrence of metallic species, their possible mobility, and their availability for interactive actions.[18] Sequential leaching separates the ash-forming matters into dissolved salt, organically bound matter and lastly included and excluded minerals.[18, 23] Batch water leaching is the first step in sequential leaching for determination of dissolved salt.

Biomass Water Leaching as Fuel Pre-treatment Strategy

Water leaching is largely employed for removal or reduction of alkali metals and chlorine in biomass[20, 22, 32, 33, 53, 63, 106-110] as the majority of them are water soluble thus can be removed by water leaching. For example, Turn and co-workers reported that combination of leaching and mechanical dewatering of banagrass achieved 45% ash reduction in addition to 98% removal of Cl, 90% of K, 55% of S, 68% of Na, 72% of P and 68% of Mg in original biomass. Dayton and co-workers found that leaching of rice straw, wheat straw, switchgrass, wood fuel and banagrass on average, removed 55% of Na_2O, 83% of K_2O, 91% of Cl, 69% of SO_3, 51% of MgO ash elements in biomass studied. The removal of these elements significantly reduced the ash-related issues associated with combustion and gasification of biomass. For instance, work carried out by Arvelakis and co-workers[20] showed that combustion of water-washed olive residual did not show any sign of deposition or agglomeration problem during the test period compared to the untreated samples.

Table 2.4: Summary of application of water leaching and the modes of leaching used

Ref	Purpose of water leaching/washing	Methods	Additional notes
24	To quantify the removal and recycling of nutrients from mallee biomass components and their derived biochars	Batch	Reported the leaching of organic matter from biomass and biochars. Leached thrice sequentially.
106	As a pre-treatment method for removal of Na, K Cl in straw biomass to reduce slagging and fouling to furnace and other thermal conversion system	Batch Water Spray Flushing	Batch is 100g in 7L water for 24 hours. Water was spray over 30mm of 100g straw bed of. Flushing 20 L water through 100g of a thin sample
63	As a pre-treatment method to remove water-soluble N, K and Cl from olive residue to prevent agglomeration-deposition problem in gasifier	Batch	Ash content of the olive residue was reduced by almost half
33	As a pre-treatment method to remove inorganic elements in biomass which contributes to ash related issues in thermos-chemical energy conversion of biomass (Banagrass).	Mechanical dewatering and leaching	Monomer sugars constituted up to 4% of dry matter is detected in the leachate. 45% ash, 90% K, 98% Cl, 55% S, 68% Na, 72% P and 68% Mg reduction.
20	As a pre-treatment method to reduce ash content to reduce the ash related problems during fluidised bed combustion of wheat straw and olive residue	Not reported	
22	As a pre-treatment method to reduce N, K and Cl from olive residue to study its effect on agglomeration during biomass gasification in fluidised bed system	Batch	
107	As a pre-treatment method to leach water-soluble N, K and Cl from peach stone that contributes to ash related problem during gasification	Batch	The pH of the leachate is about 6 to 6.5.
108	As a method to remove alkali metal from biomass to study its effect on release of alkali during pyrolysis	Semi-batch	Leached with 80°C hot water in batch for cellulose sample.
32	As a method to remove alkali metal and chlorine from rice straw, wheat straw, switchgrass and wood to study the release of alkali metal in combustion	Batch	Leaching leads to reduction in alkali metal vapour during combustion

Ref	Purpose of water leaching/washing	Methods	Additional notes
[109]	For the removal of water-soluble and ion-exchangeable inorganic elements such as Na, K, Ca, Cl and S in biomass	Batch	Decrease in pH during leaching of wheat straw
[113]	To remove AAEM species and chlorine in biomass. Investigate the effect of water leaching of hydrogen production during biomass steam gasification	Batch	
[23]	Batch water leaching as first step of chemical fractionation to determine the form or occurrence of inorganic species in biomass	Batch	The pH of the water is between 4.4 and 5.0 for all the samples studied
[110]	Use to remove inorganic matter from biomass in order to reduce the fouling and slagging potential due to alkali metal	Batch	
[18]	Batch water leaching as first step of chemical fractionation to determine the form or occurrence of inorganic species in biomass	Batch	
[111]	Water-washing is employed to study the decomposition behaviour of raw and washed-straw	Batch	
[112]	Water leaching is used to study the effect of KCl on wheat straw pyrolysis.	Batch	Hot and cold water were used. For the case of hot water, 300mL of water is used to rinse afterwards.
[114]	Water leaching is used to removed water-soluble AAEM species to study its effect on the yield and composition of bio-oil	Batch	

Leaching of Organic Matter from Biomass: An Overlooked Process

In addition to inorganic species, organic matter is also removed when biomass is pre-treated via water washing. A study carried out by Turn, Kinoshita and Ishimura[33] demonstrated that monomeric sugars accounted up to 4wt% (dry basis) of biomass can be leached. A recent study by Wu and co-workers[24] also reported that the amount of organic matter leached from biomass can be significant. More than 30% of organic matter on carbon basis were leached from mallee leaf and bark component while ~2% of organic matter (carbon basis) were leached from wood component[24]. The high organic matter removed from bark and leaf might be due to the high extractive content in these components (refer to Table 2.1).

Furthermore, various studies concerning the use of biomass as adsorbent for metal contaminant also reported that organic matter was leached during adsorption study. Organic matters was reportedly leached from absorbent prepared from seaweed.[115, 116] Other studies[117-119] also reported that organic matter waw leached from algal biomass used to remove metal contaminants. Sciban et al.[120, 121] and Gaballah et al.[122] also found that organic matter can be leached from wood and bark material.

Although these studies[24, 33, 115-122] indicate that organic matter can be leached from biomass, only few studies[24, 33] reported on the leaching of organic matter during biomass pre-treatment by water washing. The leaching of this organic matter might be due to the removal of some compounds in biomass extractive component soluble in water at room temperature. The removal of organic matter can result in significant weight loss during water washing of biomass where 49% weight loss is reported by Figueira and co-workers.[116] Even though water washing of biomass can be effective on removal of alkali metal and Cl,[22, 33, 55, 63, 106] weight loss during biomass washing has to be considered due to losses of fuel and may introduce additional cost associated to treatment biomass washing effluent. However, it is seldom discussed in open literatures concerning water washing for biomass pre-treatment.

Moreover, the leaching of organic matter from biomass during water washing can result in acidic leachate. Arvelakis and co-workers[109] found that the pH of the water leachate decreased during leaching of wheat straw. Study on water leaching of various biomass fuels by Werkelin and co-workers[23] found that the pH of these leachates range between 4.4 and 5.0. On the other hand, Vassilev et al. [41] demonstrate that the pH of water leaching leachate can range from 5 to close to neutral. These shows that depending on the type or species of biomass subjected to washing, the leachate can be acidic possibly due to the leaching of organic acids from biomass. During batch leaching of biomass, if these organic acids are not removed, the acidic condition might lead to leaching of some organic bounded inorganic species through ion-exchange. This can result in inaccurate quantification of water-soluble inorganic species in biomass during chemical fractionation.

2.5.2 Biochar Leaching

Biochar Leaching for Recycling of Biochar Inorganic Nutrient Species

With the growing interest in using biochar as soil amender and potential of recycling part of the nutrient adsorbed by biomass during it growth to soil, biochar leaching is carried out to access the recyclability of various inherent nutrient species in biochar. Wu et al.[24] and Kong et al.[27] studied the removal and recycling of inherent nutrient species in mallee biochar prepared under various pyrolysis conditions (pyrolysis temperature, heating rate, biomass component and particle size) via water. It is also important to note that Kong and co-workers[27] also used Mehlich-1 solution to quantify total plant available nutrient. Extraction with Mehlich (Mehlich-1 or Mehlich-3) solutions has long been used for quantification of bioavailable micronutrient in soil.[123-128] Although it is designed for soil analysis, various studies also attempted to quantify bioavailable micronutrient in biochar. Gaskin and co-workers[129] used Mehlich-1 extraction to quantify potential plant available micronutrient such as P, K, Mg and Ca. Mukherjee and co-workers[130] leached biochar with Mehlich-1 solution for 24 hours to quantify plant available P.

Leaching of Organic Matter from Biochar

Other than inorganic matter, organic matter are also leached from biochar.[131] The leaching of organic matter from biochar is studied due to two reasons. First, the leaching of organic matter from biochar can lead to reduction of C being sequestrated when biochar is amended to soil.[24] Second, some of bio-oil compounds may condense within the pores of biochar or its surface. Some of these compounds such as phenol can be leached from biochar when applied to soil. Significant leaching of organic matter from biochar can potentially contaminate the soil due to the leaching of harmful organic compound.[24, 28, 132, 133]

Although the leachability of inorganic matter has been actively studied, the leaching of organic matter from biochar is rarely discussed. Organic matter leached from biochar via water were also quantified by Wu el al.[24] who studied the recycling of nutrient in slow pyrolysis biochars. They found that < 2% of total carbon in these biochars is leachable by water. A separate study by Lievens et al.[28] found that aromatic compound ranging from 2 to 5 fused rings can be leached from fast pyrolysis biochar via water. The amount of leachable aromatic compounds is highly dependent on the feedstock and pyrolysis temperature. The leaching of organic matter from biochar can take up to a month to reach equilibrium.

Retention of Inorganic Matter in Biochar

The amount of AAEM species in biomass that are retained in biochar during pyrolysis thus available for nutrient recycling can be influenced by pyrolysis temperature, heating rate, type of biomass[134] and reactor configurations. Studies by Sonoyama et al.[135] and Okuno et al.[136] showed the volatilisation of AAEM species during pyrolysis can be significant at higher temperatures (>500 °C). Slow pyrolysis of pine saw dust at 800 °C in a fixed-bed reactor showed no significant release of AAEM species compared to >50% release of K and up to 20% release of Mg and Ca when the pyrolysis was carried out in a mesh wire reactor where a forced flow of gas was present.[136] The high AAEM retention in fixed-bed reactor is due to rapid desorption of AAEM species from and adsorption of AAEM species on char surface,[135] forming a more stable and less volatile compound. In reactors where volatile and char interaction are significant such as the drop-tube fixed-bed reactor used by Rahim and co-workers,[137] the interaction between volatile and hot nascent char can induce the release of AAEM species with the release being prominent for monovalent alkali species.[137, 138] Increase in temperature and heating rate lead to lower retention of AAEM species. This is due to the increase in the availability of H radical during volatilisation which can induce the release of AAEM species bound to char matrix thus the volatilisation of these species.[134, 136] Moreover, the retention of AAEM species during pyrolysis may differ from biomass to biomass. A study by Keown and co-workers[134] demonstrated that the release of Mg and Ca in pine sawdust is higher compared to bagasse. The difference in AAEM species retention might be due to the difference in the composition of other inorganic species such as Cl and Si which can form a more stable compound with Mg and Ca.[134, 139]

Nevertheless, the majority of the AAEM species in mallee biomass are retained when the biochar is produced at 500 °C[24, 27, 67, 137, 140] which is within the temperature range of the optimum bio-oil yield.[65] Wu and co-workers[24] reported that the retention of AAEM species in wood, leaf and bark component of mallee biomass is 90-100% while the data reported by Gao et al.[67] and Rahim et al.[137] indicated that the retention of AAEM species in fast pyrolysis biochar ranged from 80 to100%.

The influence of pyrolysis parameters is not only limited to the retention of AAEM species but also on other nutrient species in biomass such as Cl, S, P and N. For example, pyrolysis temperature and reactor configuration can affect the retention of Cl in biochar. During the slow pyrolysis of mallee biomass in a fixed-bed reactor, most of the Cl is released at a temperature as low as 400 °C.[24, 137] However, when the fast pyrolysis is carried out under a drop-tube fixed-bed condition, part of the Cl is retained in biochar. An experiment carried out by Rahim and co-workers[137] indicated that the retention of Cl increased to ~44% when the fast pyrolysis temperature increased from 400 °C to 600 °C before it declined at higher temperatures. The prolonged volatile-char interaction in drop-tube fixed-bed reactor caused the Cl released as volatile to recombine into the char thus higher retention in fast pyrolysis biochars.[141, 142] This also indicates that depending on the pyrolysis condition, biochar obtained can be depleted of Cl thus not available for nutrient recycling when applied to soil. The P in mallee biomass, on the other hand, is largely retained (> 90%) in biochar after pyrolysis and unaffected by the pyrolysis temperature. For S and N, as the temperature increases, the retention of these elements in mallee biochar decreases. Unlike Cl, a significant portion of these species can be retained in biochar at 500 °C even when undergoing slow pyrolysis.[24]

The Influence of Pyrolysis Parameters on Leaching of Inorganic and Organic Matter

Although, most of the AAEM species and part of crucial plant nutrient such as N, S, Cl and P in mallee biomass is retained in biochar, not all of these nutrient species are leachable from biochar to soil and made available for plant uptake. Pyrolysis process parameters such as pyrolysis temperature[24] and heating rate[27] can play a key role in the occurrence of these inorganic nutrient species thus their leachability.

Work carried out by Wu and co-workers[24] demonstrated that the amount of AAEM species leachable from biochar via water dropped when the pyrolysis temperature increased from 300°C to 500 °C. However, with further pyrolysis temperature increase to 750 °C, the amount of water-soluble K and Ca increased noticeably for leaf and bark biochar. During pyrolysis, part of the AAEM species originally present in the form of water-soluble salts become organically bounded (attached to carboxylate group on biochar) during pyrolysis. As the temperature increased, the O and H content in biochar reduced, hence these AAEM species may become directly bounded to the char matrix. Part of these metallic species may also be transformed into carbonates or oxides at high temperatures.[24] The substantial increase in water-soluble Ca in leaf and bark biochars prepared at 750 °C might be due to the formation of calcium bicarbonate which has a high solubility in water compared to its carbonate. This observation prompts Wu et al.[24] to point out that thermal treatment can be used to tune biochar to increase the leachability of Ca in biochars. It is also important to note that, while the amount of water-soluble Na and K in biochar prepared between 300 °C and 750 °C range between approximately 40% and 90%, the amount of water leachable Mg and Ca is generally < 20% and < 5% for Mg of leaf and bark char at temperature ≥ 500 °C. With Ca being the major AAEM species in mallee biomass, its low water solubility may indicate that Ca in biochar is not readily available for plant uptake.

The pyrolysis heating rate can also influence the available nutrient for plant uptake. A study carried out by Kong and co-workers[27] demonstrated that the biochar produced from fast pyrolysis can have lower water-soluble Na and K while there is no noticeable difference on Mg and Ca. It is also found that while water-soluble Ca in leaf and bark biochar prepared under slow heating condition is < 20%, > 80% of Ca in those biochar can be extracted via Mehlich-1 solution, indicating that most of the Ca in these biochar is bioavailable. Although part of the Na and K become water-insoluble when prepared via fast-pyrolysis, they are leachable via Mehlich-1 solution thus available for plant uptake. The reduction in Na and K water solubility in fast pyrolysis biochar might be due to the transformation of these species to organically bounded form, rendering them water-insoluble but soluble in Mehlich-1 (double dilute acid) solution. Moreover, fast pyrolysis also produces biochar with higher plant available Mg and Ca, possibly due to the lesser degree of carbonisation of fast pyrolysis biochar compared to that produced from slow pyrolysis. In addition, Kong et al.[27] also demonstrated that biomass particle size can affect the leachability of AAEM species from the resultant biochar. The total plant available AAEM species in fast pyrolysis biochar prepared from large wood particle is lower compared to that prepared from fine particle biomass and similar to biochar prepared under slow pyrolysis. This is attributed to the poor thermal conductivity of biomass leading to part of the biomass undergoing pyrolysis at lower heating rate thus its total plant available AAEM species is similar to biochar produced from slow pyrolysis.

Although majority of the P in mallee biomass are retained during pyrolysis, half of P in wood biochar prepared at 300 °C is water soluble.[24] However, this water-soluble portion diminishes quickly with increase of pyrolysis temperature. <30% of P is water soluble in leaf and bark biochar. When pyrolysis temperature increases to 500 °C and higher, hardly any P remains water soluble. The amount of water leachable S in wood biochar decreases with increasing pyrolysis temperature. In the case of leaf and bark biochar, the percentage of water-soluble S increases with the pyrolysis temperature. However, with less S retained at higher temperatures, the total amount of S recoverable from biochar at higher temperatures normalised to S content in biomass is lower. The low water solubility of P and S in biochar produced from increasing temperature might be due to these elements become increasingly organic bounded thus insoluble at higher pyrolysis temperature.[24] N retained in biochar prepared at temperature ranges from 300 °C to 750 °C is hardly water soluble. This is because the N in biomass largely exists in organically bounded form and remained organically bounded following pyrolysis. As aforementioned, part of the Cl is retained in fast pyrolysis biochar. Although the information on water solubility of chlorine in fast pyrolysis mallee biochar at different temperature is limited, the Cl in fast pyrolysis bark biochar prepared at 600 °C is mostly water soluble (~90%).[137]

2.5.3 Leaching of Inorganic Matter from Biomass in HCW

Although the hydrolysis of lignocellulosic biomass in HCW for recovery of sugar is widely studied,[30, 90, 94, 95, 100-102, 143] the leaching or removal of inorganic species from biomass is seldom discussed.[29, 30, 144, 145] Bai et al.[144] and Reza et al.[29] demonstrated that more than 87% of AAEM species in saw dust of Japanese cedar can be removed during hydrolysis in HCW under batch condition at temperature ranging from 200 °C to 260 °C. Other elements such as phosphorus, sulphur, iron and manganese were also removed in the process.[29, 145] During hydrolysis of biomass in HCW under semi-continuous condition, the inorganic species can co-elute with oligosaccharides at a temperature of 200 °C and below.[30, 145] The leaching of inorganic matter is a hypothesis to be correlated to the removal of hemicellulose during hydrolysis.[29, 145]

The leaching of inorganic matter can result in an undesirable impact on biomass hydrolysis. High amount of inorganic species in liquid product stream resulted from hydrolysis of high ash biomass might lead to additional effort to remove this compound from liquid product streams.[145] The solubilisation of organic species during hydrolysis of biomass in HCW can potentially increase the tendency of equipment fouling and corrosion. In addition, inorganic elements (especially trivalent and divalent species[31]) can catalyse the decomposition of saccharide in liquid product.[31, 146, 147] If their concentration in liquid product is high, this might result in more extensive decomposition of saccharide thus limited recovery of saccharides from lignocellulosic biomass.

2.6 Conclusions and Research gaps

From the literature review above, the following key conclusions can be drawn:

- Mallee biomass can be a key second-generation biomass feedstock in Western Australia.
- Biomass can be utilised for energy production through various thermochemical production. This includes but not limited to combustion and gasification of biomass, conversion of biomass to biochar, bio-oil and pyrolysis gas which can be used as a fuel via pyrolysis and hydrothermal conversion of biomass for bio-ethanol production.
- Large scale production of renewable fuels from biomass will lead to deterioration of soil and water quality resulted from removal of crop residues. By returning biochar to soil, such consequences can be avoided and potentially lead to various agronomic benefits.
- Water leaching of biomass had been widely used to remove ash forming species in biomass. Batch water leaching is the first step of sequential leaching to quantify water-soluble inorganic species. However, the leaching of organic matter from biomass during water leaching was generally overlooked.

- Various nutrient species can be leached from biochar and available for plant uptake. Organic species have also been leached from biomass during water leaching. The leaching of these compounds can potentially pose a threat for the application of biochar as soil amender.
- Depending on pyrolysis parameters such as pyrolysis heating rate, temperature and reactor configuration, a significant amount of inorganic species mainly AAEM species in biomass are retained in biochar. Pyrolysis parameters also have profound influence in the leachability of inorganic species from biomass.
- AAEM species can be leached during hydrothermal conversion of biomass to oligosaccharides.

From the review on the leaching of inorganic and organic matter from biomass and biochar, it is clear that **(1)** significant portion of organic matters can be leached from biomass but little is known on its leaching characteristics and implications. **(2)** Various studies had been carried out to investigate the effect of pyrolysis parameters on the retention and leachability of AAEM species in biochar but the retention and leachability of P, N and S in biochar produced from fast pyrolysis is rarely discussed. **(3)** Although majority of AAEM species in mallee biomass is retained in biochar, the percentage of water-soluble Mg and Ca in mallee biochar (both slow and fast pyrolysis biochar) remains low. **(4)** Even though aromatic compounds are known to be leached from fast pyrolysis biochars, the total organic matter can be removed from fast pyrolysis biochar is unknown. **(5)** Few studies had indicated that inorganic species in biomass can be leached in HCW. Yet, the knowledge on the leaching characteristics of these inorganic species in HCW and its implication is limited. Therefore, further research and development is required to address the research gaps identified above, including:

- Better understanding on the equilibrium, kinetic and implication on leaching of inorganic and organic matter from biomass. It is known that the organic matter leached from biomass can be acidic. This can potentially cause batch leaching of biomass to overestimate water-soluble AAEM species during sequential leaching for chemical fractionation. A better approach for quantification of water-soluble AAEM species in biomass is required.

- Leachability and retention of P, N and S in a fast pyrolysis biochar. P, N and S are important micronutrients for biomass. A systematic study on the retention and leachability of these elements in biochar when pyrolysis is carried out at different heating rate and reactor configuration.
- Improve water-soluble Mg and Ca portion in mallee Biochars. Although most of the AAEM species is retained in biochar, a significant portion of Mg and Ca present in the form that is either not water-soluble or not available to plant. Various thermal treatment methods should be explored as a mean to tune the biochar to enhance the leachability and leaching characteristics of AAEM species in biomass.
- Leaching of organic matter from fast pyrolysis mallee biochar. As the leaching of aromatic compound from biochar can potentially contaminate soil amended with biochar, a method has to be developed to eliminate or reduce water-soluble aromatic compound in biochar.
- To investigate the leaching characteristics of AAEM species in biomass in HCW. A better understanding of this area might lead to a better understanding on the occurrence of organically bonded AAEM species in biomass.

2.7 Research Objectives of Current Study

From the literature review carried, a number of research gaps in the field had been identified. However, it is impossible to address all the research gaps identified in a PhD study. Therefore, the scope of current study is limited to the equilibrium, kinetics and implication on leaching of inorganic and organic matter from biomass and biochars under various conditions. The main objectives of current study are:

- To study the leaching characteristics of inorganic and organic matter from biomass and the influence of the leaching of organic matter on the leaching of inorganic matter from biomass.

- To investigate the potential of partial steam gasification of fast pyrolysis biochar as a method to tune biochar properties and reduce the leaching of harmful organic matter from biochar.
- To examine the suitability of partial steam gasification as a method to enhance the recyclability of nutrients from fast pyrolysis biochars
- To provide better understanding on the leaching characteristics of AAEM species in biomass under HCW condition and the occurrence of water-insoluble AAEM species in biomass.

Chapter 3: Research Methodology and Analytical Techniques

3.1 Introduction

This chapter will provide the research methodology employed to achieve the objectives outlined in Section 2.7. The experimental setups and analytical techniques used will be described in detailed in this chapter.

3.2 Methodology

To achieve the main research objectives outlined in Section 2.7, a series of experiments had been carried out. These include:

- Leaching of mallee wood and leaf in batch and semi-continuous mode. The leachate samples were analysed for inorganic and organic species.
- Pyrolysis of fine particle (150 – 250 µm) mallee wood and leaf in drop-tube/fixed-bed reactor to produce fine particle biochar. The pyrolysis experiments were also carried out with fluidised-bed reactor to produce biochar from 1 – 2 mm mallee wood.
- Tuning of biochar via secondary pyrolysis of raw biochar at 725 °C to produce secondary pyrolysis biochars and partial steam gasification of raw biochar at 725 °C to produce partial steam gasified biochar at 5% and 10% carbon conversion.
- Analysis of the biochar via a series of analytical techniques for its proximate, ultimate analysis data, chemical composition and surface area.

- Leaching of the raw and tuned biochars in water, Mehlich-1 solution and solvents. A series of analysis were carried out on the leachate samples collected.
- Hydrolysis of mallee wood in hot-compressed water (HCW). Liquid products collected were analysed for inorganic species, total organic carbon (TOC) and saccharides.

To ensure the repeatability of the results obtained from this research, all experiments were carried out at least in duplicates. The average value along with the error bar of the data is reported. Figure 3.1 depicts the overall research methodology employed to achieve the research objectives.

3.2.1 Leaching of Organic and Inorganic Matter from Biomass by water: Differences between Batch and Semi-continuous Operations

In order to study the leaching characteristics of inorganic and organic matter from biomass and its influences on biomass inorganic leaching, a series of experiments were carried out. First, the leaching of mallee wood and leaf in water were carried out in batch operation. The concentration of inorganic and organic matter in leachates sampled was quantified. The low leachate pH observed lead to the hypothesis that the organic matter leached might lead to an overestimation of water-soluble inorganic species from biomass. Therefore, leaching of biomass in semi-continuous mode was also carried out to verify this hypothesis. The content of inorganic and organic matter in leachates sampled was also analysed. From the data collected, the leaching kinetic of inorganic and organic matter from biomass and their different leaching characteristics in batch and semi-continuous operation were studied and discussed in Chapter 4.

