Western Australian School of Mines: Minerals, Energy and Chemical Engineering

Rapid Pyrolysis of Biomass, Biomass Components and Biomass Derived Products in a Drop-tube Furnace at High Temperature

**Changya Deng** 

This thesis is presented for the degree of

**Doctor of Philosophy** 

of

**Curtin University** 

December 2020

## 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.

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

Signature: ....

Date: ...

To by beloved family

### ABSTRACT

Biomass is an important renewable energy resource in the global energy mix. It has great potential as part of fuels solving energy and environmental crisis. To make the utilization of biomass more economic, some problems like low energy density, poor grindability, high transport cost and mismatch with other fuels should be addressed. Fast pyrolysis is an effective way to convert the bulky biomass into bio-oil and biochar, which are high-energy density fuels. Stationary application like combustion could effectively transfer biomass and its derived products into energy. During stationary application, pyrolysis is the first step of these thermochemical processing. Clarifying the characteristics of biomass, biochar and bio-oil during high temperature (i.e. >1000 °C) pyrolysis is crucial important for biomass utilization for bioenergy. Pertinent to stationary applications, studies and data on biomass, biochar and bio-oil at high temperature are insufficient for practical applications. Therefore, there is an urgent need to carry out a systematic study on rapid pyrolysis of these biomass and its derived materials (i.e. biochar and bio-oil) in drop-tube furnace (DTF) at high temperatures, which is the key research work of this PhD. study.

To achieve the goal of this PhD. study, a scientific progress was developed for collecting and analyzing pyrolyzed products (i.e. soot) after high temperature pyrolysis in a DTF. The effect of feeding rate on soot formation was also discussed. After these, systematic experiments were designed and conducted for rapid pyrolysis of biomass, biomass model components and biomass derived products at high temperature. Six key objectives have been achieved, including (1) Developing a scientific progress for collecting and analyzing size-segregated pyrolyzed product (i.e. soot) after high temperature pyrolysis in a DTF; (2) Characterizing rapid

pyrolysis products of biomass wood at high temperature; (3) Investigating the factors (i.e. feeding rate) that influence the soot formation during rapid pyrolysis of different kinds of feedstock at high temperature; (4) Clarifying the differences in soot produced from main biomass model components; (5) Understanding rapid pyrolysis of biochar at high temperature, collecting and analyzing particulate matter (PM) produced during pyrolysis. (6) Studying the soot formation and synergies of bio-oil and its fractions at high temperature pyrolysis.

First, a Dekati low-pressure impactor (DLPI) was applied to separate soot from pyrolysis of pine wood in a DTF at 1300 °C according to its aerodynamic diameter for subsequent characterization. Under the experimental conditions, it was determined that the total amount of pine wood fed into the reactor must be 150 mg or less for effective soot separation without overloading the DLPI. The result shows that the carbonaceous materials with aerodynamic diameters  $\leq 10 \ \mu m \ (CM_{10})$ from pine wood pyrolysis have a unimodal distribution with a fine mode of 0.077 $\mu$ m. The carbonaceous materials with aerodynamic diameters between 1 and 10  $\mu$ m  $(CM_{1-10})$  are primarily char fragments but only account for < 2% of CM<sub>10</sub>. The CM with aerodynamic diameters  $\leq 1 \,\mu m$  (i.e. CM<sub>1</sub>) accounts for >98% of the CM<sub>10</sub> and are soot. Further analysis shows that the key elements present in soot (i.e. CM<sub>1</sub>) are Na, K and Cl, due to condensation of these inorganic species during the cooling of flue gas or as the result from the incorporation between soot and alkali metals to form inorganic bonds, but these inorganic species only contribute to  $\sim 0.2$  % of the soot yield. The (Na+K)/Cl molar ratios of >3 in the segregated soot samples indicate most of the alkali metals in soot are not in the form of NaCl and KCl. The result also shows ~85 % of Na in soot is water-soluble while only ~12 % of K in soot is watersoluble, indicating that soot preferentially incorporates with K over Na to form

organic bonds. Moreover, the contents of water-insoluble Na and K in incipient soot are higher than those in mature soot and soot cluster. Transmission electron microscopy of the soot sample shows the soot has disordered inner core(s) and clear fringe structure. There are slight increases in soot fringe and tortuosity during soot growth.

Second, the significant effect of feeding rate on soot formation during rapid pyrolysis of water-washed cellulose and acid-washed lignin (denoted as W-cellulose and A-lignin, respectively) in a DTF at 1300 °C were studied, Soot produced during W-cellulose pyrolysis has a unimodal distribution, with only a fine mode that its modal diameter increases from 0.043 to 0.246 µm as the feeding rate increases from 40 to 280 mg/min. However, at feeding rates of 12 - 200 mg/min, soot produced from A-lignin pyrolysis has a bimodal distribution with two fine modes located at  $0.077 \,\mu\text{m}$  and  $0.246 \,\mu\text{m}$ , respectively. As the A-lignin feeding rate further increases from 200 to 280 mg/min, the fine mode at 0.077  $\mu$ m disappears and the particle size distribution of soot becomes unimodal with only a fine mode with diameter of 0.246 µm. Increasing feeding rate increases the yield and particle size of total soot but decreases the yield of non-mature soot for W-cellulose at feeding rates < 280 mg/min and A-lignin at feeding rates < 40 mg/min. The results suggest that a high feeding rate produces high concentration of soot precursors and enhances the collisions for increased formation of incipient soot to large mature soot. As the feeding rate further increases to be more than 40 mg/min, the soot yield from A-lignin pyrolysis levels off, the particle sizes of overall soot decrease and the yields of non-mature soot increase. Under such conditions, further results show that soot growth is limited by the availability of soot-forming carbonaceous materials (including small gas molecules e.g. C<sub>2</sub>H<sub>2</sub> and polycyclic aromatic hydrocarbons).

Third, the properties of size-segregated soot from rapid pyrolysis of three biomass model compounds (i.e. xylan, cellulose and lignin) in a DTF under pulverized fuel conditions in argon at 1300 °C were clarified. Lignin (100.7 mg/g) yields much more soot than xylan and cellulose (7.0 and 11.6 mg/g, respectively) during pyrolysis. While all soot samples have a unimodal size distribution, lignin soot has a considerably larger mode diameter (0.246 µm) than soot from xylan and cellulose  $(0.043 \text{ and } 0.077 \text{ }\mu\text{m}, \text{ respectively})$ , attributing to the enhanced agglomeration of soot formed from lignin pyrolysis. The fringe of soot from lignin pyrolysis is longer and straighter than those of xylan soot or cellulose soot. Additionally, soot from cellulose pyrolysis contains little inorganic species as cellulose contains little ash. However, for xylan and lignin that contain abundant inorganic species, substantial Na, K, Cl and S are present in the soot samples. Even though the yield of inorganic species in CM<sub>1</sub> from xylan pyrolysis is lower than that from lignin pyrolysis, xylan soot has higher content of inorganic species than lignin soot. The presence of Na and K in soot is attributed to incorporation of these inorganic species in soot through organic bonds and/or condensation. K is more likely to incorporate with soot than Na. More Na and K are incorporated with soot from xylan pyrolysis compared to those with soot from lignin pyrolysis. Non-mature soot contains higher contents of Na and K than mature soot.

Fourth, the emission characteristics of leaf and wood biochar (LC500 and WC500) pyrolysis in a DTF at 1300 °C in argon atmosphere were studied. The char yields at 1300 °C are  $\sim 65\%$  and  $\sim 73\%$  respectively for LC500 and WC500. Over 60% Mg, Ca, S, Al, Fe and Si are retained in char after pyrolysis at 1300 °C. The retentions of Na and K in the char from LC500 pyrolysis are lower than those in the char from WC500 pyrolysis due to release via enhanced chlorination as a result of much higher

Cl content in LC500. PM with aerodynamic diameter of  $< 10 \ \mu m$  (i.e. PM<sub>10</sub>) from LC500 and WC500 pyrolysis exhibits a bimodal distribution with a fine mode diameter of 0.011  $\mu$ m and a coarse mode diameter of 4.087  $\mu$ m. The PM<sub>10</sub> yield for LC500 pyrolysis is ~ 8.2 mg/g, higher than that of WC500 pyrolysis (~2.1 mg/g). Samples in PM<sub>1-10</sub> (i.e. PM with aerodynamic diameter 1  $\mu$ m – 10  $\mu$ m) are char irregular shapes and fragments that have similar molar ratio of (Na+K+2Mg+2Ca)/(Cl+2S+3P) as the char collected in the cyclone. In PM<sub>1</sub> (i.e. PM with aerodynamic diameter  $< 1 \mu m$ ), the main components in the sample are inorganic species, and carbon only contributes to  $\sim 5$  % and  $\sim 8$  % the PM<sub>1</sub> produced from rapid pyrolysis of LC500 and WC500, respectively. Na, K and Cl are main inorganic species in PM<sub>1</sub>, contributing  $\sim 98.8\%$  and  $\sim 97.5\%$  to all inorganic species. Na, K and Cl from rapid pyrolysis of biochar have a unimodal distribution with a mode diameter of 0.011 µm. In PM<sub>1-10</sub>, Ca is the main inorganic specie, contributing to ~71.2% and ~65.3% to all inorganic species in  $PM_{1-10}$  from pyrolysis of LC500 and WC500, respectively.

Fifth, the soot formation of bio-oil and its fractions during rapid pyrolysis in a DTF at 1300 °C was investigated. Formulated samples were applied and they effectively represented the water-soluble fractions in bio-oil. Pyrolysis samples with aerodynamic diameter less than 1  $\mu$ m are soot, while those with aerodynamic diameter between 1  $\mu$ m and 10  $\mu$ m are carbon cenospheres. Soot yield from bio-oil is ~31 mg/g. Water-insoluble fraction (PL) and formulated water-soluble fraction (FWSF) of bio-oil have negative interactions after mixing for soot formation during pyrolysis. PL and FWSF have the soot yield of ~77 mg/g and ~23 mg/g, respectively. Organics in FWSF have a positive synergetic effect with PL for soot formation during pyrolysis. The soot yield of mixture is ~150 % to the estimated one calculated

by individuals (Organics in FWSF and PL) according to their contents. Water in FWSF has a significantly negative effect on soot formation. It could decrease the soot yield to ~53 % comparing with the one without water. Soot produced from bio-oil, PL, FWSF, organics in bio-oil, organics in FWSF have a unimodal distribution with a fine mode dimeter at 0.077  $\mu$ m, 0.043  $\mu$ m, 0.077  $\mu$ m, 0.246  $\mu$ m and 0.246  $\mu$ m, respectively. Analysis of average soot cluster size shows the degree of soot coagulation and agglomeration from bio-oil and its fractions varies and it is heavily dependent on the concentration of soot in the reactor. Because soot concentration reflects the collision chance among soot particles. Water in bio-oil significantly decreases the average size of soot clusters through decreasing the soot yield and suppressing soot coagulation.

## ACKNOWLEGEMENTS

I gratefully acknowledge the Curtin International Postgraduate Research Scholarship (CIPRS) provided by Curtin University to support my PhD study and Australian Research Council through its Discovery Projects Scheme to partially support my PhD research project.

I would like to especially thank my supervisor, Professor Hongwei Wu and Cosupervisor, Dr. Sui Boon Liaw for their guidance, teaching, training, inspiration, patience and constant support during my PhD. studying project.

I would like to express my great thanks to staff from Western Australian School of Mines: Minerals, Energy and Chemical Engineering for their assistance. I would like also to deeply acknowledge other members in our group: Yun Yu, Mingming Zhang, Bing Song, Matthew Witham, Chao Feng, Chua, Yee Wen, Wenran Gao, Sigit Abdurrakhman, Yu Long, Mingyang Li, Jinxiu Cao, Rashedul Khondakar, Zhiliang Wu, Qiqing Shen, Victor Olet, and Maksudur Rahman. Thanks for your help during my life of PhD study. I also want to give my gratitude to Andrew Chan, Melina Miralles, Xiao Hua, Jennifer Wang, Roshanak Doroushi, Ann Carroll and Araya Abera for their laboratory assistance and work on lab safety issues. My thanks also to the John de Laeter Centre, Curtin University in providing analysis instrument of SEM and TEM.

Finally, I would thank my families for their support. I love you.

## LIST OF PUBLICATIONS

Papers Published in Referred International Journals:

[1] **Deng, C.** and H. Wu, Mechanistic insights into effect of feeding rate on soot formation during rapid pyrolysis of biomass model components in a drop-tube furnace at high temperature. Proceedings of the Combustion Institute, 2021. 38(4): p. 5191-5199.

[2] **Deng, C.**, S.B. Liaw, and H. Wu, Fundamental investigation into characteristics of particulate matter produced from rapid pyrolysis of biochar in a drop-tube furnace at 1300 °C. Proceedings of the Combustion Institute, 2021. 38(4): p. 5229-5236.

[3] **Deng, C.**, et al., Differences in soot produced from rapid pyrolysis of xylan, cellulose and lignin under pulverized-fuel conditions. Fuel, 2020. 265: p. 116991.

[4] Deng, C., S.B. Liaw, and H. Wu, Characterization of Size-Segregated Soot from Pine Wood Pyrolysis in a Drop Tube Furnace at 1300 °C. Energy & Fuels, 2019.
33(3): p. 2293-2300.

[5] Liaw, S.B., C. Deng, and H. Wu, A Novel Two-Stage Alumina Reactor System for Burning Volatiles Generated in Situ from Biosolid: Effect of Pyrolysis Temperature and Combustion Conditions on PM<sub>1</sub> Emission. Energy & Fuels, 2018. **32**(9): p. 9438-9447.

Paper to be submitted to refereed international journals:

[6] **Deng, C**. and H.Wu, Soot formation and synergy study during rapid pyrolysis of bio-oil and its fractions in a drop-tube furnace at 1300 °C.

# **TABLE OF CONTENTS**

DECLARATION	I
ABSTRACT	III
ACKNOWLEGEMENTS	IX
LIST OF PUBLICATIONS	X
TABLE OF CONTENTS	XI
LIST OF FIGURES	XVI
LIST OF TABLES	XXII
CHAPTER 1 INTRODUCTION	1
1.1 Background and Motive	1
1.2 Scope and Objectives	2
1.3 Thesis outline	3
CHAPTER 2 LITERATURE REVIEW	6
2.1 Introduction	6
2.2 Biomass and its components	7
2.2.1 Cellulose	8
2.2.2 Hemicellulose	9
2.2.3 Lignin	10
2.2.4 Inorganic species	13
2.2.5 Organic extractives	13
2.3 Biomass pyrolysis	14
2.4 Biochar	15
2.5 Bio-oil	16
2.6 Description of soot formation at high temperature	19
2	KI   Page

2.6.1 Cracking and polymerization to form PAHs	
2.6.2 Incipient soot formation, soot growth and soot a	gglomeration21
2.6.3 Soot formation from biomass	
2.6.4 Characteristics of soot	23
2.6.5 Factors that influence soot formation	24
2.7 Conclusions and research gaps	
2.8 Research objectives of current study	
CHAPTER 3 RESEARCH METHODOLOGY	AND ANALYTICAL
TECHNIQUES	
3.1 Introduction	
3.2 Methodology	
3.2.1 A new method for size-segregated soot collectio	ns31
3.2.2 Effect of feeding rate on soot formation	
3.2.3 Biomass model component pyrolysis	
3.2.4 Pyrolysis of biomass	
3.2.5 Biochar pyrolysis	
3.2.6 Bio-oil pyrolysis	
3.3 Experimental	
3.3.1 Sample preparations	
3.3.2 Experimental Rigs	
3.3.3 Sample Analysis	46
3.4 Summary	
CHAPTER 4 CHARACTERIZATION OF SIZE-S	SEGREGATED SOOT
FROM PINE WOOD PYROLYSIS IN A DROP TUBE	FURNACE AT 1300 °C
4.1 Introduction	
	XII   P a g e

4.2 Optimized conditions for size-segregated CM10 collection54
4.3 PSD and yields of size-segregated CM and soot collected from pine wood
pyrolysis
4.4 Chemistry of size-segregated soot collected from pine wood pyrolysis58
4.5 Inorganic species in size-segregated soot collected from pine wood pyrolysis
60
4.6 Nanostructure analysis of soot from pine wood pyrolysis
4.7 Conclusions
CHAPTER 5 MECHANISTIC INSIGHTS INTO EFFECT OF FEEDING
RATE ON SOOT FORMATION DURING RAPID PYROLYSIS OF
BIOMASS MODEL COMPONENTS IN A DROP-TUBE FURNACE AT
HIGH TEMPERATURE71
5.1 Introduction
5.2 PSDs and yields of soot produced during pyrolysis of W-cellulose and A-
lignin at various feeding rates75
5.3 Yields of non-mature soot from rapid pyrolysis of W-cellulose and A-lignin at
various feeding rates81
5.4 Diameter distributions of individual soot particles from rapid pyrolysis of W-
cellulose and A-lignin at various feeding rates84
5.5 Soot clusters from fast pyrolysis of W-cellulose and A-lignin at various
feeding rates
5.6 Conclusions
CHAPTER 6 DIFFERENCES IN SOOT PRODUCED FROM RAPID
PYROLYSIS OF XYLAN, CELLULOSE AND LIGNIN UNDER
PULVERIZED-FUEL CONDITIONS91
6.1 Introduction
XIII   P a g e

mpounds	yrolysis of biomass model c	rties of soot from fast pyr	nd prope	6.2 Yields ar
93			•••••	
95	f biomass model compound	t from fast pyrolysis of b	es of soo	6.3 Propertie
ass model	ot from fast pyrolysis of bion	s in size-segregated soot f	c species	6.4 Inorgani
				compounds
fbiomass	in soot from fast pyrolysis	on on inorganic species in	liscussic	6.5 Further of
			ounds	model comp
			ions	6.6 Conclus
INTO	INVESTIGATION	FUNDAMENTAL	7	HAPTER
) FROM	TE MATTER PRODUCE	S OF PARTICULATE	RISTIC	HARACTE
ACE AT	N A DROP-TUBE FURN	S OF BIOCHAR IN A	OLYSIS	APID PYR
			••••••	300 °C
			tion	7.1 Introduc
	s species	retentions of inorganics s	lds and 1	7.2 Char yie
	nar pyrolysis	ds of $PM_{10}$ from biochar	and yie	7.3 PSDs
M <sub>10</sub> from	vidual inorganic species in l	Ds and Yields of individ	ental PS	7.4 Elem
			olysis	biochar pyro
			ions	7.5 Conclus
DURING	ND SYNERGY STUDY	F FORMATION AND	8 <b>SOO</b> T	HAPTER 8
P-TUBE	<b>IS FRACTIONS IN A DRO</b>	OF BIO-OIL AND ITS	DLYSIS	APID PYRC
		С	Г 1300 °	URNACE A
			tion	8.1 Introduc
s fractions	st pyrolysis of bio-oil and it	l yields of soot from fast	tions and	8.2 Distribut
127				
sis at high	oot yield during rapid pyroly	g bio-oil fractions on soot	es among	8.3 Synergie
130			s	temperatures
/ Page	ХГ			

8.4 Characterization of soot clusters during rapid pyrolysis at high temperatures
8.5 Conclusions
CHAPTER 9 CONCLUSIONS AND RECOMMENDATIONS137
9.1 Introduction
9.2 Conclusions
9.2.1 Characterization of Size-Segregated Soot from Pine Wood Pyrolysis in a
DTF at 1300 °C137
9.2.2 Mechanistic insights into effect of feeding rate on soot formation during
rapid pyrolysis of biomass model components in a DTF at high temperature
9.2.3 Differences in soot produced from rapid pyrolysis of xylan, cellulose and
lignin under pulverized-fuel conditions139
9.2.4 Fundamental investigation into characteristics of particulate matter
produced from rapid pyrolysis of biochar in a DTF at 1300 $^{\circ}$ C140
9.2.5 Soot formation and synergy study during rapid pyrolysis of bio-oil and its
fractions in a DTF at 1300 °C140
9.3 Recommendations
REFERENCES143
APPENDIX I: COPYRIGHT PERMISSION STATEMENTS160
APPENDIX II: ATTRIBUTION TABLES164

# **LIST OF FIGURES**

Figure 1-1. Thesis map5
Figure 2-1. Cellulose chemical structure [7]8
Figure 2-2. Main components of hemicellulose9
Figure 2-3. Microstructure of typical plant cell wall [19]11
Figure 2-4. Structure of lignin molecule from hardwood [21]12
Figure 2-5. Mechanism of PAH formation. (a) HACA mechanism; (b) Addition of
benzene rings [63]21
Figure 2-6. Soot formation mechanisms from biomass [70-72]. VOC: volatile
organic compounds. CPD: cyclopentadienes
Figure 2-7. Microstructure of soot [102]24
Figure 3-1. Methodology for research objectives in this thesis
Figure 3-2. Schematic diagram of drop-tube/fixed-bed quartz reactor
Figure 3-3 Schematic diagram of DTF with two feeders: (a) feeding system for solid
particle samples; (b) feeding system for liquid samples. (1) sample tube; (2) primary
Argon; (3) feeding tube; (4) secondary argon; (5) cooling water; (6) two-heating
zone furnace; (7) alumina tube; (8) cooling water; (9) quench helium; (10) make up
argon; (11) cyclone; (12) DLPI; (13) vacuum pump; (14) exhaust tube; (15) syringe.
Figure 3-4. Double-tube configuration in DTF42
Figure 3-5. Image of DLPI. (a) Assembled, (b) Disassembled44
Figure 3-6. Aerodynamic principles of DLPI45
XVI   P a g e

Figure 3-7. Aerodynamic size of cluster
Figure 3-8. Temperature program for proximate analysis in TGA47
Figure 3-9. Temperature program for ashing of bio-oil in Muffle furnace [123]48
Figure 4-1: PSDs of the $CM_{10}$ from pyrolysis of pine wood at 1300 °C with sample
size of 70, 150, 350 and 400 mg55
Figure 4-2: (a) PSD and (b) yields of $CM_{10}$ from pyrolysis of pine wood at 1300 °C 57
Figure 4-3 Micromorphology of CM sample from pyrolysis of pine wood with
aerodynamic diameters of (a) 6.863 $\mu$ m, (b) 0.612 $\mu$ m, (c) 0.077 $\mu$ m and (d) 0.011
μm. Panel (a1) is the zoom in picture from (a)
Figure 4-4: H/C molar ratio of size-segregated soot (i.e. CM1) from pine wood
pyrolysis in DTF at 1300 °C60
Figure 4-5: PSDs of major elements in size-segregated soot (i.e. CM1) from pine
wood pyrolysis in DTF at 1300 °C61
Figure 4-6 Yields of Na, K and Cl and water-soluble Na and K in size-segregated
soot (i.e. $CM_1$ ) from pine wood pyrolysis in DTF at 1300 °C62
Figure 4-7 Dependence of (Na + K)/Cl molar ratio on the size of size-segregated
soot (i.e. $CM_1$ ) from pine wood pyrolysis in DTF at 1300 °C63
Figure 4-8 Contents of Na (a), K (b) and Cl (c) in size-segregated soot (i.e. $CM_1$ )
collected on each impactor stage, expressed as % of total mass on each impactor
stage
Figure 4-9 Contents and distribution of water-soluble and water-insoluble Na and K
in size-segregated soot sample collected on various impactor stages during pine

wood pyrolysis in DTF at 1300 °C. Panel (a) and (b): contents of water-soluble (a)
and water-insoluble (b) Na and K; Panel (c) and (d): distribution of water-soluble
and water-insoluble Na (c) and K (d) in each impactor stage, expressed as the
percentage of respective total Na or K66
Figure 4-10 TEM micrographs of soot (on the stage with aerodynamic diameter
0.077 $\mu$ m) from pine wood pyrolysis in DTF at 1300 °C. Panels (b)-(d) are the zoom-
in images of panel (a)67
Figure 4-11 Nanostructural parameters including fringe length (a), fringe tortuosity
(b) and fringe layer spacing (c) of size-segregated soot (i.e. CM <sub>1</sub> ) from pine wood
pyrolysis in DTF at 1300 °C69
Figure 5-1. PSDs of W-cellulose and A-lignin before pyrolysis in DTF74
Figure 5-2. PSDs of soot from rapid pyrolysis of (a) W-cellulose and (b) A-lignin
with different feeding rates at 1300 °C76
Figure 5-3. Micromorphology analysis of pyrolysis products with aerodynamic
diameter less than 1 $\mu$ m from biomass model component pyrolysis at 1300 °C: (a)
feeding rate: 40 mg/min W-cellulose, (b) feeding rate: 120 mg/min W-cellulose, (c)
feeding rate: 280 mg/min W-cellulose, (d) feeding rate: 12 mg/min A-lignin, (e)
feeding rate: 40 mg/min A-lignin, (f) feeding rate: 280 mg/min A-lignin77
Figure 5-4. TEM analysis of pyrolysis products with aerodynamic diameter less than
1 $\mu$ m from biomass model component pyrolysis at 1300 °C: (a) feeding rate: 40
mg/min W-cellulose, (b) feeding rate: 120 mg/min W-cellulose, (c) feeding rate: 280
mg/min W-cellulose, (d) feeding rate: 12 mg/min A-lignin, (e) feeding rate: 40
mg/min A-lignin, (f) feeding rate: 280 mg/min A-lignin78
Figure 5-5. Soot yields from rapid pyrolysis of W-cellulose and A-lignin with

different feeding rates at 1300 °C
Figure 5-6. Soot yield during A-lignin pyrolysis at 1300 °C with different residence
times
Figure 5-7. Total carbon in remaining carbonaceous materials for soot forming ( $C_{soot}$ -
$_{\rm forming})$ and $\rm H_2$ in gas product after rapid pyrolysis of (a) W-cellulose and (b) A-lignin.
Figure 5-8. Chemical analysis of soot samples during pyrolysis of W-cellulose and
A-lignin
Figure 5-9. Non-mature soot yields from rapid pyrolysis of W-cellulose and A-lignin
with different feeding rates at 1300 °C83
Figure 5-10. Diameter distribution of soot particles from rapid pyrolysis of W-
cellulose and A-lignin with different feeding rates at 1300 °C85
Figure 5-11. Mean aerodynamic diameter of soot from rapid pyrolysis of W-
cellulose and A-lignin at 1300 °C with (a) different feeding rates and (b) soot
concentration
Figure 6-1. PSDs of CM from pyrolysis of biomass model compounds at 1300°C.
Figure 6-2. H/C molar ratio of size-segregated soot from pyrolysis of biomass model
compounds in DTF at 1300 °C97
Figure 6-3. Micromorphology of soot samples from pyrolysis of biomass model
compounds: (a) cellulose soot at 3 <sup>rd</sup> impactor stage, (b) xylan soot at 3 <sup>rd</sup> impactor
stage, (c) lignin soot at 3 <sup>rd</sup> impactor stage and (d) lignin soot at 5 <sup>th</sup> impactor stage.
$3^{rd}$ impactor stage: aerodynamic collection diameter 0.077 $\mu m;5^{th}$ impactor stage:
aerodynamic collection diameter 0.246 µm98
XIX   P a g e