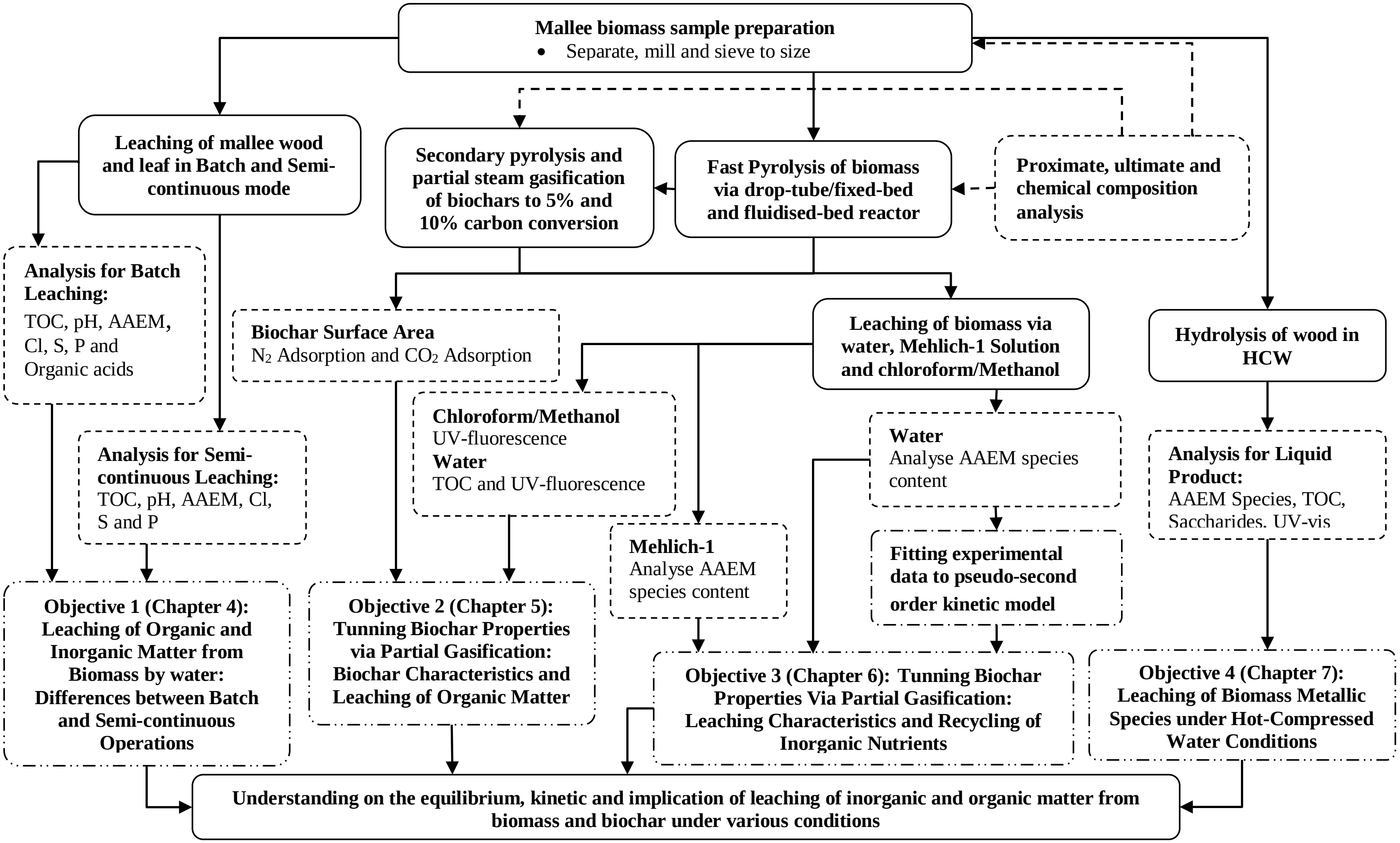


Figure 3.1: Overall research methodology

3.2.2 Tuning of Biochar Properties

To achieve the second and third objectives of this research, a series of systematic experiments were performed. The fast pyrolysis wood and leaf biochar were prepared from drop-tube/fixed-bed reactor and fluidised-bed reactor described in Section 3.3.3 below. Next, the raw biochar were subjected to secondary pyrolysis and partial steam gasification to tune the biochar properties. Then, proximate, ultimate and chemical analysis of all biochar prepared were carried out. Biochar surface areas were also measured through combination of nitrogen and carbon dioxide adsorptions. Finally, the raw biochar and tuned biochar were subjected to leaching in water, Mehlich-1 solution and methanol/chloroform solvent. The TOC, alkali and alkaline earth metal (AAEM) species and Cl content in water leachates were analysed and normalised to those available in biochar. The water and Mehlich-1 solution leachate samples were also analysed via UV-fluorescence spectrometer for soluble aromatic compounds. The AAEM species leached by Mehlish-1 solution were determined for plant available nutrient species. The solvent leachates were analysed with UV-fluorescence for leachable aromatic compound.

The results for biochar surface area, the leaching of organic matter and aromatic compounds will be discussed in Chapter 5. The leaching of inorganic species and the recyclability of inorganic nutrient will be discussed in Chapter 6. Additional effort was taken to fit the experimental data from leaching of AAEM species via water to a pseudo-second order kinetic model to study the effect of tuning on leaching kinetic. The findings are also discussed in Chapter 6.

3.2.3 Leaching of Biomass Water-Insoluble Metallic Species under Hot-Compressed Water Conditions

To study the leaching characteristics of inorganic species from biomass in HCW, hydrolysis of mallee wood in HCW at a series of temperatures (150 °C, 180 °C, 230 °C and 270 °C) were carried out. The liquid products sampled at designated time intervals were analysed for AAEM species content. The leaching equilibrium and kinetic were discussed. To further investigate the occurrence of organically bounded AAEM species in biomass, the decomposition of hemicellulose, cellulose and lignin in mallee wood were also investigated. Additional analyses were carried out for TOC and saccharide content. The findings from this part of the study are discussed in detailed in Chapter 8.

3.3 Experimental

3.3.1 Biomass Sample Preparation

The wood and leaf components were separated from mallee eucalyptus loxophleba (subspecies *lissophloia*) trees which were harvested from Narrogin, Western Australia. The samples were then subjected to size reduction using a cutting mill (model: Fritsch Cutting Mill Pulverisette 15) and sieved to prepare the final samples of size 150-250 µm and 1-2 mm. The samples were kept in plastic bottles and stored below -9 °C before experiments. It is noted that the use of such small particles (150-250 µm) in Chapter 4 is for the purpose of fundamental study in order to reduce the effect of mass transfer limitation during leaching.

3.3.2 Biomass Leaching under Batch and Semi-continuous Operations

Biomass leaching experiments were conducted using a batch leaching reactor. During each leaching experiment, approximately 5 g of a biomass sample was weighed then soaked in 1 L of ultrapure water (resistivity >18.2 MΩ-cm) in a bottle. The mixtures were gently agitated with a magnetic stirrer for a series of leaching times. At a given leaching time, a fixed volume of sample was drawn from the bottle and an equal amount of fresh ultrapure water was added to the mixtures. This process continued till the leaching reached equilibrium (no further increase in the total amount of organic matter and AAEM species leached out from biomass). The leaching experiments were done at least in duplicates.

The semi-continuous leaching experiments were carried out using a continuous flow reactor, which is similar to the one used for hydrolysis of cellulose in a previous study[92] but operated at room temperature and atmospheric pressure. Briefly, in each experiment, ~30 mg of biomass was loaded into a SUS316 stainless steel tubular reactor cell, which was sandwiched by two silver-plated stainless steel filters. The reactor cell was then connected with an HPLC pump (model: Alltech Model 627) at the inlet while the outlet was used for leachate collection. A stream (flow rate: 100 mL/min) of ultrapure water was then delivered by the HPLC pump and flowed through the reactor cell. Leaching equilibrium is considered to be reached when no TOC and inorganic species can be detected in the leachate. The leachate samples were collected at a series of leaching times and then subjected to the analysis of pH, TOC, contents of AAEM species and anions.

3.3.3 Preparation of Biochars

The pyrolysis experiments were carried out to prepare biochar from mallee biomass using 2 types of reactors, (1) drop-tube/fixed-bed quartz reactor and (2) fluidised bed quartz reactor. A drop- tube/fixed-bed reactor was used to prepare fine particle fast pyrolysis wood and leaf biochar. A fluidised bed reactor was used to prepare large particle fast pyrolysis biochar from 1 - 2 mm wood particle.

Drop-tube/Fixed-bed Quartz Reactor

A schematic of the drop-tube/fixed-bed quartz reactor system is shown in Figure 3.2. For preparation of fast pyrolysis wood and leaf biochars at 500 °C, the quartz reactor was pre-heated to 500 °C with a consistent flow of 2 L min^{-1} of ultra-high purity argon through the reactor. Approximately 20 g of biomass was loaded to the feeder and purged with ultra-high purity argon for 15 min before it was fed to the reactor through a water-cooled feeding probe at the rate of 2 g min^{-1} for 10 min. The reactor was held at 500 °C for 10 min before it was lifted then cooled at room temperature. The flow of argon through the reactor was maintained until the reactor was cooled to room temperature. The wood biochar produced is referred as “FWB-500-P” while the leaf biochar obtained is referred as “FLB-500-P” in Chapter 5 and Chapter 6. Pyrolysis experiments above were repeated to obtain the amount of biochars required.

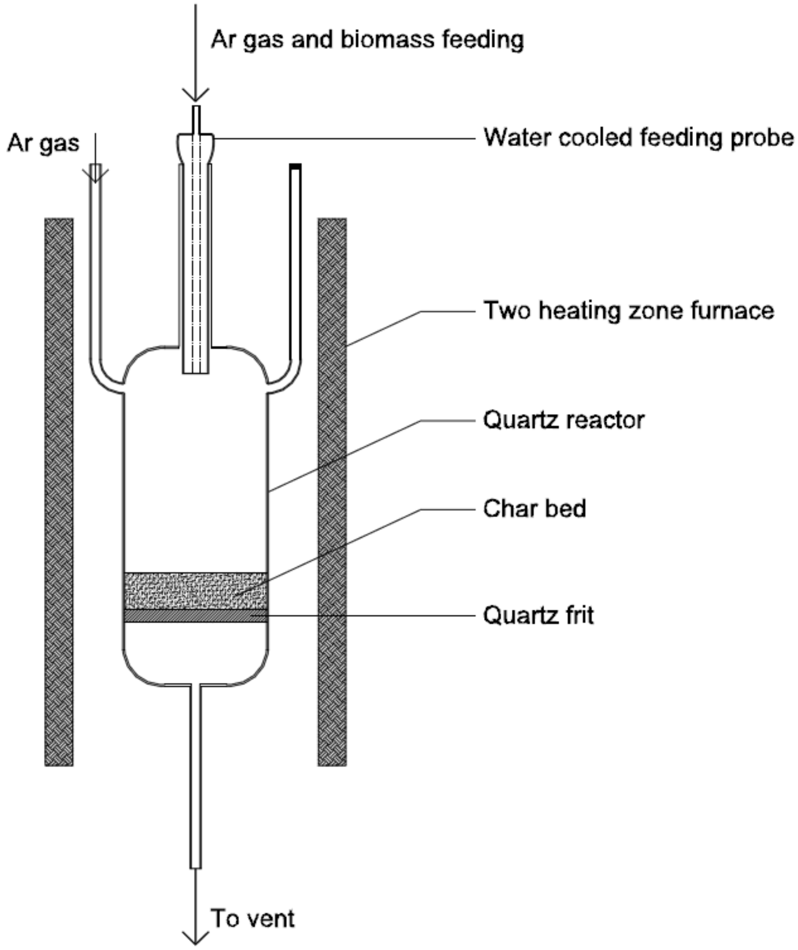


Figure 3.2: Schematic of drop-tube/fixed-bed reactor. The internal diameter middle section of the reactor is 60 mm.

Fluidised Bed Reactor

The schematic of the fluidised bed system used to prepare fast pyrolysis biochar from 1 – 2 mm wood biomass is shown in Figure 3.3. Briefly, the fluidised-bed reactor consists of a vertical tube furnace large enough to heat up the 80 mm diameter quartz reactor. The fluidising medium used is high-purity fine silica sand (125 – 355 μm). A stream of argon is fed from the bottom of the reactor to fluidise the sand at pyrolysis temperature. In order to prevent the quartz reactor from shuttering due to sand rapid thermal expansion during heating, the reactor had to be heated to pyrolysis temperature at a heating rate less than 10 K/min. The biomass was fed to the reactor from the top of the reactor. A stream of argon was flowed through the biomass feeder to prevent the backflow of pyrolysis volatiles to the feeding system. The volatiles produced during the pyrolysis were vented to the extraction system via two side tubes of the quartz reactor.

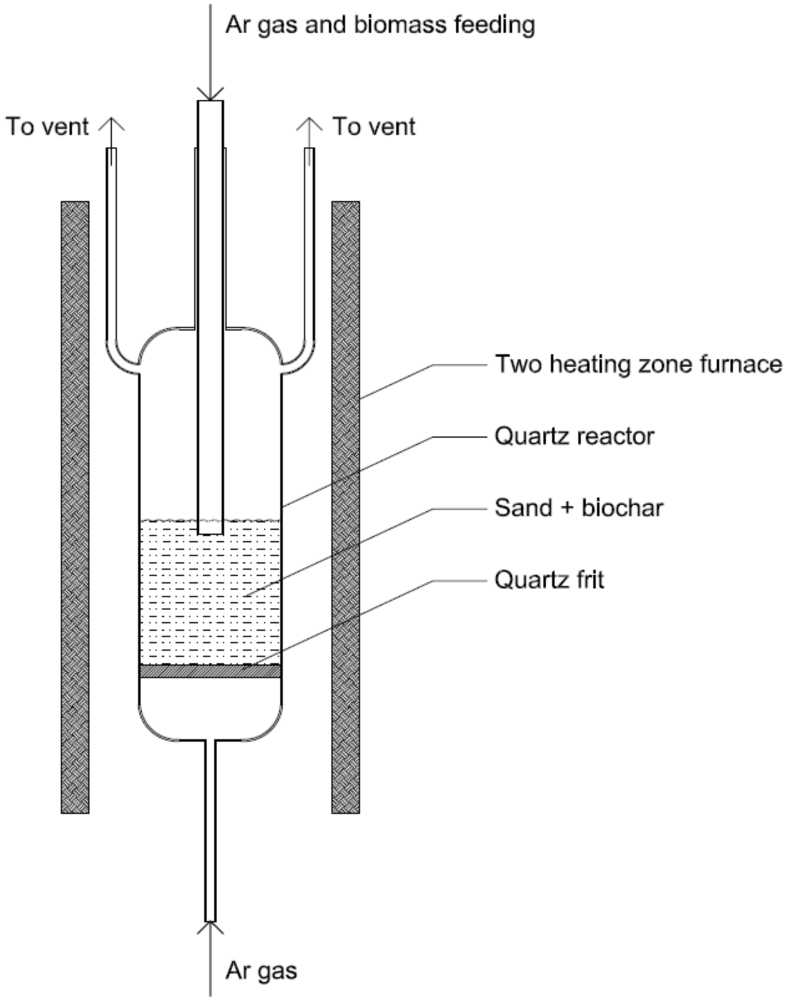


Figure 3.3: Schematic of a fluidised-bed reactor system. The internal diameter of the middle section of the reactor is 80 mm.

To prepare fast pyrolysis biochar from 1 – 2 mm wood biomass, the reactor was first loaded with approximately 450 g of high purity fine silica sand (125 – 355 μm) before it was heated to 500 °C within 70 min. A flow of ultra-high purity argon was used to maintain the fluidisation of sand in the reactor and additional 1 L min^{-1} of Argon was used as a carrier gas in the feeder. ~45 g of biomass was loaded to the feeder. The system was purged with argon for 15 min before the biomass was fed to the reactor at a rate of 2 g min^{-1}. The reactor was held at pyrolysis temperature for 10 min before it was lifted and cooled to room temperature while the flow of carrier gases were maintained. The biochar was carefully separated from the sand by using a 500 μm sieve. The biochar produced from fluidised-bed system was ground manually and sieved to the size fraction of 105 – 250 μm prior to any leaching, secondary pyrolysis and gasification experiments. Pyrolysis experiments above were repeated to obtain the amount of biochars required. The wood biochar produced from this reactor is denoted as "LWB-500-P".

3.3.4 Secondary Pyrolysis Biochar

Secondary pyrolysis biochar used in Chapter 5 and Chapter 6 in this study was produced using a drop-tube/fixed-bed quartz reactor aforementioned. Briefly, ~1.5 g of raw biochar were loaded to the reactor and purged with 3 L min^{-1} of ultra-high purity argon for 15 min before it was lowered to a pre-heated furnace. The reactor was held for 10 min at 725 °C before it was lifted from the furnace and cooled to room temperature while maintaining the flow of argon. These procedures were repeated to obtain sufficient biochar amount required. The biochar produced are denoted accordingly as shown in

Table 3.1. The meaning of the sample labels are given as "XXX-DDD-YY", in which XXX indicates the type of biochar, DDD is the processing temperature (°C) and YY indicate the conditions of biochar tuning via particle gasification. XXX can be FWB for fine wood biochar, FLB for fine leaf biochar, LWB for biochar produced from large particle wood, respectively. DDD can be either 500 for pyrolysis at 500 °C or 725 for re-pyrolysis or partial gasification at 725 °C. YY can be P for the raw fast-pyrolysis biochars, RP for the re-pyrolysed biochars, or 5%-PG and 10%-PG for tuned biochar after 5% and 10% partial gasification at 725 °C, respectively.

Table 3.1: The label for biochars produced from secondary pyrolysis and partial steam gasification

Raw Biochars	Secondary Pyrolysis at 725 °C	Partial Steam Gasification	
		5%	10%
FWB-500-P	FWB-500-RP	FWB-500-5%-PG	FWB-500-10%-PG
FLB-500-P	FLB-500-RP	FLB-500-5%-PG	FLB-500-10%-PG
LWB-500-P	LWB-500-RP	LWB-500-5%-PG	LWB-500-10%-PG

3.3.5 Partial Steam Gasification of Biochar

The partial steam gasification of biochar was performed with a fixed-bed reactor system as shown in Figure 3.4, similar to that used by Yip and co-workers.[148] Please note that the quartz reactor used in this experiment is 60 mm in internal diameter. Briefly, about 0.4 g of raw biochar were loaded to the reactor and purged with 3 L min^{-1} of ultra-high purity argon for 15 min before it was lowered to a furnace pre-heated to 725 °C. The gasification began when the temperature of the reactor reached 725 °C by feeding the steam at the concentration of 8.2 vol% in argon. The steam gasification was first carried out for 40 min to determine the time required to achieve 5% and 10% carbon conversion relative to the carbon content in biochar repyrolysed at 725 °C with no holding time. For partial steam gasification, the steam flow was cut off at the required gasification time and the reactor was immediately lifted and cooled to room temperature. Multiple experiments were carried out to collect sufficient biochar amount for various leaching experiments and analysis.

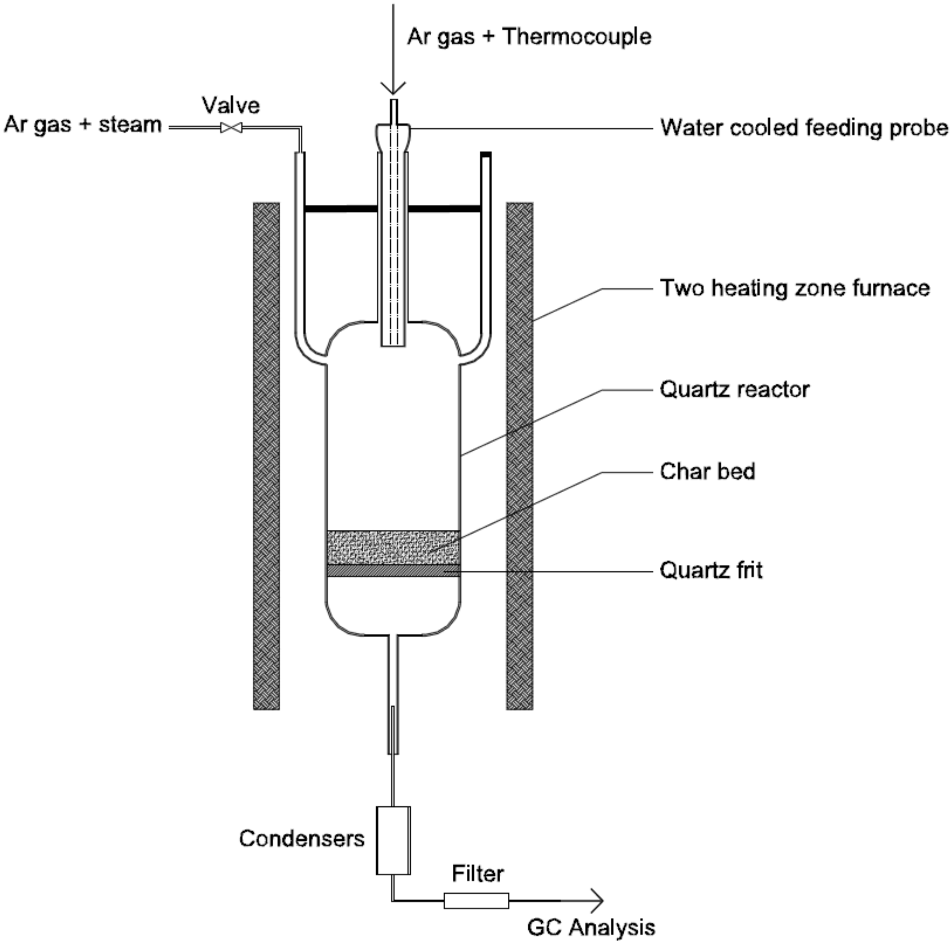


Figure 3.4: Schematic of fixed-bed reactor system for steam gasification. The internal diameter middle section of the reactor is 60 mm.

The gas produced during the steam gasification was cooled with two condensers submerged in ice water in series to remove condensable gas products and water. The gas was then passed through tube packed with glass wool to remove particles suspended in gas stream before it was collected with gas bags for analysis. The gas collected was analysed for H_2, CO, CO_2, and CH_4 as described in Section 3.4.8 below. The biochar produced are denoted accordingly as shown in Table 3.1

3.3.6 Biochar Leaching

Biochar leaching was carried out with different leaching mediums. They are water, Mehlich-1 solution and chloroform/methanol mixture. The leaching of inorganic and organic matter from biochar via water were conducted under batch condition at solid to liquid ratio of 1 g/L. Briefly, about 1 g of biochar was weighed and soaked with 1 L of ultra-pure water (18.2 M Ω) in a plastic bottle. The content was stirred gently with a magnetic stirrer bar at room temperature to minimise the solution concentration difference. A fixed amount of water sample was drawn from the bottle with a needle and syringe at a designated time interval. The sample was then centrifuged. The supernatant was carefully decanted to sample container while the solid retained was mixed with an equal amount of fresh ultra-pure water before adding them into the bottle. The leaching experiment was carried out for 28 days (4 weeks). Therefore, the water leachable inorganic and organic matter in biochar is defined as amount of inorganic and organic matter leached at equilibrium or 28 days. The TOC content was quantified using TOC analyser and AAEM and Cl content in water leachate were analysed with 2 ion-chromatographs.

Total plant available AAEM species were quantified by leaching with Mehlich-1 solution (0.05 N HCl and 0.025 N H2SO4) for extended period of 24 h following the procedure used in previous study.[27] Briefly, ~35 mg of biochar was weighed and immersed in 35 mL of solution. The content was stirred gently with a magnetic stirrer bar at room temperature for 24 h. The solution was then filtered with a 0.45 µm PVDF syringe filters before the concentration of the AAEM species and Cl was analysed with ion chromatographs.

The solvent leaching of biochars was conducted by immerging 0.2 g of biochar in 10 mL of chloroform and methanol mixture (4:1 v/v). The samples were then shook in an orbital shaker for 24 h. Immediately, the samples were filtered with a 0.45 µm filters before UV-fluorescence spectra of the sample were recorded. The leaching experiments were conducted in duplicate.

3.3.7 Hydrolysis of Biomass in HCW

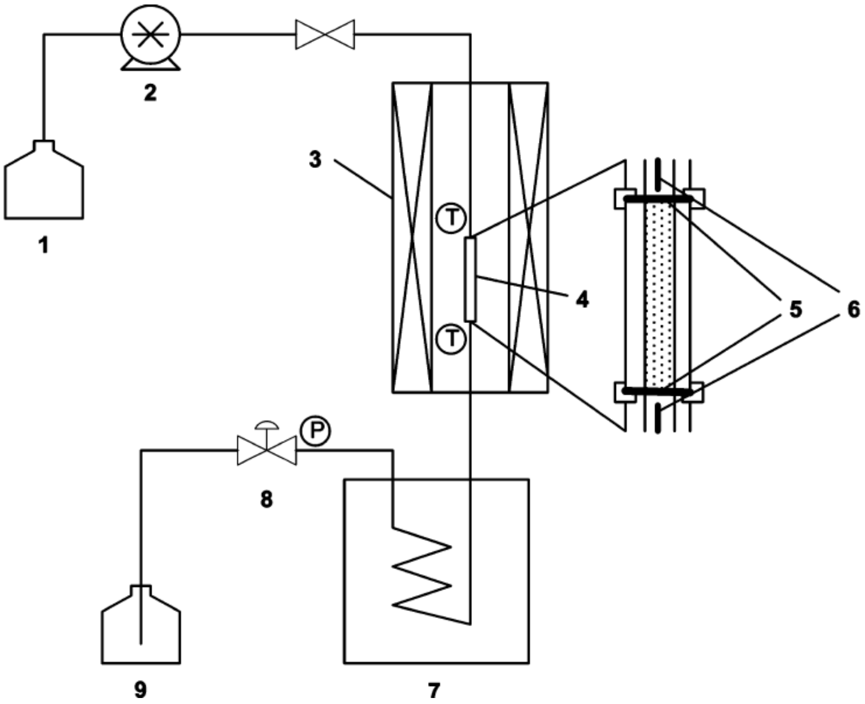


Figure 3.5 Schematic diagram of the semicontinuous reactor system used for biomass hydrolysis: (1) Water reservoir; (2) HPLC pump; (3) infrared image furnace; (4) reactor; (5) sintered stainless steel filter; (6) thermocouple; (7) cooling unit; (8) back-pressure regulator; (9) liquid product collector.

The hydrolysis of mallee wood was carried out using the same semi-continuous reactor system used in a study by Yun and Wu.[92] The schematic of the system used is shown in Figure 3.5. The setup mainly consisted of a HPLC pump, an infrared gold image furnace, an ice water bath and a pressure regulator. The HPLC pump (Alltech 627 HPLC pump) is used to deliver a constant flow (Example, 10 mL/min) of water to the system. The water was preheated to the hydrolysis temperature in the furnace before it entered the reactor cell located at the lower section of the furnace. The reactor cell used was a SUS316 stainless steel tubular reactor cell with two silver-plated stainless steel gasket filters to sandwich the biomass sample in the reactor. The effluent from the reactor was rapidly quenched to 0 °C in a cooling unit. The cooling unit was made up of a stainless steel coil with known dead volume submerged in ice water bath. The back pressure regulator located right after the cooling unit was used to regulate the pressure of the HCW (for example, 10 MPa). The liquid samples were collected from the liquid outlet.

To carry out the biomass hydrolysis experiment, ~50 mg of mallee wood sample was weighted and charged into the reactor cell. Prior to hydrolysis in HCW, the sample was leached with water at room temperature with 10 mL/min of ultrapure water (resistivity >18.2 MΩ-cm) delivered by a HPLC pump for 30 min to remove water-soluble AAEM species. Then the pressure in the reactor was pressurised to 10 MPa. The hydrolysis began by heating reactor and water rapidly (in 2 minutes) to hydrolysis temperatures (150°C, 180°C, 230°C and 270°C) and the temperature was held constant for 70 min. The reactor effluent was immediately quenched with an ice water bath to minimise any subsequent secondary reaction of the liquid product. The liquid product was sampled at designated time intervals. It is important to note that the time scale on the figures presented in Chapter 7 represents the holding time. The TOC, pH, saccharide and AAEM content of the liquid product were analysed swiftly after each experiment. The TOC content was analysed by a TOC analyser. The total saccharide in the liquid sample was analysed via HPAEC-PAD system following post-hydrolysis. The AAEM species was analysed by an ion chromatograph. The details of the instrument and analytical techniques used are given in Section 3.4 below.

3.4 Instrument and Analytical Techniques

3.4.1 Proximate and Ultimate Analysis

The proximate analysis of biomass and biochar samples was conducted using a thermogravimetric analyser (TGA, model: METTLER) according to ASTM E870-82. The carbon, hydrogen and nitrogen contents of all biomass and biochar samples were analysed using a CHNSO elemental analyser (model: Perkin Elmer 2400 Series II). The chlorine content was quantified using the Eschka and combustion method specified in AS1038.8.1.[149] The sulphur and phosphorous content in biomass used in Chapter 4 were analysed by external laboratory (ChemCentre, Bentley). The biomass samples were firstly microwave digested with concentrated nitric acid, followed by the quantification of sulphur and phosphorous using inductively couple plasma optical emission spectrometry (ICP-OES). The oxygen (O) content was then determined by difference from Carbon, hydrogen, nitrogen and sulphur on a dry and ash-free (daf) basis. The sulphur content in other biomass and biochar sample used in Chapters 5, 6 and 7 were analysed following the method specified in AS1038.6.3.1.[150]

3.4.2 Quantification of AAEM Species in Biomass and Biochar Samples

The amount of AAEM species in biomass and biochar were quantified according to a method that was used previously.[148] Briefly, ~5 mg of biomass or biochar sample was loaded in a platinum crucible which was first ashed using a specifically-designed ashing temperature program to prevent the loss of ash-forming species. The ash sample was then digested with a mixture of concentrated acid (HF/HNO_3=1:1). Excessive acids in the solution obtained after acid digestion was evaporated, followed by dissolving the residue with 0.02 M methasulphonic acid. The solution was then subjected to the quantification of AAEM species (Na, K, Mg and Ca) using an ion chromatograph (IC) detailed in Section 3.4.5.

3.4.3 Analysis of Biomass Structural Carbohydrate and Sugar Content in Liquid Products

The structural carbohydrate composition (arabinan, galactan, glucan, xylan, mannan) in wood sample were analysed via acid hydrolysis based on a NREL method.[151] About 100 mg of biomass was charged to a pressure tube and 1 mL of 72% sulphuric acid was then added to the sample. The pressure tube was then immerged in 30 °C water bath for 1 h. The acid concentration was later adjusted to 4% by addition of 28 mL ultrapure water before it was autoclaved for 1 h at 121 °C. For every batch of analysis, a recovery standard was prepared to correct the loss of saccharide during hydrolysis. 348 µL of 72% sulphuric acid was added to 10 mL of liquid standard containing arabinose, galactose, glucose, xylose and mannose in a pressure tube. The content was autoclaved along with the samples.

Post hydrolysis of HCW liquid product was carried out similar to the recovery standard to decomposed oligosaccharides into their respective monosaccharides for quantification of total saccharides in liquid product. The content of monosaccharides in the hydrolysed sample was filtered with 0.45 µm syringe filter before being analysed via HPAEC-PAD system following the procedure outline in Section 3.4.7. The concentration of saccharides in the liquid sample was adjusted based on the recovery of the standard to account for the lost during hydrolysis.

3.4.4 Quantification of Organic Matter in Liquid Samples

The concentration of organic matter in water samples (biomass/biochar washing leachates and liquid products collected from hydrolysis in HCW) were analysed immediately after collection using a TOC analyser (model: Shimadzu TOC-VCP$_H$) equipped with inorganic carbon reaction vessel. The TOC in water samples was calculated through subtraction of inorganic carbon from total carbon in water sample. To enable direct comparison, the amount of TOC in liquid samples was then normalised to the total carbon contained in the respective biomass/biochar sample.

3.4.5 Quantification of Inorganic Species in Liquid Samples

The AAEM species (Na, K, Mg and Ca) content in water samples and aliquot from acid digestions were quantified using an ion chromatograph (IC, model: DIONEX ICS-3000) equipped with suppressed conductivity detection system. Separation was achieved with IonPac CS12A 4x250mm column and IonPac CS12AG 4x50mm guard column using 0.02 M methasulphonic acid as eluent. Chloride, sulphate and phosphate were analysed using another IC system (model: DIONEX ICS-1100) equipped with suppressed conductivity detection system. The anions were separated with IonPac AS22-fast

4x150mm column and IonPac AS22G 4x30mm guard column using 45 mM sodium carbonate and 14 mM sodium bicarbonate as eluent.

3.4.6 Quantification of Organic Acids in Leachates

Anion for organic acids (formate, acetate and oxalate) in leachate from batch leaching of biomass experiments in Chapter 4 were quantified using an ion chromatograph (IC, model: DIONEX ICS-3000) equipped with a suppressed conductivity detection system. Separation was achieved with IonPac AG20 2 × 250 mm column and IonPac AG20 2 × 50 mm guard column using 5mM Potassium Hydroxide as eluent. The analysis was carried out by an external laboratory (ChemCentre, Perth).

3.4.7 Quantification of Monosaccharides

The monosaccharides (arabinan, galactan, glucan, xylan, mannan) content in water sample were analysed using a HPAEC-PAD system. The acid hydrolysis samples required a minimum of 5 times dilution with ultrapure water to bring the concentration of sulphuric acid down to ≤0.8wt%. The HPAEC-PAD is essentially a Dionex ICS-3000 ion chromatography system equipped with pulsed electrochemical detection (PAD with Au electrode and Ag/AgCl reference). In order to achieve an adequate separation of arabinose, galactose, glucose, xylose and mannose with CarbonPac PA20 analytical and guard columns, a gradient program listed in Table 3.2 was used. The total flow rate of the eluent was maintained at 0.5 mL/min. To ensure sufficient linearity of the detector respond, post-column base addition was required. 0.4 mL/min of 300 mM NaOH was added to analytical column effluent by using a PEEK flow path HPLC pump.

Table 3.2: HPAEC-PAD gradient program used for separation of monosaccharides

Time	Eluent		
	A (%) 0.3M NaAc in 0.1M NaOH	B (%) 0.3 M NaOH	C (%) Water
0.0	0	0	100
20.0	0	0	100
20.5	100	0	0
23.5	100	0	0
24.0	0	100	0
30.0	0	100	0
30.5	0	0	100
40.5	0	0	100

3.4.8 Gas Chromatography

The CH_4, CO, CO_2 and H_2 content in the gas collected during gasification were analysed using two Perkin Elmer gas chromatographs (GC). The H_2 content was analysed with Perkin Elmer AutoSystem XL GC equipped with molecular sieved column using argon as the carrier gas. CH_4, CO and CO_2 in gas sample were quantified using Perkin Elmer AutoSystem GC with dual columns (molecular sieve column and Porapak-N column) and helium as carrier gas. The GCs were calibrated with certified standard gas purchased from BOC Australia prior to each analysis sequence.

3.4.9 UV-fluorescence Spectroscopy

UV-fluorescence spectroscopy had been widely used to determine the relative size and concentration of the aromatic compound in liquid samples.[152, 153] The synchronous spectra of the solvent wash and water washing leachate were recorded with Pekin Elmer LS55B spectrometer at constant energy different of -2800 cm^{-1}. The slit width and scan speed were set to 2.5 nm and 200 nm min^{-1} respectively. All the spectra presented are the average of 5 scans.

3.4.10 Biochar Surface Area

The BET N_2 surface area of biochar was analysed by N_2 adsorption based on Brunauer-Emmett-Teller (BET) equation.[154, 155] The N_2 adsorption was carried out with Micromeritics Tri-star II Model 3020. About 200 mg of biochar samples were carefully measured in a sample tube then the sample was outgassed for at least 12 h at 120 °C. The weight loss during outgassing was measured prior to the analysis. The analysis was done with N_2 gas as adsorbate at liquid N_2 temperature. The range of P/P_0 used was limited to 0.05 to 0.35. The surface area was determined with Micromeritics ASAP 3020 software using BET equation at the linear range of the isotherm.

The micropore surface area of biochar was analysed by CO_2 adsorption based on Dubbin-Radushkevich (DR) equation.[156] The CO_2 adsorption was carried out with Micromeritics Gemini with approximately 100 – 150 mg of sample. The sample was outgassed following the same procedure prior to analysis. The analysis was carried out with CO_2 as adsorbate at 273 K (ice water bath) using multi relative pressure points between 0.005 and 0.3. The micropore surface area was determined via DR equation from the linear region of the $\ln W$ versus $\log(P_0/P)$ plot.

3.5 Kinetic Model

Previous study by Kong and co-worker[27] demonstrated that pseudo-second order kinetic model could be used to describe the leaching of AAEM species from biochar.[27] The experimental data for leaching of AAEM species from biochar via water was fitted to this kinetic model to determine the pseudo-second order leaching rate constant and initial leaching rate. The pseudo-second order leaching model is shown in Eq 1[157-159].

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

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

To determine the leaching parameter from the experimental data, Eq 1 had to be expressed in linear form. By integrating Eq 1 with the boundary condition $t = 0$ to t and $C_t = 0$ to C_t, integrated rate law Eq 2 could be obtained. By rearranging Eq 2, the linear form of Eq 1 could be obtained as shown in Eq 3. By fitting the data into t vs t/C_t, leaching parameter C_s could be obtained from the slope and k could be calculated from the intercept. As t approaching 0, the initial leaching rate could be expressed by Eq 4. The initial leaching rate h could be determined through Eq 4.

$$C_t = \frac{C_s^2 kt}{1 + C_s kt} \qquad -(Eq\ 2)$$

$$\frac{t}{C_t} = \frac{t}{C_s} + \frac{1}{kC_s^2} \qquad -(Eq\ 3)$$

$$h = kC_s{}^2 \qquad -(Eq\ 4)$$

3.6 Summary

Mallee wood and leaf were carefully separated and prepared into the desired size fractions (150 – 250 µm and 1 – 2 mm). Leaching of fine biomass was carried in both batch and semi-continuous modes. The biomass samples were also pyrolysed to produce fast pyrolysis biochar. Secondary pyrolysis and partial steam gasification of biochar were also used to tune the biochar. All the biochars produced were then subjected to leaching in water, Mehlich-1 solution and solvents. In addition, hydrolysis of biomass in HCW was also carried out to study the leaching of AAEM species in HCW. The raw biomass and its derived biochar were characterised with various analysis discussed in Section 3.4. The leachate samples collected from leaching experiment were also analysed. The results from these experiments led to a better understanding on the equilibrium, kinetic and implication of leaching of inorganic and organic matter from biomass and biochar under various conditions.

Chapter 4: Leaching of Organic and Inorganic Matter from Biomass by water: Differences between Batch and Semi-continuous Operations

4.1 Introduction

One key feature of biomass is that during its growth biomass extracts various inorganic nutrients species (e.g. Cl and alkali and alkaline earth metallic species, i.e. AAEM species, including K, Mg, Ca etc) from soil as inherent inorganic species in biomass. Knowledge on the leaching behaviour of these species during biomass water leaching is essential to biomass utilisation for at least four important reasons as described below.

First, the inherent inorganic species in biomass as precursors of ash formation are known to be responsible for notorious ash-related issues during biomass combustion/gasification.[18, 19, 56-62] The transformation of these inorganic species during biomass combustion/gasification strongly depends on the chemical forms (e.g. water-soluble, organically-bound etc) of these species in biomass.[18, 160-163] Chemical fractionation is a common method used for determining the forms of inorganic species in solid fuels. It is a sequential extraction method initially used by Benson and Holm,[164] later modified by Baxter[165] and recently improved by Zevenhoven et al.[18] The first-step of the method uses batch water washing to quantify the water-soluble inorganic species in biomass. However, as demonstrated in previous studies,[24, 121, 158] batch water washing of biomass may also leach out a substantial amount of organic matter from biomass. Such leaching of organic matter may result in an acidic leachate, which may in return interact with biomass to possibly remove some organically-bound (water-insoluble) inorganic species in biomass. Unfortunately, little work has been done on this aspect so far.

Second, it was demonstrated in previous studies[18, 20, 32, 33, 106-108, 111, 166, 167] that water washing may be an effective pretreatment strategy to remove inherent inorganic species in biomass for mitigating the ash-related issues. Such water washing of biomass was conventionally carried out under batch operations, with the removal performance reported to be dependent on the properties of biomass materials. [18, 20, 32, 33, 101-103, 106, 164, 165] Likewise, if water washing can produce an acidic leachate, such a leachate will possibly alter the leaching performance of these inorganic species in biomass. Most importantly, the leaching of organic matter from biomass during such a pretreatment step also means the loss of fuel materials. Surprisingly, little has been discussed on these aspects in the open literature.

Third, batch water leaching was also used to remove water-soluble inorganic (such as AAEM) species in biomass to investigate the effect of these species on the pyrolysis behaviour of biomass.[111, 112, 166, 167] Similarly, if batch washing of biomass leads to the loss of fuel materials,[24, 121, 158] such loss of organic matter in fuel may also influence the pyrolysis behaviour of the water-washed biomass. However, the effect of such organic matter loss (as results of water leaching) on biomass pyrolysis was unknown and not considered previously.

Fourth and last, the continuous growth and harvest of biomass in land result in continuous export of the inorganic species from soil, potentially leading to depletion of these inorganic nutrients in soil. Therefore, it is important to recycle at least part of these inherent inorganic species in biomass in order to maintain the sustainability of biomass production. It was reported that during mallee biomass production about half of key inorganic nutrients exported are in the leaf component so that recycling of these nutrients may be achieved via incorporating mallee leaf materials back into the soil.[168] Therefore, it is beneficial to understand the leaching behaviour of inherent inorganic species in biomass by water.

Therefore, it is the objectives of this chapter to carry out a series of fundamental study on the leaching characteristics of organic and inorganic matter from mallee biomass by water, employing both a batch leaching reactor and a semi-continuous leaching reactor. A unique feature of the semi-continuous leaching reactor is that the leachate is rapidly swept out of the reactor while the biomass remains inside the reactor. Such a design minimises the contact between the leachate with the biomass particles being leached, offering significant advantages over the conventional batch leaching. The experimental program considers both wood and leaf components of mallee. Leaching characteristics of organic carbon, AAEM species and anion species (e.g. Cl) are discussed.

4.2 Leaching of Organic and Inorganic Matter in a Batch Reactor

Table 4.1: Properties of mallee wood and leaf biomass samples used in this chapter

Sample	Moisture (wt% after air-dried)	Proximate (wt % dry basis)			Ultimate (wt% dry ash free)				
		Ash	VM[a]	FC[b]	C	H	N	S	O[c]
Leaf	5.6	3.6	76.5	19.9	59.1	7.4	1.30	0.12	32.08
Wood	4.0	0.5	83.6	15.9	48.8	6.7	0.42	0.02	44.06

[a]VM–volatile matter; [b]FC–fixed carbon; [c]By difference

Table 4.2: Contents of inorganic species in biomass samples

Samples	Inorganic Species (wt% dry basis)					
	Na	K	Mg	Ca	Cl	P
Leaf	0.5927	0.3057	0.1699	0.7876	0.1949	0.1165
Wood	0.0246	0.0689	0.0355	0.1376	0.0244	0.0115

Table 4.1 and

Table 4.2 show the data on the proximate, ultimate and ash analysis of mallee wood and Leaf used in this chapter. Figure 4.1 presents that data on the total organic carbon leached from mallee wood and leaf samples in the batch reactor under equilibrium conditions. A substantial amount of organic matter, about 32% of the total carbon in the mallee leaf sample, can be leached from mallee leaf. However, only a small amount of organic matter (~2% of the total carbon in the mallee wood sample) can be leached from mallee wood. The results are in consistent with those reported by Wu et al.[24] for mallee biomass samples prepared from different batches. The data for the leaching of inorganic species are presented in Figure 4.2. At equilibrium under batch leaching conditions, Na and K were almost completely leached out from both mallee wood and leaf samples (i.e. ~100% and ~92% of Na, 95% and 98% of K were leached out from wood and leaf, respectively). However, the leaching of Mg and Ca are considerably less under the same batch leaching conditions (~45% and 58% of Mg, 29% and 5% of Ca were leached out from wood and leaf, respectively). Therefore, after batch water washing, there are significant quantities of water-insoluble Mg and Ca remained in the biomass samples while all Cl can be leached out from both wood and leaf.

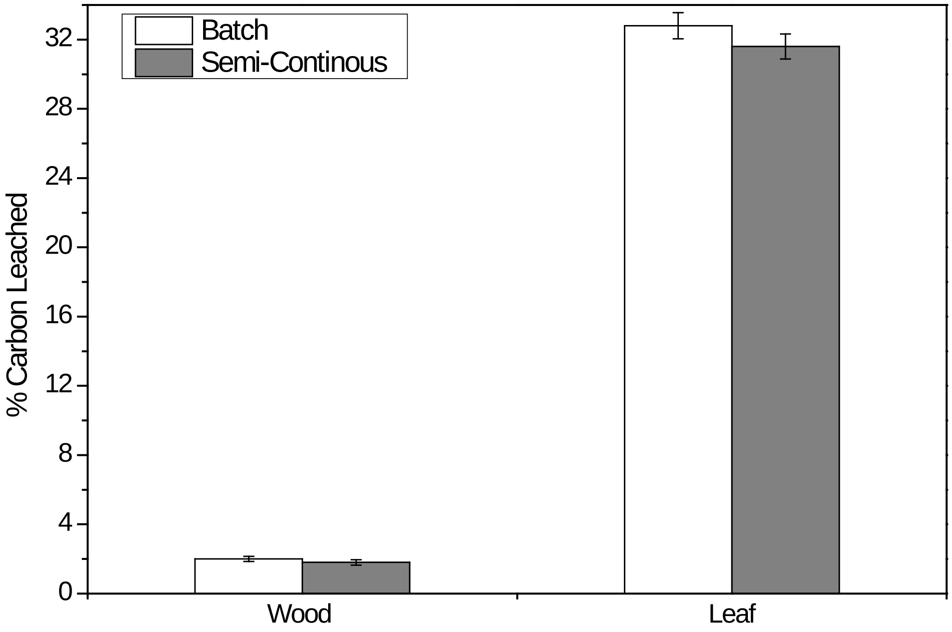


Figure 4.1: Percentages of total organic carbon leached from the water washing of mallee wood and leaf biomass samples under batch and semi-continuous leaching conditions

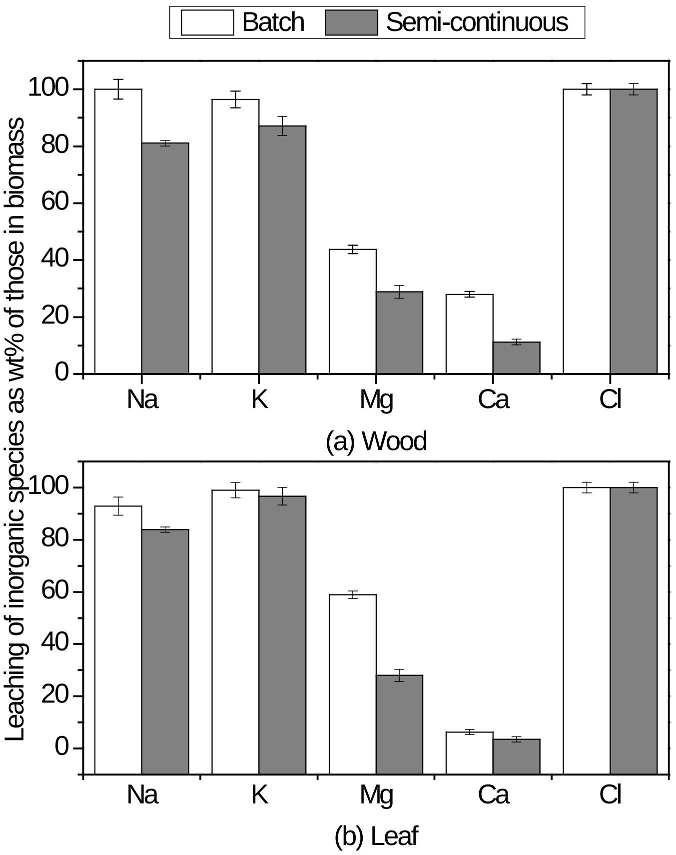


Figure 4.2: Percentages of various inorganic species leached from the water washing of mallee wood (a) and leaf (b) biomass samples under batch and semi-continuous leaching conditions

Table 4.3 lists the pH, concentrations of organic acids and cation/anion ratio of the leachates obtained from the batch water washing of leaf and wood samples at equilibrium. Clearly, the leachates are acidic as the pH values of the leachates collected from wood and leaf leaching are 5.5 and 4.2, respectively. The results suggest that at least some organic acids are present in the organic matter leached from the biomass samples. Analysis using ion chromatography (see the method detailed in section 3.4.6) shows that the leachate samples contain organic acids including acetate, formate and oxalate etc. As shown in Table 4.3, the identified organic acids contribute to 2.06% and 0.79% of total organic carbon leached from wood and leaf, respectively. Also listed in Table 4.3 is the cation/anion ratio of the leachate (Na + K +2Mg + 2Ca)/(Cl +2S +3P). The cation/anion ratios are 2.3 and 3.1 for wood and leaf, respectively, suggesting at least some of the AAEM species leached out from the biomass samples do not exist in the biomass samples as water-soluble salts. Overall, the results presented so far clearly demonstrate that under batch water leaching conditions, the organic acids leached from biomass samples remain in the leachates system and leach out some of the acid-soluble (but water-insoluble) AAEM species (e.g. organically-bound AAEM species via ion exchange). It is likely that batch water washing of biomass overestimates the contents of the water-soluble inorganic species in biomass samples. Therefore, a new method is needed for the correct quantification of these water-soluble inorganic species, eliminating the effect of the interactions between the leachate and the leaching biomass sample.

Table 4.3: Properties (pH, concentrations of organic acids and cation/anion ratio) of the leachates obtained from water washing of leaf and wood samples at equilibrium under batch leaching conditions

Items	Leachate from batch washing of wood	Leachate from batch washing of leaf
pH	5.5	4.2
concentrations of organic acid anions (% of TOC in leachate)		
acetate	1.13	0.03
formate	0.11	0.02
oxalate	0.82	0.74
Total	2.06	0.79
cation/anion ratio, ie (Na + K +2Mg + 2Ca)/(Cl +2S +3P)	2.2	3.1

4.3 Leaching of Organic and Inorganic Matter under Semi-continuous Operations

Efforts were then taken to carry out a series of leaching experiments using a semi-continuous leaching reactor. As aforementioned, the key innovation of the semi-continuous leaching reactor is the realisation of rapidly separating the leaching products from the biomass particles being leached. This ensures it is the fresh water (rather than acidic leachate) that continues to perform the leaching action on the biomass sample.

The results of leaching experiments using the semi-continuous leaching reactor are also plotted in Figure 4.1 and Figure 4.2, along with those using the batch leaching reactor. It can be seen in Figure 4.1 that there is a small (but appreciable) reduction in the amount of total organic carbon leached using the semi-continuous reactor, in comparison to that using the batch reactor. Additionally, there are considerable reductions in the percentages of AAEM species leached from both wood and leaf using the semi-continuous leaching reactor, in comparison to those leached using the batch reactor. For example, the percentages of Na, K, Mg and Ca leached from biomass samples are reduced by an absolute 20, 10, 15 and 18% for wood (and 15, 3, 30 and 4% for leaf), respectively. Therefore, it is clearly demonstrated that in the batch leaching reactor, as results of extensive and lengthy contact (hence interactions) between the acidic leachates and the biomass samples, various amounts of water-insoluble inorganic species (but soluble in the acidic leachates) have been leached out. In addition, Figure 4.2 also shows that all the chlorine in the biomass samples was leached out under both batch and semi-continuous leaching conditions, clearly indicating that all Cl in biomass is truly in water-soluble forms.

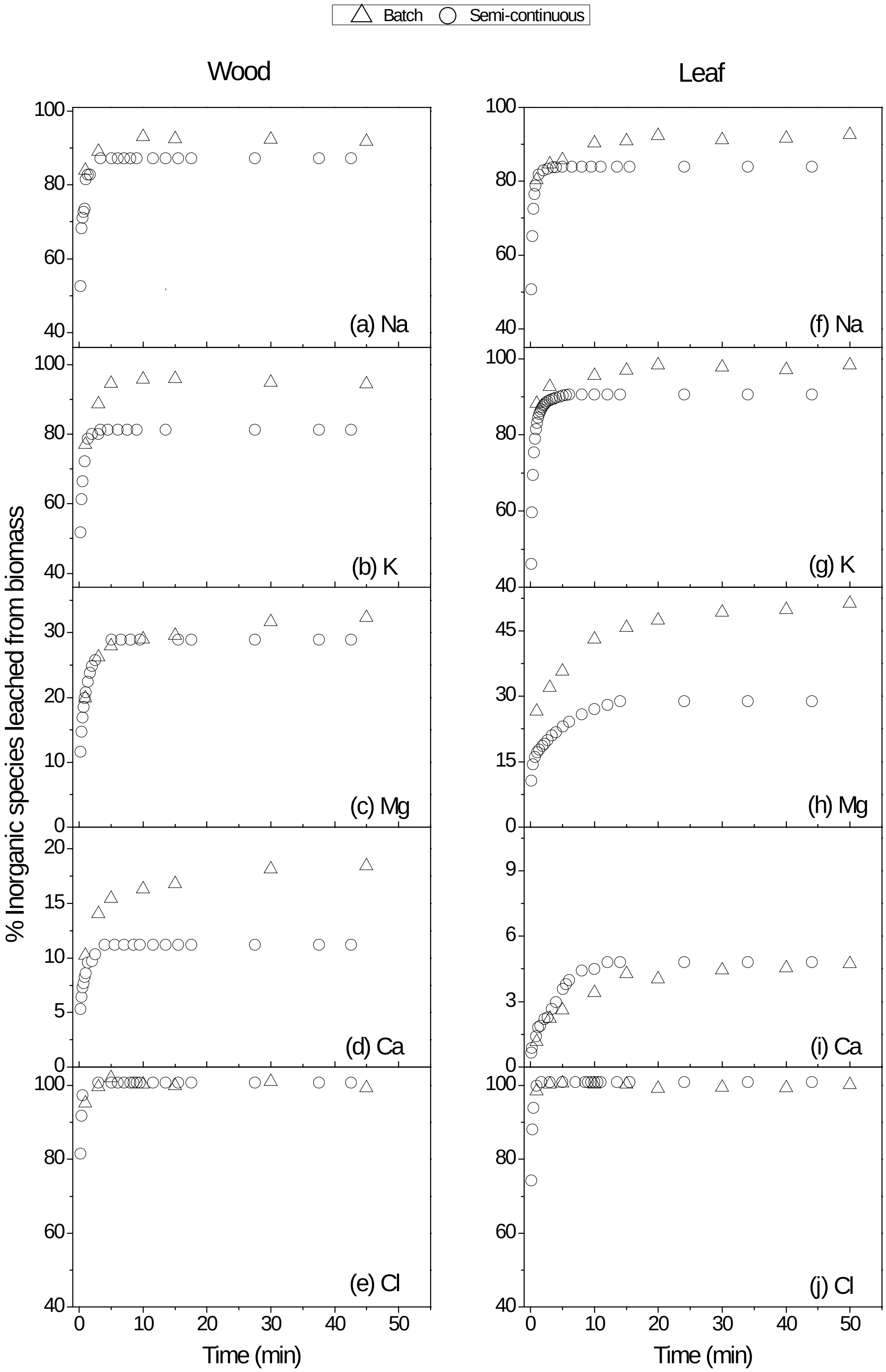


Figure 4.3: Percentage of various inorganic species leached from the water washing of mallee wood (panels a-e) and leaf (panels f-j) as a function of leaching time.