Figure 6-4. PSDs of major elements including Na (a), K (b), Cl (c), S (d) in size-
segregated soot from pyrolysis of biomass model compounds in DTF at 1300 °C.
Figure 6-5. Yields of major inorganic species (a) Na, (b) K, (c) Cl and (d) S in size-
segregated soot from pyrolysis of biomass model compounds in DTF at 1300°C.
Figure 6-6. Contents of inorganic species in size-segregated soot collected on each
impactor stage, expressed as % of total mass on each impactor stage. Panel (a) $-$ (d):
(a) Na, (b) K, (c) Cl and (d) S103
Figure 6-7. Dependence of (Na + K)/(Cl+2S) molar ratio on the size of size-
segregated soot from pyrolysis of biomass model compounds in DTF at 1300°C

Figure 7-4 Elemental PSD of (a) Na, (b) K, (c) Cl, (d) Ca, (e) Mg, (f) S and (g) P in
PM <sub>10</sub> from rapid pyrolysis of biochars at 1300 °C119
Figure 7-5. Elemental Yield of (a) Na, (b) K, (c) Cl, (d) Ca, (e) Mg, (f) S and (g) P
in $PM_{10}$ from rapid pyrolysis of biochars at 1300 °C120
Figure 8-1. PSDs of CM during rapid pyrolysis of bio-oil, FB, PL and FWSF at
1300 °C
Figure 8-2. Micromorphology analysis of CM <sub>10</sub> samples during rapid pyrolysis at
1300 °C. (a)-(d): CM <sub>1</sub> (i.e. soot) samples from pyrolysis of bio-oil (a), FB (b), PL (c)
and FWSF (d). (e)-(h): $CM_{1-10}$ sample from pyrolysis of bio-oil (e), FB (f), PL (g)
and FWSF (h)129
Figure 8-3. PSDs of CM from rapid pyrolysis of bio-oil fractions at 1300 °C131
Figure 8-4. Micromorphology analysis of CM <sub>10</sub> samples during rapid pyrolysis at
1300 °C. (a)-(c): CM <sub>1</sub> (i.e. soot) samples from pyrolysis of FWSF-2 (a), PL + FWSF-
2 (b), FB-2 (c). (d)-(f): $CM_{1-10}$ sample from pyrolysis of FWSF-2 (d), PL + FWSF-
2 (e), FB-2 (f)
Figure 8-5. SMD of soot samples from rapid pyrolysis of bio-oil and its fractions at
1300 °C

# LIST OF TABLES

Table 2-1. Product distribution from different modes of pyrolysis [29].    15
Table 2-2. Classification of tars [59, 60]
Table 3-1 Nominal cut-off size of each stage in DLPI45
Table 4-1 Properties of pine wood used in this study
Table 5-1 Properties of cellulose, lignin and water-washed lignin. The water-washed
lignin was prepared from raw lignin by repeatedly washing using deionized water.
Table 5-2 Properties of the W-cellulose and A-lignin samples used in this study. The
W-cellulose sample was prepared from the raw cellulose by repeatedly washing
using deionized water while the A-lignin sample was prepared from the raw lignin
by acid-washing
Table 6-1. Proximate, ultimate and ash analyses of xylan, cellulose and lignin92
Table 6-2. Yields of non-mature soot and mature soot and their contributions to $CM_1$
generated from fast pyrolysis of xylan, cellulose and lignin in a DTF at 1300 °C.94
Table 6-3. Nanostructure parameters of soot (with particle diameters of 20-30 nm)
generated from fast pyrolysis of xylan, cellulose and lignin
Table 7-2 Properties of fast pyrolysis biochars (i.e. LC500 and WC500) prepared
from fast pyrolysis of wood and leaf at 500 °C and the derived chars (i.e. LC500-
1300 and WC500-1300) after rapid pyrolysis of these biochars in the DTF at 1300 °C.
Table 7-3 Char yields during rapid pyrolysis of biochars in the DTF at 1300 °C in
argon, determined either directly by experiments or indirectly by ash tracer method.
XXII   P a g e

Table 7-4 Cation to anion molar ratio of PM1 and PM1-10 samples from pyrolysis of
LC500 and WC500 biochars in the DTF at 1300 °C in argon
Table 7-5 Carbon and inorganic species content in PM1 from pyrolysis of biochar in
DTF at 1300 °C
Table 8-1. Properties of bio-oil and PL. PL is the water-insoluble fraction of filtered
bio-oil
Table 8-2. Compositions of FB, FWSF and FWSF-2.    127

### **CHAPTER 1 INTRODUCTION**

#### 1.1 Background and Motive

Bioenergy is a very important renewable energy resource in the global energy mix [1, 2]. According to WBA's Global Statics 2019 [3], renewable energy accounts for 17.8 % of the gross final energy consumption globally, and 70 % of renewable energy is from biomass. Biomass is carbon neutral as fuel because photosynthesis during biomass growth could assimilate carbon, which compensates the carbon dioxide emitted during biomass utilization as bioenergy. It is also a clean fuel as it contains less nitrogen and sulfur than fossil fuels, resulting less emission of NO<sub>x</sub> and SO<sub>x</sub> [4].

In Western Australia, biomass like mallee trees and pine trees are widely spread and are important resources for future development of the state. However, biomass is hard for grinding and co-combustion with other fuels such as coal, has low energy density and high transport cost. Some pre-processes were conducted to transfer biomass into biomass derived products (i.e. biochar and bio-oil). These biomass derived products have higher energy density than biomass. In some cases [5, 6], it could be more economic comparing with direct utilization of biomass.

Stationary applications (e.g. combustion and gasification) are good ways for utilization of biomass and its derived products for energy. Pyrolysis is crucial as the first step of these thermochemical processing. Clarifying the characteristic of biomass, biochar and bio-oil during high temperature (i.e. >1000 °C) pyrolysis is very important for biomass utilization for bioenergy. Pertinent to stationary applications, studies and data on biomass, biochar and bio-oil at high temperature are insufficient. Therefore, it is urgently needed to clarify the rapid pyrolysis of biomass and its derived materials in drop-tube furnace (DTF) at high temperatures. The PhD. work reported in this thesis focus on this.

### **1.2 Scope and Objectives**

The research work intends to characterize the pyrolysis of biomass, biomass model components, biochar and bio-oil in a laboratory-scale DTF at high temperature. The detailed objectives of this study are listed below:

- Developing a scientific progress for collecting and analyzing sizesegregated pyrolyzed product (i.e. soot) after high temperature pyrolysis in a DTF;
- Characterizing rapid pyrolysis products of biomass wood at high temperature;
- Investigating the factors (i.e. feeding rate) that influence the soot formation during rapid pyrolysis of different kinds of feedstock at high temperature.
- Clarifying the differences in soot produced from the main biomass model components;
- 5) Understanding the biochar rapid pyrolysis at high temperature, collecting and analyzing particulate matter (PM) produced during pyrolysis.

 Studying the soot formation and synergies of bio-oil and its fractions at high temperature pyrolysis.

### 1.3 Thesis outline

To fully achieve the research objectives in section 1.2, research works were conducted, and 9 chapters were included in this thesis (including this chapter). The thesis map is presented in Figure 1-1 with brief introduction of each chapter clarified below.

- Chapter 1 gives the background and objectives of the thesis;
- Chapter 2 reviews the literature on biomass and its model components, its derived products (i.e. biochar and bio-oil), up-to-date researches on high temperature pyrolysis of biomass, biomass components, biochar and bio-oil, soot formation mechanism, and factors that influence soot formation, finally introducing the key research gaps and outlining of specific objectives of the present study;
- Chapter 3 reports the research methodology and techniques applied in this thesis. The detailed description of the experiment apparatus and equipment, analyzing method and process and sample preparation are also included;
- Chapter 4 develops a new method for analyzing size-segregated soot from pyrolysis of wood biomass in a DTF at high temperature. The characteristics of high temperature rapid pyrolysis of a biomass wood in the DTF are also

investigated;

- Chapter 5 provides the results and discussions for the effect of feeding rate on soot formation during high temperature rapid pyrolysis of two respective biomass model components.
- Chapter 6 investigates the differences in soot produced from rapid pyrolysis of biomass model components (i.e. xylan, cellulose and lignin) under pulverized fuel conditions. The distributions of alkali and alkaline earth metals (AAEMs) are also studied;
- Chapter 7 reports the characterization of particular matters produced from high temperature pyrolysis of two kinds of biochars.
- Chapter 8 demonstrates the results and discussions on soot formation from bio-oil and its fractions during high temperature rapid pyrolysis. The synergies for soot formation among different fractions in bio-oil were also clarified.
- Chapter 9 summarizes the major outcomes in this thesis and proposed some recommendations for future research work.



Figure 1-1. Thesis map.

## **CHAPTER 2 LITERATURE REVIEW**

#### **2.1 Introduction**

Biomass as an important source of bioenergy is sustainable and environmentally friendly. In Western Australia, biomasses like pine tree and mallee tree are widely spread as important plants that help to protect the land. These plants yield abundant biomass resources every year and have considerable potential for energy application. However, biomass has some disadvantages during utilization. It is bulky for transportation and storage, hard for grinding into small pieces and has low energy density and high moisture. These characteristics increase the cost of utilization of biomass. To address these problems of biomass and make it competitive with conventional fossil fuels, pyrolysis is a widely recognized way for biomass processing. Through pyrolysis, biomass is transferred into bio-oil and biochar. These biomass derived products are easy for transportation or grinding. Their energy densities are also higher than biomass. In some cases, the utilization of biomass.

Stationary applications (i.e. combustion and gasification) are potentially good options for biomass utilization as bioenergy. The applications are usually processed at high temperature to improve the efficiency of energy transformation. Pyrolysis is crucially important as the first step in thermochemical processing.

Accordingly, the objective of this chapter is to give a review of the high temperature pyrolysis of biomass and its derived products (i.e. biochar and bio-oil). The literature review of this thesis will start with describing the characteristics of biomass and its model components, biochar and bio-oil. Then the up-to-date researches of high temperature pyrolysis of biomass and its derived products will be summarized. The formation mechanism, characteristics of high temperature pyrolysis products (i.e. soot) will also be introduced.

#### 2.2 Biomass and its components

The concept of biomass is general. It could have numerous forms including agricultural wastes (e.g. straw), forestry wastes (e.g. bark), solid wastes (e.g. sewage sludge), leather wastes, energy crops (e.g. miscanthus and sorghum), olive pits and nutshells. For biomass wood, there are terms of "hardwood" and "softwood". Hardwood is not a very precise concept, it roughly identifies the broad class of angiospermae trees, and "softwood" is defined as gymnospermae trees [7]. The component varies in different biomass.

Western Australia (WA) has great biomass potential for utilization for bioenergy. Taking mallee biomass as example. Since the early 1990s, 14000 ha of mallee eucalyptus have been planted across the wheatbelt in WA [8, 9]. It could supply biomass with ~10 million dry tons every year [10]. Mallee biomass is estimated to provide energy with more than 200 GJ ha<sup>-1</sup> year<sup>-1</sup>. It could strongly increase the energy ratio (the ratio of total energy output and total nonrenewable energy inputs) to 41.7 [11]. The mallee biomass is initially developed in wheatbelt to tackle conservation issues like dryland salinity [5]. It is well adapted to the warm temperature winter rainfall climates where the amount of water from rainfall is much less than lost from evaporation most of time in the year.

Biomass is composed 35 % - 38 % of cellulose, 23 % - 32 % of hemicellulose, 15 % - 25 % of lignin and 5 % - 13 % of other components like inorganic species and extractives [12]. They have different structures and thus different properties. During pyrolysis, many factors influence the thermochemical process of biomass components, making it complex. The introduction will first summarize the studies on biomass chemical components. Their thermal decomposition during pyrolysis is also discussed.

#### 2.2.1 Cellulose

Cellulose is a linear polymer of  $\beta$ -(1 $\rightarrow$ 4)-D-glucopyranose units in the  ${}^{4}C_{1}$  conformation. The molecular weight of cellulose could be 10<sup>6</sup> or more. Cellulose consists of long cellulose chains, which are formed through polymerization of glucose anhydride. Cellulose contains 5000 – 10000 glucose units. Cellobiose, as featured in Figure 2-1, is the basic repeating unit in cellulose polymer. It is composed of two glucose anhydride units [7].



Figure 2-1. Cellulose chemical structure [7].

Groups of cellulose chains twist in space to form ribbon-like microfibril sheets, these sheets are the basic construction units to compose a variety of complex fibers. The

fibers formed then make up tubular structures which run along a longitudinal tree axis.

Cellulose is only soluble in some exotic solvents and completely insoluble in most of the solutions [13, 14]. The crystalline structure of cellulose makes its thermal resistance stronger than that of hemicellulose. The decomposition of cellulose during pyrolysis starts at 240  $^{\circ}$ C - 350  $^{\circ}$ C. During the thermal decomposition, anhydrocellulose and levoglucosan are produced.

### 2.2.2 Hemicellulose

Hemicellulose is also called as polyose. The composition of hemicellulose in different wood varies. In softwood it has the content of 28 %, while in hardwood the content could be 35 % [15]. Hemicellulose is a mixture of various polymerized monosaccharides and Figure 2-2 lists some of these components in hemicellulose. In hardwood, hemicellulose is rich in xylan and poor in glucomannan. In softwood, hemicellulose is poor in xylan, and has large amounts of galactoglucomannan.



Figure 2-2. Main components of hemicellulose.

Comparing the number of repeating units in cellulose (i.e. 5000 - 10000), hemicellulose only has ~150 repeating saccharide monomers. Therefore, the molecular weight of hemicellulose is much lower than that of cellulose. However, the composition of hemicellulose is more complex than cellulose. Cellulose only consists of glucose, whereas hemicellulose is composed of a heteropolysaccharide and some contains short side-chain "branches" pendent along the main polymeric chain.

Hemicellulose is easier to decompose during thermal process than crystalline cellulose. It starts to decompose at 130 °C – 194 °C. When the temperature is above 180 °C, most of hemicellulose is decomposed [16]. Comparing with cellulose, during pyrolysis, hemicellulose releases less chars, less tars and more volatiles [17]. The decomposition of hemicellulose contributes much of the acetic acid released from wood pyrolysis.

#### 2.2.3 Lignin

Lignin is a three-dimensional, highly branched, polyphenolic substance that consists of an irregular array of variously bonded "hydroxy-" and "methoxy-" substituted phenylpropane units [18]. The structure of these monomeric phenylpropane units is in form of the p-coumaryl, coniferyl and sinapyl. During agglomeration of fibrous cellulose components, lignin is the main binder. Figure 2-3 illustrates a cell wall composed of lignin, cellulose and hemicellulose [19]. Lignin also helps to prevent the destruction of cellulosic fibers from rapid microbial or fungal attack.



Cellulose Bundles

Figure 2-3. Microstructure of typical plant cell wall [19].

In softwood and hardwood, the structures of lignin are different. "Guaiacyl" lignin is usually found in softwood while hard wood mainly contains "Guaiacyl-syringyl" lignin. "Guaiacyl" lignin is formed from polymerization of a higher fraction of coniferyl phenylpropane units. "Guaiacyl-syringyl" lignin is a copolymer of both the coniferyl and sinapyl phenylpropane units. The structure of lignin is amorphous. The radical reactions are nonselective random condensations. Therefore, numerous possible interlinkages are formed between individual units. Ether bonds are predominated between lignin units, which is different with the acetal functions in cellulose and hemicellulose. Some covalent links could be found between lignin and polysaccharides [20]. They could help to enhance the adhesive bond strength between cellulose fiber and its lignin "potting matrix". A typical section of lignin polymer is presented in Figure 2-4.



Figure 2-4. Structure of lignin molecule from hardwood [21].

The extraction or isolation technology applied for lignin could influence the properties of lignin, making its physical and chemical properties different. When studying the thermal decomposition of lignin, one thing which should be notified is that the decomposition of separated lignin and lignin in biomass as a component is different. It is because the properties of lignin are inevitably changed during lignin isolation from biomass.

Comparing with hemicellulose or cellulose, lignin is harder to dehydrate. Lignin was found to begin decomposing in wood at 280 °C [7]. Phenols could be formed and released during the process through the carbon-carbon linkages and cleavage of ether. The char yield from lignin pyrolysis is higher than that from cellulose and
hemicellulose. Pyroligneous acid as a liquid product could also be found during lignin pyrolysis, based on dry lignin, it contributes ~15 % on tar residue and ~20 % on aqueous components. The aqueous portion mainly contains acetic acid, methanol, acetone and water. The main components in tar include homologous phenolic compounds. Lignin pyrolysis also yields ~10 % gaseous product on original lignin basis, and the product contains methane, ethane and carbon monoxide.

## 2.2.4 Inorganic species

Biomass also contains many kinds of inorganic species. The main inorganic species in biomass include Na, Mg, Si, Cl, S, Al, K, P, Fe, Ca, Mn and Ti [22]. Some trace elements are also detected including Ba, Co, Ni, As, Sn, Cr, U, Mo, Se, Zn, V and Cu [23]. The environmental conditions, variety of biomass and obtaining time and method could influence the kinds and contents of these inorganic elements [24]. In biomass, inorganic species could be in numerous forms, including salts, covalent bonds between inorganic elements, free ion and the organic biomass structure [24].

The inorganic species due to nutrient uptake is important for biomass growth. During thermal chemical process, the inorganic species could influence the process through catalytic effects [25]. It could also cause some problems like slagging or adverse impacts on environment and human health through emission of PMs.

## 2.2.5 Organic extractives

Organic extractives are also important for biomass as energy reserves, as intermediates in metabolism and as defense against microbial and insects attack. These organic extractives includes fats, mucilages, saponins, alkaloids, phenolics, pectins, gums, resins, waxes, simple sugars, terpenes, starches, glycosides, proteins, and essential oils [7, 20]. They could be extracted through polar solvents or nonpolar solvents [7, 20].

#### 2.3 Biomass pyrolysis

Biomass has some disadvantages during utilization as a fuel. It has high moisture content and low energy density. Besides, biomass is bulky and fibrous [6]. Therefore, strategies are needed to make utilization of biomass more economic. Pyrolysis is thermal decomposition of materials in the absence of oxygen or when significantly less oxygen is present than required for complete combustion. It is an effective method for biomass processing [7]. It could turn the bulky, low energy biomass into bio-oil and biochar. Bio-oil could turn into high quality fuel after further upgrading and refining [7, 26, 27]. Biochar could also be a fuel with good properties [6]. The reaction mechanisms are complex and could be simplified in three main steps [28]:

$$Biomass \rightarrow Water + Unreacted residue$$
(2-1)

Unreacted residue 
$$\rightarrow$$
 (Volatile + Gases)<sub>1</sub> + (Char)<sub>1</sub> (2-2)

$$(Char)_1 \rightarrow (Volatile + Gases)_2 + (Char)_2$$
 (2-3)

In Eq. 2-1, moisture and some volatiles are lost in the initial pyrolysis. In Eq. 2-2, primary biochar is formed. In Eq. 2-3, Secondary biochar is formed after volatilechar interaction and chemical rearrangement. The process parameters could affect the properties and yields of pyrolyzed products. Table 2-1 presents the product distributions obtained from different modes of pyrolysis.

Mode	Conditions	Liquid	Solid	Gas
Fast	~500 °C, short hot vapour	750/ 100/ -		. 120/
	residence time ~1 s	/ 3 70	1270 Char	1370
Intermediate	~500 °C, hot vapour	500/in 2 mbases	250/ abor	250/
	residence time $\sim 10 - 30$ s	50% III 2 phases	23% char	2370
Carbonisation (Slow)	~400 °C, long vapour	200/	250/ abor	250/
	residence hours /days	30%	55% char	3370
Gasification	~750 - 900 °C	5%	10% char	85%
Torrefaction (Slow)	~290 °C, solids residence	$\frac{1}{2}$	200/ an1:1	200/
	time ~10 - 60 min	up 10 5%	80% SOI10	20%

Table 2-1. Product distribution from different modes of pyrolysis [29].

Fast pyrolysis is of particular interest among these modes because the liquid yield after pyrolysis is the highest [7]. Bio-oil is from these pyrolyzed liquid. It is an environmentally friendly product and could be used for energy, chemicals or as energy carriers [30, 31]. Different kinds of reactors such as rotating cone, transported beds, circulating fluid beds, bubbling fluid beds, etc. were developed for fast pyrolysis[29].

## 2.4 Biochar

Biochar is the solid residues formed during the thermochemical decomposition of biomass. It is inexpensive and environmentally friendly. The surface functional groups, specific surface area and porous structure in biochar are large. The mineral content is also very high. It could be applied for waste management in water or air [32, 33], producing biodiesel, removing tar as a catalyst [34, 35] and soil remediation [32, 36]. Biochar has the similar mass energy density as traditional solid fuel like

coal [6]. It could be used for stationary application for energy production. Biochar is also used for greenhouse gas reduction. Some researches on the application of biochar as fuel cells [37, 38] and supercapacitors [39, 40] have also been reported. The elemental composition in biochar is depended on the raw biomass and pyrolysis conditions [32, 41, 42]. Carbon is the main element in biochar. It also contains other elements like hydrogen, oxygen, nitrogen and sulfur [43].

Many parameters could influence the pyrolysis process, thus influence the properties of biochar. These parameters include residence time, heating rate and reaction temperature. In general, with the increasing of pyrolysis temperature, the yield of biochar decreases but the yield of syngas increases [28, 44-46]. The pH, carbon stability and ash content increase, whereas functional groups decreases at the same time [46, 47]. The increase in pH is because of the reduction of organic functional groups like -COOH and -OH. The residence time of pyrolysis could also affect the composition of biochar. When increasing the residence time, the yield of biochar decreases [47]. Lu et al. [48] found that within temperature range from 500 °C to 900 °C, the pore area and specific surface area increase with the increase of residence time is below 2 h, but these factors decrease with the increase of residence time when it is above 2 h. Bandosz et al. [49] reported that during the pyrolysis of sewage sludge, with the increase of residence time at 950 °C, the pore volume and specific surface area decrease. It is because of the sintering of char during pyrolysis [48].