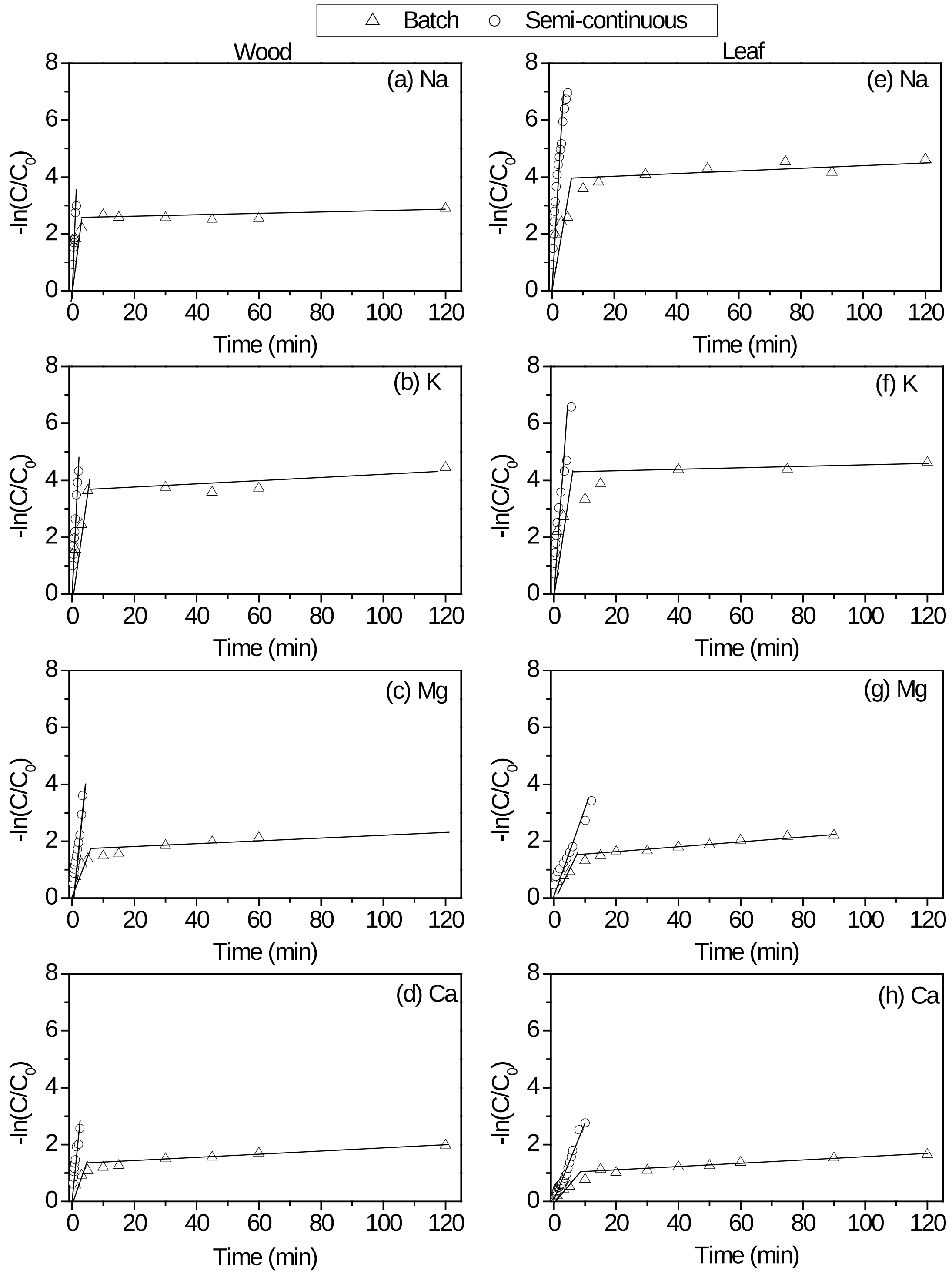


Figure 4.4: Correlation between $-\ln(C/C_0)$ and leaching time under both batch and semi-continuous leaching conditions: Panel (a-d) for Na, K, Mg and Ca in wood, Panel (e-h) for Na, K, Mg and Ca in leaf

4.4 Differences in Leaching Kinetics between Batch and Semi-continuous Leaching Operations

Figure 4.3 presents the percentages of inorganic species leached out from the mallee wood and leaf samples as a function of leaching time under both batch and semi-continuous leaching conditions. The results clearly demonstrate the substantial differences in the leaching kinetics between batch and semi-continuous leaching conditions. Leaching of Na and K from both leaf and wood is rapid within the first 10 minutes and almost reaches equilibrium under both batch and semi-continuous leaching conditions. Similarly, the leaching of Mg and Ca is also rapid during the first 10 minutes and further leaching becomes slow. All chlorine in biomass can be leached within less than 5 minutes for batch leaching and within one minute for semi-continuous leaching. The longer leaching time for batch leaching suggests that Cl leaching appears to be influenced by the Cl concentration in the bulk leachate.

Assuming the leaching follows the first-order kinetics, $C_{i,0}$ is the total amount of species i which can be leachable and $C_{i,t}$ is the total amount of species i remained after a leaching time t, we have

$$-\ln(\frac{C_{i,t}}{C_{i,0}}) = k_i t$$

where k_i (min^{-1}) is the leaching rate and t (min) is the leaching time. For first-order kinetics, the plot of $-\ln(C_{i,t}/C_{i,0})$ against time t should give a straight line. Figure 4.4 presents such plots for Na, K, Mg and Ca based on the experimental data. Clearly, the overall leaching process does not follow first-order kinetics under batch operations. It consists of two distinct first-order leaching steps (represented by two straight lines for each species in Figure 4.4) for the leaching of these species from both wood and leaf. The first step is a rapid leaching step within the first several minutes, followed the second step which is slow. The two-step leaching suggests that two different leaching mechanisms govern the leaching process during batch water leaching of biomass. The first step corresponds to rapid dissolution of inorganic species which are in the form of water-soluble salts while the second step reflects the slow leaching of inorganic species via ion-exchange with H$^+$ from organic acids. However, under semi-continuous leaching conditions, Figure 4.4 shows that the leaching process consists of only one single step, i.e. the first rapid leaching step. The slow second-step leaching is absent because the acidic leachate was swept out of the semi-continuous reactor rapidly hence its contact with the biomass particles was minimised.

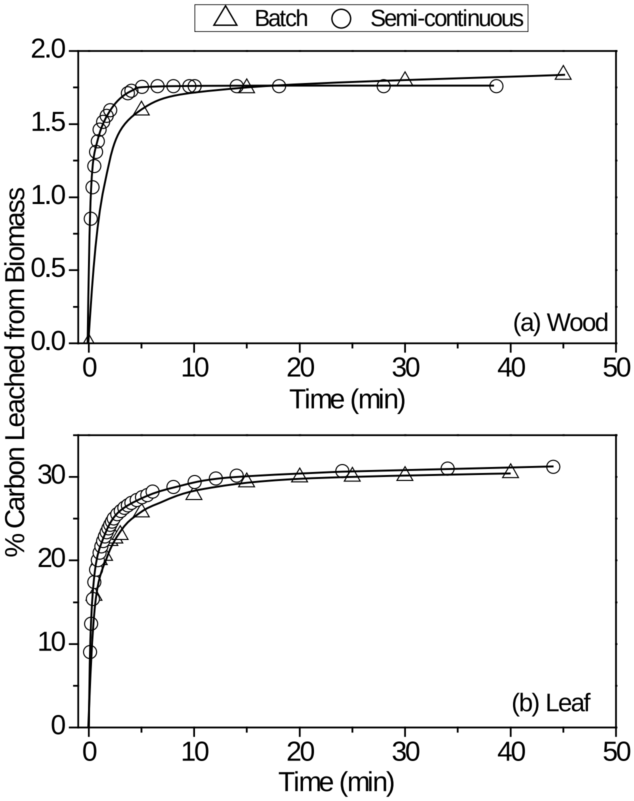


Figure 4.5: Percentage of total organic carbon leached from the water washing of mallee wood (a) and leaf (b) as a function of leaching time, under both batch and semi-continuous leaching conditions.

Similar trends of two-step leaching are also observed in the leaching of total organic carbon from the biomass samples under batch conditions. As shown in Figure 4.5, under batch leaching conditions, ~80% of leachable total organic carbon was leached out within 5 minutes, followed by a slow leaching process towards equilibrium. As shown in Figure 4.6, the leaching of organic matter from wood also shows a one-step leaching process under semi-continuous operation conditions, However, Figure 4.6 shows a two-step leaching process for the water leaching of leaf under semi-continuous conditions. The data in Figure 4.1 show that the amount of water-leachable organic matter in leaf is substantial, equivalent to ~32% of the total carbon in the biomass. Therefore, as far as water leaching is concerned, 80% of this water-leachable organic matter in leaf can be dissolved and leached quickly by water in the first rapid step. The subsequent leaching of the rest 20% of the water-leachable organic matter in leaf is slow.

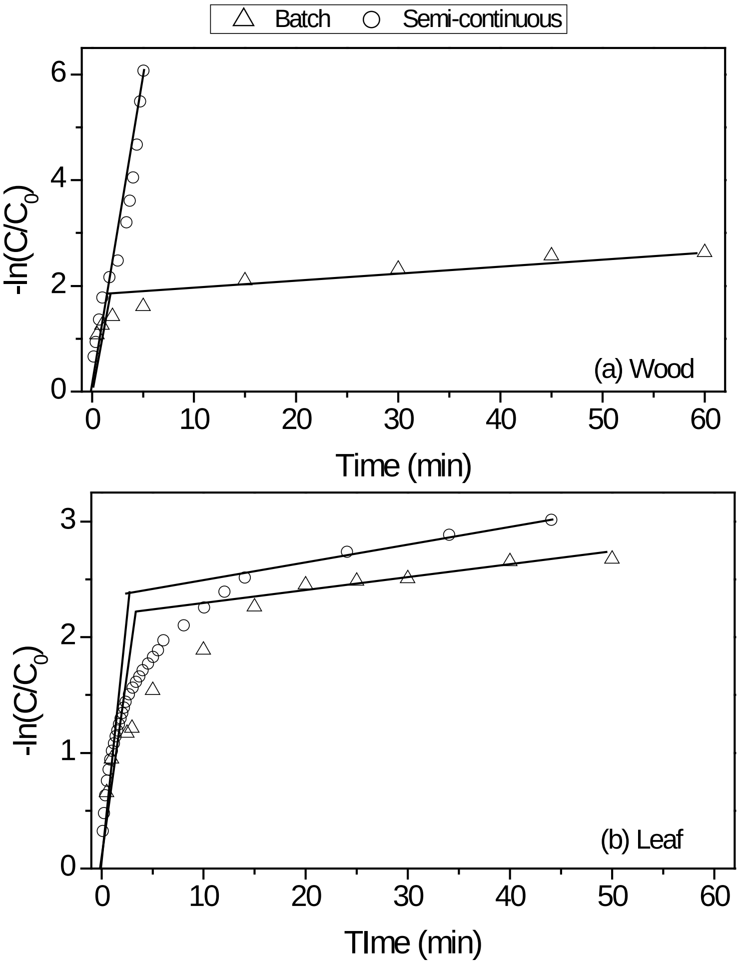


Figure 4.6: Correlation between $-\ln(C/C_0)$ and leaching time for total organic carbon leached from the water washing of mallee wood (a) and leaf (b) under both batch and semi-continuous leaching conditions.

4.5 Differences in the Evolution of Leachate pH and Cation/Anion Molar Ratios between Batch and Semi-continuous Leaching Operations

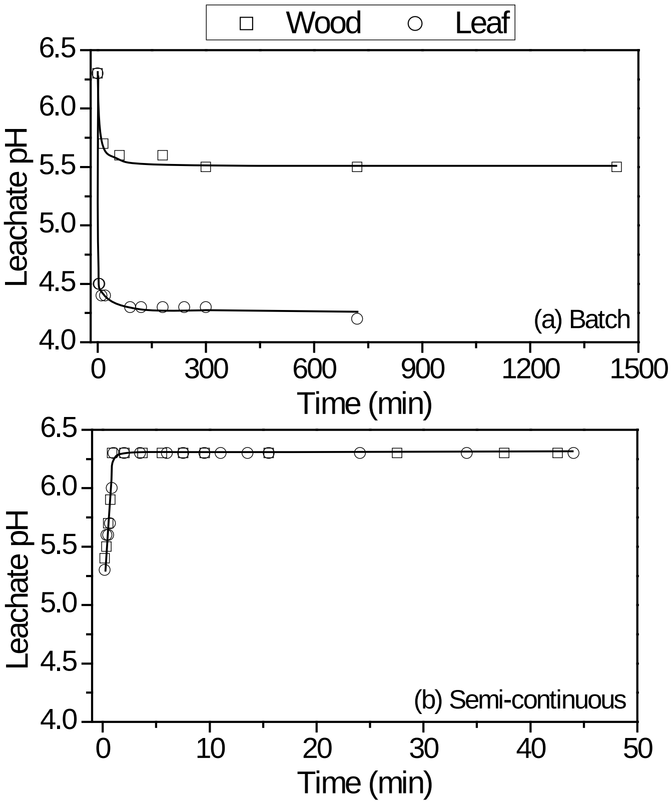


Figure 4.7: Evolution of leachate pH during water washing of mallee biomass sample under batch (a) and semi-continuous (b) leaching conditions

Further work was then carried out to analyse the pH and the cation/anion molar ratios of various leachate samples as a function of leaching time. As shown in Figure 4.7a, under batch leaching conditions, the leachate pH decreases sharply as soon as leaching begins for a period of 5 mins, coinciding with the rapid TOC leaching during the same period (see Figure 4.5). A further increase in leaching time leads to a much slower decrease in pH of the leachate till reaching equilibrium. At equilibrium, the pH value (4.2) of the leachate from leaf is much lower than that (5.5) of the leachate from wood. This is in consistence with the fact that there is substantially more organic matter leached from leaf than wood (see Figure 4.1). On the other hand, under semi-continuous leaching conditions (see Figure 4.7b), the pH value of the leachate increases with the leaching time within the first several minutes, reaches a value of 6.3 and remains unchanged with leaching proceeding further. Two points should be noted from the data presented in Figure 4.7b. One is that a pH value of 6.3 is close to neutral because the pH of the ultrapure water was ~6.5 that is below 7 (known to be the results of ambient carbon dioxide inevitably dissolved in the water[169]).The other is that water-soluble organic matter can be indeed leached out within a period of several minutes, after which little organic matter can be further leached out, resulting in a leachate with pH close to that of the ultrapure water.

Figure 4.8 further presents the cation/anion molar ratio of the leachate samples, i.e. (Na + K +2Mg + 2Ca)/(Cl +2S +3P), as a function of leaching time. Under batch conditions, the data in Figure 8a shows that the cation/anion molar ratio in the leachate from the water washing of wood is close to parity initially, indicating that the inorganic species in biomass leached at the beginning are mainly in the forms of water-soluble inorganic salts. As the leaching process proceeds, the cation/anion molar ratio quickly increases to above 2, clearly showing that the acidic leachate leaches out some of the organically-bound inorganic species in biomass under batch leaching conditions. For the same reasons, the cation/anion ratio under batch leaching conditions is considerably higher than those under semi-continuous leaching conditions. For leaf biomass, the differences in the cation/anion molar ratios between batch and semi-continuous leaching conditions are more significant. This apparently due to the considerably larger amount of total organic carbon leached out of leaf (~32%) in comparison to wood (~2%).

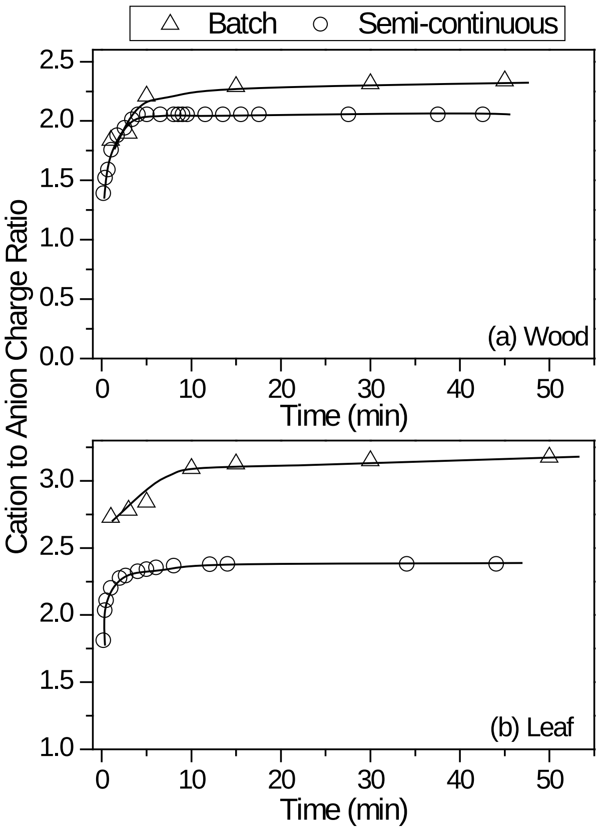
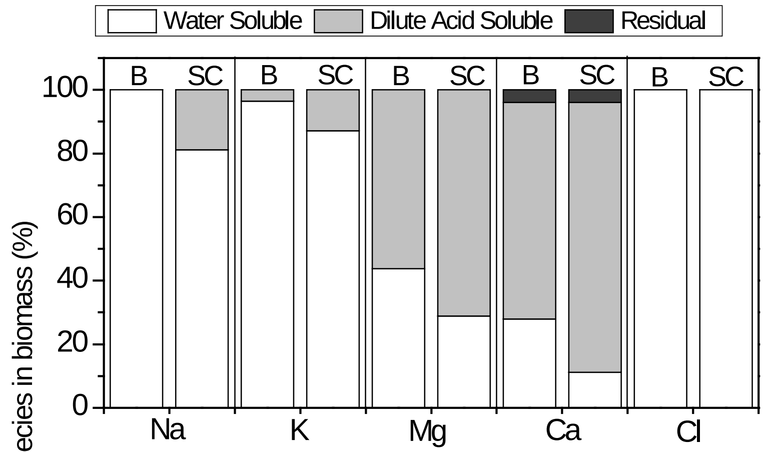


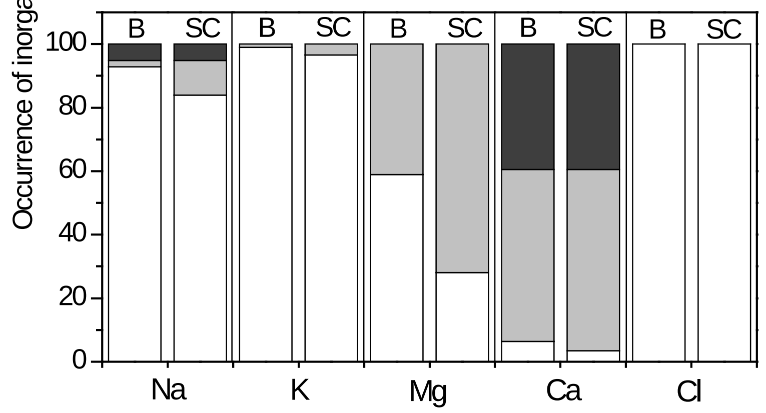
Figure 4.8: Evolution of leachate cation/anion ratio during the water washing of mallee wood (a) and Leaf (b) samples under batch and semi-continuous leaching conditions

4.6 Further Discussion and Practical Implications

The results presented in this chapter have important practical implications on several aspects. First, the findings in this chapter have significant implications to the method used for determining the chemical forms of inorganic species in biomass or other solid fuels. Generally, the occurrence of inorganic species in biomass can be categorised into 3 categories, the water-soluble portion (including salts readily soluble in water), the dilute-acid leachable portion (including organically-bound inorganic species and minerals which are water-insoluble but acid dissolvable, e.g. carbonates) and the residual (other acid-insoluble minerals e.g. silicates). The quantification of water-soluble portion is conventionally done by water leaching of biomass under batch operations. In this study, for illustration purpose, the dilute acid leachable portion was determined via the leaching of biomass using 0.01 M HCl solution (initial solid concentration: 5 g biomass per 1 L dilute acid solution) for 24 hours. It should also be noted that for chlorine, acid leaching of biomass was carried out using 0.01 M H_2SO_4 solution. The residual portion was then calculated by difference. Considering the two different cases of water leaching, i.e. batch leaching as used commonly and semi-continuous leaching reported in this study, the distribution of the three categories of inorganic species are plotted in Figure 4.9 for comparison. It can be seen that both methods can accurately quantify the water-soluble inorganic species if such species are present in biomass only in water-soluble form (e.g. Cl). Otherwise, the conventional method via water batch leaching leads to a clear overestimation. For example, while water leaching using the semi-continuous reactor shows the true water-soluble portion of Na in wood is 80%, batch water leaching results in the conclusion that all Na are water soluble as results of the leaching of 20% organically-bound Na by the acidic leachate in the batch reactor. Similarly, the water-soluble portion of Mg in leaf is considerably overestimated, by almost one fold. Therefore, in the sequential extraction scheme deployed in chemical fractionation, the semi-continuous instead of batch water leaching should be used for quantifying the water-soluble inorganic species.



(a) Wood



(b) Leaf

Figure 4.9: Occurrence of inorganic species in mallee biomass via batch and semi-continuous leaching methods: (a) wood; (b) leaf; B and SC stand for batch and semi-continuous leaching, respectively.

Based on the semi-continuous leaching method, the data in Figure 4.9 (panels a and b) indicate that the majority of Na and K in both wood and leaf are water soluble but large proportions of Mg and Ca are only leachable via dilute acid. These water-insoluble but acid-leachable Mg and Ca might be bonded with the organic structure of the biomass which was only leachable through ion exchange with hydrogen ion from dilute acid or present as water-insoluble salt such as calcium/magnesium oxalate[170] and or calcium/magnesium carbonate. It is also noted that ~4% of Ca in wood, 5% of Na and 40% of Ca in leaf are not leachable even by dilute acid. Therefore, these sodium and calcium are present in acid-insoluble forms, e.g. silicates.

Second, under semi-continuous leaching conditions, the kinetic plots in Figure 4.4 suggest that the leaching of water-soluble mono-valence species (Na and K) is much faster than that of di-valence species (Mg and Ca). For water leaching of a species i within porous materials such as biomass, the leaching kinetics of the species is dependent on the diffusion coefficient D_i of the species within the complex micro-pore network of the biomass particle. Based on the previous work on ion transport in porous media,[171, 172] the overall diffusion coefficient D_i can be calculated as $D_i = D_i^u/\tau$, where D_i^u is the diffusion coefficient of the ion species in free water and τ is the tortuosity of the complex micro-pore network within the porous media. For the same biomass materials, τ can be considered to be same for all ionic species. Therefore, the overall diffusion is determined by D_i^u that is an intrinsic attribute of an ionic species. According to the classic chemistry handbook (such as reference[173]), the values of D_i^u of Na^+ and K^+ (mono-valence species) at 25 °C are 1.334×10^{-9} and 1.957×10^{-9} m^2/s, respectively, considerably higher than 0.706×10^{-9} and 0.792×10^{-9} m^2/s of Mg^{2+} and Ca^{2+} (di-valence species), respectively. Therefore, the leaching of Mg and Ca are slower than Na and K, as indicated by the data in Figure 4.4.

Third, the results reported in this chapter also have important implications to the use of water batch washing as a pretreatment strategy for removing inorganic species in biomass fuels for mitigating ash-related issues during thermochemical processing of biomass. Such a strategy was considered in various previous studies. [18, 20, 32, 33, 101-103, 106, 164, 165] Based on the results in this chapter, it is true that under this condition, water leaching removes most of Cl, Na and K as well as considerable portions of Mg and Ca. However, water leaching may also remove substantial amounts of organic matter in biomass, depending on the origin of biomass. For example, for mallee biomass, while water leaching removes 2% TOC from wood, it can remove and ~32% of TOC from leaf. It was also reported that over 30% of TOC can be removed from mallee bark by water batch leaching.[24] Considering that the bulk biomass from the harvest of mallee trees has 40% of wood, 25% of bark and twig, and 35% of leaf,[174] this can translate to a substantial loss of fuel if water washing is adopted as an attempt to remove inherent inorganic species in biomass. Therefore, from energy applications’ point of view, the fuel loss due to organic matter removal from the water leaching of biomass cannot be neglected.

Fourth, the findings in this chapter may also have an important implication to the conventional method used in investigating the effect of water-soluble inherent inorganic species on chemical reaction mechanisms during thermochemical processing of biomass. In such studies,[106, 107, 164, 165] water washing of biomass was typically carried out under batch operations to prepare a so-called "washed" biomass sample which is considered to be free of water-soluble inorganic species. The effect of water-soluble inorganic species on thermochemical reactions (e.g. pyrolysis) of biomass was then investigated by comparing the behaviour of the raw and the washed samples. Unfortunately, the removal of potentially substantial organic matter from biomass during the water washing of the raw biomass under batch conditions was not quantified and discussed.

4.7 Conclusions

This chapter demonstrates that various amount of organic matter can be leached out from biomass during water washing, depending on biomass materials. The leaching of organic matter from biomass produces an acidic leachate. During batch leaching, the acidic leachate is in continuous contact with biomass particles being leached, resulting in at least some of the water-insoluble (e.g. organically-bound) inorganic species being leached out and being quantified as water-soluble. A semi-continuous leaching reactor was then developed to overcome this issue. It rapidly sweeps the leachate out of the reactor while keeps the biomass sample within the reactor, effectively minimising the contact between the acid leachate and the biomass sample. This leads to accurate quantification of water-soluble inorganic species in biomass and demonstrates that the conventional method using batch washing can lead to an overestimation. The batch leaching of inorganic species in biomass is a two-step process, which include a rapid leaching step for an initial short period and a followed slow leaching step for a long period. However, the semi-continuous leaching of inorganic species in biomass is a single-step process that only includes the first rapid leaching step. The second slow-leaching step disappears as results of minimised interaction between acidic leachate and biomass. It was also found that the leaching of water-soluble di-valence species (Ca and Mg) is slower than mono-valence species (Na and K) due to the smaller diffusion coefficients of di-valence ionic species. The overestimation of water-soluble species suggests that semi-continuous (instead of batch) water leaching should be deployed in the sequential extraction scheme used in chemical fractionation for quantifying water-soluble inorganic species in biomass. As results of potentially substantial loss of fuel matter, care must be taken in using water batch washing as a potential strategy for removing inorganic species in biomass (for fuel quality improvement) and as a method for studying the effect of water-soluble inorganic species on thermochemical reactions of biomass.

Chapter 5: Tuning Biochar Properties via Partial Gasification: Biochar Characteristics and Leaching of Organic Matter

5.1 Introduction

As discussed in Section 2.4.2, large scale utilisation of biomass for bioenergy production may lead to various undesirable impacts on soil and water quality,[25, 26, 81] resulted from continuous harvesting of biomass or removal of biomass residual. This includes reduction of soil fertility due to significant losses of plant nutrients like alkali and alkaline earth metallic (AAEM) species from soil argo-ecosystem. Unless part of these plant nutrients is returned or recycled to the soil, continuous removal of plant nutrient from pyrolysis lifecycle might render sustainability of biomass pyrolysis in doubt. Bio-oil is normally produced from fast pyrolysis of biomass at temperature of 450 °C to 550 °C for optimum yield. While bio-oil can be burned in diesel engine[72, 74] and potentially upgraded to transportation fuel,[68, 70, 77] the vast quantity of biochar produced during commercial production of bio-oil can be applied to soil.[26] As the majority of AAEM species in biomass are retained in biochar during pyrolysis[24, 137] this will enable part of AAEM species uptake by biomass during its growth to be recycled to soil[24, 27] and improves the quality of the soil at the same time.[26]

Although the overall recyclability of Mg and Ca in fast pyrolysis mallee biochar (based on Mehlich-1 leaching) is high, a major portion of them are water insoluble. This is due to the combination of encapsulation of these AAEM species in biochar structure and possible transformation of AAEM species into water-insoluble form.[27] The fact that a large portion of these Mg and Ca being water-insoluble indicates that depending on the soil pH, the overall recyclability of these AAEM during soil amendment can be low.

As steam gasification is known to promote the formation of porous structure of biochar,[154] partial steam gasification can potentially tune the biochar from fast pyrolysis to enhance the overall recycling of biomass inherent AAEM species retained in biochar by exposing those AAEM species which are encapsulated during pyrolysis. Furthermore, the inherent AAEM species in biochar are known to be the catalyst for char gasification and participate in the gasification reaction.[175] Coupled with increase in oxygen containing functional groups on biochar surface,[175, 176] there is a possibility those AAEM species in the form that is water-insoluble to transform into water-soluble form thus increase in the overall recyclability of these AAEM species in biochar at a wider range of soil conditions.

While partial steam gasification is a promising method for biochar tuning, basic characteristics of the tuned biochar such as its surface area and leaching of organic matters have to be understood. Application of biochar in soil will certainly affect the soil physical properties.[177] For instance, surface area and pore size distribution can affect the amended soil microbial activity[177] and water holding capacity (WHC). In addition, it is known that small amount organic matter can be leached from mallee biochar[24] which can be harmful to the environment. Although complete identification of these organic matters leached from biochar is not practical, at least basic nature of these compound have to be understood.

The option to tune the properties of biochar from fast pyrolysis mallee biochar via partial stream gasification will be investigated in current and following chapter. This chapter will focuses on the evolution of biochar characteristics following partial gasification and the leaching of organic matter from raw and tuned biochar. Chapter 6 will emphasise on the leaching characteristics and recycling of inorganic nutrients in biochar.

In this chapter, the raw biochars were prepared from fast pyrolysis of small particle mallee wood and leaf using drop-tube fixed-bed (DTFB) reactor system and large particle wood using fluidised-bed (FB) reactor system. The raw biochar were tuned via 5% and 10% partial steam gasification. Then the properties of biochar such as char yield, carbon content and surface area were analysed and discussed. To better understand the leaching of organic matter from biochar during soil application, the biochars were subjected to water and solvent (chloroform methanol mixture at 4:1 v/v ratio) washing. The total organic carbon (TOC) content of water leachate was quantified to determine the amount of organic matter leachable by water. Finally, the leachates from water and solvent washing of biochar were analysed using UV-florescence spectroscopy to study the leaching of aromatic compound from raw and tuned biochar.

5.2 Char Yield and the Characteristics of Biochar from Secondary Pyrolysis and Partial Gasification

Table 5.1 shows the proximate and ultimate analysis data for the raw biomass and biochars used in this chapter. Figure 5.1 shows the progression of steam gasification of three different biochars as percentage carbon conversion over time at 725 °C. The steam gasification was carried out at a mild temperature (725 °C) rather than 750 °C used in previous studies[148, 154] to slow down the gasification process, especially the gasification of leaf biochar so that the conversion of the biochar could be controlled precisely.[148, 154] Compared to gasification of wood derived biochar, the gasification rate of leaf biochar (FLB-500-P) was highest followed by wood biochar prepared from FB (LWB-500-P) and lastly DTFB (FWB-500-P) system. This is due to the catalytic effect from high AAEM content in leaf biochar and slightly higher AAEM content in LWB-500-P biochar compared to FWB-500-P biochar as shown in Table 5.2.

Table 5.1: Proximate and ultimate analysis of the raw biomass and various biochars used in this study. The meaning of the sample labels are given as "XXX-DDD-YY", in which XXX indicates the type of biochar, DDD is the processing temperature (°C) and YY indicate the conditions of biochar tuning via particle gasification. XXX can be FWB for fine wood biochar, FLB for fine leaf biochar, LWB for biochar produced from large particle wood, respectively. DDD can be either 500 for pyrolysis at 500 °C or 725 for re-pyrolysis or partial gasification at 725 °C. YY can be P for the raw fast-pyrolysis biochars, RP for the re-pyrolysed biochars, or 5%-PG and 10%-PG for tuned biochar after 5% and 10% partial gasification at 725 °C, respectively.

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

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

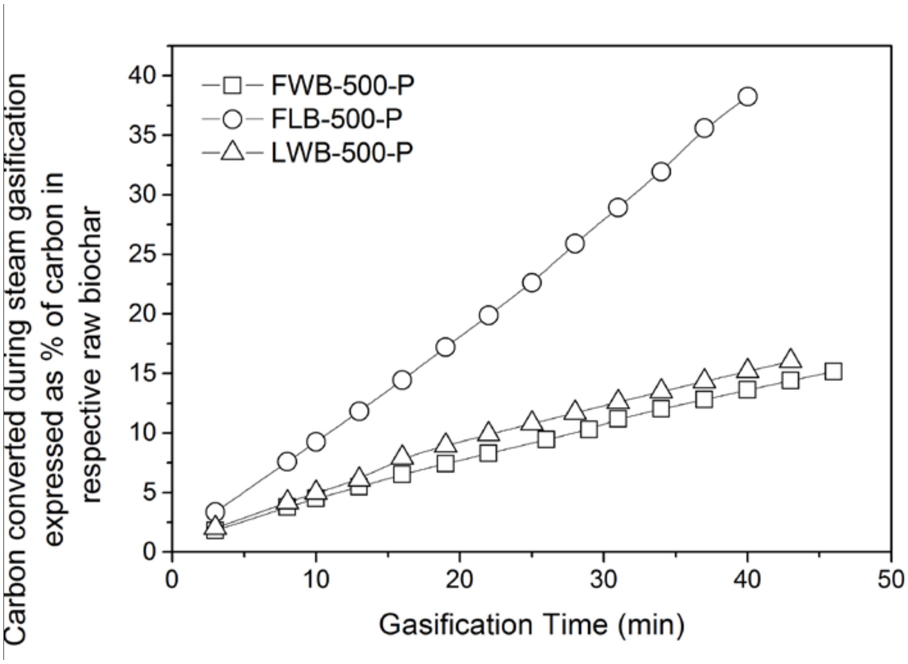


Figure 5.1: % carbon conversion as a function of gasification time for various biochars at 725°C

The char yield of biochar from pyrolysis at 500 °C and biochar from subsequent re-pyrolysis then partial steam gasification at 725 °C is shown in Figure 5.2. As expected, re-pyrolysis and gasification of biochar at a higher temperature cause the biochar to experience additional weight loss due to release of volatiles and conversion of some biochar into syngas. The magnitude of weight loss of these biochar is in the order of FWB-500-P > FLB-500-P > LWB-500-P derived biochar. The biochar produced from LWB-500-P experienced a higher weight lost during secondary pyrolysis and gasification compared to FWB-500-P derived biochar. This might due to the higher volatile content in LWB-500-P biochar as this biochar was produced from pyrolysis of larger particle size biomass. An increase in biomass feedstock particle size caused some of the volatile from pyrolysis to trap within biochar structure due to mass transfer limitation imposed by pyrolysis of large particle biochar. However, as the biochar was grounded to smaller particle size prior to secondary pyrolysis and steam gasification, these trapped volatile matters were released during treatment at an elevated temperature.

Table 5.2: Contents of inorganic species in biomass and various biochars, expressed as wt% on a dry basis. The meanings of the sample labels are given in the caption of Table 5.1

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

In addition, the weight loss experienced during these processes also indicated the loss of carbon in biochar. Figure 5.2b shows the retention of carbon after secondary pyrolysis and 5% to 10% carbon conversion partial steam gasification. It is clear that biochar tuning via partial gasification comes at an appreciable cost, with losses of 8 – 23% of carbon available for sequestration. While only 75% of carbon is retained in leaf biochar following 10% partial steam gasification (FLB-725-10%-PG), the carbon retained in FWB-725-10%-PG and LWB-725-10%-PG biochars is at 88% and 80%, respectively. Lower carbon retention in leaf biochar is coincided with higher weight loss. Moreover, subsequent treatment of raw biochar also increases the ash content of the biochar due to accumulation of inorganic species as indicated in Table 5.2. Although, partial steam gasification generally resulted in biochar with higher inorganic species content, a slight decrease in Na content is observed which attributed to the volatilisation of Na during gasification. This may result in ash-related issue in gasification system during large scale implementation.

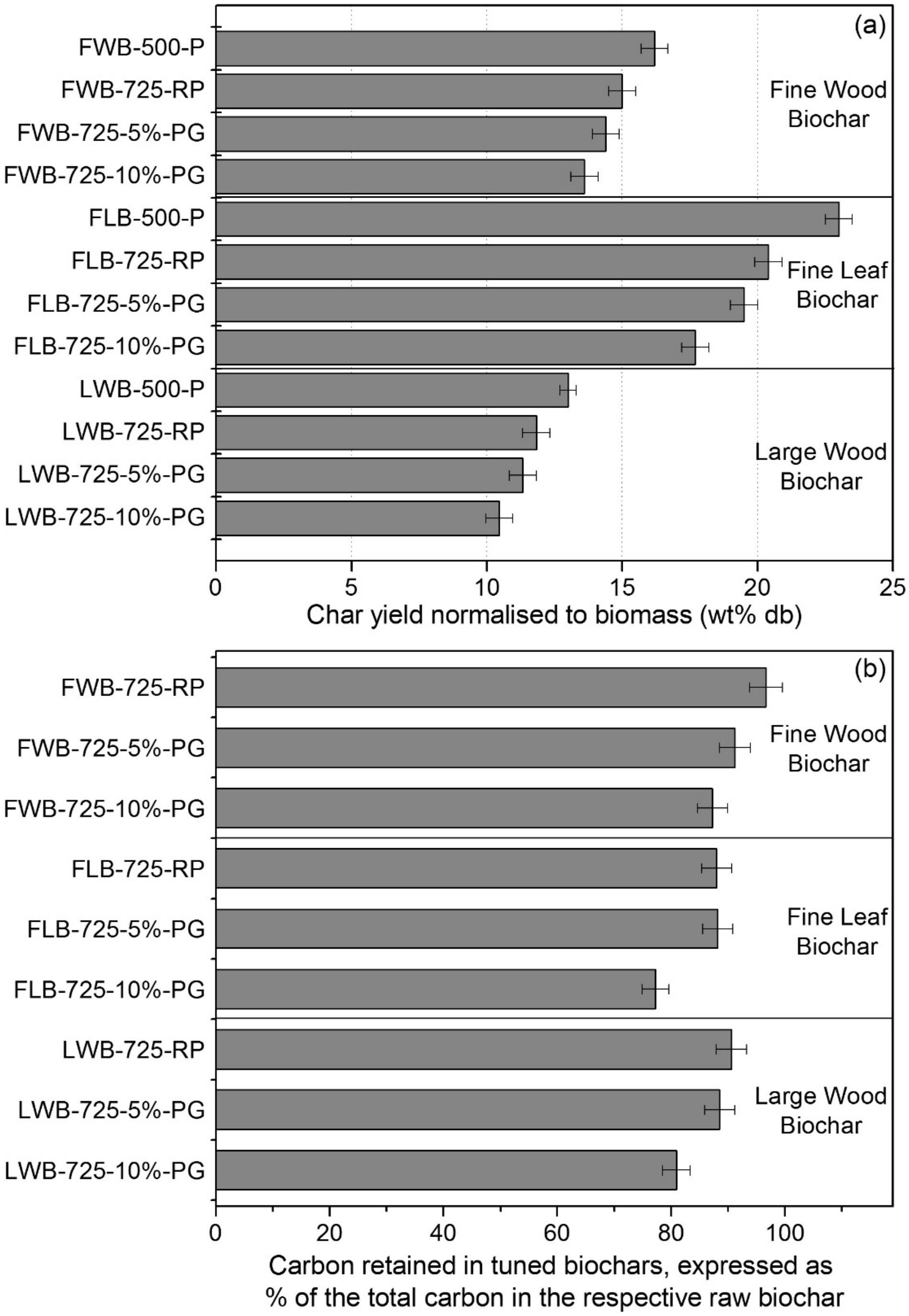


Figure 5.2: Weight and carbon retention of various biochars. (a) Char yield from pyrolysis and partial steam gasification normalised to biomass feedstock mass (wt% dry-basis). (b) Carbon retained in the tuned biochars, expressed as % of the total carbon in the respective raw biochar. The meanings of the sample labels are given in the caption of Table 5.1.

It should be noted that for the biochar to be stable and recalcitrant from degradation when applied to soil, the H/C and O/C molar ratios of biochar need to be below 0.6 and 0.4, respectively.[178-180] The Van Krevelen diagram in Figure 5.3 clearly shows the tuned biochars have the O/C molar ratio (~0.1) and H/C molar ratio (0.05–0.2), which are well below the threshold values, suggesting that the carbon in the tuned biochars will be stable.

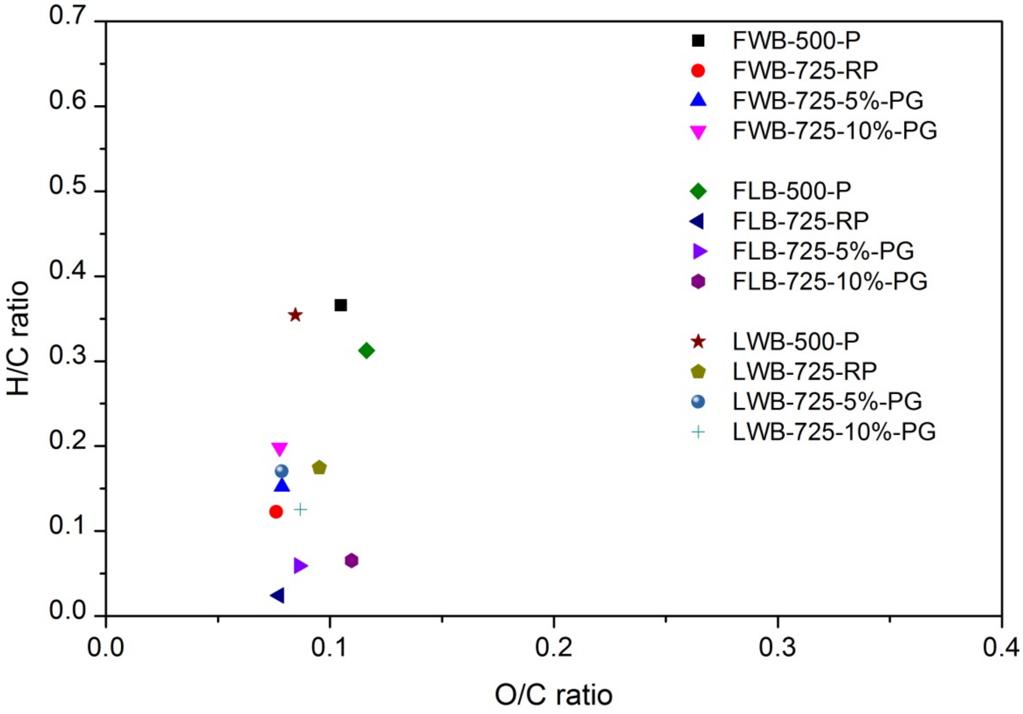


Figure 5.3: Van Krevelen diagram for the raw, re-pyrolysed and tuned (via partial gasification at 5% and 10% carbon conversions, respectively) biochars. The meanings of the sample labels are given in the caption of Table 5.1.

5.3 Evolution of Biochar Surface Area

Biochar porosity and surface area play important roles in amended soil WHC and bioactivity.[177] Figure 5.4 presents the evolution of biochar surface area following partial steam gasification. The data clearly shows the dissimilarity between surface areas obtained N_2 (BET N_2 surface area) and CO_2 (micropores surface area) adsorption isotherm. For raw biochar, the surface area obtained with CO_2 adsorption isotherm is higher compared to surface area obtained from N_2 adsorption isotherm. This indicates that the surface area of raw biochar is dominantly contributed by narrow-micropores as the diffusion of N_2 to these pores is kinetically restricted at liquid nitrogen temperature (77K).[181, 182] The micropores surface area is within the range of 120 – 180 m^2/g while BET N_2 surface area is less than 50 m^2/g. Please note that the BET N_2 surface area for biochar re-pyrolysis at 725°C is not presented as the BET surface area cannot be accurately determined due to the limited linearity of the N_2 adsorption isotherm of these samples. Following secondary pyrolysis at 725 °C, the micropores surface area of all biochar increases by about 100 m^2/g . This shows significant development of micropores in biochar structure during pyrolysis. On the other hand, there is no significant change in micropores surface area in wood biochar during partial steam gasification. The micropores surface area between 5% and 10% partial steam gasified wood char is relatively close. Leaf component derived biochar on the contrary, experience a sizable increase in micropore surface area at 5% conversion while further gasification of the leaf biochar does not contribute to significant increase in micropore surface area.

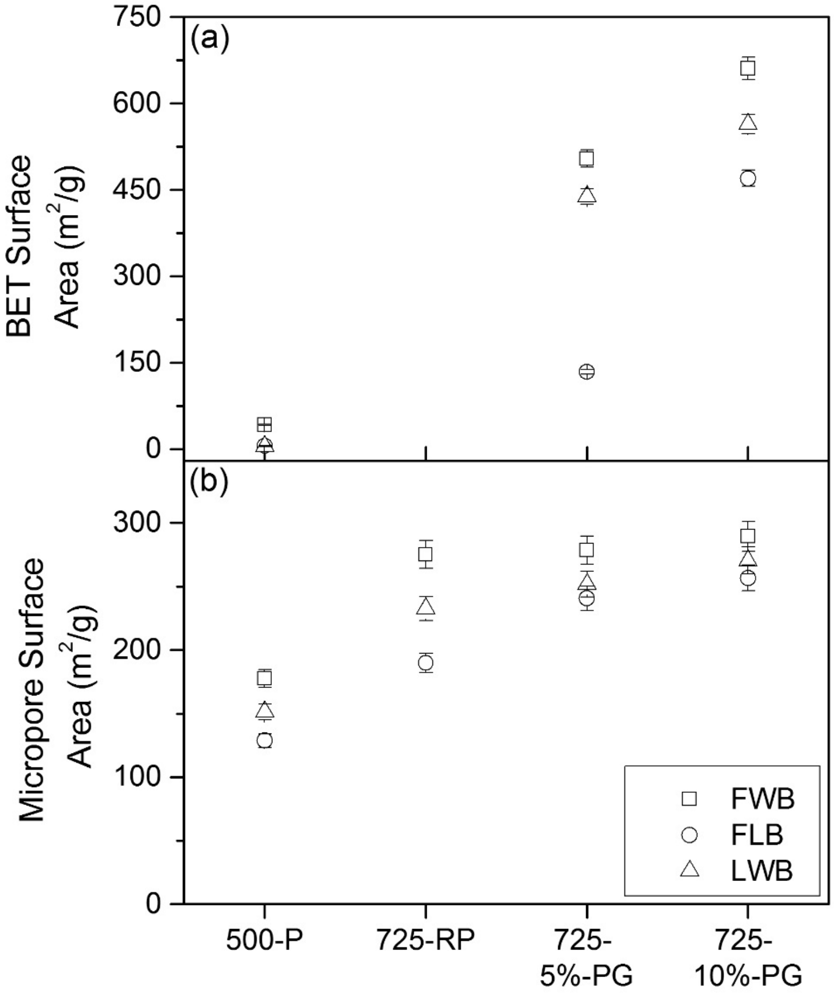


Figure 5.4: Surface area of various biochars: (a) BET surface area, determined via N_2 adsorption at 77K using BET Method (b) micropore surface area, determined via CO_2 adsorption at 273K using D-R Method. FWB, FLB and LWB stand for fine wood biochar, fine leaf biochar and large wood biochar, respectively. “500-P” indicates raw biochars, “725-RP” indicates repyrolysed biochar while “725-5%-PG” or “725-10%-PG” indicate tuned biochars via partial gasification at 5% and 10% conversions, respectively.

Although further partial steam gasification does not lead to further increase in micropores surface area, partial steam gasification at higher conversion lead to significant increase in BET N_2 specific surface area, coincide with the finding in the previous study on steam gasification of slow pyrolysis mallee biochars.[154] A substantial increase in BET N_2 specific surface area while micropores surface area is relatively unchanged can point towards two possible explanations. 1) Steam gasification leads to enlargement of existing micropores into mesopores and macropores while new micropores continue to form as no reduction in micropores surface area is observed during steam gasification at the carbon conversions studied.[183] 2) Pyrolysis at higher temperatures often results in melting of initial biochar structure[184] and more pronounce secondary reaction[72] which might cause the formation of secondary char within micropores. These can result in partial blockage of micropores. Steam gasification at low conversion might lead to removal of carbon deposits which restrict the penetration of N_2 into micropores.[185] However, while gasification might lead to opening of partially blocked pore, formation or larger pores during partial steam gasification at 5% and 10% might be a dominant process as BET N_2 surface area is significantly higher compared to micropores surface area of partial gasified biochar with the exception of FLB-725-5%-PG biochar.

In addition, the data also show that the surface area of biochar produced from large biomass particles (LWB-500-P) is lower compared to the biochar produced from small biomass particles (FWB-500-P). This suggests that effect of feedstock particle size on the structure of the resultant biochars. This is because the heat- and mass-transfer limitations arising from the fast pyrolysis of large biomass particles might lead to slowed devolatilisation of the biomass core[186] and thus, a reduction in surface area.

5.4 The Lechability of Carbon from Treated biochar

Figure 5.5 shows that some organic matter was leached from the raw biochar and tuned biochars. Similar to biochar produced from slow pyrolysis,[24] the amount of organic matter leachable via water in these biochars is <1.5% (on a carbon basis), demonstrates the recalcitrant nature of carbon in biochar. The organic matter leached from biochar might be due to the removal of the polar component of pyrolytic product retained on biochar during pyrolysis. A recent study by Lin and co-workers[187] characterised the organic matter leached from biochar prepared at temperature ranging between 380°C and 600°C indicates that these organic matter are mainly low molecular weight protic organic acids, alcohol, ketone, aldehyde and sugar.

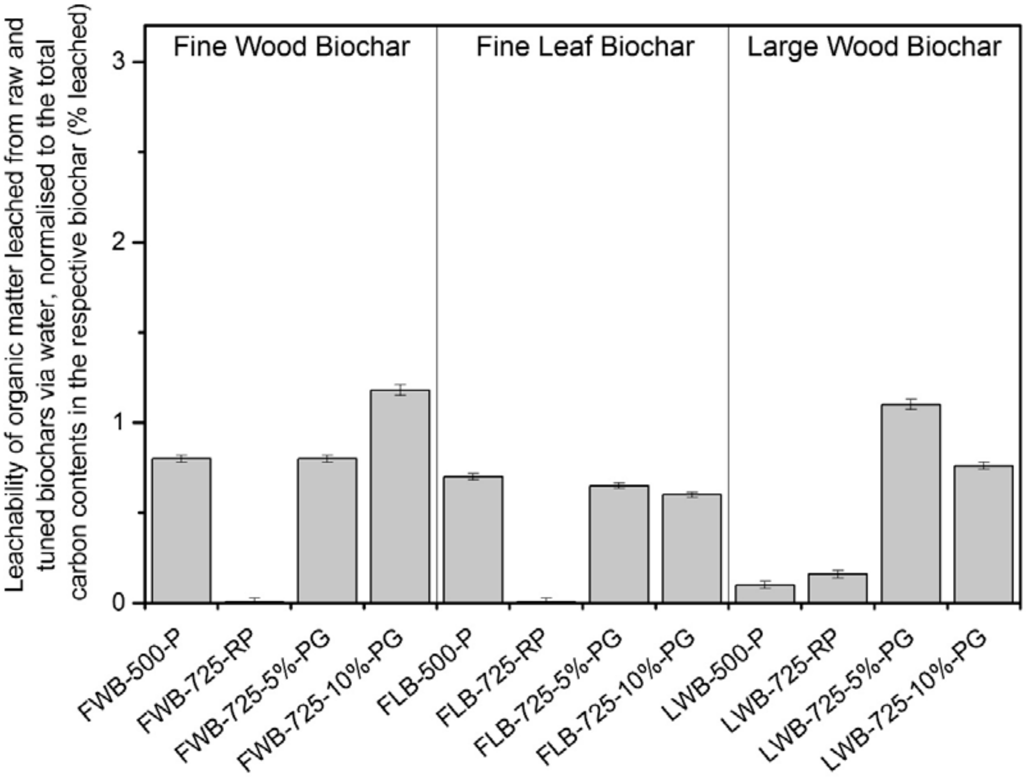


Figure 5.5: Leachability of organic matter leachable from the raw and tuned biochars via water, normalised to the total carbon contents in the respective biochars. The meanings of the sample labels are given in the caption of Table 5.1.

It is important to note that the raw biochars prepared from fast pyrolysis (at 500 °C), the tuned biochars (particularly for FWB-725-RP and FLB-725-RP biochars) after the re-pyrolysis of the raw biochars at 725 °C reduces the amount of leachable organic matter to below the quantification limit of our method (0.06% of C in biochar). This is plausible because re-pyrolysis at a higher temperature might result in the cracking of heavy tars in raw biochar[188] and/or the release of at least some organic matter on biochar surface. However, there is no reduction of the amount water-soluble organic matter in LWB-725-RP biochar, probably due to difference characteristics of the organic matter present in LWB-500-P biochar as it was prepared from large particle feedstock in fluidised bed reactor. It is interesting to note that after partial gasification at low conversions, there are actually significant amount of organic matter leached from the tuned biochars. The data clearly demonstrate that there are leachable organic matter locked in at least part of the pore system within the biochars and such organic matter is inaccessible to leaching medium as that part of the pore system is either closed or blocked (e.g. by carbon deposition during pyrolysis). Partial gasification opens these closed/blocked pore systems so that the locked organic matter becomes accessible. In addition, partial gasification leads to the formation of larger pores such as macropore and mesopore[181] which also act as transport system for leaching.

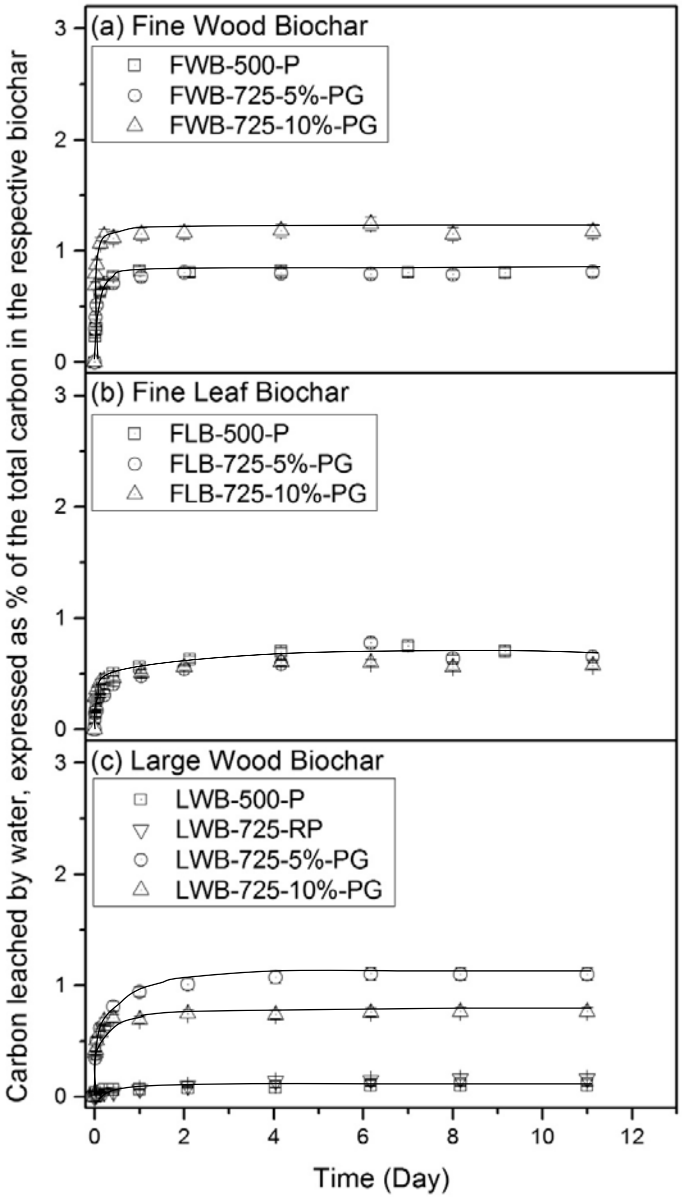


Figure 5.6: Leaching kinetics of organic matter (on a carbon basis) from the raw and tuned biochars. Panel (a) fine wood biochars, (b) fine Leaf biochars and (c) large wood biochars. The meanings of the sample labels are given in the caption of Table 5.1.