## 2.5 Bio-oil

Bio-oil is a dark brown, free-flowing organic liquid which is composed of highly

oxygenated compounds [26, 50, 51]. It is an important liquid product from pyrolysis of biomass. During biomass pyrolysis, biomass model components including hemicellulose, cellulose and lignin in biomass experience rapidly and simultaneously depolymerization and fragmentation. The intermediate pyrolysis products of cellulose, hemicellulose and lignin then "freeze in" through rapid quenching. If the high temperature residence time is extended, the products could further react, like to cleave, degrade or condensate with other molecules. Therefore, many reactive species are in bio-oil. Bio-oil is a complex mixture which contains catecols, furancarboxaldehydes, water, vanillins, guaiacols and other carboxylic acids, etc. [52]. The water during pyrolysis could shred the feed particles and aid heat transfer. Free water could explosively vaporize under fast pyrolysis conditions. Hemicellulose and cellulose could also lose water during pyrolysis. Oligomeric species may simply "blown apart" into aerosols as decomposition rapidly occurs and never be vaporized. They are derived mainly from lignin, but also cellulose. The weight of oligomer molecule varies from several hundred to 5000 or more. The factors like temperature, residence time, heating rate, particle size and biomass species used could influence the molecular weight of oligomers.

Bio-oil could be regarded as a microemulsion in which the continuous phase stabilizes the discontinuous phase. The small molecules from lignin decomposition and products from holocellulose decomposition compose the continuous phase. While the pyrolytic lignin macromolecules consist of discontinuous phase [52]. The hydrogen bonding and nanomicelle and micromicelle formation could help to stabilize the microemulsion. Bio-oil as a liquid could be stored and transported as the similar way as petroleum-based products [26].

Bio-oil contains most of the oxygen originally composed of biomass. The oxygen content of bio-oil is typically 45 - 50 % [53]. Water content could also have an effect on the oxygen content of bio-oil. Oxygen could be in more than 300 compounds which have been identified in bio-oil [17]. These compounds could be roughly classified into five categories: hydroxyaldehydes, carboxylic acids, hydroxyketones, sugars and dehydrosugars, and phenolic compounds [52].

The phenolic compounds in bio-oil are in form as monomeric units and oligomers derived from the coniferyl and syringyl building blocks of lignin. These organic compounds could be classified in details as: aldehydes, acids, furans, sugars, esters, ketones, aromatics, phenols, alcohols, guaiacols, syringols, alkenes, nitrogen compounds and miscellaneous oxygenates [52, 54]. Besides water, hydroxyacetaldehyde has the highest content in bio-oil as single chemical compound, which could be as much as 10 wt.%. The contents of acetic and formic acid could also be typically  $\sim 5$  wt.% for acetic and  $\sim 3$  wt.% for formic acid [52]. Because of these components, the bio-oil becomes acidic with pH 2.0 - 3.0.

The properties of bio-oil could be manipulated by adjusting the thermal conditions of the process or using catalysts. It yields different kinds of compounds under different temperatures [55]:

Mixed oxygenates (400 °C)  $\rightarrow$  phenolic ethers (500 °C)  $\rightarrow$  alkyl phenolic (600 °C)  $\rightarrow$  heterocyclic ethers (700 °C)  $\rightarrow$  polycyclic PAH (800 °C)  $\rightarrow$  larger PAH (900 °C) (2-4) Alkyl groups cleave from aromatic compounds when the temperature is increased,

and polycyclic aromatic hydrocarbons (PAHs) could be formed from aromatic

compounds with further increase of temperature.

## 2.6 Description of soot formation at high temperature

Soot is a carbonaceous material generated from the gas phase during fuel thermochemical processing. Soot could have several important implications to process operations and environment. First, soot can enhance radiative heat transfer at high temperatures. Such a condition is desirable in a furnace or boiler where high radiative heat transfer is required but become undesirable when radiative heat transfer needs to be restrained (e.g., internal combustion engines) [56]. Second, soot mainly contains carbon. Therefore, significant soot formation reduces the overall process efficiency, as part of carbon from fuel forms soot rather than being oxidized and converted to useful energy. Third, the release of soot to atmosphere can result in an adverse impact to local community cardiovascular and pulmonary health, as the fine soot particles could be easily inhaled [57]. Last, soot can exacerbate global warming, as soot absorbs strongly over ultraviolet, visible, and infrared spectral regions [58].

Soot formation is widely studied and could be roughly summarized into four steps. (1) Cracking and polymerization to form PAHs; (2) PAHs form into incipient soot; (3) soot growth (including coagulation); and (4) soot agglomeration to form clusters or chains.

## 2.6.1 Cracking and polymerization to form PAHs

During thermal processing, complex cracking reactions happen and organic molecules are broken into smaller molecules. Bonds of C-C or C-H could break

when heat is inputted. This process leads to the formation of free radicals on some carbon atoms. Large hydrocarbons like tar are especially affected by cracking reaction, Table 2-1 classifies the primary, secondary and tertiary tars by Evans and Mine [59, 60]. With the increase of severity during reaction, primary tars could further decompose into secondary tars and tertiary tars. Light hydrocarbons, mainly  $CH_4$  and olefins like  $C_2H_2$ , along with non-hydrocarbon gases like  $H_2$  and CO could be produced during decomposition of tar. Light hydrocarbon molecules could also decompose during thermal processing. The decomposition of them trends to the formation of  $C_2H_2$ , which could form aromatic compounds [61].

	Secondary Tertiary tars		rtiary tars	
Primary Tars	tars	Substituted	Condensed	
Derived products from cellulose and hemicellulose (e.g. levoglucosan, furfural, etc.)	Olefin and phenolics	Methyl derived aromatics (e.g. methyl acenaphtylene,	Aromatic hydrocarbons without substitute (e.g. benzene, naphthalene, acenaphthylene,	
lignin (e.g. methoxyphenol)		toluene) and indene	phenanthrene, pyrene)	

Free radicals formed from cracking reactions could reform new large hydrocarbon chains through polymerization. It could be regarded as the opposite reaction of cracking. When the temperature is high enough (i.e. above 900 °C), PAHs could be formed and continue to grow to larger PAH molecules. Aliphatic hydrocarbons could form  $C_6H_6$  for PAH formation [62]. Figure 2-5 describes two examples of mechanism for PAH formation. The most accepted mechanism for PAH formation

is HACA mechanism (i.e. hydrogen abstraction acetylene addition).



Figure 2-5. Mechanism of PAH formation. (a) HACA mechanism; (b) Addition of benzene rings [63].

## 2.6.2 Incipient soot formation, soot growth and soot agglomeration

The primary soot particles start to nucleate when a critical size of PAH is reached. The homogeneous phase then transforms into heterogeneous phase. The primary soot starts with a rather small mass, which is  $\sim 3.10^{-21}$  g [64]. Then the primary soot grows to bigger particle size by surface growth mechanism. It is reported that surface growth attributes up to 98 % of the total growth of soot [65-67]. Two relevant mechanisms are reported for soot growth and they are not isolated. One is the surface growth by the addition of acetylene [68]. The other is the addition of PAHs. When the acetylene and the PAHs collide with the soot particles, they are polymerized with the surface of soot growth by acetylene, in which C<sub>soot</sub>H is an active site on soot surface on which C<sub>2</sub>H<sub>2</sub> can polymerize [68].

$$C_{\text{soot}}H + H \cdot \leftrightarrow C_{\text{soot}} \cdot + H_2 \tag{2-5}$$

 $C_{\text{soot}} \cdot + H \cdot \rightarrow C_{\text{soot}} H \tag{2-6}$ 

21 | P a g e

$$C_{\text{soot}} \cdot + C_2 H_2 \to C_{\text{soot}} H + H \cdot$$
(2-7)

Coagulation could also contribute to soot growth. When two soot particles collide, they could form a new nearly spherical particle with further growth. Finally, soot particles could stick to each other to form soot clusters or chains through agglomeration. Soot agglomeration is just a loose connection that can easily be broken [69].

## 2.6.3 Soot formation from biomass

Biomass is made up with complex components, which include hemicellulose, cellulose, lignin, inorganic species and extractives. It is more complex than pure fuels, making soot formation from biomass pyrolysis more complex than those from pure fuels. Some researchers have analyzed the soot formation from biomass and Figure 2-6 summarizes soot formation mechanisms from biomass [70-72].



Figure 2-6. Soot formation mechanisms from biomass [70-72]. VOC: volatile organic compounds. CPD: cyclopentadienes.

Hemicellulose, cellulose and lignin in biomass begin to decompose and crack at high temperatures. The process releases small molecules (e.g. CH4, CO and H2) and heavy tar with large molecules. Hemicellulose and cellulose largely decompose into molecular pieces including furans, saccharides, ketones and acids. These species undergo further decomposition like ring-opening interactions, polymerization and aromatization to form compounds with benzene rings like phenol, methylbenzene and styrene. Unlike hemicellulose and cellulose, the decomposition of lignin could directly lead to products with benzene rings like phenols and aromatics. These small aromatic molecules then further develop into precursors of nascent soot particles through reported mechanisms below: (1) small molecules react with C<sub>2</sub>H<sub>2</sub> for growth into larger PAHs through HACA mechanism; (2) cyclopentadienes (CPDs) generated from phenols further react into naphthalenes and indenes, then form PAHs through HACA mechanism; (3) Formed naphthalenes and indenes further interact with CPDs and grow into larger PAHs; (4) 'ring-ring condensation' among small molecules with aromatic rings to form PAHs. All these mechanisms are not isolated and could happen at the same time for soot formation [70].

#### 2.6.4 Characteristics of soot

Soot is a black solid sphere. Carbon and hydrogen are the main elements in soot. It may also contain some traces of nitrogen, oxygen and sulfur [73]. The incipient soot usually has H/C molar ratio of 0.4 - 0.7 [74-81] with the size range from 1 nm to 6 nm [68, 82-88]. When soot becomes mature, the H/C molar ratio decreases to 0.05 – 0.1 as hydrogen is lost during this process [73-75, 80, 81, 89], the interlayer spacing of soot decreases [74, 90, 91], the graphite crystallite size increases [92-94], the fine structure become more ordered [90-92, 95, 96] and the size of mature soot

increases to 10 - 50 nm in diameter [82, 95, 97, 98]. Mature soot has the similar fine structure to polycrystalline graphite.

Figure 2-7 illustrates the micro structure of soot. It could be seen that soot spherule structures could be essentially divided into inner core and outer shell. The inner core is composed of spherical nucleus, some fine particles could be observed in the inner core, which is the early primary soot particles. The outer shell is consisted of concentric layer of graphitic crystallites. They are formed during growth stage of soot and are chemically and structurally stable [78, 99-101].



Figure 2-7. Microstructure of soot [102].

Soot particles usually have a very low porosity with 8 - 14 %, the maximal pore size is 1 nm. However, after agglomeration. The porosity of soot clusters could be as high as 95 %, and the pore size in the magnitude order could range from 10 nm to 100 nm [103].

# 2.6.5 Factors that influence soot formation

Some factors including physical parameters and fuel compositions could influence the soot formation. These factors include temperature, pressure, fuel properties, and inorganic species etc. They are summarized in detail below.

## 2.6.5.1 Temperature

Temperature has great effect on soot formation by affecting the reaction rate. Glassman [104] found that soot inception begins around 1400 K. Xuebin Wang etc. [105] reported that soot is significantly formed when temperature is above 1000 °C during biomass pyrolysis. They also found that when the temperature of pyrolysis is increased, soot particles become small and uniform, it has higher carbon content and more ordered structure of carbonization [105]. The reactivity of soot is decreased with increasing temperature [106]. Vander Wal [107] also reported when the temperature is below 1300 °C, PAHs mainly contribute to soot mass growth, whereas at higher temperature, the decomposition of PAHs to  $C_2H_2$  is enhanced, making the contribution of mass growth from  $C_2H_2$  greater. The structural order of soot is also increased with increasing temperature.

# 2.6.5.2 Pressure

Changing the pressure could influence soot formation. An increase in pressure could increase soot formation with the rate as high as  $P^2$  [108]. Higher pressure during pyrolysis means higher concentration of soot precursors and more collisions, leading to higher reaction rates [108].

#### 2.6.5.3 Fuel composition and structure

Many research works report that the composition and structure of fuel could affect the formation of soot. The literature suggests that the composition of fuel plays more important role in soot formation than structures [108]. Generally, high content of carbon in fuel means it is more likely to produce soot, while high content of oxygen in the fuel leads to a low yield of soot [108]. The influence of hydrogen is less than oxygen. High content of hydrogen in a fuel could suppress the formation of soot. For sulfur, it has no direct effect on soot formation. It could attach to soot particles and result in increasing particle size and mass [109].

Molecular structure is an important factor for soot formation [110]. Ring structures could significantly influence the formation of soot and fuels with fused cyclic molecules having higher soot yield. For fuel without aromatics, the properties of the chain could also influence soot formation. It is reported that carbon double bond (C = C) has a substantial influence on soot formation tendency [108].

## 2.6.5.4 Inorganic species

Biomass and its derived products also contain some inorganic species. Some of these species could also affect the soot formation. Xuebin Wang [105] reported that when biomass was pretreated with water-washing to remove potassium in biomass, this process leads to higher yield of soot, the particle size and carbon content of soot particles are also increased. It indicates the potassium has strong catalytic effect on soot formation and consumption. Ann trubetskaya [111] also found the dominating role of potassium on the soot reactivity.

#### 2.7 Conclusions and research gaps

Based on the literature review above, several capital conclusions are organized below. The research gaps are also proposed for study:

Firstly, High temperature pyrolysis of biomass is critically important for utilization. More researches are needed for characterization of biomass rapid pyrolysis at high temperatures, especially for the soot formation and distribution.

Secondly, Soot is an important product during pyrolysis of carbonaceous material at high temperatures. Soot formation mechanisms are widely studied. For pyrolysis in flow reactors, sampling and analyzing methods need to be developed for study.

Thirdly. The effect of feeding rate is an important factor during pyrolysis of biomass and its model component. There is little research on the effect of this factor on soot formation during pyrolysis at high temperature.

Fourthly, biomass is composed of biomass model components. Clarifying the rapid pyrolysis of biomass model components at high temperature could help further understanding biomass pyrolysis at high temperatures. However, according to the literature review, more research work is needed to characterize high temperature pyrolysis of biomass model components.

Fifthly, biochar applied in stationary application is an effective way for utilization, there is little literature related to high temperature pyrolysis of biochar pertinent to stationary application situations.

Sixthly, bio-oil is a high-density energy, environmentally friendly and renewable

energy source. The application of bio-oil through combustion in boiler is a good way for utilization of bio-oil. Little research is related to the high temperature pyrolysis of bio-oil pertinent to stationary application.

In summary, further investigation is required to fill in the research gaps in the field of pyrolysis of biomass, biomass model components and biomass derived products in a DTF at high temperatures.

# 2.8 Research objectives of current study

As listed in the section 2.7, several research gaps in the field have been identified from the literature review. Nevertheless, it is practically impossible to fill all the research gaps due to the limited timeframe of the PhD study. Thus, the scope of this thesis aims to achieve six objectives as follows:

- Developing a scientific progress for collecting and analyzing pyrolyzed products (i.e. soot) after high temperature pyrolysis in a DTF;
- 2) Characterizing the biomass wood rapid pyrolysis at high temperature;
- Investigating the factor (i.e. feeding rate) that affects soot formation during high temperature pyrolysis of two typical biomass model components.
- Clarifying the differences in soot produced from main biomass model components (i.e. hemicellulose, cellulose and lignin);

- Understanding the rapid pyrolysis of biochar at high temperature. Characterizing its pyrolysis products.
- 6) Studying the soot formation from rapid pyrolysis of bio-oil and its fractions.Discussing the synergies among fractions in bio-oil during soot formation.

# CHAPTER 3 RESEARCH METHODOLOGY AND ANALYTICAL TECHNIQUES

# **3.1 Introduction**

In this chapter, research methodology is reported for achieving the objectives listed in Chapter 2. Experimental and analytical techniques are illustrated in detail below.

# 3.2 Methodology

A biomass wood, three main biomass model components, two kinds of biochar and a bio-oil are applied in this thesis. The derived biomass pyrolysis products include biochar and bio-oil. A series of systematical experiments are then carried out, including:

- Pre-treatment of sampling including cutting samples into small sizes, sieving, water-washing or acid washing.
- Pyrolysis of mallee wood and mallee leaf in a drop-tube/fixed-bed reactor system to produce biochar for further experiments.
- High temperature pyrolysis of biomass, biomass model components, biochar and bio-oil are conducted through a laboratory-scale DTF.
- Size-segregated samples collected through a sampling system, which includes a Dekati cyclone and a Dekati low pressure impactor (DLPI).

• Analysis of the collected samples including chemical composition, micromorphology analysis and structure analysis, etc.

All the experiments in this research were conducted at least in duplicate for the reproducibility of the results. Figure 3-1 presents the overall research methodology for research objectives.



Figure 3-1. Methodology for research objectives in this thesis.

# 3.2.1 A new method for size-segregated soot collections

As introduced in Chapter 2, soot is an important high temperature pyrolyzed product. A key issue needs to be addressed for the objectives in the thesis is developing a proper method for the sampling of soot produced from pyrolysis. As soot particles are very small, the diameter of soot is usually less than 100 nm. Soot could also agglomerate to form chains or clusters to become bigger. However, the traditional sampling system usually consists of a cyclone for separation of coarse particles and a filter for collection of fine particles that are regarded as soot [112, 113]. Such systems have at least two drawbacks that may have significant impact on the determination of soot yield and the characteristics of collected soot samples. One is that it is unclear whether all the char fragments could be separated by cyclone. Most importantly, it is unclear on the contribution of char fragments to the collected soot. The other is that the properties of soot or soot clusters are dependent on soot growth stage (hence soot size) so that there are great needs to collect and characterize sizesegregated soot samples for revealing insights into soot formation during fuel thermochemical processing. Therefore, a new sampling method via a DLPI for collecting size-segregated soot samples was developed, the detailed work and discussion are reported in Chapter 4.

## 3.2.2 Effect of feeding rate on soot formation

During biomass pyrolysis, the feeding rate of feedstock is likely to have significant effect on soot formation and properties. Such effect may also be highly dependent on the biomass components such as cellulose and lignin. From the literature review, there has been little research dedicated to understanding the effect of feeding rate on soot formation and properties during rapid pyrolysis of biomass model compounds under high-temperature conditions pertinent to stationary applications. Consequently, to achieve object 3, the effect of feeding rate on soot formation during rapid pyrolysis of biomass model components under non-catalytic conditions was investigated. The detailed work and results are illustrated in Chapter 5.

### 3.2.3 Biomass model component pyrolysis

Biomass feedstock is complex. It is known [114] to consist of three major components (i.e., hemicellulose, cellulose, and lignin) plus minor extractives and inorganic species. Previous experimental work as introduced in chapter 2 also suggested that the formation routes of soot precursor (PAHs) may vary from biomass component to component. To achieve object 4, systematically work was done to investigate the emission behavior of soot from pyrolysis of three major biomass model compounds (i.e., xylan, cellulose and lignin) at 1300 °C in a DTF. The detailed results and discussion are reported in Chapter 6.

#### **3.2.4 Pyrolysis of biomass**

As introduced in Chapter 2, biomass as a renewable resource plays an important role in future sustainable energy supply. To achieve object 2. The new sampling method was applied to characterize biomass pyrolysis in a DTF at 1300 °C. The chemical compositions, occurrence of inorganic species, and nanostructure of the sizesegregated soot samples are analysed. The detailed work and results are presented in Chapter 4.

#### **3.2.5 Biochar pyrolysis**

When biochar is fed into a DTF at high temperature, solid fuel particles experience rapid pyrolysis as the first step of the reactions. During rapid pyrolysis, part of released volatiles form fine particles at high temperature such as soot [10], which influences the operating conditions during application [11]. In addition, some inorganic elements also form fine particles with organic or inorganic species that have crucial effect on practical applications including undesired emissions into the environment. Because biochar is produced from biomass fast pyrolysis at relatively low temperature (450–550 °C), most of the inherent inorganic species are retained in biochar. The ash content of biochar typically ranges from ~5 % to ~60 %, depending on the type of biomass feedstock [12]. Biochar is also expected to experience secondary pyrolysis at high temperature in the DTF. To achieve Objective 5, two biochars were prepared from fast pyrolysis of mallee wood and mallee leaf at 500 °C. The biochars were then pyrolyzed in the DTF at 1300 °C in argon atmosphere. Focuses are on char yield, retention of inorganic species, characteristics and properties of PM with aerodynamic diameter of < 10  $\mu$ m (i.e. PM<sub>10</sub>). The detailed results and discussion are reported in Chapter 7.

## 3.2.6 Bio-oil pyrolysis

To achieve Objective 6, a bio-oil as well as its fractions including water-insoluble fraction, formulated water-soluble fraction, organics in bio-oil, etc. were applied in a DTF with a novel sampling method at 1300 °C to clarify the soot formation and internal synergies during bio-oil rapid pyrolysis at high temperature. The detailed results and discussion are presented in Chapter 8.

## 3.3 Experimental

## 3.3.1 Sample preparations

**Biomass.** The wood component was separated from pine trees harvested from Western Australia. The wood sample was dried at 40 °C in an oven overnight, cut in a cutting mill, and then sieved to yield the size fraction of 90–150  $\mu$ m for use in this study. Prior to pyrolysis experiments, the pine wood samples were kept in freezer at -9 °C to avoid spoilage. The properties of the pine wood sample are listed in Table 4-1, Chapter 4, including proximate and ultimate analyses, concentrations of major elements, and contents of structural carbohydrates, extractive, and lignin.

**Biomass model component.** Xylan (representing hemicellulose), cellulose and lignin samples were purchased from Sigma-Aldrich. Xylan and cellulose are extracted from beechwood and cotton linters, respectively, while the lignin is alkali lignin in the form of brown powders. Prior to pyrolysis, each of these biomass model compounds was sieved to the size fraction of 90–150  $\mu$ m, Basic properties of the biomass model compounds are shown in Table 6-1, Chapter 6.

**W-cellulose and A-lignin.** Raw cellulose and lignin samples were purchased from Sigma-Aldrich, with the properties presented in Table 5-1, Chapter 5. To eliminate the effect of inorganic species on soot formation, the raw cellulose and lignin samples were pre-treated to remove these inorganic species. Briefly, the raw cellulose sample was washed repeatedly with deionised water until no inorganic species can be detected in the washed solutions. For lignin, as the water-washed lignin still contains relatively high ash content comparing with cellulose (see Table 5-1 in Chapter 5), the raw lignin sample was further washed with 0.1 M HCl for 24 h, followed by repeated washing with deionised water to remove the acid. The pre-treated cellulose and lignin samples were then dried in an oven at 60 °C for 24 h. After sieving, the samples were sealed in containers and stored in fridge for

35 | P a g e

subsequent use. The particle size distributions (PSDs) of these initial biomass samples are presented in Figure 5-1 in Chapter 5. Hereafter, the pre-treated cellulose and lignin samples are referred to as "W-cellulose" and "A-lignin" samples, respectively. The properties of the W-cellulose and A-lignin samples are listed in Table 5-2, Chapter 5. Indeed, as shown in Table 5-2, there is little ash-forming species in the W-cellulose and A-lignin samples.

**Biochar.** The wood and leaf components of mallee tree, which is widely distributed in Western Australia (WA), were separated, air dried, size reduced with a cutting mill and sieved into the size fraction of 90–150  $\mu$ m, their properties are listed in Table 7-1. Fast pyrolysis biochars were prepared from wood and leaf samples using a quartz drop-tube/fix-bed reactor (detailed in section 3.3.2.1) at 500 °C in argon. Briefly, after the reactor was preheated to 500 °C, ~1 g of biomass sample was fed into the reactor using a stream of argon at ~ 0.1 g min<sup>-1</sup>. Once the feeding was completed, the reactor was held at 500 °C for 15 minutes before it was lifted from the furnace and allowed to cool to ambient temperature while maintaining the flow of argon gas to the reactor. The char yield was determined by weighing the reactor before and after a pyrolysis experiment, taken in account the moisture in biomass and char. The yields of leaf biochar and wood biochar (hereafter termed as LC500 and WC500) are ~19 % and ~14 %, respectively. After pyrolysis, the biochar samples were collected, well mixed, sealed and stored in a fridge. The properties of the biochar samples are listed in Table 7-2, Chapter 7.