Figure 5.6 presents the leaching profile of organic matters from the biochars studied. Compared to leaf biochar, the leaching wood biochars (except LWB-725-5%-PG) achieves equilibrium within 2 days. Leaf biochars on the other hand, require 4 to 6 days for the leaching process to reach equilibrium. While the leaching of the organic matter from biochars might require up to 6 days to reach equilibrium, >70% of the leachable amount is removed during first days of leaching. This further supports that the leachable organic matters in these biochars are mainly consisted of low molecular weight compounds with fair solubility in water. The difference in leaching equilibrium time between wood and leaf biochar is probably due to the dissimilarities in their organic matter characteristics.

5.5 Leaching of Aromatic Compounds

Aromatic compounds such as polyaromatic hydrocarbons (PAH) are known to be present in biochar.[189] The leaching of aromatic compounds from biochar during soil application may result in undesirable environmental impact. Therefore, the raw and tuned biochars were leached with chloroform methanol mixture (4:1 v/v) for 24 hours for characterisation of leachable aromatic compound. The UV-fluorescence synchronous spectra of the resultant leachate are presented in Figure 5.7. The spectra show raw biochar contain solvent leachable aromatic compound. The maxima centred at ~350 nm for the spectra of raw fine wood (FWB-500-P) and leaf (FWB-500-P) biochar indicates the leaching of 2-3 fused rings aromatic compounds while the maxima centred at ~390 nm for the spectrum of large wood (LWB-500-P) biochar indicate the leaching of larger 3-5 fused rings aromatic compounds. The higher intensity in the raw fine leaf biochar and large wood biochar spectra suggest higher amount of aromatic compounds can be leached from these biochars compared to raw fine wood biochar. However, no leaching of aromatic compound in the re-pyrolysed and tuned biochar is detected. It is also noted that UV spectra of the leachates collected from the leaching of turned biochars using water showed the absence of aromatic compounds. The absence of these aromatic compounds suggests that those aromatic compounds were mostly likely depolymerised or cracked during re-pyrolysis or partial gasification (as results of more intense reactions at higher temperature[188]). In addition, it is known that steam gasification can lead to selective removal of smaller and reactive components within biochar at low conversions, resulting in the tuned biochars with a stable and highly-aromatic structure.[154] Therefore, partial gasification at low conversions tunes the raw biochar to be virtually free of leachable aromatic compounds.

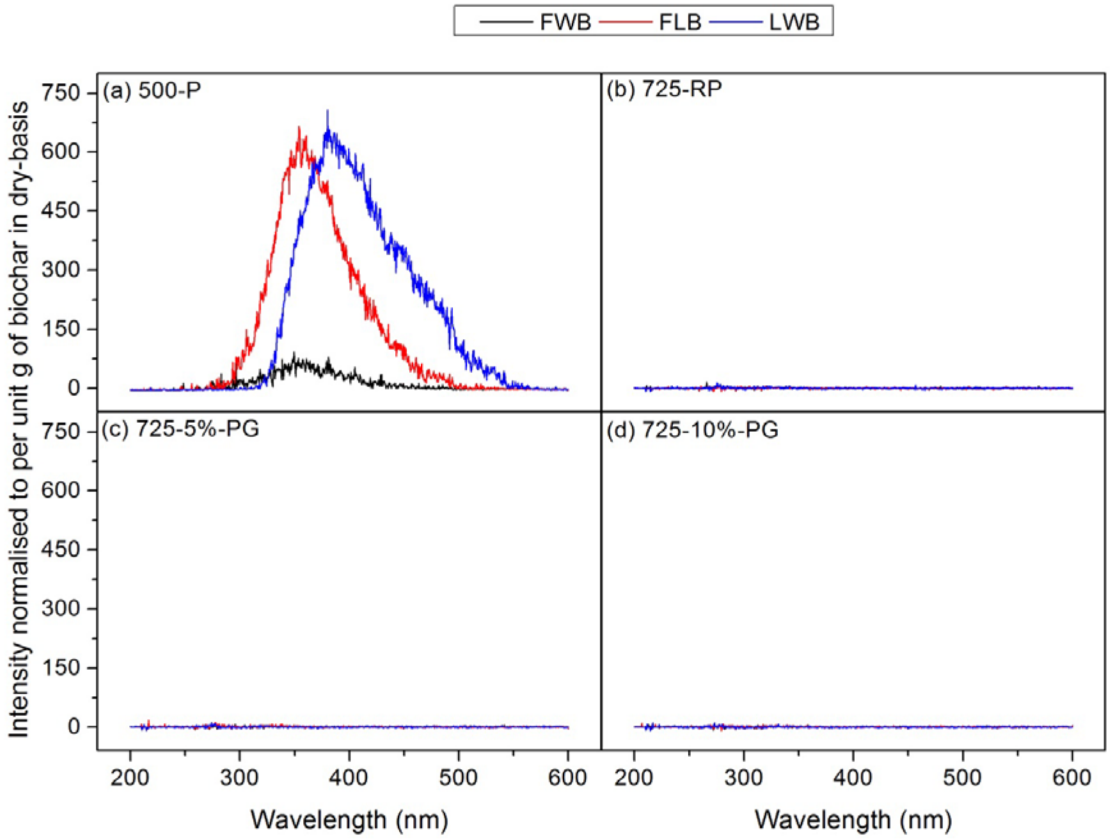


Figure 5.7: UV/Fluorescence spectrums of Methanol/Chloroform wash solution normalised to per g of biochar (dry-basis). The wavelength of the spectra shown is the wavelength of the excitation monochromator. Penal (a) shows the spectra for raw biohcar, (b) biochar after re-pyrolysis, (c) 5% gasification biochar and (d) 10% gasification biochar.

5.6 Further Discussion and Practical Implications

Tuning biochar via partial gasification also leads to positive changes in the pore structure of biochar, with several practical implications. First, it is known that biochar porosity and surface area play important roles in amended soil water holding capacity and bioactivity[177] and a surface area of > 150 m^2/g has been recommended and considered as preferable for good performance in soil.[178, 179] The results in this study show that partial gasification at low conversions can tune the biochar structure to have surface area significantly larger than 150 m^2/g. Second, it was postulated that soil microbes activity is unlikely to benefits from addition of biochar with micropore (<2 nm) as these pores is inaccessible by most bacteria and fungi[190, 191] (with sizes of 0.5 – 5 µm[192]). The results in this study show that tuning via partial gasification leads to the formation of larger pores in tuned biochars (hence potentially providing more habitat for soil microbes and protect them from their gazers[177]). Third, Biochar with a large surface area and rich in macropore with pore diameter >50 nm are known to potentially have high water holding capacity.[193] The higher surface area and formation of large pores in tuned mallee biochars (via partial gasification reported in this chapter) can bring significant benefits when the tuned biochars are applied to soil. This is of great importance and highly desired to the sandy soil (abundant in the agriculture land in Western Australia[194]) which suffers from low water holding capacity due to its low surface area.[192]

A small amount (<1.5% on carbon basis) of organic matter can be leached from raw and tuned biochar. With the typical application rate of biochar at 5 to 50 t/ha[195] and >70% of water leachable organic matter leached within a day, large quantity or organic matter will leach to soil. This can also lead to potential contamination to local water way and ground water. Therefore, it is important to access the quantity of water leachable organic matter in biochar intended for soil application. Strategic application should also be employed for biochar with high water leachable organic matter. Although some organic matter can be leached from biochar tuned with partial steam gasification, UV-fluorescence study demonstrates that there is no detectable aromatic compounds leachable via water and organic solvent. This clearly demonstrates that partial steam gasification fast pyrolysis mallee biochar has little or no aromatic compounds such as polyaromtic hydrocarbons (PAHs).

5.7 Conclusion

This study investigates the evolution of the characteristics and leaching of organic matter from mallee biochars tuned via partial steam gasification at low carbon conversion of 5% and 10%. Tuning of biochar via partial steam gasification causes a loss of up to 25% of carbon available for sequestration in raw biochar. However, the remaining carbon is postulated to be stable with the H/C ratio and O/C ratio of these biochars well below 0.6 and 0.4 respectively. While raw biochar is dominantly microporous, partial steam gasification leads to significant increase in surface area and formation of larger pore structure owing to enlargement of micropores and opening of partially blocked pores. Partial steam gasification does not remove water leachable organic matters from biochar while secondary pyrolysis generally reduces them to below detection limit. However, only <1.5% of organic matter on carbon basis can be leached from raw and tuned biochar. The leaching of organic matters in tuned biochar is possibly due to the increase in accessibility of water leachable organic matter within biochar. UV-fluorescence spectroscopy study of water and organic solvent leachates demonstrate that partial steam gasification is able to produce tuned fast pyrolysis mallee biochar with little or no leachable aromatic compound thus reduce the risk of possible contamination from aromatic compounds such as PAHs during soil application. The results further show this tuning method can produce mallee biochar with characteristics that will improves its performance in soil such as promoting soil microbial activity and improving soil water holding capacity. High application rate of biochar in soil should proceed with care due leaching of organic matter from biochar.

Chapter 6: Tuning Biochar Properties via Partial Gasification: Leaching Characteristics and Recycling of Inorganic Nutrients

6.1 Introduction

In the effort to reduce greenhouse gases emission related to energy generation, increasing number of countries are moving toward increasing the contribution of renewable energy in their country energy mix. This consequently led to a growing interest in utilisation of biomass for energy. Unlike fossil fuels, combustion of biomass or its derived biofuels is relatively carbon neutral as the carbon dioxide released will be reabsorbed by plant during its growth.[196]

The literature review in Section 2.2 shows that mallee biomass is postulated to be a promising bioenergy feedstock due to its potential for large scale and near carbon neutral production.[9, 10, 40] Recent studies also showed that pyrolysis of mallee biomass can produce biochar and bio-slurry suitable as a fuel.[12, 14, 15, 67, 140] Fast pyrolysis can also be employed for production of bio-oil. While bio-oil can be processed into transportation fuels,[197] the biochar produced can be applied to soil and delivered numerous agronomical[25, 82, 125, 155, 198, 199] and environmental benefits.[25, 79, 80] In addition, majority of the plant nutrient species such as alkali and alkaline earth metallic (AAEM) species mainly Na, K, Mg and Ca adsorbed by plant during its growth is retained in biochar.[24, 137] Applying biochar to soil can potentially return part of these plant nutrients to soil[27] thus improves the sustainability of biomass pyrolysis process.

Earlier study on overall recycling of AAEM species in fast pyrolysis mallee biochar demonstrated that while overall recycling based on Mehlich-1 leaching is high, a significant portion of Mg and Ca are water-insoluble.[27] Furthermore, Mg and Ca account for at least half of AAEM species in biomass by weight and are important plant nutrients.

The limited water solubility of these species signifies that much of these AAEM species might not available to plant under certain soil condition.

However, the recovery of Mg and Ca from fast pyrolysis mallee biochar can be improved by tuning the biochar via partial steam gasification. The development of highly porous structure[154] during gasification might expose the AAEM species trapped in biochars structure that render them inaccessible by water. As biochars AAEM species are known as catalyst and take part in catalytic gasification reaction,[175] partial steam gasification can potentially transform part of these water-insoluble Mg and Ca into water-soluble form.

As discussed in Chapter 5, fast pyrolysis biochar tuned via partial steam gasification at carbon conversion of 5% and 10% have desirable characteristics for a good biochar performance in soil. Moreover, the amount of water leachable organic species is <1.5% and no detectable aromatic compound is leachable via water or organic solvent. In this chapter, the effect of partial steam gasification on the leachability and overall recyclability of AAEM species in various fast pyrolysis biochars will be investigated. The raw biochars are prepared from fast pyrolysis of small particle mallee wood and leaf using drop-tube fixed-bed (DTFB) reactor system and large particle wood using fluidised-bed (FB) reactor system. The raw biochar will be tuned via re-pyrolysis, 5% and 10% partial steam gasification. The leachability of AAEM species in biochar will be accessed via batch leaching with water and Mehlich-1 solution. Lastly, the overall recyclability between raw and partial steam gasified biochars will be compared.

6.2 AAEM Retention in Biochar

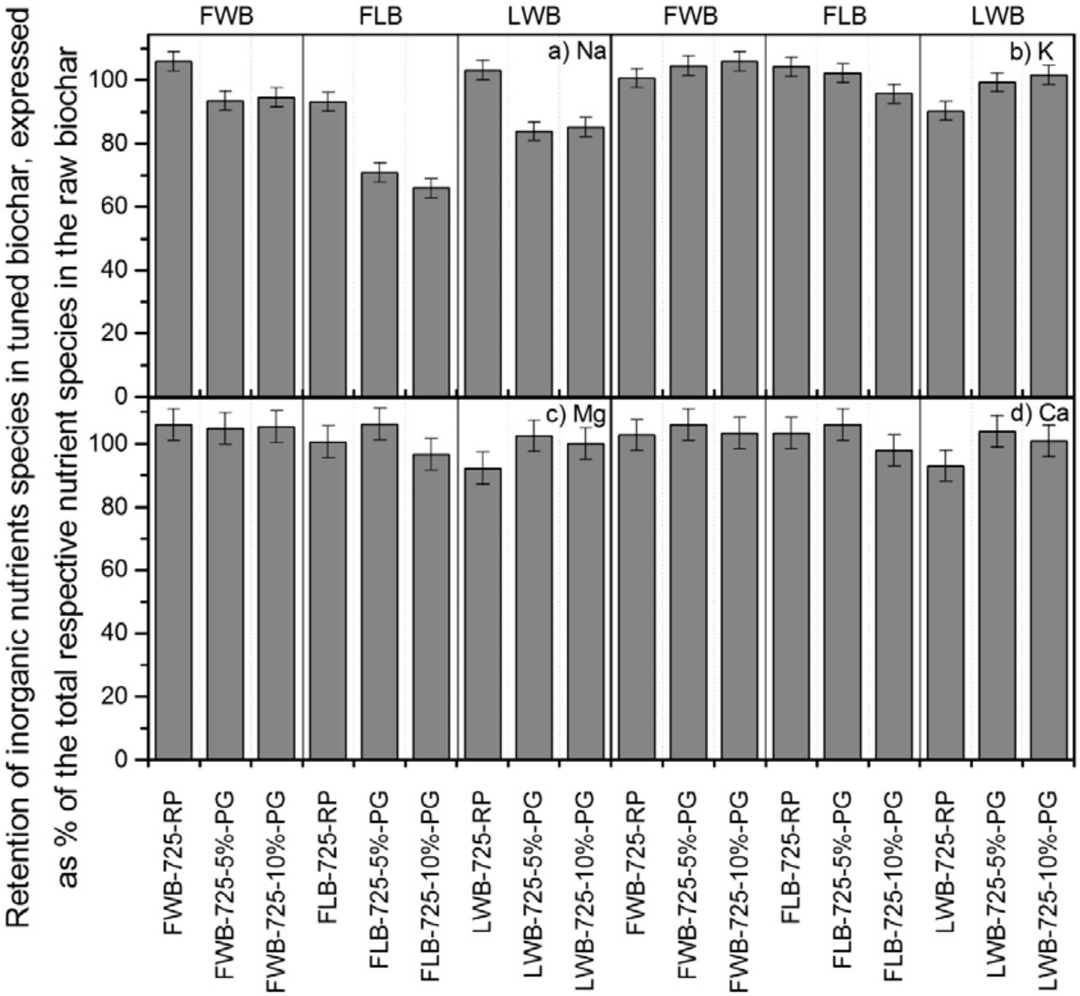


Figure 6.1: Retention of inorganic nutrients species in the tuned biochars, normalised to the total respective nutrients species in the raw biochars. The meanings of the sample labels are given in the caption of Table 5.1.

Figure 6.1 shows the retention of AAEM species in biochars compared to its content in raw biochars. At least 88% of K, Mg and Ca and more than 80% of Na in wood biochar are retained during re-pyrolysis then partial gasification. However, the retention of Na in partial steam gasified leaf biochar can be as low as ~66% which indicates significant volatilisation of Na during gasification reaction. The release of Na during re-pyrolysis of the FLB-500-P biochar is slightly higher compared to wood biochars (FWB-500-P and LWB-500-P) produced from both reactor configurations possibly due more intense volatile-char interaction.[138] Similar trend is also observed during fast pyrolysis of bark with DTFB system where significantly higher amount of Na is volatilised compared to K, Mg and Ca. Higher volatile matter content in FLB-500-P biochar and comparatively significant reduction of volatile matter between FLB-500-P and FLB-725-RP biochar both suggest that more volatile is released during the re-pyrolysis and steam gasification of 500LC biochar. In addition, Na content FLB-500-P biochar is comparatively higher (see Table 5.2 in chapter 5). Coupled with a forced gas flow through the thin char bed, this might result in the significant losses of Na.[135, 200] The volatilisation of Mg and Ca is insignificant due to their higher atomic mass and divalent nature.[201] Furthermore, the majority of Mg and Ca in fast pyrolysis biochar are water insoluble[24, 27] which indicates that a large portion of these species is organically bounded to char matrix. Two bonds have to be broken before the alkaline earth metallic species can be released from char matrix and volatilised during gasification. While K is not a divalent species, the volatilisation of K is insignificant possibly due its more pronounced intercalating properties compared to Na.[202]

Table 6.1: Chlorine content in biomass and raw biochars as % wt in dry basis. The data is extracted from Table 5.2 of Chapter 5

Sample	Chlorine Content (% wt db)
Wood	0.0146
Leaf	0.1576
FWB-500-P	0.0159
FLB-500-P	0.5427
LWB-500-P	0.0512

In addition to high retention of AAEM species, considerable amount of Cl is retained in fast pyrolysis wood biochar as shown in Table 6.1 while most of the Cl in wood biochar prepared from slow pyrolysis is not detectable.[24] Furthermore, the Cl content of raw leaf biochar is also higher compared to that prepared from slow pyrolysis.[24] Higher Cl retention in biomass prepared from fast pyrolysis is resulted from prolonged volatile-char interaction, causing the Cl released as volatile to recombine with nascent char as pointed out by Rahim and co-worker.[137] Moreover, the chlorine retained in wood biochar prepared from fluidised-bed reactor (FB) is lower compared to that prepared from drop-tube/fixed-bed (DTFB). This might due to less significant volatile-char interaction as higher gas flow rate required for fluidisation of bed material greatly reduced the residence time of volatile in the reactor thus reduction in Cl retention.

6.3 The Lechability of AAEM Species in Raw and Treated Biochar

Figure 6.2 presents the data on the leachability of inorganic nutrient species by water or Mehlich I medium. It can be seen that over 70% of Na and K in the raw biochars are water leachable and similar amount of Na and K are observed to be leached by Mehlich I medium. This suggests that in the raw biochar, water leaching can recycle close to 100% of the total plant available Na and K in the raw biochar. However, less than 30% of Mg and Ca are water leachable from the raw biochar while close to 50% and 90% of Mg and Ca in the raw char can be leached by Mehlich I medium, respectively. Therefore, water leaching can only recycle less than less than 60% and 30% of the total plant available Mg and Ca in the raw biochars, respectively.

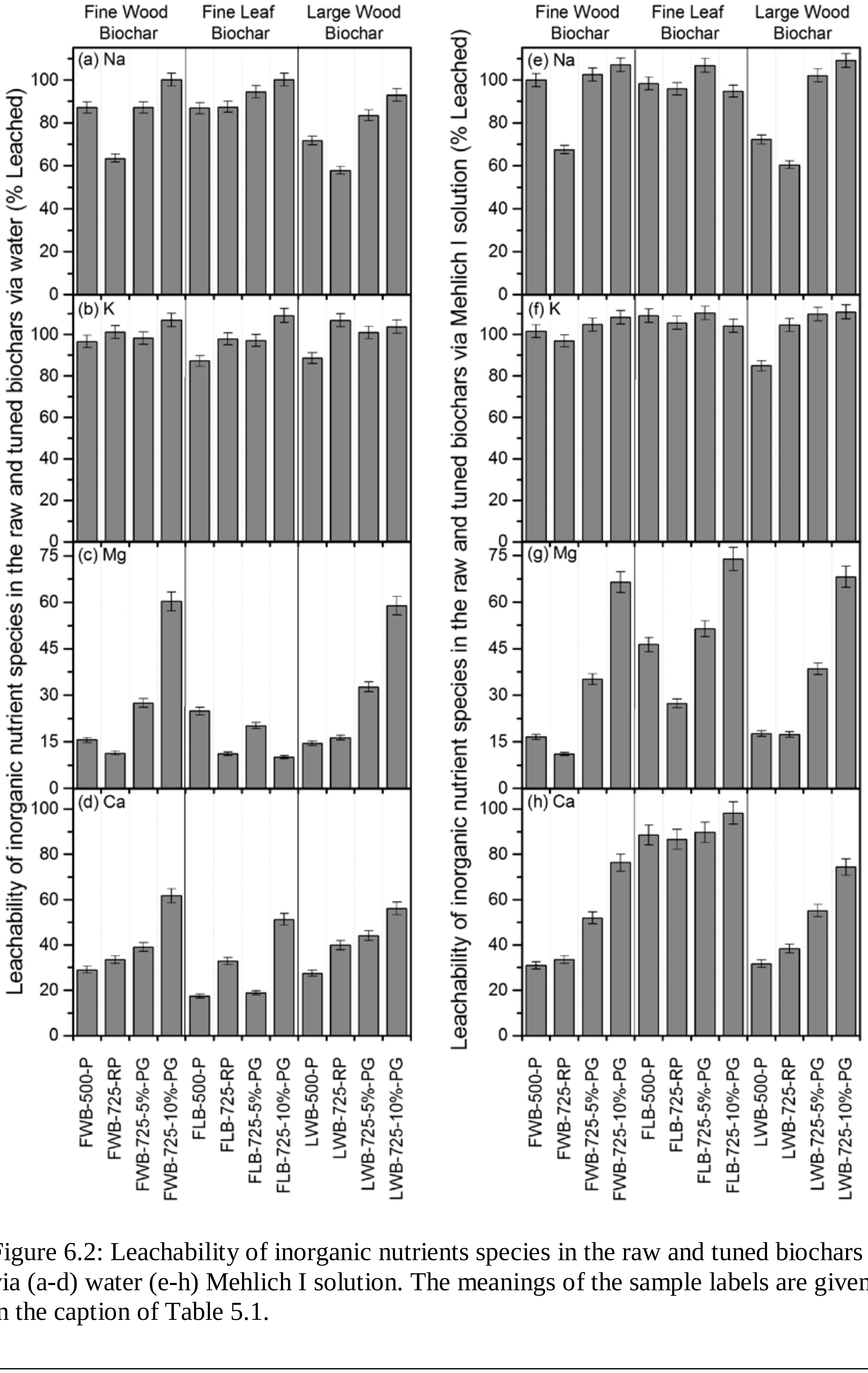


Figure 6.2: Leachability of inorganic nutrients species in the raw and tuned biochars via (a-d) water (e-h) Mehlich I solution. The meanings of the sample labels are given in the caption of Table 5.1.

The most important finding in Figure 6.2 is that partial gasification at low carbon conversions (5% and 10%) can have significant effect on the leachability of inorganic nutrients in the biochars. For water leaching, there are potentially substantial increases in the amount of water leachable Mg and/or Ca in biochars. For example, the water leachable Mg in tuned fine (FWB) and large (LWB) wood biochar almost quadrupled (from ~16% to 60%) after 10% gasification and the water leachable Ca increases from ~30% to ~60%. However, the trend for Mg in leaf biochars (FLB) following partial gasification is not clear. The partial gasification process also brought the amount of water-soluble Na and K to ~100%. It is clear that partial gasification of the raw biochar can facilitate the recovery of inorganic nutrient species from biochars prepared from fast pyrolysis. For Mehlich I medium leaching, partial gasification can also significantly increase the total plant available Mg and Ca. For example, the total plant available Mg in fine and large wood biochar increases from ~15% to ~65% while it increase from 46% to 74% for fine leaf biochar. The plant available Ca in both fine and large wood biochar increases from ~30% to ~75%. The increases in the leachability (by water or Mehlich I solution) of inorganic nutrients as results of partial gasification may be attributed to at least two reasons. One is that partial gasification opens the closed or blocked micropore and also enlarges micropore due to the gas-solid reactions as aforementioned. Therefore, the inorganic nutrient species which was encapsulated in the char structure during fast pyrolysis[27, 184] and inaccessible would have become accessible by the leaching medium. The other is that the gasification reactions may have changed some of the inorganic nutrient species in biochars to more leachable chemical forms.[175]

It is further noted in Figure 6.2 that there is a noticeable difference in water-soluble and total plant available (Mehlich I extracted) Na and K between the FWB-500-P and LWB-500-P biochars. This is likely due to the differences in the conditions for biochar preparation. LWB-500-P was prepared from large wood particles in a fluidised-bed (FB) reactor while FWB-500-P was prepared from fine wood particles in a drop-tube/fixed-bed (DTFB) reactor. During pyrolysis, the mass transfer resistance for the volatiles within the pyrolysing large wood particles promotes the secondary reactions of volatiles within the particles. These result in more carbon deposition within the micropore hence more encapsulation of inorganic nutrients species in the blocked pores.[27, 72] The data in Figure 6.2 show that grinding the LWB-500-P biochar particles into fines then followed up by biochar tuning via partial gasification can improve the leachability of inorganic nutrient species. It can be seen that the water soluble Na and K in LWB-500-P biochar increase from ~72% and ~88% to ~93% and ~103%, respectively while all Na and K become leachable in the Mehlich I solution medium.

The leachability of chlorine from the raw and tuned biochars by water is presented in Figure 6.3. Please note that the data on chlorine leached by the Mehlich I solution medium are not available because the Mehlich I solution itself contains chlorine. It can be seen that while all the chlorine in biomass is water soluble,[203] ~80% of the chlorine in raw biochar is water soluble. This is consistent with the previous report that during pyrolysis, a proportion of chlorine bound to biochar is transformed into water-insoluble form.[137] Furthermore, re-pyrolysis and partial gasification has an insignificant effect on the distribution of water-soluble chlorine in biochar.

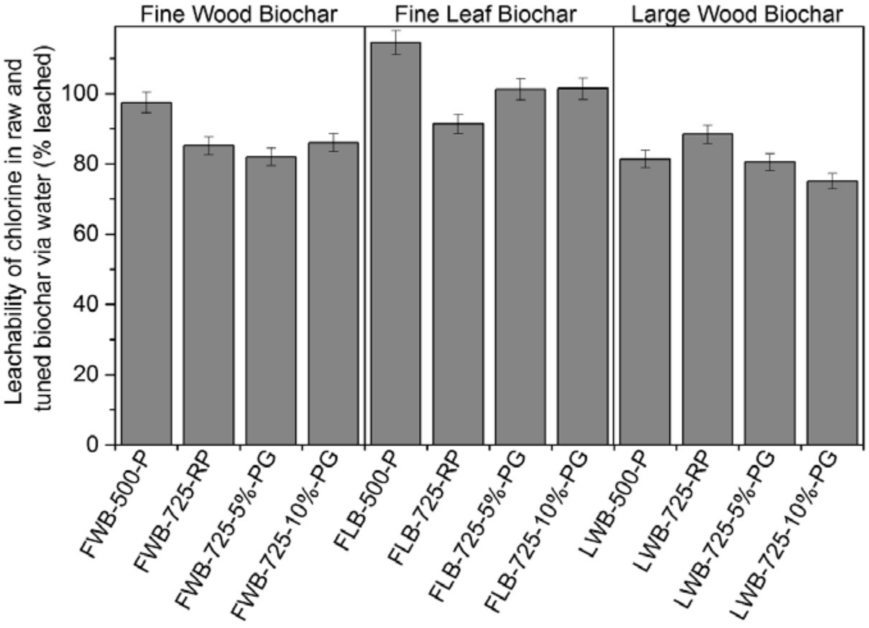


Figure 6.3 Leachability of chlorine in raw and tuned biochar via water. The meanings of the sample labels are given in the caption of Table 5.1.

6.4 Leaching Kinetic and Kinetic Model

Figure 6.4 shows the leaching kinetic of inorganic matter from the raw and tuned biochars. The experimental data was then fitted to the pseudo-second order kinetic model, with the values of the fitted parameters tabulated in Table 6.2. It can be seen that the r^2 of the data fitting are all above 0.98, suggesting that the pseudo-second order kinetic model is suitable to describe the leaching kinetics of inorganic nutrient species and organic carbon from the raw and tuned biochars. The data in Table 6.2 further shows that partial gasification generally increases the overall leaching rate constant and the initial leaching rate. This is reflected by the fact that, in Figure 6.4 there is a sharp increase in the leaching of inorganic nutrient species from tuned biochars within the first 2 days of the 28-day leaching period. Therefore, partial gasification enhances not only the recycling but also leaching kinetics of the inherent inorganic nutrients in the biochars. This is a desired but expected outcome, due to at least two reasons. One reason is that partial gasification leads to the formation and enlargement of the pore system and the opening of closed/blocked pores, as discussed in Chapter 5. This tunes the raw biochar into a highly porous tuned biochar with a high surface area. Such porous structure of the tuned biochar reduces the intra-particle mass-transfer resistance of the inorganic nutrient species during leaching. A higher surface area in the tuned biochar also promotes the ionisation or dissolution of the inorganic nutrient species due to the increased exposures of these species to the leaching medium. The other reason is that partial gasification has changed the occurrence forms of the inorganic nutrient species within the tuned biochar. For example, at least part of Mg and Ca have been transformed from water insoluble form into water soluble form and become water leachable.

Table 6.2: Kinetic parameters for water leaching of various biochars. In the table, k is overall leaching rate (unit: L mg^{-1} day^{-1}) and h is initial leaching rate (unit: L mg^{-1} day^{-1}) at time close to 0 while r^2 is the goodness of fit from kinetic parameter fitting. The meanings of the sample labels are given in the caption of Table 5.1.

Samples	Kinetic parameter for each element											
	Na			K			Mg			Ca		
	k	*h*	r^2	*k*	*H*	r^2	*k*	*h*	r^2	*k*	*h*	r^2
FWB-500-P	0.711	0.864	0.998	0.523	6.022	0.999	3.470	0.239	0.991	0.757	2.803	0.995
FWB-725-RP	1.073	0.783	0.990	0.694	9.248	0.998	4.098	0.194	0.994	1.502	8.372	0.998
FWB-725-5%-PG	3.418	3.948	0.998	6.494	98.230	0.999	14.702	4.111	0.999	3.339	30.613	0.999
FWB-725-10%-PG	5.601	8.550	0.999	16.856	299.100	0.999	5.183	7.201	0.999	1.390	30.681	0.999
FLB-500-P	0.113	32.482	0.998	0.241	23.242	0.998	0.512	1.043	0.990	0.824	17.709	0.998
FLB-725-RP	0.112	30.687	0.998	0.280	40.782	0.999	5.843	3.065	0.997	0.745	67.241	0.999
FLB-725-5%-PG	0.396	80.421	0.999	1.107	163.950	1.000	39.997	57.570	0.998	0.284	9.004	0.993
FLB-725-10%-PG	0.836	200.360	1.000	2.032	404.510	1.000	1.482	0.5881	0.971	26.163	6775.501	0.999
LWB-500-P	0.397	0.391	0.984	0.161	2.161	0.995	0.488	0.104	0.990	0.095	0.717	0.986
LWB-725-RP	0.296	0.283	0.990	0.574	10.366	0.999	1.408	0.268	0.993	0.443	5.185	0.994
LWB-725-5%-PG	3.255	3.786	0.999	4.398	87.680	0.999	4.028	3.989	0.999	0.646	13.275	0.998
LWB-725-10%-PG	14.287	24.479	0.999	38.902	1059.0	0.999	1.7313	6.343	0.999	0.930	33.231	0.999

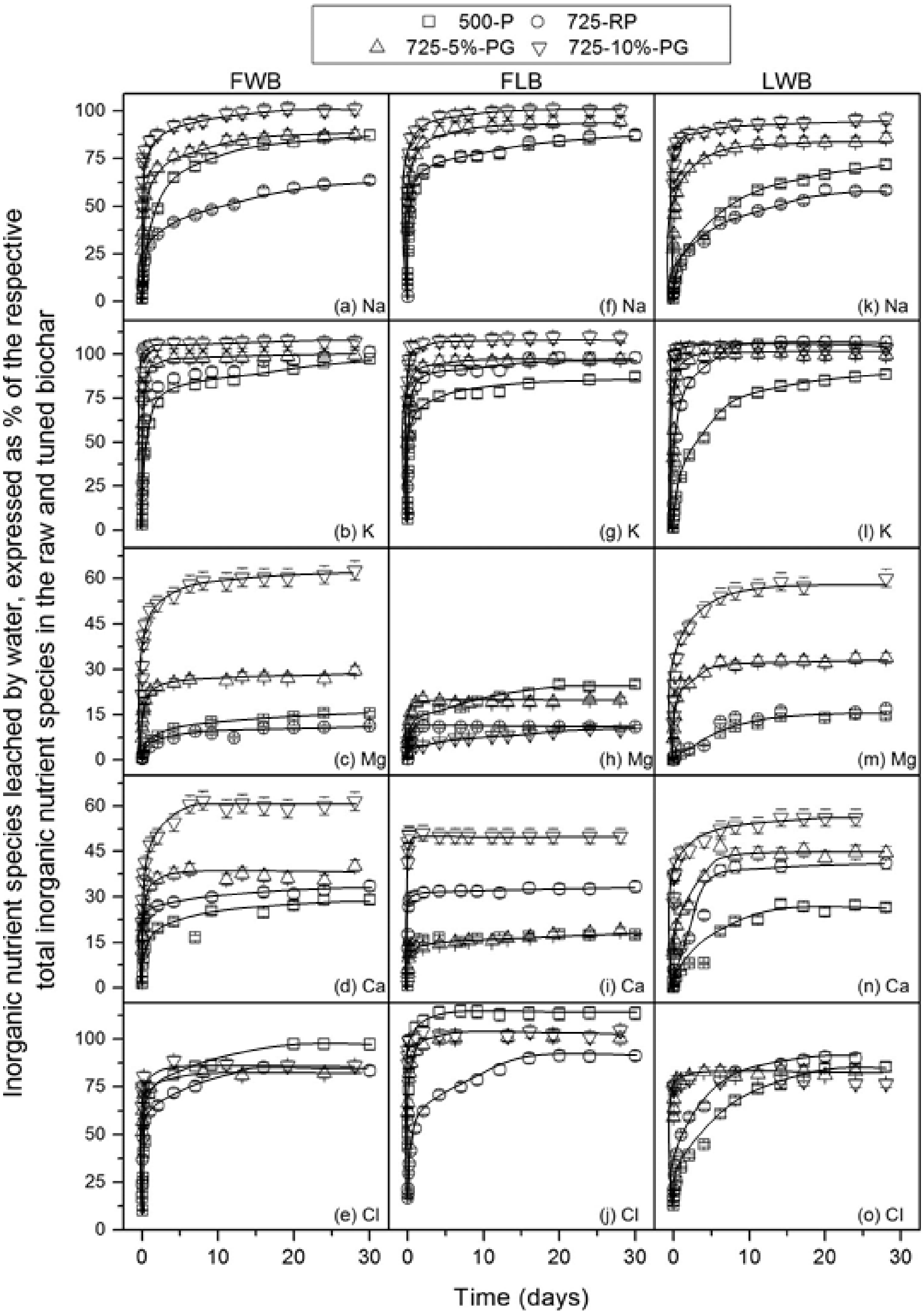


Figure 6.4: Leaching kinetics of inorganic nutrient species from various biochars. Panel (a-e) for fine wood biochars(FWB), (f-j) for fine Leaf biochars(FLB) and (k-o) for large wood biochars(LWB). "500-P" indicates raw biochars, "725-RP" indicates repyrolysed biochar while "725-5%-PG" or "725-10%-PG" indicate tuned biochars via partial gasification at 5% and 10% conversions, respectively.

6.5 Further Discussions

The results presented so far show that K (and Na) in the raw biochar prepared by biomass pyrolysis at 500 °C is generally plant available and its recycling can be achievable via water leaching while the plant availability and recyclability of the inherent Mg and Ca in the raw biochars are poor (see Figure 6.2). It can further be seen in Table 5.2 (on page 84) that Mg and Ca accounted for more than 65% and 50% of the total major inorganic nutrient species in the raw wood and leaf biochars, respectively. K, Mg and Ca are crucial to plant growth.[194, 204, 205] The poor plant availability of Mg and Ca translate to only ~50% of the all major inorganic nutrient species (Na, K, Ca, Mg and Cl) in the raw biochar can be returned during the direct soil application of the raw biochars.

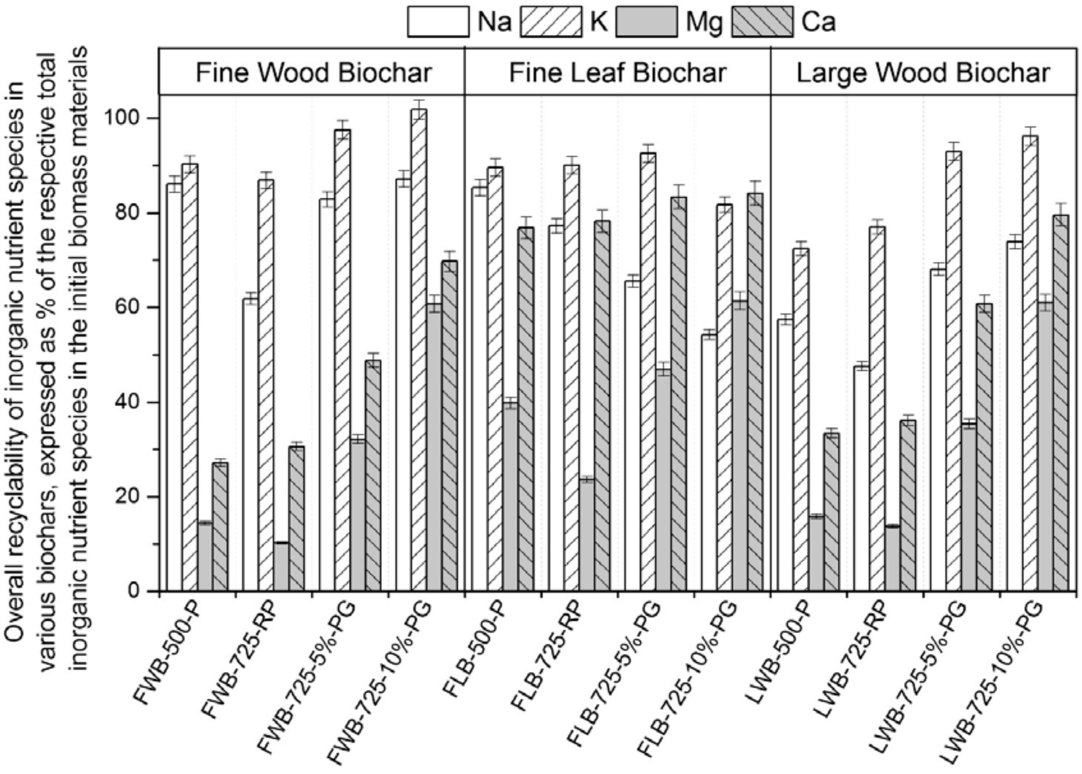


Figure 6.5: Overall recyclability of inorganic nutrient species in the raw and tuned biochars (measured via leaching by Mehlich I solution), normalised to the respective total inorganic nutrient species in the initial biomass materials. The meanings of the sample labels are given in the caption of Table 5.1.

The results presented so far also show that tuning the raw biochars via partial gasification can potentially increase the plant availability of the inorganic nutrient species in the biochars substantially. To further illustrate and evaluate the overall recyclability of the inorganic nutrient species in the raw and tuned biochars, the amounts of plant available inorganic nutrient species (measured via Mehlich I solution leaching) in various biochars are normalised to those present in the raw biomass materials. As shown in Figure 6.5, partial gasification at low conversions can be a good strategy for tuning biochar because it clearly enhances the overall recyclability of inorganic nutrient species, particularly Mg and Ca. The overall recyclability of Na is low after tuning via partial gasification due to the release of Na during gasification. This is not a concern because in Western Australia, mallee is planted in agricultural land for managing dryland salinity and there are over supply of Na (in the form of NaCl salt[205]).

There are also several important considerations in choosing the process parameters of partial gasification for tuning biochars structure and facilitating inorganic nutrients recycling. There are mainly three parameters of consideration, i.e. conversion, temperature and particle size. The first important consideration is biochar conversion during tuning via partial gasification. To make the tuning strategy meaningful and practically useful, it is critical to achieve the desired structural tuning with minimised weight loss of the biochar which would be subsequently returned to soil for carbon sequestration and minimised losses of inherent inorganic nutrients. Therefore, the gasification should be done at low conversions and the data in this study show that 5-10% conversion is sufficient. A too low conversion may not achieve the desired objectives of tuning while a too high conversion leads to significant loss of carbon which would be otherwise available for sequestration. The second important parameter is the choice of a suitable gasification temperature, considering a balance among processing time, energy consumption and potential loss of useful inorganic nutrient species. At a too low temperature, gasification reaction is slow, the process would benefit from a low energy input, favourable retention of inorganic nutrient species in the tuned biochar and good process controllability but suffer from a prolonged tuning time. However, at a too high temperature, gasification reaction is fast, the process benefits from a fast tuning time but it becomes difficult to control, demands high energy input and suffers from potential release of useful inorganic nutrients species during the tuning process. Therefore, the application of partial gasification for tuning biochars is recommended to be done at low conversions (below 10%) and a suitable temperature. The third and last consideration is particle size. Gasification of small biochar particles can be significantly faster than that of large biochar particles as small particles reduce intraparticle mass-transfer limitations and provide considerably more surface area available for gasification reactions.[206] It is known that while the grindability of mallee biomass is poor, the biochar produced from biomass pyrolysis has excellent grindability so that size reduction of biochar (instead of biomass) is favoured.[12] It was also reported that direct leaching of inorganic nutrients species from large biochar particles are slow due to intraparticle mass transfer limitations.[27] Therefore, the results in this study show that for tuning purpose, the biochar produced from the pyrolysis large biomass particles can be firstly ground into small particles, followed by partial gasification for tuning. This leads to not only a fast process for biochar tuning but also improved leaching kinetics of tuned biochar. Of course, care should be taken during biochar size reduction because extensive grinding leads to the ground biochar containing increased contents of fine particulate matter which can remain airborne for significant period of time during soil application and poses potential health risk to workers and neighbouring environment.[207]

6.6 Conclusion

The study in this chapter demonstrate that the volatilisation of AAEM species in biochar when tuned via partial steam gasification is minimal with exception for leaf biochar where the retention of Na is as low as ~66%. Biochar produced from 500 °C fast pyrolysis of biomass generally has a low fraction of water and Mehlich-1 solution leachable Mg and Ca. This result in approximately half of AAEM species in biochar is recovered through water leaching. This study demonstrates that partial steam gasification at low carbon conversions (e.g. 5% and 10%) and mild temperature (725 °C) can greatly improve the amount of water and Mehlich-1 solution leachable AAEM species and consequently more AAEM species can be recycled to the soil during soil amendment application. This effectively boosted the total plant available AAEM species in wood biochar and leaf biochar to about 85% and 96%, respectively. The increment in leachability of AAEM in biochar can be attributed to two main factors, (1) the development of pore structure and (2) transformation of the occurrence of biochar inherent AAEM species during partial steam gasification from the form that bonded to char matrix to the forms that are soluble in water or dilute acid solution. These factors also result in increase of overall and initial AAEM species leaching rate. The overall AAEM species recycling demonstrate that partial gasification can be employed to minimise the loss of AAEM species in biomass utilisation cycle and thus the sustainability of biomass pyrolysis process. Furthermore, partial steam gasification of grounded fast pyrolysis biochar produced from large particle wood also increases the overall recycling of AAEM species and enhances leaching kinetic compared to its raw biochar.

Chapter 7: Leaching of Biomass Water-Insoluble Metallic Species under Hot-Compressed Water Conditions

7.1 Introduction

Utilisation of fossil fuels for energy generation results in significant release of CO_2 to the atmosphere, accounting for 69% of the total greenhouse gases emitted in 2010.[208] Therefore, the government in develop and developing countries are moving toward replacing fossil fuels with carbon-neutral and renewable fuel[209] such as bioethanol.[210] However, majority of bioethanol in US and Brazil is produced from corn and sugarcane[83, 84] while wheat, sorghum and molasses are the feedstock for bioethanol in Australia.[84] Yet, the production of bioethanol from food crops at the scale that can replace significant amount of fossil fuels use can result in competition of land use for food production[36], creating food/fuel dilemma. Hence, the production at such scale is only sustainable with lignocellulose biomass as feedstock.[45]

Biomass hydrolysis in hot-compressed water (HCW) for the liberation of fermentable sugars has been extensively studied,[90, 100, 143] but little attention is paid on the leaching of alkali and alkaline earth metallic (AAEM) species from biomass during hydrolysis process[29, 30, 144, 145]. Lignocellulosic biomass such as mallee can have high contents of AAEM species depending on the biomass component (wood, leaf and bark)[24]. The removal of these AAEM species might potentially catalyse the decomposition of sugar products into other secondary products during hydrolysis in HCW,[146, 147, 211] thus reduction of fermentable sugars. As majority of Na and K in mallee biomass is water soluble (see Chapter 4), simple water washing is able to remove these alkali metallic species. However, only a small amount of Mg and Ca are water soluble (see Chapter 4). Therefore, it is important to understand the leaching characteristics of these water-insoluble Mg and Ca during biomass hydrolysis under HCW conditions.

In this study, the leaching characteristics of AAEM species and degradation of lignin, cellulose and hemicellulose in mallee wood will be investigated. The hydrolysis will be carried out at 150 − 270 °C to understand the leaching behaviour of AAEM species and decomposition of lignin, cellulose and hemicellulose in biomass at different temperatures. As lignin, hemicellulose and lignin start to decompose at different temperatures, this study will provide an insight to the occurrence of organically bounded AAEM species in biomass.

7.2 Leaching of AAEM Species during Biomass Conversion in HCW

Before mallee wood is hydrolysed in HCW, the biomass was washed at room temperature for 30 minutes to remove water-soluble AAEM species from biomass. Figure 7.1 shows almost 90% of Na and K in mallee wood are water soluble while the amount of water-soluble Mg and Ca are low. Only ~21% of Mg and ~14% of Ca in mallee wood are water soluble. The remaining AAEM species in mallee wood is mainly organically bounded and leachable via dilute acid (see chapter 4). In addition, small amount of organic matters (~2% in carbon basis) were also leached from biomass at room temperature. The removal of this organic matter can be associated with the leaching of extractive in biomass.

Table 7.1: Proximate and ultimate analysis of mallee wood sample

Moisture[a]	Proximate (wt%, db)			Ultimate (wt%, daf[d])				
(wt%)	Ash	VM[b]	FC[c]	C	H	N	S	O[e]
4.0	0.5	83.6	15.9	47.7	6.2	0.51	0.03	45.6

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

Table 7.2: Saccharides and inorganic species content (wt% in dry basis) of mallee wood used in this study.

Saccharides content (wt%, db)					Inorganic species content (wt%, db)			
Arabinan	Galactan	Glucan	Xylan	Manan	Na	K	Mg	Ca
1.06	2.21	40.66	17.95	0.38	0.024	0.066	0.033	0.128

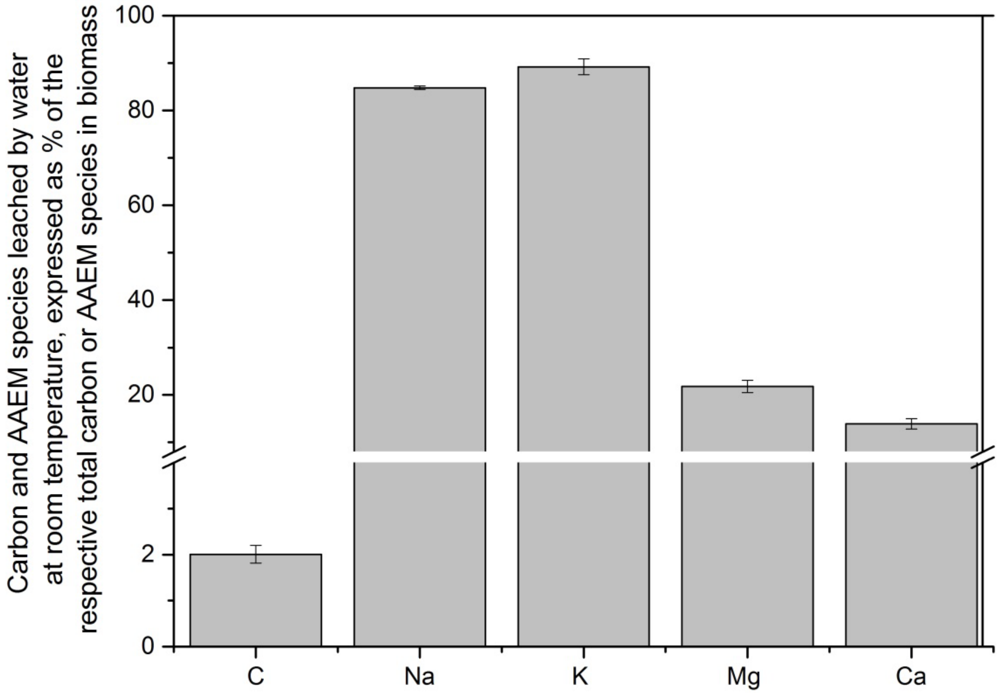


Figure 7.1: Organic matter (on a carbon basis) and AAEM species leached by water from mallee wood at room temperature, expressed as % of the total of those in biomass, respectively.

However, these water-insoluble alkaline earth species can be leached from biomass during hydrolysis in HCW. The leaching profile of Mg and Ca under HCW conditions is presented in Figure 7.2. About 90% of the total Mg and ~95% of the total Ca in biomass can be recovered. Due to majority of Na and K are removed during leaching at room temperature, the amount of Na and K leached at high temperature cannot be accurately quantified and therefore not reported in this study. At 150 °C, the leaching of Mg and Ca remained in biomass occurs slowly spanning throughout 70 minutes of the reaction time. When the reaction temperature increased to 180 °C, the leaching of

Mg and Ca take place swiftly with ~90% of leachable metallic species in biomass under HCW condition removed within 10 minutes. At 230 °C, a steeper raise of Mg and Ca was observed as compare to those at 180 °C. However, there is no significant change in the leaching kinetic observed with further increase of temperature to 270 °C, indicating that the leaching of AAEM species is temperature independent at temperature above 230 °C.

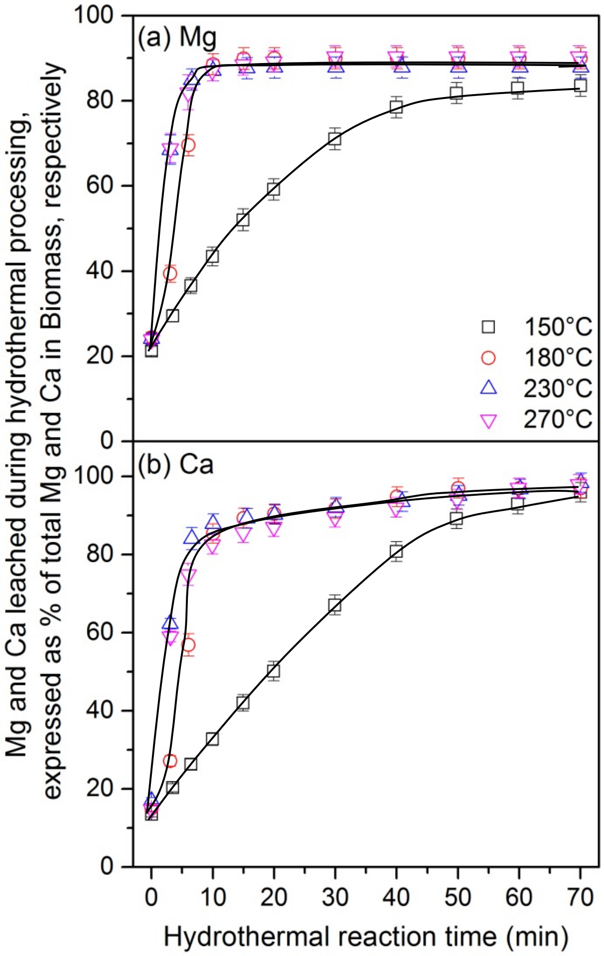


Figure 7.2: Leaching of (a) Mg and (b) Ca from mallee wood as a function of reaction time during hydrothermal processing at various reaction temperatures (150, 180, 230 and 270 °C), expressed as % of the total Mg and Ca in biomass, respectively.

Although an increase in water temperature under HCW conditions results in the increase of water ionic product[16, 212], the abundance of hydronium ion (H_3O^+) in HCW alone does not explain the significant removal of Mg and Ca under HCW condition. The pH of HCW ranges from ~6 at 150 °C to ~5.6 at 270 °C.[16, 212] Result in Chapter 4 demonstrates that the pH of the leachate during batch water leaching of mallee wood was ~5.5, which is close to the pH of HCW at 200 – 270 °C. However, only ~44% of Mg and ~ 28% of Ca in biomass are removed from batch leaching compare to ~90% of Mg and ~95% of Ca under HCW conditions. Moreover, the total amount of Mg and Ca leached is similar to the total amount of Mg and Ca leachable via dilute acid (0.01M HCl) reported Chapter 4. It is known that strong acid leaching can result in biomass physiochemical structural changes,[213] exposing the organically bound AAEM species that are not available for ion-exchange by weaker organic acids. The relatively similar leaching kinetic of Mg and Ca at the temperature range of 180 °C to 270°C also indicates that the leaching of water-insoluble AAEM species under HCW conditions might correlate to the decomposition and removal of organic compounds in mallee wood. Therefore, the TOC, saccharide and lignin content in liquid product were also analysed.