**Bio-oil.** The raw bio-oil applied in this study is produced from fast pyrolysis of pinewood under 500  $^{\circ}$ C in a pilot scale pyrolyser. To remove the fine char particles in bio-oil, it was filtered through a 0.45  $\mu$ m filter. Water-insoluble fraction of bio-oil

(PL) was separated from the filtered bio-oil via cold-water precipitation, which was detailed elsewhere [115, 116]. Briefly, ~10 mL filtered bio-oil in a syringe was added into  $\sim$ 500 mL cold water by using a syringe pump with the rate of 0.5 mL/min. Magnetic stirring was conducted during the mixing process at the speed of 750 rpm. After the addition of bio-oil, the stirring was continued for one day for dissolution, followed by filtration of mixture via ashless filter paper (Whatman, grade 540). The residue on the filter paper was flushed with deionized water to washout the watersoluble fraction of bio-oil, then dried at room temperature for two weeks until no further weight loss was detected. The dried PL sample was then selected by a 25  $\mu$ m sieve for samples with diameters less than 25 µm. The properties of filtered bio-oil (hereafter referred as bio-oil) and PL were presented in Table 8-1, Chapter 8. As it is impossible to separate water-soluble fraction from bio-oil directly, it was formulated according to the main components in water-soluble fraction of bio-oil [117] and termed as FWSF. A little CaCl<sub>2</sub> was also doped as the representative of inorganic matters. To verify the representability of FWSF, formulated bio-oil (FB) was prepared via mixing PL and FWSF according to their contents in the bio-oil. FWSF-2 was also prepared by removing the water, levoglucosan and CaCl<sub>2</sub> in FWSF. The components of FB, FWSF and FWSF-2 were illustrated in Table 8-2, Chapter 8. All the samples prepared were sealed and stored at 4 °C in fridge for further use.

## **3.3.2 Experimental Rigs**

## 3.3.2.1 A drop-tube/fixed-bed quartz reactor system

Biochars were prepared from mallee wood and mallee leaf samples through fast pyrolysis at 500 °C in a quartz reactor system. Figure 3-2 presents the schematic

diagram of the reactor system. The system mainly consists of a quartz reactor and an electrical furnace with two heating zones. The system could be applied to the pyrolysis experiments both under fast heating rate and slow heating rate conditions [118]. In this thesis, the reactor system is used for preparing biochar samples through fast pyrolysis. The quartz reactor was first preheated and an external thermal couple was applied to adjust the temperature of zone above the frit is 500 °C. A stream of argon gas with flowrate of 1 L/min continuously flows through the reactor for at least 10 min to create inert atmosphere in the reactor. ~1 g of biomass particles was then fed into the reactor at the feeding rate of ~0.1 g/min with a feeder for solid samples (see section 3.3.2.2). The biomass particles undergo fast pyrolysis at 500 °C. Volatiles formed were swept away and biochar was left on the frit. Once the feeding process was completed, the reactor was held at 500 °C for 15 minutes before it was lifted from the furnace and allowed to cool to room temperature while maintaining the flow of argon gas to the reactor.



Figure 3-2. Schematic diagram of drop-tube/fixed-bed quartz reactor

# 3.3.2.2 A High-Temperature DTF System

All the rapid pyrolysis experiments at high temperatures in this thesis study were conducted via a laboratory-scale DTF system. The basic system of the furnace was shown in Figure 3-3. Thermochemical experiments could be conducted in the furnace with various atmospheres. The DTF system consists of three parts (i.e. a feeding system, a main furnace and a sampling system). Further detailed descriptions are given below.

Feeding system. The feedstock samples are in different forms. Two types of feeding

systems are applied in this study to meet the requirements. Figure 3-3(a) is the feeding system for solid samples, which includes biomass, biomass model components, W-cellulose, A-lignin, biochar and PL in this study. Figure 3-3(b) illustrates the feeding system for liquid samples, including bio-oil and its formulated water-soluble fraction solutions. For solid particle feeding system, samples are fed into the furnace at various feeding rates through a feeding tube using a stream of primary argon gas (flowrate: 1 L/min) by adjusting the moving speed of the sample tube. A secondary argon was introduced to prevent the back flow of the volatiles produced from pyrolysis. The feeding tube is protected by a water-cooling jacket and secondary argon to prevent sample pyrolysis and retention in the feeding tube. For liquid sample, samples are pumped into the feeding tube through a syringe pump (model: KDS LEGATO 210) within a 20 mL stainless steel syringe. A primary argon was supplied for the atomization of liquid sample via a two-fluid nozzle set (model: VLA-3, VLT-3 and VLB, Paasche Airbrush). The size of liquid particles could be controlled by adjusting the flowrate of primary argon, which is detailed elsewhere [119]. A secondary argon was also introduced to prevent the back flow of the fume in the furnace tube. The feeding tube was protected by both the water-cooling jacket and the secondary argon to keep the outlet of nozzle less than 70 °C to avoid coking [120].



Figure 3-3 Schematic diagram of DTF with two feeders: (a) feeding system for solid particle samples; (b) feeding system for liquid samples. (1) sample tube; (2) primary Argon; (3) feeding tube; (4) secondary argon; (5) cooling water; (6) two-heating zone furnace; (7) alumina tube; (8) cooling water; (9) quench helium; (10) make up argon; (11) cyclone; (12) DLPI; (13) vacuum pump; (14) exhaust tube;

(15) syringe.



Figure 3-4. Double-tube configuration in DTF

**High temperature pyrolysis zone.** The high temperature rapid pyrolysis takes place in a vertical dense mullite tube. The length of the tube is 1.2 m and its inner diameter is 56 mm. It was placed in two heating zones with 6 electrical elements in total. The pyrolysis zone was heated to 1300 °C before pyrolysis experiments were conducted and the length of isothermal zone is ~600 mm. The whole system was purged with argon gas at least 15 min before pyrolysis experiment. In order to obtain the accurate char yield from pyrolysis, a novel double-tube configuration was employed for experiments at the same conditions. The schematic diagram of it is illustrated in Figure 3-4. It is important to note the key innovation of this novel DTF is it has a double-tube configuration that achieves complete collection of char for accurate quantification of char yield during rapid pyrolysis of solid fuels at 1300 °C.

**Sampling system.** The pyrolysis products were sampled via a sampling system that consists of a stream of make-up argon, a water-cooled helium-quenched sampling tube, a Dekati cyclone (model: SAC-65, with a size-cut of 10 µm in aerodynamic dimeter), a 13-stage DLPI with back filter assembly, and a vacuum pump (model: Leybold Sogevac SV25). The whole sampling line was maintained at 115 °C to prevent possible acid gas condensation [121]. The flowrate of fume gas that goes through the cyclone and DLPI should be limited at 10 L/min to achieve collection and separation of samples in the fume gas. A stream of make-up argon gas was supplied to control the flowrate of total fume gas in the sampling system. The particles with aerodynamic diameter > 10  $\mu$ m are collected in the cyclone, and the others go through the cyclone and enter the DLPI. The image of DLPI is shown in Figure 3-5. The particles with aerodynamic diameter  $< 10 \ \mu m$  are separated according to the aerodynamic principles illustrated in Figure 3-6. The smaller aerodynamic diameter of the particles, the easier these particles could make a sharp turn to continue to flow between the plates. Therefore, particles with large aerodynamic diameters are captured in high plates and particles with small aerodynamic diameters go further and be captured in low plates. The cut-off particle sizes on each stage in DLPI are presented in Table 3-1. It should be noted that cluster could be regarded as a real particle for aerodynamic diameter in DLPI, which is illustrated in Figure 3-7. Hereafter, in this thesis, carbonaceous materials (CM) with an aerodynamic diameter of <0.1, 0.1-1, <1, 1-10 and  $<10 \mu m$  are referred to as CM<sub>0.1</sub>, CM<sub>0.1-1</sub>, CM<sub>1</sub>, CM<sub>1-10</sub>, and CM<sub>10</sub>, respectively. PM with aerodynamic diameter of  $< 0.1 \ \mu\text{m}$ ,  $0.1 \ \mu\text{m} - 1 \ \mu\text{m}$ ,  $< 1 \ \mu\text{m}$ ,  $1 \ \mu\text{m} - 10 \ \mu\text{m}$  and  $< 10 \ \mu\text{m}$  are regarded as  $PM_{0.1}$ ,  $PM_{0.1-1}$ ,  $PM_1$ ,  $PM_{1-10}$  and  $PM_{10}$ , respectively.

Soot particles are usually in form of clusters because of agglomeration. Polycarbonate and quartz filters were used as substrates in the DLPI. The polycarbonate filters were used to enable the quantification of inorganic species in the collected size-segregated samples, whereas those samples collected using quartz filters were used for H/C molar ratio determination, micromorphology, and nanostructure analysis. The diluted Apiezon-H vacuum grease was used on each polycarbonate filters to prevent the bounce of particles during collection [121] for polycarbonate filters. A vacuum pump was also applied to maintain the work pressure above the back filter as 100 mbar.



Figure 3-5. Image of DLPI. (a) Assembled, (b) Disassembled.



Figure 3-6. Aerodynamic principles of DLPI

	Cast off size (D50
Cut-off size (D50)	
stages	μm)
13	10.174
12	6.852
11	4.087
10	2.438
9	1.624
8	0.955
7	0.61
6	0.372
5	0.246
4	0.138
3	0.077
2	0.043
1	0.022
Back filter	0.011

Table 3-1 Nominal cut-off size of each stage in DLPI



Figure 3-7. Aerodynamic size of cluster

## 3.3.3 Sample Analysis

3.3.3.1 Proximate analysis.

Proximate analysis quantifies the contents of water, volatile, fixed carbon and ash in the sample. The analysis was conducted via a thermogravimetric analyzer (model: Mettler Toledo) according to American Society for Testing and Materials (ASTM) international standard ASTME870-82 [122]. The temperature program applied in TGA is illustrated in Figure 3-8. Briefly, ~6 mg samples were weighted and loaded in a 150  $\mu$ L alumina crucible for TGA analysis. After purging argon for 15 min to build the inert atmosphere at 40 °C, the sample was heated to the temperature of 110 °C with holding time of 20 min until no further weight loss was observed. The weight loss in this stage was regarded as the weight of moisture in the sample. The temperature was then increased to 950 °C with a heating rate of 50 °C/min, with holding time of 20 min. After that, the temperature was decreased to 600 °C. The weight loss during the stage from the end of 110 °C and start of 600 °C was regarded as volatile matter in the sample. The sample was then further burned at 600 °C for 30 min with 100 mL/min air until no further weight loss was observed. The residual left in the crucible was ash and its weight was regarded as the ash content of sample. The difference of the weight before and after burning was calculated as the fixed carbon content in the sample.



Figure 3-8. Temperature program for proximate analysis in TGA

Bio-oil in this study have high water and volatile contents and low ash contents. It is hard to distinguish water and volatiles, as well as quantify ash content via TGA method above. Therefore, different methods were applied here for determination of water and ash content in bio-oil. The method of Karl Ficher titration is applied here for quantifying water content in bio-oil, which is detailed elsewhere [120]. Briefly, ~0.25 g bio-oil was injected into a solution (mixture of Hydranal methanol and chloroform with mass ratio of 3:1) and titrated in a titrator (model: Mettler V30) with additive of Hydranal Composite 5K which works to prevent fading of the titration end point. For the ash content analysis, ~500 mg bio-oil was ashed in a Muffle furnace with a temperature program shown in Figure 3-9 [123]. Then the

residual ash after ashing was weighted for ash content determination.



Figure 3-9. Temperature program for ashing of bio-oil in Muffle furnace [123].

## 3.3.3.2 Ultimate analysis

Ultimate analysis is used to quantify the contents of carbon, hydrogen and nitrogen in the sample. It was conducted via an element analyzer (model:PerkinElmer CHNSO 2400 Series II) according to Australian standard AS 1038.6.1-1997 (R2013) [124]. Sometimes the contents of Cl and S are also included in ultimate analysis. They were analyzed via an improved Eschka method [125]. Specifically, ~30 mg sample was first mixed with ~50 mg Eschka flux (sodium carbonate and magnesium oxide, Sigma Aldrich, 00166) in a Pt crucible, then the mixture was covered by ~100 mg Eschka flux on the top. For Cl determination, it was heated in a Muffle furnace to 675 °C and hold the temperature for 2 hours. After that, the sample was dissolved in deionized water. The solution was then injected into an IC (model: Dionex ICS-1100) equipped with an IonPac AS22 fast analytical column for Cl analysis. While for S determination, it was heated in a Muffle furnace to 800 °C to achieve the complete
transformation of S, then the sample after ashing was dissolved and analyzed in IC as Cl determination.

3.3.3.3 Soot chemistry analysis

The chemistry analysis of size-segregated soot samples collected in various stages of DLPI was conducted in an element analyzer (model:PerkinElmer CHNSO 2400 Series II). As the quartz filter was used for soot collection and it was not possible to separate soot samples from the substrates for sample collection. Therefore, while the absolute contents of C, H, N, and O in soot samples could not be determined, the research achieved the determination of the H/C molar ratio (considered as an important factor for soot chemical characteristics [73-75, 77, 80, 89]) for the size-segregated soot sample.

3.3.3.4 Contents of extractives, structural carbohydrates, and lignin

The National Renewable Energy Laboratory (NREL) methods [126] were applied in this study to quantify the contents of extractives, structural carbohydrates, and lignin in biomass wood.

3.3.3.5 Mass-based particle size distribution in DLPI

The mass-based particle size distribution in this thesis was achieved by weighing the mass of size-segregated samples collected from each stage in DLPI. A Mettler MX5 microbalance (accuracy: 0.001 mg) was applied for weight determination.

#### 3.3.3.6 Contents of inorganic species

For quantification of major inorganic elements in this thesis including Na, K, Mg, Ca, Al, Si, Fe and P. Different analysis methods were applied. For determination of Na, K, Mg and Ca, samples were load into a Pt crucible for ashing in a Muffle furnace with the designed ashing program illustrated in Figure 3-8 and Figure 3-9. The residual ash with Pt crucible was then put into a Teflon vial for ash digestion by using a mixture of concentrated hydrofluoric acid (HF) and nitric acid (HNO<sub>3</sub>) with mass ratio of 1:1. After digestion at 120 °C for 12 h. The excessive acid was removed through evaporation and the residual samples were further dissolved in 0.02 M methanesulfonic acid (MSA) solution. The solution was quantified in an ion chromatography (IC, model: Nionex 3000). For Si, Al and Fe, sample loaded in a Pt crucible was ashed with the same method introduced above in a Muffle furnace. The ash was then mixed with X-ray flux (50 % lithium tetraborate and 50 % lithium metaborate) and the mass ratio of ash to X-ray flux were controlled at 1:30. The Pt crucible which contains the mixture was then covered with Pt lid and heated at 950 °C for 2 h for ash decomposition in a Muffle furnace. After cooling, the residual samples were dissolved in 2 % nitric acid solution with continuous stirring at 60 °C. After that, the solution was injected into an inductively coupled plasma optical emission spectrometry (ICP-OES, model: PerkinElmer Optima 8300) for quantification. For the content of total phosphorus (P), samples were directly digested by using concentrated HNO<sub>3</sub>/HF/H<sub>2</sub>O<sub>2</sub> mixture. Hydrogen peroxide was added here to enhance the oxidation capacity with nitric acid to break down organic matters including fatty components. Briefly, samples were loaded into a Teflon digestion vessel with mixture concentrated HNO3 and HF acid with mass ratio of 3:1. After being sealed with lid and holding temperature at 120 °C for 4 h. the

mixture was cooled and  $H_2O_2$  was added into the mixture with same amount as HF. The Teflon vessel was sealed again and heated at 120 °C for another 4h. After that, the lid was opened and the excessive liquid was evaporated at 120 °C. The residual sample in the vessel was re-dissolved in 2 % nitric acid solution and quantified in ICP-OES.

#### 3.4 Summary

This chapter introduces the methodology and analytical techniques. To achieve the objectives listed in Chapter 2, biomass, biomass components and biomass derived produces (i.e. bio-oil and biochar) were carefully selected and prepared. We used a DTF with a novel double-tube configuration to conduct high temperature rapid pyrolysis in a DTF. Various analytical methods were also applied for characterizing the feedstock and pyrolysis products.

### CHAPTER 4 CHARACTERIZATION OF SIZE-SEGREGATED SOOT FROM PINE WOOD PYROLYSIS IN A DROP TUBE FURNACE AT 1300 °C

#### 4.1 Introduction

Lignocellulosic biomass as a renewable resource plays an important role in future sustainable energy supply. Thermochemical processing of biomass (e.g. combustion and gasification) can produce soot that may have several important implications to process operations and environment as introduced in Chapter 2.

For solid fuels, precursors for soot formation during pyrolysis that is the first step of any solid fuel thermochemical processing are complex. For example, biomass consists of various components including cellulose, hemicellulose, lignin and some mineral matter and extractives [127]. At high temperature (i.e. >1000 °C), experiments on the pyrolysis of solid fuels (e.g. biomass) were typically conducted in DTFs. Under such conditions, various components in biomass experience complex reactions, part of which lead to soot formation [71, 112, 113, 128, 129].

As introduced in section 3.2.1. The traditional sampling systems have at least two drawbacks that may have significant impact on the determination of soot yield and the characteristics of collected soot samples. Therefore, the key objective in this chapter is to deploy a DLPI for collecting size-segregated soot samples from pine wood pyrolysis at 1300 °C in a DTF and to characterize chemical compositions, occurrence of inorganic species, and nanostructure of the size-segregated soot samples. The properties of the pine wood sample are listed in Table 4-1, including

proximate and ultimate analyses, concentrations of major elements, and contents of structural carbohydrates, extractive, and lignin.

Proximate Analysis (wt % db <sup>b</sup> )         Ash       0.41         Volatile Matter       90.22         Fixed Carbon       9.37         Ultimate analysis (wt % daf°)       47.95         L       C       47.95         H       6.53       0.08         O <sup>d</sup> 45.44         Major Elements (mg/kg, db <sup>b</sup> )       41.03 ± 6.49         Fe       29.18 ± 0.20         Si       399.26 ± 142.69         K       575.44 ± 2.17         Mg       213.84 ±10.12         Na       164.90 ± 16.29         Ca       617.41 ± 39.64         P       38.90 ± 6.65         Cl       28.42 ± 2.57         S       n.d.         Contents of Structure Carbohydrates (wt % db <sup>b</sup> )       20.02         Arabinan       1.41         Galactan       2.16         Glucan       3.40         Xylan       4.31         Manan       8.74         Cellulose       37.85	Moisture (wt % ad <sup>a</sup> )	0.56
Ash         0.41           Volatile Matter         90.22           Fixed Carbon         9.37           Ultimate analysis (wt % daf°)            C         47.95           H         6.53           N         0.08           O <sup>d</sup> 45.44           Major Elements (mg/kg, db <sup>b</sup> )            Al         41.03 ± 6.49           Fe         29.18 ± 0.20           Si         399.26 ± 142.69           K         575.44 ± 2.17           Mg         213.84 ±10.12           Na         164.90 ± 16.29           Ca         617.41 ± 39.64           P         38.90 ± 6.65           Cl         28.42 ± 2.57           S         n.d.           Contents of Structure Carbohydrates (wt % db <sup>b</sup> )            Extractives         5.35           Hemicellulose         20.02           Arabinan         1.41           Galactan         2.16           Glucan         3.40           Xylan         4.31           Manan         8.74           Cellulose         37.85	Proximate Analysis (wt % db <sup>b</sup> )	
Volatile Matter       90.22         Fixed Carbon       9.37         Ultimate analysis (wt % daf°) $         C       47.95         H       6.53         N       0.08         Od       45.44         Major Elements (mg/kg, dbb)                Al       41.03 ± 6.49         Fe       29.18 ± 0.20         Si       399.26 ± 142.69         K       575.44 ± 2.17         Mg       213.84 ±10.12         Na       164.90 ± 16.29         Ca       617.41 ± 39.64         P       38.90 ± 6.65         Cl       28.42 ± 2.57         S       n.d.         Contents of Structure Carbohydrates (wt % dbb)                Extractives       5.35         Hemicellulose       20.02         Arabinan       1.41         Galactan       2.16         Glucan       3.40         Xylan       4.31         Manan       8.74         Cellulose       37.85   $	Ash	0.41
Fixed Carbon9.37Ultimate analysis (wt % daf°)CC47.95H6.53N0.08O <sup>d</sup> 45.44Major Elements (mg/kg, db <sup>b</sup> )41.03 $\pm$ 6.49Fe29.18 $\pm$ 0.20Si399.26 $\pm$ 142.69K575.44 $\pm$ 2.17Mg213.84 $\pm$ 10.12Na164.90 $\pm$ 16.29Ca617.41 $\pm$ 39.64P38.90 $\pm$ 6.65Cl28.42 $\pm$ 2.57Sn.d.Contents of Structure Carbohydrates (wt % db <sup>b</sup> )Extractives5.35Hemicellulose20.02Arabinan1.41Galactan2.16Glucan3.40Xylan4.31Manan8.74Cellulose37.85	Volatile Matter	90.22
Ultimate analysis (wt % daf*)C47.95H6.53N0.08Od45.44Major Elements (mg/kg, db <sup>b</sup> )41.03 $\pm$ 6.49Fe29.18 $\pm$ 0.20Si399.26 $\pm$ 142.69K575.44 $\pm$ 2.17Mg213.84 $\pm$ 10.12Mg213.84 $\pm$ 10.12Na164.90 $\pm$ 16.29Ca617.41 $\pm$ 39.64P38.90 $\pm$ 6.65Cl28.42 $\pm$ 2.57Snd.Contents of Structure Carbohydrates (wt % db <sup>b</sup> )Extractives5.35Hemicellulose20.02Arabinan1.41Galactan2.16Glucan3.40Xylan4.31Manan8.74Cellulose37.85	Fixed Carbon	9.37
C47.95H $6.53$ N $0.08$ $O^d$ $45.44$ Major Elements (mg/kg, db <sup>b</sup> ) $1103 \pm 6.49$ Fe $29.18 \pm 0.20$ Si $399.26 \pm 142.69$ K $575.44 \pm 2.17$ Mg $213.84 \pm 10.12$ Na $164.90 \pm 16.29$ Ca $617.41 \pm 39.64$ P $38.90 \pm 6.65$ Cl $28.42 \pm 2.57$ Sn.d.Contents of Structure Carbohydrates (wt % db <sup>b</sup> )Extractives $5.35$ Hemicellulose $20.02$ Arabinan $1.41$ Galactan $2.16$ Glucan $3.40$ Xylan $4.31$ Manan $8.74$ Cellulose $37.85$	Ultimate analysis (wt % daf <sup>c</sup> )	
H $6.53$ N $0.08$ Od $45.44$ Major Elements (mg/kg, db <sup>b</sup> ) $41.03 \pm 6.49$ Fe $29.18 \pm 0.20$ Si $399.26 \pm 142.69$ K $575.44 \pm 2.17$ Mg $213.84 \pm 10.12$ Na $164.90 \pm 16.29$ Ca $617.41 \pm 39.64$ P $38.90 \pm 6.65$ Cl $28.42 \pm 2.57$ Sn.d.Contents of Structure Carbohydrates (wt % db <sup>b</sup> )Extractives $5.35$ Hemicellulose $20.02$ Arabinan $1.41$ Galactan $2.16$ Glucan $3.40$ Xylan $4.31$ Manan $8.74$ Cellulose $37.85$	С	47.95
N $0.08$ $O^d$ $45.44$ Major Elements (mg/kg, db <sup>b</sup> )Al $41.03 \pm 6.49$ Fe $29.18 \pm 0.20$ Si $399.26 \pm 142.69$ K $575.44 \pm 2.17$ Mg $213.84 \pm 10.12$ Na $164.90 \pm 16.29$ Ca $617.41 \pm 39.64$ P $38.90 \pm 6.65$ Cl $28.42 \pm 2.57$ Sn.d.Contents of Structure Carbohydrates (wt % db <sup>b</sup> )Extractives $5.35$ Hemicellulose $20.02$ Arabinan $1.41$ Galactan $2.16$ Glucan $3.40$ Xylan $4.31$ Manan $8.74$ Cellulose $37.85$	Н	6.53
Od         45.44           Major Elements (mg/kg, db <sup>b</sup> )         41.03 ± 6.49           Al         41.03 ± 6.49           Fe         29.18 ± 0.20           Si         399.26 ± 142.69           K         575.44 ± 2.17           Mg         213.84 ±10.12           Mg         213.84 ±10.12           Na         164.90 ± 16.29           Ca         617.41 ± 39.64           P         38.90 ± 6.65           Cl         28.42 ± 2.57           S         n.d.           Contents of Structure Carbohydrates (wt % db <sup>b</sup> )         1.41           Galactan         2.16           Ghucan         3.40           Xylan         4.31           Manan         8.74           Cellulose         37.85	Ν	0.08
Major Elements (mg/kg, dbb)Al $41.03 \pm 6.49$ Fe $29.18 \pm 0.20$ Si $399.26 \pm 142.69$ K $575.44 \pm 2.17$ Mg $213.84 \pm 10.12$ Na $164.90 \pm 16.29$ Ca $617.41 \pm 39.64$ P $38.90 \pm 6.65$ Cl $28.42 \pm 2.57$ Sn.d.Contents of Structure Carbohydrates (wt % dbb)Extractives $5.35$ Hemicellulose $20.02$ Arabinan $1.41$ Galactan $2.16$ Glucan $3.40$ Xylan $4.31$ Manan $8.74$ Cellulose $37.85$	$O^d$	45.44
Al $41.03 \pm 6.49$ Fe $29.18 \pm 0.20$ Si $399.26 \pm 142.69$ K $575.44 \pm 2.17$ Mg $213.84 \pm 10.12$ Na $164.90 \pm 16.29$ Ca $617.41 \pm 39.64$ P $38.90 \pm 6.65$ Cl $28.42 \pm 2.57$ Sn.d.Contents of Structure Carbohydrates (wt % db <sup>b</sup> )Extractives $5.35$ Hemicellulose $20.02$ Arabinan $1.41$ Galactan $2.16$ Glucan $3.40$ Xylan $4.31$ Manan $8.74$ Cellulose $37.85$	Major Elements (mg/kg, db <sup>b</sup> )	
Fe $29.18 \pm 0.20$ Si $399.26 \pm 142.69$ K $575.44 \pm 2.17$ Mg $213.84 \pm 10.12$ Na $164.90 \pm 16.29$ Ca $617.41 \pm 39.64$ P $38.90 \pm 6.65$ Cl $28.42 \pm 2.57$ Sn.d.Contents of Structure Carbohydrates (wt % db <sup>b</sup> )Extractives $5.35$ Hemicellulose $20.02$ Arabinan $1.41$ Galactan $2.16$ Glucan $3.40$ Xylan $4.31$ Manan $8.74$ Cellulose $37.85$	Al	$41.03\pm6.49$
Si $399.26 \pm 142.69$ K $575.44 \pm 2.17$ Mg $213.84 \pm 10.12$ Na $164.90 \pm 16.29$ Ca $617.41 \pm 39.64$ P $38.90 \pm 6.65$ Cl $28.42 \pm 2.57$ Sn.d.Contents of Structure Carbohydrates (wt % db <sup>b</sup> )Extractives $5.35$ Hemicellulose $20.02$ Arabinan $1.41$ Galactan $2.16$ Glucan $3.40$ Xylan $4.31$ Manan $8.74$ Cellulose $37.85$	Fe	$29.18\pm0.20$
K $575.44 \pm 2.17$ Mg $213.84 \pm 10.12$ Na $164.90 \pm 16.29$ Ca $617.41 \pm 39.64$ P $38.90 \pm 6.65$ Cl $28.42 \pm 2.57$ Sn.d.Contents of Structure Carbohydrates (wt % db <sup>b</sup> )Extractives $5.35$ Hemicellulose $20.02$ Arabinan $1.41$ Galactan $2.16$ Glucan $3.40$ Xylan $4.31$ Manan $8.74$ Cellulose $37.85$	Si	$399.26 \pm 142.69$
Mg $213.84 \pm 10.12$ Na $164.90 \pm 16.29$ Ca $617.41 \pm 39.64$ P $38.90 \pm 6.65$ Cl $28.42 \pm 2.57$ Sn.d.Contents of Structure Carbohydrates (wt % db <sup>b</sup> )Extractives $5.35$ Hemicellulose $20.02$ Arabinan $1.41$ Galactan $2.16$ Glucan $3.40$ Xylan $4.31$ Manan $8.74$ Cellulose $37.85$	K	$575.44\pm2.17$
Na $164.90 \pm 16.29$ Ca $617.41 \pm 39.64$ P $38.90 \pm 6.65$ Cl $28.42 \pm 2.57$ Sn.d.Contents of Structure Carbohydrates (wt % db <sup>b</sup> )Extractives $5.35$ Hemicellulose $20.02$ Arabinan $1.41$ Galactan $2.16$ Glucan $3.40$ Xylan $4.31$ Manan $8.74$ Cellulose $37.85$	Mg	$213.84 \pm 10.12$
Ca $617.41 \pm 39.64$ P $38.90 \pm 6.65$ Cl $28.42 \pm 2.57$ Sn.d.Contents of Structure Carbohydrates (wt % db <sup>b</sup> )ExtractivesS $5.35$ Hemicellulose $20.02$ Arabinan $1.41$ Galactan $2.16$ Glucan $3.40$ Xylan $4.31$ Manan $8.74$ Cellulose $37.85$	Na	$164.90 \pm 16.29$
P $38.90 \pm 6.65$ Cl $28.42 \pm 2.57$ S       n.d.         Contents of Structure Carbohydrates (wt % db <sup>b</sup> ) $5.35$ Extractives $5.35$ Hemicellulose $20.02$ Arabinan $1.41$ Galactan $2.16$ Glucan $3.40$ Xylan $4.31$ Manan $8.74$ Cellulose $37.85$	Ca	$617.41 \pm 39.64$
Cl $28.42 \pm 2.57$ S       n.d.         Contents of Structure Carbohydrates (wt % db <sup>b</sup> )         Extractives $5.35$ Hemicellulose $20.02$ Arabinan $1.41$ Galactan $2.16$ Glucan $3.40$ Xylan $4.31$ Manan $8.74$ Cellulose $37.85$	Р	$38.90\pm 6.65$
Sn.d.Contents of Structure Carbohydrates (wt % db <sup>b</sup> )Extractives5.35Hemicellulose20.02Arabinan1.41Galactan2.16Glucan3.40Xylan4.31Manan8.74Cellulose37.85	Cl	$28.42 \pm 2.57$
Contents of Structure Carbohydrates (wt % db <sup>b</sup> )Extractives5.35Hemicellulose20.02Arabinan1.41Galactan2.16Glucan3.40Xylan4.31Manan8.74Cellulose37.85	S	n.d.
Extractives5.35Hemicellulose20.02Arabinan1.41Galactan2.16Glucan3.40Xylan4.31Manan8.74Cellulose37.85	Contents of Structure Carbohydrates (w	vt % db <sup>b</sup> )
Hemicellulose20.02Arabinan1.41Galactan2.16Glucan3.40Xylan4.31Manan8.74Cellulose37.85	Extractives	5.35
Arabinan1.41Galactan2.16Glucan3.40Xylan4.31Manan8.74Cellulose37.85	Hemicellulose	20.02
Galactan2.16Glucan3.40Xylan4.31Manan8.74Cellulose37.85	Arabinan	1.41
Glucan3.40Xylan4.31Manan8.74Cellulose37.85	Galactan	2.16
Xylan4.31Manan8.74Cellulose37.85	Glucan	3.40
Manan8.74Cellulose37.85	Xylan	4.31
Cellulose 37.85	Manan	8.74
	Cellulose	37.85