7.3 Conversion of Biomass Organic Matter in HCW Conditions

Further effort had been taken to analyse the total carbon present in the liquid products. Figure 7.3 depicts the biomass hydrothermal conversion on a carbon basis at various temperatures. At 150 °C, the total carbon conversion increases slightly with reaction time, suggesting part of the biomass structure starts to decompose even at 150 °C. The carbon conversion is ~34% after 70 minutes. At 180 °C, there is a steep incline of carbon conversion at time < 15 minutes followed by a gradual increase to settle at ~56% after 70 min. The carbon conversion for hydrolysis at 230°C and 270°C follows a similar trend with the conversion of ~69% at 230 °C and ~88% at 270 °C after 70 min. The specific reactivity of the organic matter (on a carbon basis) in biomass at various temperatures is plotted in Figure 7.4. At 150 °C, the low specific reactivity and its gradual increase with carbon conversion show the slow decomposition of biomass organic matter. As the reaction temperature increases to 180 °C, the specific reactivity and carbon conversion increases, indicating a more rapid decomposition of some reactive biomass components (such as hemicellulose and lignin). A further increase in temperature to 230 °C continues to speed up the decomposition of those reactive components in biomass. However, the specific reactivity decreases significantly at biomass conversions of 40-60%, suggesting the reactivity of the remaining biomass component (mostly cellulose, see discussion below) is slow at 230 °C. At 270 °C, although the specific reactivity also decreases at biomass conversions of 40-60%, but the specific reactivity is higher than that at 230 °C, confirming the promotion of biomass conversion at increased temperatures.

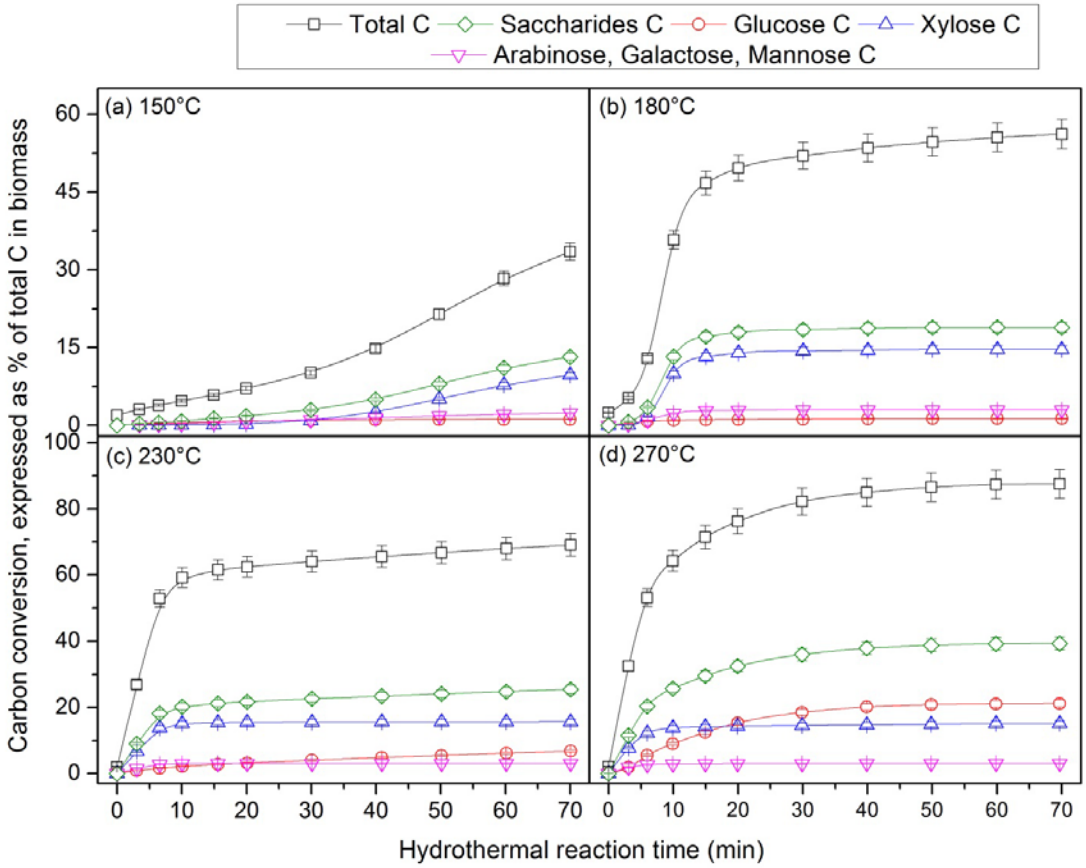


Figure 7.3: Carbon conversion as a function of reaction time during hydrothermal processing at various reaction temperatures: (a) 150°C, (b) 180°C, (c) 230°C and (d) 270°C, expressed as % of total C in mallee wood.

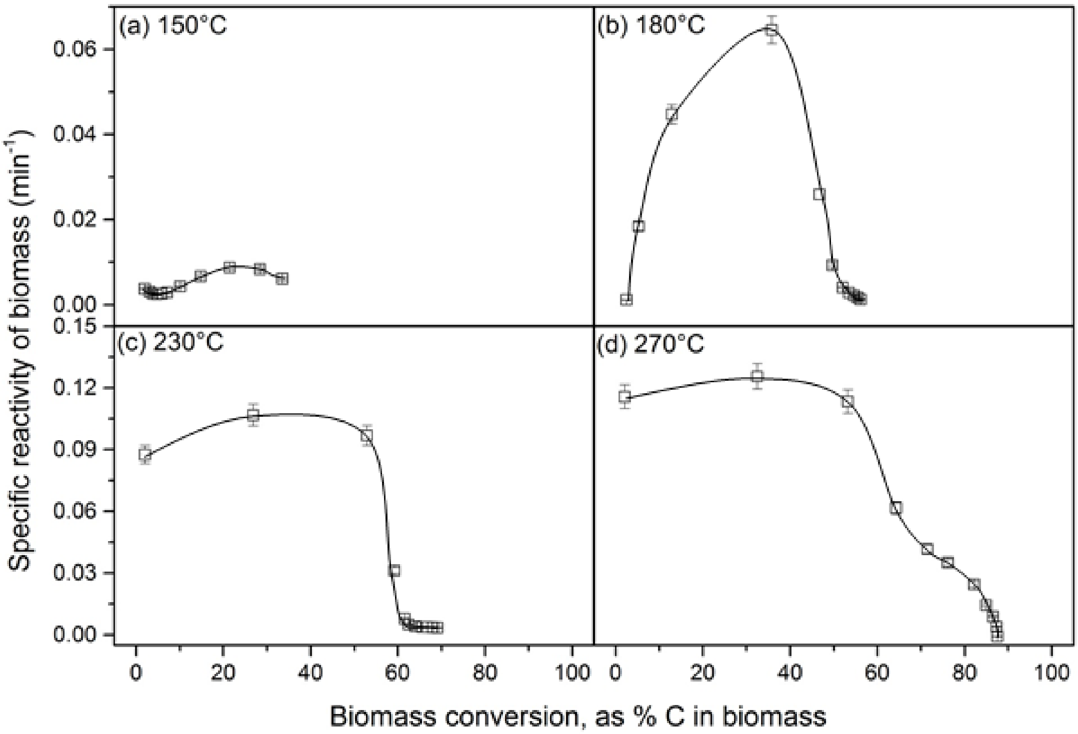


Figure 7.4: Specific reactivity of biomass as a function of biomass conversion (on a carbon basis) during hydrothermal processing at various reaction temperatures: (a) 150°C, (b) 180°C, (c) 230°C and (d) 270°C

To better understand the composition of the liquid product, the saccharide contents were analysed following post-hydrolysis. The recovery of arabinose, galactose, xylose and glucose at various temperatures is presented in Figure 7.3 and Figure 7.5. Arabinose, galactose and small amount of glucose oligomers started to form in the liquid products collected from hydrolysis of biomass at 150 °C (Figure 7.3a and Figure 7.5a). However, only significant amount of xylose oligomers is recovered after 15 minutes of hydrolysis (Figure 7.3a). The formation of significant amount of these oligomers at 150 °C demonstrates that the hemicellulose in mallee wood starts to decompose at temperatures as low as 150 °C. It is known that the typical structure of hemicellulose consists of xylan chain as backbone with the present of various compounds such as mannose, arabinose, galactose and sugar acid (just to name a few) on the brunches, depending on the type of plant.[45, 209] It is also known that lignin structure can also be covalently bonded to hemicellulose.[45] A schematic of typical hemicellulose structure is shown as Figure 2.1 in Chapter 2. Therefore, the formation of mannose, galactose and glucose oligomers prior to xylose oligomers indicates that the decomposition of hemicellulose brunches and lignin starts before xylan backbone is exposed and available for hydrolysis.

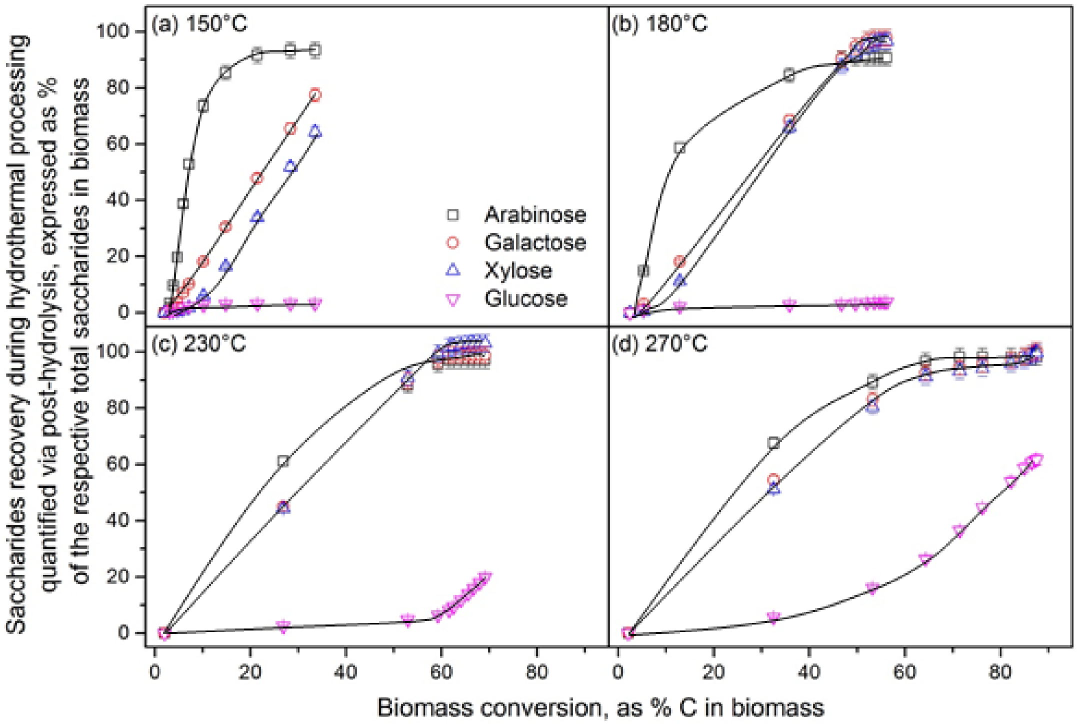


Figure 7.5: Recovery of arabinose, galactose, xylose and glucose during hydrothermal processing at various reaction temperatures: (a) 150°C, (b) 180°C, (c) 230°C and (d) 270°C as a function of biomass conversion, quantified via post-hydrolysis, expressed as % of the respective total saccharides in mallee wood.

At 180 °C, the decomposition of most of the hemicellulose in mallee wood completes within 20 minutes with ~98% of the xylose recovered after 40 min (Figure 7.3b and Figure 7.5b). The amount of glucose recovered remained at ~3% after 70 min, similar to that observed at 150 °C, most likely resulting from the decomposition of amorphous glucan associated with hemicellulose. The conversion of cellulose in mallee wood was not observed until the temperature increased to 230 °C and the reaction accelerated at 270 °C. The increase in glucose recovery with biomass conversion at 270 °C (Figure 7.3d and Figure 7.5d), clearly demonstrate that the higher reactivity is mainly contributed by the conversion of glucan. Although ~88% carbon conversion was achieved at 270 °C, the recovery of glucose levels off at ~62%. Such a glucose recovery is lower compared to that of ~80% achieved from microcrystalline cellulose under the same condition in previous work by Yu and Wu.[17] A low recovery of glucose was also reported by Phaiboonsilpa and co-workers[102] using a similar reactor system for hydrothermal processing of Japanese cedar. The low glucose recovery is not likely due to the secondary reactions of primary liquid product, since the xylose recovery is close to 100% at 270 °C. It is more likely due to the in situ structural changes of cellulose in biomass during hydrothermal treatment,[214] resulting in the decomposition of cellulose structure before converted into the liquid product.

Additional effort was taken to calculate the percentage of carbon contributed by saccharides to the total carbon in liquid product. The data is presented in Figure 7.3. Despite more than 30% of carbon is recovered at 150 °C, less than half of the recovered carbon are contributed by sugar products. Similarly, <35% of total carbon recovered at 180 °C is contributed by sugar products. This suggests that considerable amount of lignin start to hydrolyse at 150 °C. A gradual increase in carbon recovery after 20 minutes hydrolysis at 180 °C also suggests that additional lignin were decomposed at 180 °C as the amount of carbon contributed by saccharides had levelled off.

7.4 Relationship between the Leaching of Water-insoluble Mg and Ca and the Hydrolysis of Hemicellulose Brunches

As the water-insoluble Mg and Ca in biomass start to leach at 150 °C, the leaching of these inorganic species during hydrothermal treatment is unlikely to be correlated with the decomposition of cellulose. In addition, lignin usually consists of phenolic compounds linked via C–O–C or C–C bond,[215] thus is unlikely to be associated with inorganic species. On the other hand, hemicellulose in hardwood such as O-acetyl-4-O-methyl-glucuronoxylan contains significant amount of 4-O-methylglucuronic acids and various amounts of arabinose, galactose and glucose as side chains on the xylan backbone.[47, 215, 216] Therefore, it is more plausible that the organic-bound Mg and Ca are associated with carboxylic acid functional group on hemicellulose side chains. However, the analysis of carboxylic acid in the liquid sample was not performed in this study due to the limitation of our analytical techniques. Therefore, this study only tries to correlate the leaching of Mg and Ca with the sugar recovery to obtain some indirect evidences.

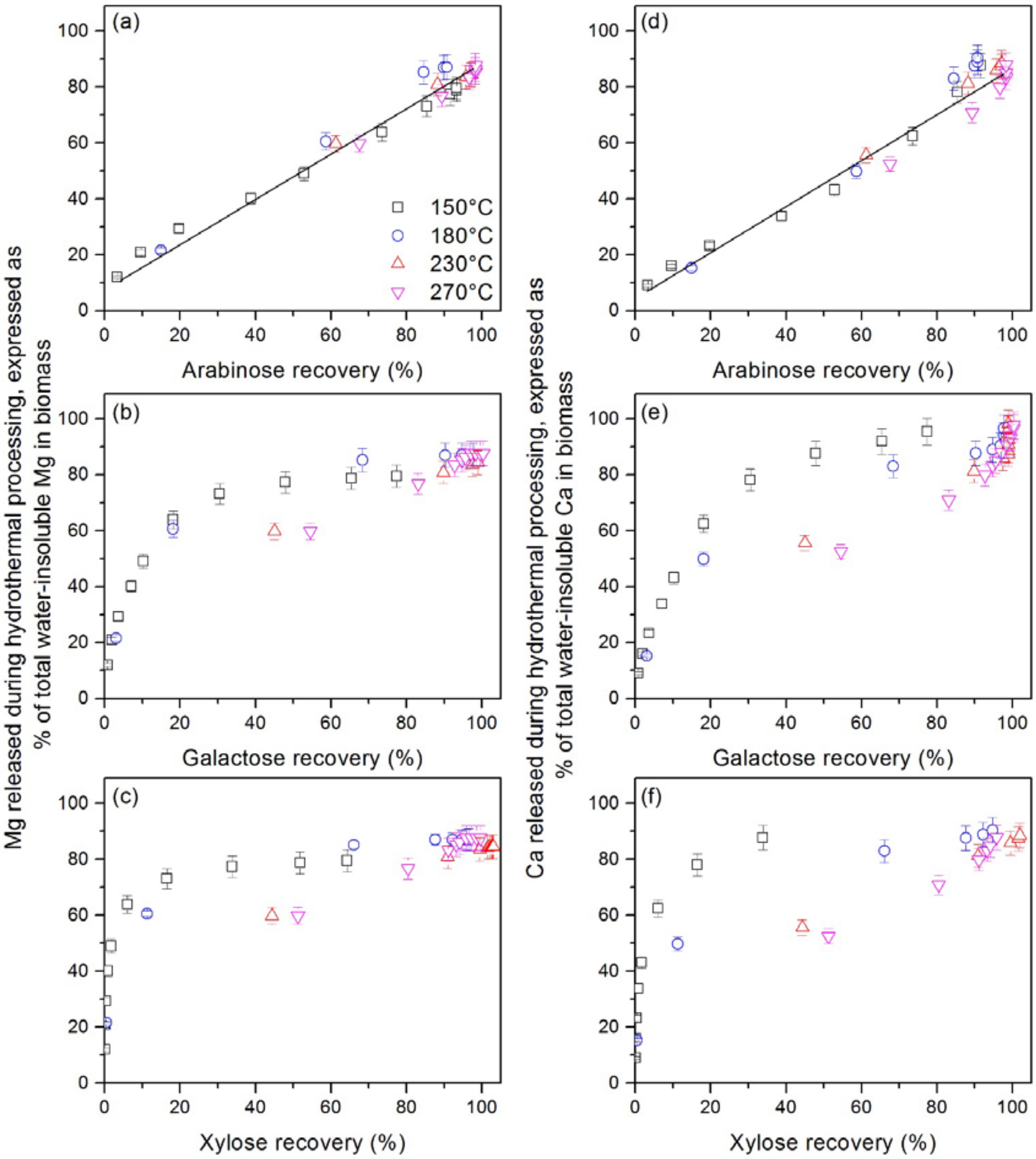


Figure 7.6: Correlation between the recovery of arabinose, galactose or xylose with the release of (panel a-c) Mg and (panel d-f) Ca during hydrothermal processing at various reaction times (0 – 70 min) and temperatures (150 – 270 °C).

Consequently, the leaching of Mg and Ca in biomass is plotted against the recovery of hemicellulose-derived sugars (e.g., arabinose, galactose and xylose), as shown in Figure 7.6. It is noteworthy that the leaching of the water-insoluble Mg and Ca in the wood sample is only linearly proportional to arabinose recovery, while the plots for galactose and xylose are non-linear. The release of arabinose prior to xylose (even galactose, see Figure 7.5) at low temperatures (i.e., 150 °C) suggests arabinose is likely associated with hemicellulose side chains, which decompose prior to the xylan backbone in hemicellulose during hydrothermal processing. It is known that Mg and Ca cannot be organically bound to arabinose directly. Thus, the linear relationship between the arabinose recovery and the leaching of Mg and Ca further suggests that the water-insoluble Mg and Ca are likely organically bound to the carboxylic acid functional group on hemicellulose side chains. As hydrothermal processing at low temperatures can convert the reactive organic matter (i.e., the hemicellulose side chains) in biomass, exposing more organic-bound inorganic species which are not accessible at room temperature. Then, the high ionic product in HCW allows the ion exchange reaction to take place, leading to the leaching of more water-insoluble Mg and Ca during hydrothermal processing. The results on the inorganic species release during wood hydrothermal processing may have some important practical implications. For example, the released inorganic species can potentially act as catalysts to promote the secondary decomposition of sugar products [31, 146, 147] and alter the reaction pathway in the aqueous phase [217]

7.5 Conclusion

This chapter investigates the leaching of water-insoluble alkaline earth metallic species in mallee wood under HCW conditions at 150 – 270 °C, using a semi-continuous reactor system. Depending on the temperature, >90% of Mg and Ca in mallee wood can be leached under HCW conditions. At 150 °C, the leaching of Mg and Ca took at least 70 min to complete but ~90% of leachable Mg and Ca were released in <15 min hydrolysis at temperature ≥180°C. The organic compounds in the liquid product were also analysed to understand the correlation of leaching of water-insoluble alkaline earth metallic species and the conversion of organic matter. The biomass conversion increase from ~34% to ~88% as temperature increase from 150 to 270 °C after reaction for 70 min, with the majority of organic compounds contributed by sugar oligomers and lignin derived compounds. Hemicellulose and lignin started to decompose at 150 °C. Almost all of the arabinose, galactose, xylose and mannose were recovered at 180 °C. Cellulose started to decompose at 230 °C with the decomposition rate increase significantly at 270 °C. Further analysis of the data clearly shows that the leaching of water-insoluble Mg and Ca are well correlated with the recovery of arabinose during mallee wood conversion in HCW, indicating the water-insoluble alkaline earth metallic species are mainly bounded the acid functional groups on hemicellulose brunch.

Chapter 8: Conclusions and Recommendations

8.1 Introduction

This chapter summarises the key findings from this PhD research. The work carried out in this research leads to a better understanding on the leaching of inorganic and organic matter from biomass and biochar under various conditions, their equilibrium, kinetics and implications. First, this research found that the leaching of organic matter from biomass leads to at least some of the water-insoluble inorganic species being leached during batch water leaching. This resulted in over estimation of water-soluble inorganic species in biomass with batch leaching. Second, partial steam gasification can effectively tune the properties of fast pyrolysis mallee biochar, producing biochar with high surface area and with little or no leachable aromatic compounds. Third, tuning biochar via partial gasification improves the leachability of alkali and alkaline earth metallic (AAEM) species in biomass. This enhances the overall recyclability of AAEM species from biochar. Lastly, ~90% Mg and ~96% Ca were leaching from mallee wood when hydrolysis under hot-compressed water (HCW) condition. The experimental data indicates that organic bounded Mg and Ca are likely to be bounded on the acid groups on hemicellulose brunches linked by arabinose. In addition, based on the outcomes from this research, several recommendations suggested for future work required to improve the knowledge in this research area.

8.2 Conclusions

8.2.1 Leaching of Organic and Inorganic Matter from Biomass by water: Differences between Batch and Semi-continuous Operations

- Various amount of organic matter can be leached from biomass during water washing, producing an acidic leachate.
- Continuous contact between acidic leachate and biomass during batch leaching leads to part of the water-insoluble (e.g. organically bounded) inorganic species being leached out and quantified as water-soluble.
- The use of semi-continuous leaching method minimises the contact between acidic leachate and biomass sample, providing an accurate quantification of water-soluble inorganic species in biomass.
- The leaching kinetics demonstrates that batch leaching of inorganic species involves two leaching steps, rapid leaching for an initial short period of time and a subsequence slow leaching step for a long period. However, the second slow leaching step is not observed for semi-continuous leaching due to minimised interaction between leachate and biomass.
- The leaching of mono-valence species (Na and K) is found to be faster compared to di-valences species (Mg and Ca). This is due to the large diffusion coefficients of mono-valence ionic species in water.

8.2.2 Tuning Biochar Properties via Partial Gasification: Biochar Characteristics and Leaching of Organic Matter

- Tuning of fast pyrolysis mallee biochar via partial steam gasification at low conversion (5 to 10%) and mild temperature (725 °C) causes up to 25% loss in carbon available for sequestration. However, the remaining carbon in tuned biochar is postulated to be stable.
- Partial steam gasification leads to significant increase in biochar surface area mainly through the formation of large pores (e.g. mesopore and macropores).

- <1.5% of organic matter on carbon basis can be leached from biochar studied. While secondary pyrolysis generally removes the water-soluble organic matter from biochar, partial steam gasification does not. The leaching of organic matter following partial steam gasification might be due to the increase of accessibility of water to water leachable organic matter in biochar.
- Small amount of aromatic compound in raw biochar can be leached from fast pyrolysis biochar via organic solvents. Tuning via partial steam gasification is able to produce biochar with no leachable aromatic compounds. This reduces the risk of possible contamination of amended soil

8.2.3 Tuning Biochar Properties via Partial Gasification: Leaching Characteristics and Recyling of Inorganic Nutrients

- Close to 90% of K, Mg and Ca in fast pyrolysis biochar are retained during tuning via partial steam gasification. Up to ~34% of Na in leaf biochar is volatilised following partial steam gasification while >80% Na in wood biochar are retained.
- Partial steam gasification enhances the leachability of AAEM species in water and Mehlich-1 solution. 85% AAEM species in wood biochar and 96% of that in leaf biochar are leachable by Mehlich-1 solution thus available to plant.
- Increase in AAEM species leachability might be due to (1) the development of pore structure, and (2) transformation of biochar inherent AAEM species from the form that bounded to char matrix to the form that are soluble in water and Mehlich-1 solution during partial steam gasification.
- Tuning of biochar via partial steam gasification increase the overall recycling of AAEM species from fast pyrolysis biochar when it is applied to soil, minimising the loss of soil nutrient during biomass utilisation cycle and improving the sustainability of biomass pyrolysis process.

8.2.4 The Leaching of Biomass Water-Insoluble Metallic Species under Hot-Compressed Water Condition

- Most of the Na and K in mallee biomass are leachable at room temperature. ~90% Mg and ~96% Ca in mallee wood can be leached under HCW conditions.
- At 150 °C, the leaching of Mg and Ca in HCW took at least 70 min to complete. At 180 °C, ~90% leachable Mg and Ca were removed in 15 min. The increase in HCW temperature does not affect the leaching kinetic of Mg and Ca.
- The carbon conversion of mallee wood is found to be at ~34%, ~56%, ~69% and ~88% following hydrolysis in HCW at 150 °C, 180 °C, 230 °C and 270 °C, respectively.
- The lignin and hemicellulose component of mallee wood start to decomposed at 150 °C. Cellulose only starts to decompose at 230 °C.
- Further analysis suggests that organic bounded Mg and Ca are likely to be bounded on the acid functional groups on hemicellulose branches.

8.3 Recommendations

Based on the finding from this research, the following future researches are suggested to close the research gaps in this area:

1. Water leaching of biomass in this study was carried out with fine biomass particle and at room temperature. The leaching equilibrium and kinetics of inorganic and organic matter from larger particle biomass and at various temperatures are not well understood. Therefore, further investigation on the leaching characteristics of inorganic and organic matter from various biomass particle size and temperature is required.

2. This study demonstrates that a small amount of labile organic matter can be leached from biochar via water and solvent. However, the nature of the organic matter leached is not well understood thus additional study has to be carried out

to characterise these organic matter. In addition, it is also important to quantify the presence of poly aromatic hydrocarbon (PAH) in raw and tune biochar. These are to ensure the application of biochar to soil will not contaminate the amended soil.

3. Current research only studies the recyclability of AAEM species from raw and tuned biochars. Biochar also contains other plant essential nutrients such as S, N and P. A systematic study is required to study the recyclability of S, N and P from fast pyrolysis biochar produced under various pyrolysis conditions and the effect of partial steam gasification on the recyclability of these nutrient species.

4. Only mallee biochars were considered in the present research. The study on the tuning of biochars to enhance the recycling of inherent nutrient species should also be extended to other biomass feedstock.

5. The study on the leaching of AAEM species during biomass hydrolysis in HCW in this research is limited to the mallee wood. As mallee leaf and bark contain high amount of AAEM species, it is important to study the leachability and leaching kinetic of AAEM species from these components under HCW conditions.

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