Table 4-1 Properties of pine wood used in this study

53 | P a g e

Lignin	36.78	
Acid-soluble lignin <sup>d</sup>	11.57	
Acid-insoluble lignin	25.21	

 $ad^a = air dried. db^b = dry basis. daf^c = dry and ash free. <sup>d</sup> By difference. n.d.=non$ detected

#### 4.2 Optimized conditions for size-segregated CM<sub>10</sub> collection

Overloading of CM samples on DLPI stages can seriously distort the PSDs of the CM<sub>10</sub> collected from pine wood pyrolysis in the DTF. Therefore, this study carried out a series of experiments to determine the optimal conditions for size-segregated CM<sub>10</sub> collection. The results are presented in Figure 4-1, with two important observations. One is that the PSDs of the CM<sub>10</sub> collected from pine wood pyrolysis clearly show the collected CM<sub>10</sub> consists of predominantly CM<sub>1</sub>. The other is that the PSDs of  $CM_{10}$  samples collected from DTF experiments are strongly dependent on the total amount of pine wood sample fed into the DTF in an experiment. Increasing the total feeding amount from 70 mg to 150 mg, there is no change in the PSD of the CM<sub>10</sub> collected from the DTF. However, a further increase in the total feeding amount from 150 mg to 350 mg (or 400 mg) results in a significant shift in the PSD of the CM<sub>10</sub> towards considerably larger sizes, accompanied with a significant shift of mode diameter from 0.077 µm to 0.246 µm. This clearly demonstrates that at least a portion of the CM with smaller aerodynamic diameters was collected and classified as CM of larger aerodynamic diameters as a result of the sample overloading on the impactor stages. When an impactor stage is overloaded, some particles may bounced off the impactor stage and adhere to the bottom of the stage jet plate, leading to partial blockage of the jet nozzle. This consequently affects the pressure drop and jet velocity profiles across the impactor

stages of the DLPI. A higher jet velocity due to partial blockage of the jet nozzle lead to particles of smaller aerodynamic sizes impacted, collected and classified as particles of larger aerodynamic sizes. Therefore, the experimental results in Figure 4-1 thus far demonstrate that when the total amount of sample fed into the reactor in each experiment is 150 mg or less, effective size segregation and collection of  $CM_{10}$ from pine wood pyrolysis can be achieved via the DLPI used in this study. Therefore, a total biomass wood sample feeding size of <150 mg used in all experiments in this chapter, with each experiment being conducted in at least triplicate.



Figure 4-1: PSDs of the CM<sub>10</sub> from pyrolysis of pine wood at 1300 °C with sample size of 70, 150, 350 and 400 mg.

# 4.3 PSD and yields of size-segregated CM and soot collected from pine wood pyrolysis

Figure 4-2 presents the PSD and yields of  $CM_{10}$  from pine wood pyrolysis at 1300 °C. The PSD (see Figure 4-2a) of the  $CM_{10}$  has a unimodal distribution with a fine mode of 0.077 µm. Figure 4-2b further shows that on a mass basis the  $CM_{10}$  is primarily  $CM_1$ , which accounts for >98 % of the  $CM_{10}$ , and contains little  $CM_{1-10}$  that only contributes to <2 % of the CM<sub>10</sub>. The CM samples collected from various impactor stages were then subjected to SEM characterization. Figure 4-3 illustrates the morphologies of the fine particulates in CM<sub>1-10</sub> and CM<sub>1</sub>, respectively. It can be seen in Figure 4-3a that the fine particulate particles in the CM<sub>1-10</sub>, represented by CMs collected from the impactor stage of aerodynamic diameter of 6.863 µm, have irregular shapes with sharp edges and are clearly fine char fragments. Further magnification of the particle (see Figure 4-3a1) illustrates that part of the particle surface is covered with some smooth spherical particles with individual particle diameter in tens of nanometres, indicating some of the soot particles formed during pyrolysis deposited on fine char fragments. The observed soot particles are in the form of clusters and chains. The panels b-d of Figure 4-3 further show that the CM<sub>1</sub> from pine wood pyrolysis, represented by CM collected from the impactor stages of aerodynamic diameters of 0.612, 0.077 and 0.011 µm, respectively, are soot and no char fragment can be observed. For large soot particles shown in Figure 4-3b (0.612  $\mu$ m) and 3c (0.077  $\mu$ m), the soot particles with a range of diameter agglomerate and coagulate to form soot clusters. However, for small soot particles shown in Figure 4-3d (0.011  $\mu$ m), those are individual soot particles <20 nm with negligible agglomeration and coagulation. While it is not surprising to see fine char fragments in CM<sub>10</sub> because those can be produced from the fragmentation of pyrolysing fuel particles (as also reported during coal pyrolysis in DTF [130]), it is interesting to see that fine char fragments are only present in  $CM_{1-10}$  and  $CM_1$  consists of soot, and the yield of soot (i.e.  $CM_1$ ) is 39.6 mg/g pine wood.



Figure 4-2: (a) PSD and (b) yields of  $CM_{10}$  from pyrolysis of pine wood at 1300 °C



Figure 4-3 Micromorphology of CM sample from pyrolysis of pine wood with aerodynamic diameters of (a) 6.863  $\mu$ m, (b) 0.612  $\mu$ m, (c) 0.077  $\mu$ m and (d) 0.011  $\mu$ m. Panel (a1) is the zoom in picture from (a).

#### 4.4 Chemistry of size-segregated soot collected from pine wood pyrolysis

To further understand the chemistry of soot samples, elemental analysis (C, H and N) of the size-segregated soot samples (i.e. CM<sub>1</sub>) was conducted. Because the

amounts of samples collected in various stages of DLPI were small (less than 1 mg), it was not possible to separate soot samples from the substrates for sample collection. Therefore, while the absolute contents of C, H, N and O in soot samples could not be determined, this study achieved the determination of the H/C molar ratio (considered as an important factor for soot chemical characteristics [73-75, 77, 80, 89]) for the segregated soot sample on a DLPI stage.

The H/C molar ratios of soot samples are presented in Figure 4-4. It shows that there is a substantial reduction in the soot H/C molar ratio from ~0.65 to ~0.15 as the size of soot increases from 0.011 to 0.022  $\mu$ m while the soot H/C molar ratio then plateaus at ~0.1 with further increase in soot size. It is known that the soot H/C molar ratio ranges from 0.4 to 0.7 in the inception stages and decreases during the growth to the range of 0.05–0.1 for mature soot [73-75, 77, 80, 89]. This is mainly due to the HACA mechanism during soot formation.[71] Therefore, the collected soot sample in the impact stage of size 0.011  $\mu$ m and 0.022  $\mu$ m is non-mature soot while those in the impact stages of larger sizes are mature soot. The plateaued H/C molar ratio in these larger impact stages of 0.043  $\mu$ m or larger shows no significant variation in the carbon structure of these soot. The results thus far also demonstrate that DLPI is able to segregate and collect soot particles with different growth stages, from non-mature soot particles to mature soot clusters.



Figure 4-4: H/C molar ratio of size-segregated soot (i.e.  $CM_1$ ) from pine wood pyrolysis in DTF at 1300 °C

#### 4.5 Inorganic species in size-segregated soot collected from pine wood pyrolysis

As shown in Table 4-1, the pine wood sample also contains abundant inorganic species. These inorganic species may be present in the form of salts or organically bonded to biomass [131]. Some of these inorganic species such as Na, K and Cl are known to be volatilised during pyrolysis [132] and released in the form of alkali metal, chlorides, hydroxides or HCl [133]. These vaporised inorganic species may be released as part of soot or interact with the soot formed during pyrolysis. As soot is predominantly present in CM<sub>1</sub> (see Figure 4-2), the inorganic species in the soot samples collected from various impactor stages for soot were then quantified, with the results presented in Figure 4-5. The PSDs of inorganic species in soot samples clearly demonstrate that Na, K and Cl are the major inorganic elements in soot and furthermore show that all elemental PSDs have a unimodal distribution with the same mode diameter of 0.077  $\mu$ m. There are little Mg, Ca, Al, P, Fe and Si present in soot because these elements form refractory compounds hence do not volatilise

during pyrolysis [134-136]. The results in Figure 4-6 further shows that the yields of Na, K and Cl in soot are ~0.03, ~0.04 and ~0.015 mg/g pine wood, respectively. Cumulatively, the total yield of these major inorganic elements accounts for only ~0.2 % of the total soot yield.



Figure 4-5: PSDs of major elements in size-segregated soot (i.e. CM1) from pine wood pyrolysis in DTF at 1300 °C



Figure 4-6 Yields of Na, K and Cl and water-soluble Na and K in size-segregated soot (i.e. CM<sub>1</sub>) from pine wood pyrolysis in DTF at 1300 °C.

Further efforts were then made to determine the (Na+K)/Cl molar ratio of sizesegregated soot samples collected on various impactor stages, with the results presented in Figure 4-7. It can be seen that (Na+K)/Cl molar ratios far exceeds 1 for all size-segregated soot samples. A (Na+K)/Cl molar ratio of >1 indicates at least part of Na and K in the soot samples are present in the forms of alkali salts or organically bonded to soot, other than in the form of water-soluble NaCl and KCl. In addition, the (Na+K)/Cl molar ratio increases from ~3.2 to ~6.0 as soot size increases from 0.011  $\mu$ m to 0.043  $\mu$ m then levelled at ~6.0 with further increase in the soot size. The results indicate that there are higher proportions of Na and K in soot with aerodynamic diameter of 0.011 µm being present in the form of chlorides. Figure 4-8 further shows that the contents of Na, K and Cl in size-segregated soot samples are low (in the range of 0.03–1.26 % for Na, 0.04–0.60 % for K and 0.02– 0.79 % for Cl, respectively). But it should be noted that while the yield of the finest soot (0.011 µm) is the lowest, the contents of Na, K and Cl are the highest (1.26%, 0.60% and 0.79%, respectively). As soot size increases to 0.043  $\mu$ m, the content of Na, K and Cl of soot decreases substantially to ~0.1%, ~0.1% and 0.05%,

respectively. Therefore, the finest soot has the highest contents of inorganic species (i.e. Na, K and Cl) and the lowest (Na+K)/Cl molar ratio (~3). Such results indicate that the presence of these inorganic species in fine soot can be due to either the heterogeneous condensation of NaCl and KCl on soot particles or the formation fine particulates as a result of homogeneous condensation of NaCl and KCl.



Figure 4-7 Dependence of (Na + K)/Cl molar ratio on the size of size-segregated soot (i.e.  $CM_1$ ) from pine wood pyrolysis in DTF at 1300 °C



Figure 4-8 Contents of Na (a), K (b) and Cl (c) in size-segregated soot (i.e. CM<sub>1</sub>) collected on each impactor stage, expressed as % of total mass on each impactor stage.

To further investigate the form of non-chlorine bond Na and K in soot, the sizesegregated soot samples were subjected to water leaching because the Na and K organically bonded to soot are water-insoluble. The yields of water-soluble Na, K and Cl in soot are presented in Figure 4-6. While ~85 % of Na in soot is water-soluble, only ~12 % of K in soot is water-soluble. Figure 4-9 further presents the distributions and contents of water-soluble and water-insoluble Na and K in the size-segregated soot samples. The majorities (1.2 % and 0.5 %, respectively) of the Na and K in the soot with an aerodynamic diameter of 0.011  $\mu$ m are water-soluble. The percentages of water-insoluble Na and K decrease with increasing soot size. This is further clearly shown in the panels c and d of Figure 4-9 which plots the distribution of water-soluble and water-insoluble Na or K in each impactor stages. It can be seen that ~95 % to the total Na in the soot with aerodynamic diameter of 0.011  $\mu m$  is water-soluble and decreases slightly to ~80 % as the soot aerodynamic diameter increases to 0.043  $\mu$ m. Overall, although only ~12% of K in the soot (i.e. CM<sub>1</sub>) is water-soluble, ~77 % of K in soot with aerodynamic diameter of 0.011 µm are watersoluble but decrease sharply to  $\sim 10$  % as aerodynamic diameter increases to 0.043 um and levels off with further increasing soot size. Such observations lead to several important findings. First, it can be seen that soot incorporates preferentially with K over Na to form organic bond as the contents of the water-insoluble K is considerably higher than those of water-insoluble Na. The fraction of total K being water-insoluble is also higher than that of Na in each size-segregated soot sample. This might due to K being more electropositive than Na, has a higher tendency to form intercalation compounds with soot [137-139]. Second, there are more Na and K incorporate with non-mature soot (with sizes of 0.011 µm and 0.022 µm, see section 4.4) to form organic bond than those with mature soot because the contents of water-insoluble Na and K are comparatively higher in incipient soot (see Figure 4-9). It is known that non-mature soot is more disordered than mature soot [69] thus more likely to interact with alkalis. Thirdly, the levelled trends in the contents of water-soluble alkalis in size-segregated soot samples with sizes  $\geq 0.043 \ \mu m$  (see Figure 4-9a) suggest that the majorities of the water-soluble Na and K may deposited on the soot particles through heterogeneous condensation as the soot and flue gas cooled during sampling. This is reasonable because the soot agglomerate is a collection of loosely connected soot particles [69], thus the specific surface area of the soot available for heterogeneous condensation of alkali species is similar in large sized segregated soot samples (agglomeration stage). On the other hand, a higher proportion of water-soluble Na and K in the soot samples of 0.011 and 0.022 µm may be more likely due to the formation of ultrafine inorganic particulate matter

from the homogeneous condensation of alkali species.



Figure 4-9 Contents and distribution of water-soluble and water-insoluble Na and K in size-segregated soot sample collected on various impactor stages during pine wood pyrolysis in DTF at 1300 °C. Panel (a) and (b): contents of water-soluble (a) and water-insoluble (b) Na and K; Panel (c) and (d): distribution of water-soluble and water-insoluble Na (c) and K (d) in each impactor stage, expressed as the

percentage of respective total Na or K.

#### 4.6 Nanostructure analysis of soot from pine wood pyrolysis

As from micro morphology analysis, the soot collected from one stage could have a wide range of diameters. An example of the TEM micrograph of one size-segregated soot sample (on the stage with an aerodynamic diameter of 0.077  $\mu$ m) is shown in Figure 4-10, which shows clear fringes in soot particles. The soot has an inner core with irregular structures (Figure 4-10b), which corresponds to the incipient soot in

early stage of soot growth. The core is surrounded with regular shells (Figure 4-10c) as the gas phase species attached on the soot surface and formed regular structure during soot growth. Figure 4-10d presents the coagulation between a small soot (11 nm) and a large soot (40 nm).



Figure 4-10 TEM micrographs of soot (on the stage with aerodynamic diameter 0.077 μm) from pine wood pyrolysis in DTF at 1300 °C. Panels (b)-(d) are the zoom-in images of panel (a)

Figure 4-11 presents the quantified soot nanostructures, including fringe length,

fringe tortuosity and layer spacing. It is noted that fringe length refers to the average length of lattice lines observed in soot; fringe tortuosity refers to the ratio of the distance between fringe end points to the fringe length; and layer spacing is the mean distance between adjacent fringes. While the standard errors are large, the average values of these structural parameters do present some broad trends. It can be seen in Figure 4-11a that the average soot fringe length increases slightly from 0.942 nm to 1.023 nm as the soot size increases from 10-20 nm to 80-90 nm. Similarly, the average soot fringe tortuosity (see Figure 4-11b) also follows a similar trend and increases from 0.849 to 0.891 as the soot size increases from 10-20 nm to 80-90 nm. As shown in Figure 4-11c, the average soot layer spacing broadly remains unchanged (around 0.342 nm). Overall, the results in Figure 4-11 indicate that during soot growth, the soot fringe has a slow trend of becoming longer and straighter. This is reasonable because incipient soot is more disordered than mature soot so that when soot becomes mature (large), the soot fine structures could become more ordered [69].



Figure 4-11 Nanostructural parameters including fringe length (a), fringe tortuosity
(b) and fringe layer spacing (c) of size-segregated soot (i.e. CM<sub>1</sub>) from pine wood
pyrolysis in DTF at 1300 °C

#### 4.7 Conclusions

This chapter shows a DLPI can be used for segregated collection of soot from pyrolysis of pine wood at 1300 °C in a DTF. The optimum biomass wood sample feeding amount was identified to be <150 mg for effective aerodynamic separation

of soot. The  $CM_{10}$  from pyrolysis of pine wood is mainly  $CM_1$  (>98%) and has a unimodal distribution with a fine mode of 0.077 µm. Micromorphology analysis shows CM<sub>1-10</sub> mainly consists of char fragments while CM<sub>1</sub> only consists of soot. In CM<sub>1</sub>, segregated soot with aerodynamic diameter 0.011 µm and 0.022 µm has a high H/C molar ratio of >0.1, indicating that it is mainly non-mature soot. The H/C molar ratio drop sharply then levelled off with further increase in aerodynamic diameter. This demonstrates that the segregated soot with larger aerodynamic size is mature soot. The inorganic species in soot (i.e. CM<sub>1</sub>) are primarily Na, K and Cl. The results further suggest that K is more likely to incorporate with soot to form organic bond than Na. Moreover, non-mature soot contains more organic bonded Na and K than mature soot does. The water-soluble inorganic species present in soot mainly due to the condensation of alkali salts during cooling of flue gas. Water-soluble alkali species in soot could form ultrafine ash particle resultant from homogeneous condensation of alkali species, or deposited on the soot particles through heterogeneous condensation. Quantitative analysis of soot structure shows that there are slight increases in fringe length and fringe tortuosity during soot growth.

## CHAPTER 5 MECHANISTIC INSIGHTS INTO EFFECT OF FEEDING RATE ON SOOT FORMATION DURING RAPID PYROLYSIS OF BIOMASS MODEL COMPONENTS IN A DROP-TUBE FURNACE AT HIGH TEMPERATURE

#### **5.1 Introduction**

Biomass is an important renewable energy source that contributes to addressing the global energy and environment problems. Stationary applications (e.g. combustion) using biomass as a fuel are important technical pathways for biomass utilization. Soot formation is inevitable during such combustion processes that typically operated at temperatures  $\geq$ 1300 °C [140].

As biomass particles are injected into a combustor, the first step of the reactions is rapid pyrolysis. Therefore, it is of critical importance to understand the fundamental mechanisms governing soot formation during biomass pyrolysis. Soot formation during biomass pyrolysis is expected to be complex because biomass consists of three key components (i.e., hemicellulose, cellulose and lignin). The formation of soot in gaseous phase requires the formation of polycyclic aromatic hydrocarbons (PAHs), which are soot precursors. As illustrated in Chapter 2, during pyrolysis of solid fuels such as biomass, two distinct mechanisms are proposed to be responsible for the formation of PAHs [70, 71]. One is that the formation of PAHs via the pathway from small molecules like C<sub>2</sub>H<sub>2</sub> that can be produced from the thermal cracking of hemicellulose and cellulose [141, 142]. The other is the formation of PAHs from the phenolic and aromatic compounds produced from lignin thermal cracking [143, 144].

During biomass pyrolysis, the feeding rate of feedstock is likely to have significant effect on soot formation and properties. Such effect may also be highly dependent on the biomass components such as cellulose and lignin. Surprisingly, from the literature review, there has been little research dedicated to understanding the effect of feeding rate on soot formation and properties during rapid pyrolysis of biomass model compounds under high-temperature conditions pertinent to stationary applications. Furthermore, in chapter 4 we developed a new method achieving separation of soot and fine char fragments and sampling size-segregated soot from rapid pyrolysis of biomass at high temperature (i.e. 1300 °C). Conventional investigation into soot agglomeration usually relies on analysis of missing important information when analysing three-dimensional soot clusters due to overlapping effect [145, 146]. The new method for sampling size-segregated soot enables size-segregated soot analysis, paving a new perspective for characterizing soot clusters and investigating soot agglomeration.

Consequently, this chapter reports the effect of feeding rate on soot formation during rapid pyrolysis of biomass model components under non-catalytic conditions. The experimental program considers two biomass model components, i.e., cellulose and lignin. Biomass model components such as cellulose and lignin typically contain alkali and alkaline earth metallic (AAEM) species such as K, Na, Mg and Ca (that are known to influence soot formation [147-149]). Therefore, as introduced in Chapter 3, Section 3.3.1, the cellulose and lignin samples used in this study were pre-treated to remove these catalytically active inorganic species. The properties of cellulose, lignin and water-washed lignin (Water-washed lignin was prepared from raw lignin by repeatedly washing using deionized water) are shown in Table 5-1 and

the properties of the W-cellulose and A-lignin samples used in this study are shown
in Table 5-2. PSDs of W-cellulose and A-lignin before pyrolysis in DTF are shown
in Figure 5-1.

Table 5-1 Properties of cellulose, lignin and water-washed lignin. The waterwashed lignin was prepared from raw lignin by repeatedly washing using deionized water.

Sample	Cellulose	Lignin	Water-washed lignin	
	Proximate analysis (wt.%, ad <sup>a</sup> )			
$M^b$	3.7	3.4	2.4	
ash	0.04	3.7	0.4	
VM <sup>c</sup>	91.3	65.2	61.8	
$FC^d$	5.0	27.7	35.4	
Ash compositional analysis (mg/kg, db <sup>e</sup> )				
Κ	$19.75\pm1.62$	$1255.46 \pm 1.99$	$120.00\pm8.00$	
Mg	$5.23\pm0.22$	$192.15\pm9.00$	$216.81 \pm 11.60$	
Na	$55.06 \pm 4.23$	$11567.10 \pm 148.17$	$484.17\pm30.63$	
Ca	Ca $5.28 \pm 0.54$ $106.77 \pm 15.63$ $117.62 \pm 7.18$			
<sup>a</sup> air o	<sup>a</sup> air dried. <sup>b</sup> moisture; <sup>c</sup> volatile matter; <sup>d</sup> fixed carbon; <sup>e</sup> dry basis.			

Table 5-2 Properties of the W-cellulose and A-lignin samples used in this study.

The W-cellulose sample was prepared from the raw cellulose by repeatedly washing using deionized water while the A-lignin sample was prepared from the raw lignin by acid-washing.

Samples	W-cellulose	A-lignin	
Proximate analysis (wt.%, ad <sup>a</sup> )			
$M^b$	3.2	2.2	
Ash	0.04	0.1	
VM <sup>c</sup>	90.3	63.9	
$FC^d$	6.5	33.8	

Ultimate analysis (wt.%, daf <sup>e</sup> )			
С	43.67	64.79	
Н	6.63	5.61	
Ν	0.00	0.23	
S	0.00	1.18	
$\mathbf{O}^{\mathrm{f}}$	49.70	28.19	
Ash compositional analysis (mg/kg, db <sup>g</sup> )			
Na	$5.48\pm0.87$	n.d.	
Κ	$13.78\pm0.18$	n.d.	
Mg	$2.71\pm0.04$	$58.29 \pm 1.54$	
Ca	$1.08\pm0.25$	$120.01\pm7.45$	
Al $27.09 \pm 0.54$ $152.74 \pm 2$		$152.74\pm2.41$	
Si $\frac{111.49 \pm}{22.50}$ $219.20 \pm 0.76$			
Fe	$14.59\pm3.66$	$43.52\pm0.54$	
Р	n.d. <sup>h</sup>	n.d.	
Cl n.d.		n.d.	
<sup>a</sup> air dried; <sup>b</sup> moisture; <sup>c</sup> volatile matter; <sup>d</sup>			
fixed carbon; <sup>e</sup> dry and ash free; <sup>f</sup> by			
difference; <sup>g</sup> dry basis; <sup>h</sup> not-detected.			



Figure 5-1. PSDs of W-cellulose and A-lignin before pyrolysis in DTF.

### 5.2 PSDs and yields of soot produced during pyrolysis of W-cellulose and Alignin at various feeding rates

Figure 5-2 presents the PSDs of CM collected during rapid pyrolysis of W-cellulose and A-lignin at different feeding rates. Micromorphology analysis was also carried out for  $CM_1$  using SEM and TEM. As shown in Figure 5-3 and Figure 5-4,  $CM_1$ samples are soot. The results in Figure 5-2 show that the CM<sub>10</sub> samples contain dominantly CM1 (i.e., soot), which contribute to close to 100% of CM10 for both Wcellulose and A-lignin at different feeding rates. For W-cellulose, the PSDs of soot samples have a unimodal distribution with a fine mode. The mode diameter increases from 0.043 to 0.246 µm as the W-cellulose feeding rate increases from 40 to 200 mg/min, and remains unchanged at 0.246  $\mu$ m with further increase at the feeding rate from 200 to 280 mg/min. However, for A-lignin, the PSDs of soot samples have a bimodal distribution with two fine mode diameters of 0.077 µm and 0.246 µm, respectively, at feeding rates of 12 - 200 mg/min. As the feeding rate further increases to 280 mg/min, the PSD of the soot sample exhibits a unimodal distribution with a fine mode diameter of 0.246 µm. Clearly, the feeding rate of feedstock affects the PSDs of soot samples from rapid pyrolysis of W-cellulose or A-lignin. An increase in feeding rate results in an increase in the mode diameter of soot. However, the extent of such effect decreases with the increasing feeding rate of feedstock.

Figure 5-5 presents the yields of soot samples produced from rapid pyrolysis of Wcellulose and A-lignin in DTF at 1300 °C at various feeding rates. The yields of soot from A-lignin pyrolysis are much higher than those from W-cellulose pyrolysis under the same conditions. It is because of the key differences in the chemical structures between W-cellulose and A-lignin. Cellulose is composed of polymers of glucose and could decompose into saccharides, acids, ketones and furans [141, 142], whereas lignin is formed of cross-linking of monolignols [143]. During rapid pyrolysis at such a high temperature, thermal cracking of cellulose produces small molecules like C<sub>2</sub>H<sub>2</sub> [141, 142], from which PAHs as soot precursors are formed via the kinetically-limited HACA mechanism [150, 151]. However, rapid pyrolysis of lignin releases abundant phenolic and aromatic compounds [144, 152], which can readily form PAHs as soot precursors.



Figure 5-2. PSDs of soot from rapid pyrolysis of (a) W-cellulose and (b) A-lignin with different feeding rates at 1300 °C.



Figure 5-3. Micromorphology analysis of pyrolysis products with aerodynamic diameter less than 1 μm from biomass model component pyrolysis at 1300 °C: (a) feeding rate: 40 mg/min W-cellulose, (b) feeding rate: 120 mg/min W-cellulose, (c) feeding rate: 280 mg/min W-cellulose, (d) feeding rate: 12 mg/min A-lignin, (e) feeding rate: 40 mg/min A-lignin, (f) feeding rate: 280 mg/min A-lignin.



Figure 5-4. TEM analysis of pyrolysis products with aerodynamic diameter less than 1 μm from biomass model component pyrolysis at 1300 °C: (a) feeding rate:
40 mg/min W-cellulose, (b) feeding rate: 120 mg/min W-cellulose, (c) feeding rate:
280 mg/min W-cellulose, (d) feeding rate: 12 mg/min A-lignin, (e) feeding rate: 40 mg/min A-lignin, (f) feeding rate: 280 mg/min A-lignin.



78 | P a g e

## Figure 5-5. Soot yields from rapid pyrolysis of W-cellulose and A-lignin with different feeding rates at 1300 °C.

As shown in Figure 5-5, during rapid pyrolysis of W-cellulose at 1300 °C, soot yield increases monotonically with feeding rate, from 6 mg/g at 40 mg/min to 24 mg/g at 280 mg/min. During fast pyrolysis of A-lignin at the same temperature, the soot yield also initially increases with feeding rate, from 75 mg/g at 12 mg/min to 105 mg/g at 40 mg/min. Such increases in soot yield with increasing feeding rate are understandable because a higher feeding rate leads to more feedstock being fed into the furnace per unit time, resulting in a higher concentration of soot-forming carbonaceous materials in gaseous phase for soot formation hence a higher soot yield.

However, Figure 5-5 also shows that during rapid pyrolysis of A-lignin at 1300 °C, as the feeding rate further increases from 40 to 280 mg/min, the soot yield remains largely unchanged. It is noteworthy that the results reported in Figure 5-5 are for soot samples collected from the DTF at a residence time of 0.75 s. As shown in Figure 5-6, the process of soot formation has largely completed at a residence time of < 0.6 s at 40 – 280 mg/min. As the soot yield in Figure 5-5 were obtained at a residence time of 0.75 s, soot formation under such conditions becomes limited by the availability of these soot-forming carbonaceous materials (including small gas molecules such as C<sub>2</sub>H<sub>2</sub>, and PAHs) in the gaseous phase. Further experiments were then carried out to quantify the yields of H<sub>2</sub> and the remaining amount of soot-forming carbonaceous materials in the gaseous phase include many small gas molecules such as C<sub>2</sub>H<sub>2</sub>, and PAHs. An indirect method was employed to determine the yield of total carbon in these species (denoted as *C<sub>soot-forming</sub>*) via

subtracting the yield of total carbon in CO and CO<sub>2</sub>, which are in the gas product but do not contribute to soot formation, from the yield of total carbon in the gas product. Experimentally, the yields of CO, CO<sub>2</sub> and also H<sub>2</sub> were directly measured while those of the total carbon in the gas product was quantified by combustion method. As shown in Figure 5-7, the yields of  $C_{soot-forming}$  become very low during A-lignin pyrolysis at feeding rates exceeding 40 mg/min so that the soot-forming carbonaceous materials in gaseous phase are largely depleted. Similar observations can also be made for W-cellulose pyrolysis at feeding rates exceeding 120 mg/min. Furthermore, it is known that soot formation involves C-H bond-breaking and C-C bond-formation, leading to the release of H<sub>2</sub> [75]. As shown in Figure 5-7, at feeding rates where soot yields plateaued, there is little additional production of H<sub>2</sub>, clearly indicating that the soot-forming carbonaceous materials in gaseous phase are largely consumed.



Figure 5-6. Soot yield during A-lignin pyrolysis at 1300 °C with different residence times.



Figure 5-7. Total carbon in remaining carbonaceous materials for soot forming (C<sub>soot-forming</sub>) and H<sub>2</sub> in gas product after rapid pyrolysis of (a) W-cellulose and (b) A-lignin.

# 5.3 Yields of non-mature soot from rapid pyrolysis of W-cellulose and A-lignin at various feeding rates

Figure 5-8 presents the H/C molar ratios of size-segregated soot samples with various aerodynamic diameters during rapid pyrolysis of W-cellulose and A-lignin at various feeding rates. The soot samples collected in the back filter and the first stage in DLPI have very small sizes of 11 nm and 22 nm, respectively. These soot

samples are non-mature soot because their H/C molar ratios (0.25 - 0.75) are higher than those of mature soot  $(0.05 - 0.1 \ [69])$ . Therefore, the yield of non-mature soot could be estimated via measuring the soot samples collected from these two stages (i.e. the back filter and the first stage) of the DLPI.



Figure 5-8. Chemical analysis of soot samples during pyrolysis of W-cellulose and A-lignin.



Figure 5-9. Non-mature soot yields from rapid pyrolysis of W-cellulose and Alignin with different feeding rates at 1300 °C.

Figure 5-9 presents the data on the yield of non-mature soot during rapid pyrolysis of W-cellulose and A-lignin in the DTF at various feeding rates. For W-cellulose pyrolysis, an increase in W-cellulose feeding rate from 40 to 280 mg/min results in a continuous decrease in the yield of non-mature soot. In contrast, during A-lignin pyrolysis, the yield of non-mature soot firstly decreases as the A-lignin feeding rate increases from 12 to 40 mg/min, reaches a minimum at 40 mg/min, then increases as the feeding rate further increases from 40 to 280 mg/min. It is well known that the growth of soot requires the essential supply of carbonaceous species such as C<sub>2</sub>H<sub>2</sub> or PAHs [103]. When the feeding rate increases from 40 to 280 mg/min for Wcellulose and from 12 to 40 mg/min for A-lignin, more small molecules (e.g. C<sub>2</sub>H<sub>2</sub>) and PAHs are generated per unit time. High concentrations of these species increase the possibility of collisions among these species and soot particles in the gaseous phase. Both surface growth and maturing process of soot are enhanced so that more non-mature soot particles grow into mature soot, leading a reduction in the yield of the non-mature soot. For A-lignin pyrolysis at feeding rates exceeding 40 mg/min, increasing feeding rate increases the concentrations of soot-forming carbonaceous materials in gases phase, resulting in an increase in the formation of incipient soot. Because the total amount of sample fed into the furnace remains constant at different feeding rates, more incipient soot formation would have consumed more soot-forming carbonaceous materials and left less of these species for soot growth. Therefore, a further increase in feeding rate results in an increase in the yield of non-mature soot during A-lignin pyrolysis.

### 5.4 Diameter distributions of individual soot particles from rapid pyrolysis of W-cellulose and A-lignin at various feeding rates

The PSDs of soot samples collected by DLPI, i.e., the results presented in Figure 5-2, are based on size segregation of soot samples via aerodynamic collection in DPLI. It reflects the mass size distribution of soot (mainly soot clusters) determined by the mass of soot samples collected in various stages of DLPI. However, it does not provide the information on the diameters of individual soot particles within those soot clusters because of soot coagulation and agglomeration. Further efforts were made to measure the sizes of individual soot particles, based on acquisition of images for soot samples using a TEM, followed by image analysis. Figure 5-10 presents the diameter distributions of individual soot particles during rapid pyrolysis of W-cellulose and A-lignin at various feeding rates. It can be seen in Figure 5-10 that the diameters of individual soot particles are < 100 nm. During rapid pyrolysis of W-cellulose, an increase in feeding rate from 40 to 120 then to 280 mg/min results in the size distribution of individual soot particles shifting to become larger. Interestingly, during rapid pyrolysis of A-lignin, the size distribution of individual soot particles shifting to become larger.
mg/min, then to become smaller when feeding rate further increases from 40 to 280 mg/min. As aforementioned, an increase in feeding rate (from 40 to 280 mg/min for W-cellulose and from 12 to 40 mg/min for A-lignin) enhances soot surface growth hence increases the diameter of soot particles. However, during rapid pyrolysis of A-lignin at feeding rates of 40 - 280 mg/min, there are insufficient supply of carbonaceous materials required for soot growth in the gaseous phase so that the size distribution of individual soot particles shifts to become smaller.



Figure 5-10. Diameter distribution of soot particles from rapid pyrolysis of Wcellulose and A-lignin with different feeding rates at 1300 °C.

### 5.5 Soot clusters from fast pyrolysis of W-cellulose and A-lignin at various

#### feeding rates

In addition to individual soot particles, there are also abundant soot clusters in the soot samples, as clearly observed in the TEM images. As aforementioned, the sizes determined by the DLPI stages only provide mass size distribution of the collected size-segregated soot samples. As shown in Figure 5-10, the sizes of most individual soot particles are less than 80 nm, considerably smaller than the corresponding size of soot collected in each DLPI stage where soot particles are mainly in form of soot clusters. Therefore, a higher mass reflects a higher degree of soot agglomeration and coagulation, which results in a bigger cluster containing many individual soot particles. Further efforts were then made to analyse the mean aerodynamic diameter of the collected soot cluster samples (SMD) during rapid pyrolysis of W-cellulose and A-lignin at various feeding rates, with the results presented in Figure 5-11. The SMD reflects the average size of soot clusters and can be calculated as SMD = $\sum_{i=0}^{i=7} d_i \times k_i$ , where  $d_i$  refers to the aerodynamic diameter of  $i^{th}$  stage in DPLI and  $k_i$  refers to the mass ratio of the soot sample collected from the  $i^{th}$  stage in DLPI to the total soot collected in CM<sub>1</sub>. In other words,  $k_i$  reflects the contribution of soot clusters with certain aerodynamic diameters to the total soot.

Figure 5-11a clearly shows that the SMD of collected soot cluster samples increases with increasing feeding rate. This is not surprising because an increase in feeding rate fundamentally increases the soot concentration in the gaseous phase. Therefore, the concentration of soot is an important parameter that influence the collisions between soot particles, soot coagulation and agglomeration hence subsequently the SMD of soot samples. Therefore, the results presented in Figure 5-11a are then replotted as Figure 5-11b that illustrates the SMD of the collected soot samples as a

function of soot concentration. It is noted that the concentration of soot in flue gas is represented by Z that is calculated as  $Z=A \times Y_A$ , where A is the feeding rate of feedstock and  $Y_A$  is the yield of soot at feeding rate A. Therefore, Z represents the average soot concentration in the reactor tube of the DTF during rapid pyrolysis.



Figure 5-11. Mean aerodynamic diameter of soot from rapid pyrolysis of Wcellulose and A-lignin at 1300 °C with (a) different feeding rates and (b) soot concentration.

Several important observations can be made Figure 5-11b. First, the SMD of soot samples increases with increasing Z during rapid pyrolysis of both W-cellulose and

A-lignin. As Z increases, collision among soot particles in the gaseous phase increases, enhancing soot coagulation or agglomeration, leading to an increase in the SMD of collected soot samples. It is noteworthy that there are key differences between coagulation and agglomeration. Coagulation refers to a collection of chemically-bond soot particles that require the essential supply of small molecules (e.g. C<sub>2</sub>H<sub>2</sub>) or PAHs during growth. However, agglomeration refers to a cluster of loosely-connected soot particles that only require collisions among these particles. Second, at the same Z, the SMD of soot from rapid pyrolysis of A-lignin is larger than that of W-cellulose. It is known that soot growth (including coagulation) requires the essential supply of PAHs as the dominant species [153]. Rapid pyrolysis of A-lignin readily produces such PAHs in volatiles but thermal cracking of Wcellulose during pyrolysis directly produce only small molecules (e.g.  $C_2H_2$ ), only from which PAHs can then be formed via extra reaction steps. Third, during fast pyrolysis of both W-cellulose and A-lignin, the SMD of soot samples increases substantially at  $Z \leq \sim 5$  mg/min. However, at  $Z > \sim 5$  mg/min, the increase in SMD with increasing Z becomes considerably slower. At low soot concentrations (i.e., Z $\leq$  ~5 mg/min, corresponding to feeding rates below 200 and 40 mg/min for Wcellulose and A-lignin, respectively), Figure 5-10 shows that the diameters of the formed individual soot particles increases with an increase in feeding rates (equivalent to an increase in Z). In addition, soot coagulation and agglomeration were also enhanced because of increased concentration of carbonaceous materials for soot growth and higher possibility of collisions among soot particles in gaseous phase. All these factors result in a substantial increase in the SMD of collected soot samples. At high soot concentrations (i.e.,  $Z > \sim 5$  mg/min, corresponding to feeding rates above 200 and 40 mg/min for W-cellulose and A-lignin, respectively), the growth of coagulation among individual soot particles becomes limited by the

availability of small molecules such as  $C_2H_2$  and PAHs. Only soot agglomeration, which is also known to be loose combination and easily broken [69], contributes to the further increase in the SMD of collected soot samples. Therefore, the increase in the SMD of collected samples becomes considerably slower as Z increases to be > ~5 mg/min.

#### 5.6 Conclusions

This chapter studies the effect of feeding rate on soot formation during rapid pyrolysis of W-cellulose and A-lignin in a DTF at 1300 °C. Soot from W-cellulose pyrolysis has a unimodal distribution and the increasing feeding rate significantly increases its mode diameter from 0. 043  $\mu$ m to 0.246  $\mu$ m. For A-lignin, when the feeding rate is 12 - 200 mg/min, soot shows a bimodal distribution with fine mode diameters of 0.077 µm and 0.246 µm. Increasing the feeding rate to 280 mg/min transforms the soot size distribution into a unimodal distribution with a fine mode diameter of 0.246 µm. When feeding rate increases from 40 to 280 mg/min for Wcellulose and from 12 to 40 mg/min for A-lignin, both soot yield and individual soot particle size increase whereas the yield of non-mature soot decreases. As A-lignin feeding rate increases further above 40 mg/min, the soot yield remains unchanged, the diameters of individual soot particles decrease and the yield of non-mature soot increases. In addition, the sizes of soot clusters are dependent on soot concentration (Z) in the flue gas. At  $Z \leq -5$  mg/min (corresponding to feeding rates less than 200 and 40 mg/min for W-cellulose and A-lignin, respectively), the size of soot clusters increases substantially as Z increases, as a result of enhanced soot growth. At  $Z > \sim$ 5 mg/min (corresponding to feeding rates above 200 and 40 mg/min for W-cellulose and A-lignin, respectively), the size of soot clusters only increases slowly with

further increase in soot concentration. The growth of soot is limited by the availabilities of small molecules (e.g.  $C_2H_2$ ) and PAHs that are required for the formation of soot.

### CHAPTER 6 DIFFERENCES IN SOOT PRODUCED FROM RAPID PYROLYSIS OF XYLAN, CELLULOSE AND LIGNIN UNDER PULVERIZED-FUEL CONDITIONS

### 6.1 Introduction

Soot produced from fuel thermochemical processing (e.g. combustion) has important process and environmental implications [1-5]. It is known that the high emissivity of soot affects process operating conditions [4]. When discharged into the atmosphere, soot absorbs visible solar radiation and thus contributes to global warming [5]. Therefore, soot formation and properties, and the effect of operating conditions on these aspects, are important considerations [6-8]. The knowledge on soot formation from gas and liquid hydrocarbon fuels [2,3] is well established as introduced in Chapter 2.

There are still considerable spaces in further research into formation mechanisms and emission behavior of soot from biomass fast pyrolysis, for addressing at least two main issues. One issue is the complexity of biomass feedstock, which is known [12] to consist of three major components (i.e., hemicellulose, cellulose, and lignin) plus minor extractives and inorganic species. Experimental work [11,13] suggested that the formation routes of soot precursor (PAHs) may vary from biomass component to component. The second issue, which is critical, lies in the conventional method for sampling and quantification of soot product from flow reactors, which typically separate the bulk sample into that collected in a cyclone and that collected on filter paper, with the latter regarded as soot. Consequently, only bulk soot samples without size segregation were collected (for examples in previous studies [11,13,14]) and fine char fragments might be possibly present in the collected soot samples. In chapter 4, we addressed this issue via the development of a new sampling method that both achieves the collection of size-segregated soot particles and differentiates soot from char fragments [15]. Therefore, it is a natural continuation to apply this new method to study soot generated from pyrolysis of individual biomass model compounds.

This chapter aims to systematically investigate the emission behavior of soot from pyrolysis of three major biomass model compounds (i.e., xylan, cellulose and lignin) at 1300 °C in a DTF. Discussion is focused on key differences in the yields and properties of soot generated from pyrolysis of these model compounds, as well as the distribution and occurrence of inorganic species in soot. The properties of xylan, cellulose and lignin used in this chapter are shown in Table 6-1.

Biomass model compound	xylan	cellulose	lignin			
Moisture (wt%						
ad <sup>a</sup> )	6.0	3.6	3.4			
	Proximate analy	ysis (wt% db <sup>b</sup> )				
ash	6.4	0.02	3.8			
VM	83.6	95.0	67.5			
FC	10.0	5.0	28.7			
Ultimate analysis (wt% daf <sup>c</sup> )						
С	45.43	43.69	65.80			
Н	6.73	6.47	6.24			
Ν	0.05	0.03	1.02			
S	0.01	0.00	2.12			
$O^d$	47.78	49.81	24.82			

Table 6-1. Proximate, ultimate and ash analyses of xylan, cellulose and lignin.

Ash analysis (mg/kg,db <sup>b</sup> )					
Al	$11.38 \pm 2.73$	$29.40\pm0.43$	$152.35\pm1.47$		
Fe	$73.68\pm0.12$	$14.11\pm0.36$	$51.68\pm4.31$		
Si	$520.92\pm42.90$	$109.33\pm2.68$	$364.14\pm7.85$		
Κ	$157.60\pm3.03$	$19.38 \pm 1.54$	$1255.46 \pm 1.99$		
Mg	$76.74\pm8.17$	$5.63\pm0.28$	$192.15\pm9.00$		
Na	$18713.97 \pm 129.29$	$53.19\pm5.41$	$11567.10 \pm 148.17$		
Ca	$4279.95 \pm 1.10$	$4.78\pm 0.22$	$106.77\pm15.63$		
Р	$97.54\pm3.98$	n.d	n.d		
Cl	$18.96\pm2.75$	$41.96 \pm 1.04$	$76.46 \pm 1.06$		

 $ad^a = air dried. db^b = dry basis. daf^c = dry and ash free. <sup>d</sup> By difference. n.d.=non-detected$ 

## 6.2 Yields and properties of soot from fast pyrolysis of biomass model compounds

Figure 6-1 and Table 6-2 illustrate the PSDs and yields of soot collected from fast pyrolysis of xylan, cellulose and lignin at 1300 °C, respectively. There are two important observations from these results. One is that the collected CM<sub>10</sub> samples contain dominantly CM<sub>1</sub> (i.e. soot) but little CM<sub>1-10</sub>, as shown in Figure 6-1. Further listed in Table 6-2, the yield of soot (i.e. CM<sub>1</sub>) from pyrolysis of lignin is ~100.7 mg/g, which is substantially higher than those from pyrolysis of cellulose and xylan (~11.6 mg/g and ~7.0 mg/g, respectively). Such an observation is of critical importance and can be attributed to the key differences in the chemical structure of these three biomass model compounds. The dissimilarity in the intermediates formed during pyrolysis results in distinctly different reaction mechanisms governing soot formation process thus a significant variation in soot yield from pyrolysis of different biomass model compounds. Lignin is a complex organic polymer formed from cross-linking of monolignols (e.g. p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol) which contain phenyl group [24]. The decomposition of lignin during

pyrolysis may release substantial amount of phenolic and aromatic compounds [25] which can readily react to form PAHs, the precursor for soot. Cellulose and xylan, on the contrary, are polymers of glucose and xylose, respectively, which are mainly decomposed into compounds such as saccharides, acids, ketones and furans [26,27]. These compounds then undergo further thermal cracking to form smaller gaseous species. In short, their decomposition does not directly give light aromatic compound. Rather, the aromatic compound required for PAH formation are only formed through HACA of small gaseous molecules such as C<sub>2</sub>H<sub>2</sub>. Furthermore, the small gaseous molecules formed during decomposition of lignin can also form aromatic compounds through HACA. Consequently, the relative abundance of gaseous species which can react to form PAH during pyrolysis of lignin results in substantial yield of soot in comparison to pyrolysis of xylan and cellulose.

The other important observation is that as shown in Figure 6-1, the soot samples from pyrolysis of xylan, cellulose and lignin have a unimodal distribution at a fine mode diameter of 0.043  $\mu$ m, 0.077  $\mu$ m and 0.246  $\mu$ m, respectively. The difference of the mode diameter for the soot is mainly due to the agglomeration of fine soot particles. As the soot yield increases, the particle number density (reflected by particle mass) increases. Soot would be more likely to agglomerate during pyrolysis and sampling. As pyrolysis of lignin has the highest soot yield followed by pyrolysis of cellulose and xylan, the mode diameters of their respective soot also show a similar trend with lignin soot being the largest, followed by cellulose soot and xylan soot.

Table 6-2. Yields of non-mature soot and mature soot and their contributions to CM<sub>1</sub> generated from fast pyrolysis of xylan, cellulose and lignin in a DTF at

1200	$^{\circ}C$
1300	U

	Biomass model compounds					
	Xylan		Cellulose		Lignin	
Samples	Viald	Contribu	Viold	Contribu	Viold	Contribu
	$(mg/g)$ $tion to  CM_1 (%)$	tion to	r r r r r r r r r r r r r r r r r r r	tion to	r rela	tion to
		$(\operatorname{IIIg/g})$ $\operatorname{CM}_1(\mathbb{C})$	CM <sub>1</sub> (%)	$(\operatorname{III} g/g) = \operatorname{CM}_1(\%)$	CM <sub>1</sub> (%)	
Mature soot	$6.42 \pm$	01.06	$11.04~\pm$	94.93	$97.63 \pm$	96.95
	0.48	91.00	1.33		5.44	
Non-mature	$0.63 \pm$	<u>  0</u>	$0.59 \ \pm$	5.07	$3.07 \pm$	3.05
soot	0.08	0.94	0.11		0.52	
Total	$7.05 \pm$	100.00	$11.63 \pm$	100.00	$100.70 \pm$	100.00
	0.56	100.00	1.44		5.96	100.00



Figure 6-1. PSDs of CM from pyrolysis of biomass model compounds at 1300°C.

### 6.3 Properties of soot from fast pyrolysis of biomass model compounds

Figure 6-2 shows the H/C molar ratio of size-segregated soot from pyrolysis of biomass model compounds. The H/C molar ratios decrease from 0.7 - 0.8 to  $\sim 0.1$ 

when aerodynamic diameter increases from 0.011  $\mu$ m to 0.043  $\mu$ m and then plateau with further increase in aerodynamic diameter. The H/C molar ratio serves as an effective indicator to differentiate incipient soot from mature soot. Specifically, the H/C molar ratio ranges from 0.4 to 0.7 for incipient soot and further decreases to 0.05–0.1 for mature soot, as a result of soot growth [28-33]. Therefore, Figure 6-2 suggests that soot with aerodynamic diameter of  $\leq 0.022 \,\mu m$  is mainly non-mature soot, while soot of larger sizes is mature. Therefore, from Table 6-2 it could be known that non-mature soot only contributed to ~8.9 %, ~5.1 % and ~3.1 % in the total soot sampled from pyrolysis of xylan, cellulose and lignin, respectively. It is also evident that for soot with aerodynamic diameter of 0.022 µm, the H/C molar ratio for xylan soot is considerably lower than that for cellulose soot and lignin soot. This discrepancy can be attributed to two factors. Firstly, xylan has the highest inorganic species content compared to cellulose and lignin (see Table 6-1). When incorporating with soot, these inorganic species might displace the hydrogen (e.g., there are oxygen-containing functional groups such as hydroxyl group which is known to present in soot [34-36]), leading to the decrease of H/C molar ratio for xylan soot. Secondly, some smaller non-mature soot might coagulate or agglomerate to form a larger soot cluster with an aerodynamic diameter of 0.022 µm. This small non-mature soot on the cluster might have a higher H/C molar ratio than that of a single soot particle with an aerodynamic diameter of 0.022 µm. This resulted in a higher H/C molar ratio. As aforementioned, soot from xylan has the least tendency to agglomerate compared to that of lignin and cellulose, thus the H/C molar ratio of xylan soot with aerodynamic diameter of 0.022 µm is the lowest.



Figure 6-2. H/C molar ratio of size-segregated soot from pyrolysis of biomass model compounds in DTF at 1300 °C.

Figure 6-3 depicts the morphology of soot from pyrolysis of biomass model compounds. The SEM images in Figure 6-3 (a-c) show clear evidence of soot agglomeration and the diameters of soot particles in soot clusters are similar for all the three compounds. Figure 6-3 (c) and (d) illustrate the morphology of lignin soot of two collection aerodynamic diameters (0.077 and 0.246  $\mu$ m). It is evident that with the increase in the collection aerodynamic diameter, there is no obvious increase in the diameter of soot particles in soot clusters. The morphology of soot further supports that the variation in soot mode diameter observed in Figure 6-1 is mainly caused by difference in the degree of agglomeration of soot particles.



Figure 6-3. Micromorphology of soot samples from pyrolysis of biomass model compounds: (a) cellulose soot at 3<sup>rd</sup> impactor stage, (b) xylan soot at 3<sup>rd</sup> impactor stage, (c) lignin soot at 3<sup>rd</sup> impactor stage and (d) lignin soot at 5<sup>th</sup> impactor stage. 3<sup>rd</sup> impactor stage: aerodynamic collection diameter 0.077 μm; 5<sup>th</sup> impactor stage: aerodynamic collection diameter 0.246 μm.

As aforementioned, xylan, cellulose and lignin have different chemical structure and fast pyrolysis of these model compounds leads to formation of soot with different yields and structures. In addition, the presence of inorganic species could also influence the soot structure which governs the soot properties. Therefore, the nanostructures of soot from pyrolysis of different biomass model compounds were analyzed. All the soot particles analyzed are chosen from the impactor stage with the

collection aerodynamic diameter of 0.077  $\mu$ m. In order to prevent the influence of soot particle diameter [15], only soot particles with diameter of 20 – 30 nm were analyzed. The fringe length, fringe tortuosity and layer spacing of xylan, cellulose and lignin soot are analyzed and shown in Table 6-3. Fringe length is defined as the average length of lattice line in soot while fringe tortuosity is the ratio of the distance between the two ends of a fringe to its total length. Layer spacing is termed as the mean distance between adjacent lattice lines in soot.

Table 6-3. Nanostructure parameters of soot (with particle diameters of 20-30 nm)generated from fast pyrolysis of xylan, cellulose and lignin.

Feedstock	Fringe length / nm	Fringe tortuosity	Layer spacing / nm
Xylan	$0.935\pm0.053$	$0.848\pm0.023$	$0.341\pm0.010$
Cellulose	$0.938\pm0.060$	$0.872\pm0.023$	$0.344\pm0.006$
Lignin	$0.993\pm0.049$	$0.879\pm0.019$	$0.347\pm0.012$

Although the standard errors are relatively high, the average values do show differences in nanostructure of soot from pyrolysis of xylan, cellulose and lignin. The results indicate that lignin soot has longer fringe compared to xylan and cellulose soot. This can be attributed to the presence of abundant aromatic rings in lignin because these aromatic rings would enhance formation of PAHs during lignin pyrolysis, as aforementioned. This consequently enhances the formation and growth of incipient soot during lignin pyrolysis, leading to higher degree of in-plane similarity. Fringe tortuosity reflects the extent of odd number (5- and 7- membered) carbon rings in the material [37,38]. The HACA process from small molecules (produced during pyrolysis of cellulose and xylan) is more likely to form odd

number carbon rings compared to that from aromatic compounds. Therefore, the fringe of lignin soot is straighter in comparison to that of cellulose soot or xylan soot. In addition, tortuosity is also a measure of disorderness within the material [21]. The abundance of inherent inorganic species in xylan might incorporate with soot during pyrolysis, making the xylan soot more disordered hence its fringe tortuosity being the lowest.

### 6.4 Inorganic species in size-segregated soot from fast pyrolysis of biomass model compounds

Although biomass model compounds were used for this study, these model compounds (particularly xylan and lignin) inevitably contain considerable amounts of inorganic species (see Table 6-1). After transformation during pyrolysis, at least some of these inorganic species could be present in soot. In Chapter 4, inorganic species such as Na and K are observed during biomass pyrolysis. Similar observations were also found by other researchers [39,40] and these inorganic species can reduce the yield and particle size of the soot in flame and enhance soot reactivity during oxidation [41-43]. In this study, analysis shows that the contents of inorganic species of xylan and lignin soot samples are 1.55 % and 0.43 %, respectively. Furthermore, there is little inorganic species present in cellulose soot, which is understandable because cellulose contains little ash (see Table 6-1). The discussion is focused on inorganic species in xylan soot and lignin soot samples.

Figures 6-4 and 6-5 present the distribution and yields of key inorganic species (i.e. Na, K, Cl and S) that are found in soot. These key inorganic species in soot are similar as those in Chapter 4, section 4.5 except S, as little S is detected in pine wood

(Chapter 4, Table 4-1). For xylan, the elemental PSDs of Na and K show a unimodal distribution with a mode diameter of 0.043 µm while Cl also exhibits a unimodal distribution but with a mode diameter of 0.077 µm. On the other hand, the elemental PSD of S shows a bimodal distribution with mode diameters of 0.011 µm and 0.043  $\mu$ m. As for lignin, the PSDs of these elements all exhibit a unimodal distribution with mode diameter of ~0.246 µm. The yields of Na, K, Cl and S in xylan soot are 0.068 mg/g, 0.017 mg/g, 0.005 mg/g and 0.019 mg/g, respectively. For lignin soot, the yields of Na, K, Cl and S are higher (0.219 mg/g, 0.152 mg/g, 0.035 mg/g and 0.023 mg/g, respectively). The higher yields of inorganic species in soot from lignin pyrolysis are associated with higher soot yields as these inorganic species might incorporate into soot or condense on soot during pyrolysis. Figure 6-6 further presents the contents of inorganic species in size-segregated soot samples. It is important to note that while the absolute yields of inorganic species in lignin soot collected in each impactor stage is higher than those in xylan soot, the contents of inorganic species (i.e. the mass of inorganic species relative to the total soot mass on each impactor stage) are actually higher for xylan soot than for lignin soot. The contents of Na, K, Cl and S in both lignin and xylan soot is the highest at aerodynamic diameter of 0.011 µm but decrease with increasing aerodynamic diameter.



Figure 6-4. PSDs of major elements including Na (a), K (b), Cl (c), S (d) in sizesegregated soot from pyrolysis of biomass model compounds in DTF at 1300 °C.







Figure 6-6. Contents of inorganic species in size-segregated soot collected on each impactor stage, expressed as % of total mass on each impactor stage. Panel (a) –

(d): (a) Na, (b) K, (c) Cl and (d) S.

Figure 6-7 shows the (Na + K) / (Cl + 2S) molar ratio of size-segregated soot. For xylan soot, the molar ratio increases from ~1.5 at aerodynamic diameter of 0.011 µm to ~3.4 at 0.043 µm and remains constant with increasing soot aerodynamic diameter. For lignin soot, the molar ratio rises from ~2.6 at aerodynamic diameter of 0.011 µm to ~8.2 at 0.043 µm. However, the (Na + K) / (Cl + 2S) molar ratio drops to ~4.0 with the increase of aerodynamic diameter to 0.138 µm before returning to and remained at ~8.5 as soot aerodynamic diameter increases to 0.61 µm. The molar

ratios at all impactor stages are >1, indicates that only a small part of Na and K are in form of Cl and S containing salts. The remaining Na and K in xylan and lignin soot could present in other forms such as oxide or hydroxide or incorporate with soot. The drop in (Na + K) / (Cl + 2S) molar ratio in lignin soot with aerodynamic diameter between 0.043 and 0.138 µm might be due to higher amount of (Na or K) chloride and sulfate present in soot at this size fraction. The relatively lower molar ratios at the first two stages also suggest that the content of (Na or K) chloride and sulfate is relatively higher at the first two stages.



Figure 6-7. Dependence of (Na + K)/(Cl+2S) molar ratio on the size of sizesegregated soot from pyrolysis of biomass model compounds in DTF at 1300°C

## 6.5 Further discussion on inorganic species in soot from fast pyrolysis of biomass model compounds

To further understand the form of Na and K presented in soot, size-segregated soot from pyrolysis of xylan and lignin were washed with deionized water and the watersoluble Na and K were analyzed. Figure 6-8 presents the contents and distribution of water-soluble and water-insoluble Na and K in size-segregated soot. The yield of water-soluble Na and K is also shown in Figure 6-5. Na or K salts in soot are water-soluble and the water-insoluble Na and K represent those incorporated with soot and become organically bonded. The experimental result indicates that water-soluble Na and K in xylan soot account for ~72.8% and ~49.8%, of the total Na and K in soot, respectively. However, they are lower for lignin soot and only contribute ~63.5 % and ~6.6 % to the total Na and K in soot, respectively.

Several important observations can be made from this additional analysis. Firstly, as shown in Figure 6-8 (d), the percentage of water-insoluble K in soot is higher than water-insoluble Na in soot. This might due to K is more electropositive than Na, and capable of forming intercalation compounds with carbons [44-46]. Secondly, it is clear from Figure 6-8 (b), non-mature soot (i.e. aerodynamic diameter 0.011  $\mu$ m) contains more water-insoluble Na and K than mature soot. It is because non-mature soot is more disordered than mature soot, thus more reactive [47,48] hence, possibly more Na and K are incorporated in the non-mature soot. In addition, water-insoluble Na and K might also be released from soot during maturation process and thus a reduction in water-insoluble Na and K content in mature soot. This property could be a useful parameter to differentiate between non-mature soot and mature soot in practice. Thirdly, Figure 6-8 (a) clearly shows that the contents of water-soluble Na and K on impactor stage with the aerodynamic diameter of 0.011 µm is the highest. This is due to formation of ultrafine particulates from homogeneous condensation of Na and K during cooling of reactor effluent gas for soot sampling. The contents of water-soluble Na and K then decreased and remained constant for size-segregated soot with higher aerodynamic diameter. Similarly, Na and K can also undergo heterogeneous condensation and deposited on larger size-segregated soot. The

contents of water-soluble Na and K remain relatively unchanged for the larger sizesegregated soot as its specific area available for heterogeneous condensation is similar. The first three conclusions are coincide with the ones for biomass wood pyrolysis in Chapter 4, section 4.5. Fourthly, Figure 6-8 (c) and (d) clearly show that the percentage of water-soluble Na and K in xylan soot decrease with increasing soot aerodynamic diameter. Similar trend is observed for K in lignin soot but it is not for Na in lignin soot. The water-soluble Na in lignin soot increases from  $\sim 70\%$  to  $\sim 80\%$ at aerodynamic diameter of 0.138  $\mu$ m, before dropping to ~45% with further increase in soot aerodynamic diameter. The increase of water-soluble Na in lignin soot at aerodynamic diameter of 0.138  $\mu$ m coincides with the sudden drop of (Na + K) / (Cl + 2S) molar ratio for lignin soot in Figure 6-7. This further supports the reduction in molar ratio is likely due to higher condensation of water-soluble Na salt such as NaCl and Na<sub>2</sub>SO<sub>4</sub> on soot with aerodynamic diameter of 0.138 µm. Lastly, soot from xylan pyrolysis is found to incorporate with relatively more Na and K than soot from lignin pyrolysis. Table 6-1 shows the content of Na and K in xylan is  $\sim 1.6$ and  $\sim 0.1$  times of the content of Na and K in lignin, respectively. However, the content of water-insoluble Na and K in soot from xylan pyrolysis is  $\sim 2.2$  and  $\sim 0.6$ times the content Na and K in soot from lignin pyrolysis, respectively. One of the possible explanations is the yield of soot from lignin pyrolysis is higher than the yield of soot from xylan pyrolysis (14 times). Therefore, the ratio of Na or K in gas phase to soot formed from xylan pyrolysis during pyrolysis is higher. Another possibility is the difference in reaction mechanism governing the formation of soot during pyrolysis of xylan and lignin aforementioned. This might affect the incorporation of Na and K during soot formation.



Figure 6-8. Contents and distributions of water-soluble and water-insoluble Na and K in size-segregated soot sample collected on various impactor stage during pyrolysis of biomass model compounds in DTF at 1300 °C. Panel (a) and (b): contents of water-soluble (a) and water-insoluble (b) Na and K; Panel (c) and (d): distribution of water-soluble (c) and water-insoluble (d) Na and K in each impactor stage, expressed as the percentage of respective total Na or K.

Comparing with the results of AAEM between biomass components pyrolysis in this Chapter and biomass pyrolysis in Chapter 4. Even though the form and contents of AAEM in biomass components and biomass are different. It could be seen that inorganics in soot are elementals (i.e. Na and K) which could easily evaporate during pyrolysis. Both of them could either condense on soot as salt or incorporate with soot. K are more likely to incorporate with soot than Na. Non-mature soot contains more Na and K than mature soot. Some differences of AAEM like distribution in soot could also be found between biomass components and biomass. It is because the distributions of soot are different between biomass components and biomass. The other reason is that biomass model components in this study come from different biomasses (Chapter 3, Section 3.3.1). They might have different characteristics to the biomass component in pine wood in Chapter 4.

### 6.6 Conclusions

A systematic set of experiments were carried out to collect size-segregated soot from fast pyrolysis of xylan, cellulose and lignin in a DTF at 1300 °C. The CM<sub>10</sub> samples collected are dominantly CM<sub>1</sub> that is soot. The yield of soot from lignin pyrolysis  $(\sim 100.7 \text{ mg/g})$  is substantially higher than the soot yields of xylan pyrolysis ( $\sim 7.0$ mg/g) and cellulose soot (~11.6 mg/g) due to dissimilarity of chemical structure of lignin, xylan and cellulose. Soot samples from pyrolysis of all biomass model compounds have a unimodal distribution with mode diameter of 0.043  $\mu$ m, 0.077 µm and 0.246 µm for xylan soot, cellulose soot and lignin soot, respectively. The difference in mode diameter is mainly due to the agglomeration of fine soot particles. Nanostructure analysis shows that the fringe of soot from lignin soot is longer and straighter compared to that of cellulose soot and xylan soot. Soot from cellulose pyrolysis contains little inorganic species because of little ash content in cellulose. For xylan and lignin which contain abundant inorganic species, Na, K, Cl and S could be found both in xylan soot and lignin soot. Na and K salts could condense on soot through homogenous or heterogeneous condensation. They could also incorporate with soot and organically bonded to soot. The data shows K is more likely to incorporate with soot compared to Na. Higher amounts of Na and K are incorporated in soot from pyrolysis of xylan compared to that from pyrolysis of lignin. Non-mature soot only takes a small ratio of soot. However, it contains higher

contents of incorporated Na and K than mature soot.

### CHAPTER 7 FUNDAMENTAL INVESTIGATION INTO CHARACTERISTICS OF PARTICULATE MATTER PRODUCED FROM RAPID PYROLYSIS OF BIOCHAR IN A DROP-TUBE FURNACE AT 1300 °C

### 7.1 Introduction

Biomass considered as an important renewable energy resource in global effort to curb carbon emission [1]. According to the Global Bioenergy Statistics by World Bioenergy Association, biomass contributes at a total of 55.6 EJ energy, equivalent to ~15% of the world's gross energy consumption in 2017 [2]. In Australia, mallee biomass is known to supply not only sustainable bioenergy but also deliver environmental and agronomic benefits [3]. However, direct utilization of biomass as a fuel faces several key challenges including high moisture content, low energy density, poor grindability, high transport cost and mismatch with other fuels such as coal [4]. Biomass fast pyrolysis at ~500 °C is an attractive technology for converting the bulky biomass into high-energy-density products including biochar and bio-oil [5]. While bio-oil can be further separated, upgraded and/or refined for production of liquid fuels and chemicals [6], biochar as a byproduct has its own suitable applications. It is desired to use biochar in value-added applications (e.g. for producing carbon-based adsorbents or materials [7,8]), such applications are however typically of small volume. Considering the large quantity of potential biochar production, it is still highly desired for biochar to find large-volume applications (typically low-value) especially use as a fuel for energy applications.

Biochar has some desired fuel properties such as high energy density (i.e. similar

mass energy density that is close to coal) and excellent grindability, which make it a potentially good option for pulverized fuel (PF) applications [4]. It is known that PF applications such as combustion in a boiler are operated at high temperature (typically  $\geq 1300$  °C) [9]. Upon being injected into such a high-temperature reactor, solid fuel particles experience rapid pyrolysis as the first step of the reactions. During rapid pyrolysis, part of released volatiles form fine particles at high temperature such as soot [10], which influences the operating conditions during application [11]. In addition, some inorganic elements also form fine particles with organic or inorganic species that have crucial effect on practical applications including undesired emissions into the environment. Because biochar is produced from biomass fast pyrolysis at relatively low temperature (450–550 °C), most of the inherent inorganic species are retained in biochar. The ash content of biochar typically ranges from  $\sim 5$  % to ~60 %, depending on the type of biomass feedstock [12]. Biochar is also expected to experience secondary pyrolysis at high temperature under PF conditions. Surprisingly, to best knowledge of the present authors, in the open literature, there have been no studies on the behaviour of biochar during rapid pyrolysis under the conditions pertinent to PF applications.

Therefore, the main objective of this study is to carry out a set of fundamental research to understand the rapid pyrolysis of biochars (prepared from biomass fast pyrolysis at 500 °C for bio-oil production) in a laboratory-scale DTF under experimental conditions pertinent to PF applications. Two biochars were prepared from fast pyrolysis of wood and leaf at 500 °C. The biochars were then pyrolyzed in a DTF at 1300 °C in argon atmosphere. Focuses are on char yield, retention of inorganic species, characteristics and properties of PM with aerodynamic diameter of < 10  $\mu$ m (i.e. PM10). The properties of leaf and wood, as well as the biochar

samples are listed in Table 7-1 and Table 7-2.

Sample name	Leaf	Wood		
Moisture (wt. % ad <sup>a</sup> )	2.32	0.49		
Proximate analysis (wt.	%, db <sup>b</sup> )			
ash	3.42	0.59		
VM	92.45	91.26		
FC	4.12	8.14		
Ultimate analysis (wt. 9	%, daf <sup>c</sup> )			
С	56.97	45.78		
Н	7.06	6.19		
Ν	1.13	0.12		
S	0.06	0.01		
$\mathbf{O}^{\mathrm{d}}$	34.78	47.9		
Ash composition analysis (mg/kg, db <sup>b</sup> )				
Al	$278.1\pm4.7$	$13.51\pm4.5$		
Fe	$271.8\pm5.4$	$20.29 \pm 1.6$		
Si	$589.3 \pm 47.1$	$78.8\pm 6.3$		
Κ	$3721.2\pm113.0$	$679.7\pm0.4$		
Mg	$1252.8\pm21.4$	$270.1 \pm 10.1$		
Na	$3361.3\pm445.8$	$126.9\pm46.1$		
Ca	$8408.3\pm121.4$	$1551.7\pm69.5$		
Cl	$2064.2\pm29.6$	$571.8 \pm 18.6$		

Table 7-1 Properties of leaf and wood for biochar preparation.

 $^{\rm a}$  air dried.  $^{\rm b}$  dry basis;  $^{\rm c}$  dry and ash free.  $^{\rm d}$  by difference

Table 7-2 Properties of fast pyrolysis biochars (i.e. LC500 and WC500) prepared from fast pyrolysis of wood and leaf at 500 °C and the derived chars (i.e. LC500-1300 and WC500-1300) after rapid pyrolysis of these biochars in the DTF at 1300 °C.

Samula	LC500	LC500 1200	WC500	WC500 1200
Sample	LC300	LC300-1300	WC300	WC300-1300
	4.10	1.62	2.10	2.22
Moisture	4.13	4.63	3.19	3.33
(wt. $\%$ ad <sup>a</sup> )				
Proximate an	alysis (wt. %, db	<sup>b</sup> )		
ash	16.75	13.87	3.75	3.89
VM	40.11	27.64	36.29	15.50
FC	43.14	58.49	59.96	80.61
Ultimate anal	lysis (wt. %, daf <sup>c</sup>	)		
С	79.94	86.42	81.35	87.47
Н	2.12	0.96	2.64	0.86
Ν	1.87	1.04	0.32	0.42
S	0.06	0.07	0.02	0.02
$O^d$	16.01	11.51	15.67	11.23
Ash composi	tion analysis (mg	g/kg, db <sup>b</sup> )		
Al	$758.2\pm5.4$	$1142.7\pm33.4$	$58.7\pm5.4$	$80.6\pm9.3$
Fe	$360.5\pm15.1$	$498.9\pm10.6$	$58.2\pm3.8$	$73.1\pm1.6$
Si	$3068.5\pm217.0$	$3034.1 \pm 210.7$	$493.0\pm25.6$	$463.9\pm45.8$
Κ	$14763.9 \pm 795.3$	$6728.1 \pm 193.8$	$5082.1 \pm 178.8$	$4083.4\pm72.5$
Mg	$5945.2\pm104.3$	$8485.0\pm22.8$	$2014.2\pm11.3$	$2349.2\pm43.7$
Na	$15407.2 \pm 1193.4$	$577.5\pm38.6$	$866.3{\pm}6.1$	$106.7\pm4.4$
Ca	$37684.8 \pm 2106.1$	$55537.5 \pm 1570.3$	$11360.8 \pm 101.5$	$13765.6 \pm 237.4$
Cl	$10416.6 \pm 125.1$	$276.4\pm45.2$	$455.0\pm0.9$	$20.8\pm2.4$
Р	$3586.3 \pm 391.6$	$1356.8\pm8.5$	$4992.2 \pm 142.2$	$1565.5\pm140.4$

<sup>a</sup> air dried. <sup>b</sup> dry basis; <sup>c</sup> dry and ash free. <sup>d</sup> by difference

### 7.2 Char yields and retentions of inorganics species

The char yields during rapid pyrolysis of LC500 and WC500 in the DTF at 1300 °C in argon are listed in Table 7-3. It is noted that complete collection of chars in flow reactors such as DTF during solid fuels pyrolysis at high temperature (> 1000 °C) is rarely achieved, ash tracer method is commonly used for determination of char yield [154]. Therefore, the char yields have also been estimated using ash tracer method with total ash, Ca and Si as tracer and presented in Table 7-3 for comparison. It can be clearly seen that ash tracer method significantly overestimates char yields

especially for LC500 biochar with total as tracer because of ash species vaporization during pyrolysis at 1300 °C.

Table 7-3 Char yields during rapid pyrolysis of biochars in the DTF at 1300 °C in argon, determined either directly by experiments or indirectly by ash tracer method.

	Char yield (%, on a dry basis)				
Samples	Directly by experiments	Indirectly by ash tracer method using total ash as tracer	Indirectly by ash tracer method using Ca as tracer	Indirectly by ash tracer method using Si as tracer	
LC500- 1300	$65.46\pm0.16$	$120.76\pm0.17$	$67.85 \pm 1.87$	$101.13\pm0.13$	
WC500- 1300	$72.88 \pm 1.25$	$96.40\pm5.85$	$82.53\pm0.69$	$106.27\pm4.97$	

From the char yield directly determined by experiments, the retentions of inorganic species in the chars after pyrolysis at 1300 °C are calculated and shown in Figure 7-1. The results clearly indicate that even some of the refractory elements (including Mg, Ca, Al and Fe) are released into gaseous phase, although over 80% of these elements are retained in LC500-1300 and WC500-1300 chars after rapid pyrolysis at 1300 °C. The retentions of Si in these chars are also ~70%, with 30% Si in these biochars are released (via mechanism such as reduction by CO or C to gaseous SiO [155]). The release of Si during pyrolysis explains significant overestimation of char yield with Si as tracer while the errors are relatively smaller for Ca as tracer (see Table 7-3). It is noteworthy that the retention of S is relatively high (~80%). This can be attributed to the S remained in the biochars after fast pyrolysis at 500 °C are most likely in the form of organically-bond S that are known to remain thermally

stable even at temperatures > 1000 °C [156, 157]. The retentions of Na, K, Cl and P in biochars are relatively low because these volatile elements volatize easily during pyrolysis under the conditions [154]. It is also noted that the retentions of Na and K in LC500-1300 are lower than those in WC500-1300. This can be attributed to the high content of Cl in LC500 (see Table 7-2) because some inherent Na and K may be released via chlorination during pyrolysis. The substantial release of Na and K leads to a significant overestimation of char yield with total ash as tracer for LC500-1300 char. The retention of carbon during biochar pyrolysis at 1300 °C is calculated and included in Figure 7-1, showing 20-30% of the organic matter in biochar being released. Such considerable amounts of inorganic species and organic matter released are therefore expected to form PM<sub>10</sub> and form soot during biochar pyrolysis at 1300 °C. It is also possible that biochar particles may experience fragmentation to produce fine char fragments. Therefore, particulate matter collection system including a 13-stage DLPI and a back filter was employed to sample the PM<sub>10</sub> formed during pyrolysis of biochar at 1300 °C.



Figure 7-1. The retention of inorganic species and C in char from rapid pyrolysis of biochars at 1300 °C.

### 7.3 PSDs and yields of PM10 from biochar pyrolysis

Figure 7-2 presents the PSDs and yields of  $PM_{10}$  from pyrolysis of LC500 and WC500 at 1300 °C. The PSDs of the  $PM_{10}$  from pyrolysis of LC500 and WC500 show a bimodal distribution with a fine mode diameter of 0.011 µm and a coarse mode diameter of 4.087 µm. The yields of  $PM_{0.1}$ ,  $PM_{0.1-1}$ , and  $PM_{1-10}$  are ~6.42 mg/g, ~0.89 mg/g and ~1.14 mg/g, respectively, for pyrolysis of LC500 and ~0.52 mg/g, ~0.01 mg/g and ~1.53 mg/g, respectively, for pyrolysis of WC500. While the  $PM_{10}$  from pyrolysis of WC500 mainly is distributed in  $PM_{1-10}$ , accounting for ~74.3 % of the total  $PM_{10}$ . PM<sub>10</sub> from pyrolysis of LC500 mainly consists of PM<sub>1</sub>, accounting for ~75.1 % of the total  $PM_{10}$ .

The collected PM<sub>10</sub> were also subjected to micromorphology analysis using SEM, with typical SEM images are shown in Figure 7-3. Figure 7-3 (a) and (c) show the morphology of PM<sub>1-10</sub> samples from pyrolysis of LC500 and WC500 at 1300 °C, respectively. It can be seen that the fine particles present in PM<sub>1-10</sub> have irregular shape with sharp edges, indicating PM<sub>1-10</sub> are mainly char fragments. Figure 7-3 (b) and (d) show that PM<sub>1</sub> from pyrolysis of LC500 and WC500 at 1300 °C, respectively, consists of agglomerated small smooth spherical particles. Therefore, PM<sub>1</sub> is likely to be soot, and/or ash particles formed through homogeneous/heterogeneous condensation of ash species (mainly Na and K) during cooling of flue gas.



Fig 7-2. (a) PSDs and (b) yield of  $PM_{10}$  from rapid pyrolysis of biochars at 1300  $^{\circ}\mathrm{C}$ 



Figure 7-3. SEM image of (a) PM<sub>1-10</sub> and (b) PM<sub>1</sub> from rapid pyrolysis of LC500 and (c) PM<sub>1-10</sub> and (d) PM<sub>1</sub> from pyrolysis of WC500.

# 7.4 Elemental PSDs and Yields of individual inorganic species in PM<sub>10</sub> from biochar pyrolysis

To understand the chemical composition of  $PM_{10}$  from the pyrolysis of biochar, the samples are ashed, acid digested and analyzed. The PSDs and yields of the individual elements are presented in Figs. 7-4 and 7-5. Na, K, Cl and S are mainly distributed in PM<sub>1</sub> with a unimodal distribution and a fine mode diameter of 0.011 µm while

Mg has a bimodal distribution with a fine mode diameter of 0.011  $\mu$ m and a coarse mode diameter of 4.087  $\mu$ m. However, Ca and P are mainly distributed in PM<sub>1-10</sub> and exhibit a unimodal distribution with a coarse mode diameter of 4.087  $\mu$ m.



Figure 7-4 Elemental PSD of (a) Na, (b) K, (c) Cl, (d) Ca, (e) Mg, (f) S and (g) P in PM<sub>10</sub> from rapid pyrolysis of biochars at 1300 °C.



Figure 7-5. Elemental Yield of (a) Na, (b) K, (c) Cl, (d) Ca, (e) Mg, (f) S and (g) P in PM<sub>10</sub> from rapid pyrolysis of biochars at 1300 °C

The yields of Na, K and Cl in PM<sub>1</sub> from pyrolysis of LC500 are  $\sim 0.95$  mg/g,  $\sim 2.12$  mg/g and  $\sim 2.35$  mg/g, respectively, while those in PM<sub>1</sub> from pyrolysis of WC500
are ~ 0.06 mg/g, ~ 0.17 mg/g and ~ 0.14 mg/g, respectively. This can be attributed to the significantly lower contents of Na, K and Cl in WC500. Na, K and Cl contribute to the majority of PM<sub>1</sub>, accounting for ~ 98.80 % and 97.47 % of the total detected inorganic species in PM<sub>1</sub> from pyrolysis of LC500 and WC500, respectively. In fact, Na, K and Cl are mainly distributed in PM<sub>0.1</sub> and account for >85% of the total Na, K and Cl in PM<sub>1</sub>. The yields of Ca in PM<sub>1-10</sub> from pyrolysis of LC500 and WC500 are 0.05 mg/g and 0.03 mg/g, respectively. As Ca is mainly retained in char, it accounts for ~71.2 % and ~65.3 % of all the quantified inorganic species in PM<sub>1</sub>. 10 from pyrolysis of LC500 and WC500, respectively. Some Mg is observed in PM<sub>1</sub> due to its partial release during pyrolysis. Although the retention of P is <30%, little P is present in PM<sub>1</sub>. The yield of P in PM<sub>1-10</sub> from pyrolysis of LC500 and WC500 are 0.002 and 0.003 mg/g biochar, respectively.

Table 7-4 shows the molar ratio of (Na + K + 2Mg + 2Ca)/(Cl + 2S + P) in PM<sub>1</sub> and molar ratio of (Na + K + 2Mg + 2Ca)/(Cl + 2S + 3P) in PM<sub>1-10</sub> during pyrolysis of LC500 and WC500 at 1300 °C. The phosphorous is counted as monovalent in PM<sub>1</sub> as it is usually present in the form of metaphosphate (PO<sub>3</sub><sup>-</sup>) while the P in PM<sub>1-10</sub> is usually in the form of phosphate [158]. Due to limited amount of sample collected on each individual stage of PM<sub>10</sub> for WC500 and that of PM<sub>1-10</sub> for LC500, the molar ratio in PM<sub>1</sub> or PM<sub>1-10</sub> is shown instead. The malar ratio remains around 1.3 - 1.6 in PM<sub>1</sub> from pyrolysis of LC500, while the molar ratio is ~1.82 in PM<sub>1</sub> from pyrolysis of WC500. The molar ratio of (Na + K + 2Mg + 2Ca)/(Cl + 2S + 3P) in PM<sub>1-10</sub> from pyrolysis of LC500 and WC500 is ~20.6 and ~5.8, respectively. It should be noticed that for both LC500 and WC500, the molar ratio in PM<sub>1-10</sub> is very similar to the molar ratios in the char samples, further proves that PM<sub>1-10</sub> are mostly char fragmentations. The molar ratios in PM<sub>1-10</sub> is significantly >1, indicating that only a small part of AAEMs is in the form of Cl, S or P containing salts, while majority of them are in the form oxides, hydroxides, react with Si, Al and Fe or organically bonded.

Table 7-4 Cation to anion molar ratio of  $PM_1$  and  $PM_{1-10}$  samples from pyrolysis of LC500 and WC500 biochars in the DTF at 1300 °C in argon

	(Na+K+2Mg+2Ca)/(Cl+2S+P)						(Na+K+2Mg+2Ca)/( Cl+2S+3P)			
Biochar DLPI stages for PM <sub>1</sub>			,		Cyclone					
Samples									PM <sub>1-10</sub>	Char
	0	1	2	3	4	5	6	7		
LC500	1.32	1.57	1.45	1.27	1.35	1.46	1.44	1.60	20.57	20.92
WC500 <sup>a</sup>				1.	82				5.79	5.95
<sup>a</sup> only the value of the total $PM_1$ from rapid pyrolysis of WC500 biochar is										

reported because all samples on the DLPI stages for  $PM_1$  have been accumulated for analysis due to the sample amount on each stage is too small.

Table 7-5 Carbon and inorganic species content in PM1 from pyrolysis of biochar

### in DTF at 1300 °C

	Detected inor	ganic species <sup>a</sup>	Carbon		
Biochar	$\mathbf{V}_{i}$ and $(\mathbf{m}_{i}, \mathbf{r}_{i})$	Contribution to Viald (may		Contribution to	
	rield (mg/g)	PM <sub>1</sub> (%)	rield (mg/g)	PM <sub>1</sub> (%)	
LC500	$5.488\pm0.322$	77.98	$0.350\pm0.028$	4.97	
WC500	$0.384\pm0.037$	74.51	$0.041\pm0.002$	7.71	
<sup>a</sup> Na, K, Mg, Ca, Cl, S and P in Figure 7-5					

The results presented thus far indicate that  $PM_{1-10}$  are mainly char fragments. However, pyrolysis of LC500 and WC500 also resulted in volatilization of organic matters which can react to form soot at 1300 °C, contributing to part of the released  $PM_1$ . Therefore, the carbon contents in  $PM_1$  released from pyrolysis of LC500 and WC500 were analyzed and presented in Table 7-5 along with the total yield of inorganic species quantified (calculated from Figure 7-5). This concludes that  $PM_1$  is mainly consist of ash forming species (~75–78 %) while carbon only contributes to 5-8% of  $PM_1$ . It is important to note that the inorganic species are not converted into their respective oxides or hydroxides form as they are released under pyrolysis condition. The ~17 % gap in the mass balance is likely to be contributed by O, N, H and trace amount of Si, Al and Fe.

#### 7.5 Conclusions

This chapter reports the PM produced from rapid pyrolysis of leaf and wood biochar at 1300 °C in a DTF in argon. A novel double-tube configuration was employed for the DTF, enabling direct determination char yields from pyrolysis of LC500 and WC500 at 1300 °C, which are ~65 % and ~73 %, respectively. It is noted that even refractory elements such as Ca, Mg, Al, Fe and Si experience up to 40% release during rapid pyrolysis of these biochars under the experimental conditions. The PSDs of PM<sub>10</sub> for pyrolysis of LC500 and WC500 have a bimodal distribution with a fine mode diameter of 0.011  $\mu$ m and a coarse mode diameter of 4.087  $\mu$ m. The elemental PSDs of Na, K, Cl and S in PM<sub>10</sub> have a unimodal distribution with a fine mode diameter of 0.011  $\mu$ m, with these elements accounting for ~98.8% and ~97.5% of the total inorganic species in PM<sub>1</sub> from pyrolysis of LC500 and WC500, respectively. The PSD for Mg exhibits a bimodal distribution with a fine mode diameter of 0.011  $\mu$ m and a coarse mode diameter of 4.087  $\mu$ m. While the PSDs of Ca and P show a unimodal distribution with a coarse mode diameter of 4.087  $\mu$ m. sharp edges. Couple with the similarity in the (Na+K+2Mg+2Ca)/(Cl+2S+3P) molar ratio in PM<sub>1-10</sub> and char collected in the cyclone, it is clear that PM<sub>1-10</sub> are fine char fragments generated during rapid pyrolysis of these biochars. Experimental results further show that PM<sub>1</sub> contains dominantly inorganic species because carbon only contributes to ~5.0 % and ~7.7 % of PM<sub>1</sub> produced from rapid pyrolysis of LC500 and WC500, respectively.

### CHAPTER 8 SOOT FORMATION AND SYNERGY STUDY DURING RAPID PYROLYSIS OF BIO-OIL AND ITS FRACTIONS IN A DROP-TUBE FURNACE AT 1300 °C

#### 8.1 Introduction

Bio-oil is an important derived liquid product from biomass pyrolysis. It helps control carbon emission, makes it easy for transportation, releases less SOx and NOx than typical fuels during application and has relatively high energy density [26, 30, 31]. Heat and power applications in boilers are good options for bio-oil utilization, and these applications in a boiler such as combustion are usually operated at high temperature (typically above 1300 °C). Pyrolysis is critically important as the first step in all these thermochemical processing. Bio-oil heavily releases volatiles into the gas phase during pyrolysis at high temperatures. These volatiles are rich in organics and soot could be generated. The soot in the fumes has great implications to operation conditions, the environment and human health [56].

The complexity of bio-oil causes soot formation from bio-oil pyrolysis at high temperature more complicated than that from fuel with simple composition. Besides the mechanism of HACA, several mechanisms including cyclopentadienes (CPDs) path and 'ring-ring' condensations are proposed in the research of soot formation, in which products with benzene rings like phenols and aromatics could be directly produced and form PAHs during pyrolysis [70, 71, 159].

Soot formation during thermochemical processing at high temperature is inevitable. However, there is little research clarifying soot formation from bio-oil during rapid pyrolysis pertinent to stationary application at high temperatures, as well as the synergies among different fractions in bio-oil. Another issue is the sampling method for soot products from flow reactors. Conventionally, paralyzed samples in fume gas go through a cyclone (interception of bulk samples) and collected on a filter paper were regarded as soot (previous studies [71, 159, 160] as examples). The new method reported in Chapter 4 achieves separation of soot and fine char fragments. Agglomeration and coagulation characteristics of soot clusters could also be analysed as illustrated in Chapter 5. Therefore, in this study, a bio-oil as well as its fractions (i.e. water-insoluble fraction, formulated water-soluble fraction, organics in bio-oil, etc.) were applied in a DTF with a novel sampling method at 1300 °C to clarify the soot formation and internal synergies during bio-oil rapid pyrolysis at high temperature. The properties of bio-oil and PL were presented in Table 8-1. The components of formulated bio-oil or fractions (i.e. FB, FWSF and FWSF-2) were illustrated in Table 8-2.

 Table 8-1. Properties of bio-oil and PL. PL is the water-insoluble fraction of filtered bio-oil.

Sample name	Bio-oil	PL
Water content (wt, %		
ad <sup>a</sup> )	26.00	1.06
Proximate a	nalysis (wt% ad <sup>a</sup> )	
ash	0.02	0.04
VM	n.d. <sup>c</sup>	81.08
FC	n.d. <sup>c</sup>	18.88
Ultimate an	nalysis (wt% ad <sup>a</sup> )	
С	41.31	66.56
Н	8.01	6.33
Ν	0.16	0.11

126 | P a g e

S	0.00	0.01				
$\mathrm{O}^{b}$	50.52	26.99				
Ash compositional analysis (mg/kg,ad <sup>a</sup> )						
Κ	13.66	9.28				
Mg	2.43	1.73				
Na	1.25	1.75				
Ca	16.15	13.78				
Cl	16.91	n.a. <sup>d</sup>				
Fractions by water extraction (wt %, ad <sup>a</sup> )						
Water-soluble	83.00	n.d. <sup>c</sup>				
Water-insoluble	17.00	n.d. <sup>c</sup>				
<sup>a</sup> As-received basis; <sup>b</sup> by difference; <sup>c</sup> Not applicable; <sup>d</sup>						

Not detected;

Table 8-2. Compositions of FB, FWSF and FWSF-2.

Composition (wt%)	FB	FWSF	FWSF-2
PL	17.00	0.00	0.00
Water	26.00	31.33	0.00
Acetic acid	18.40	22.17	34.46
Hydroxyacetone	18.40	22.17	34.46
Phenol	7.00	8.43	13.10
Furfual	7.00	8.43	13.10
Methanol	2.60	3.13	4.87
Levoglucosan	3.55	4.28	0.00
CaCl <sub>2</sub>	0.05	0.06	0.00

#### 8.2 Distributions and yields of soot from fast pyrolysis of bio-oil and its fractions

PSDs and yields of soot of the bio-oil, FB, PL and FWSF are presented in Figure 8-1 and Table 8-3. Several observations could be found in the results. Firstly, CM<sub>1</sub> is the main product of CM<sub>10</sub> which contributes to over 90 % in all CM<sub>10</sub> samples. Micromorphology analysis in Figure 8-2 shows that samples in CM<sub>1</sub> are soot, while in CM<sub>1-10</sub> they are carbon cenospheres. Secondly, Bio-oil and FB have the same PSDs and soot yields, indicating that FWSF could perfectly represent the watersoluble fractions of bio-oil during soot characterization. Thirdly, the soot distributions of bio-oil (same as FB), PL and FWSF have a unimodal distribution with a fine mode diameter at 0.077  $\mu$ m, 0.043  $\mu$ m and 0.077  $\mu$ m, respectively. Fourthly, PL has the highest soot yield of ~77 mg/g, while FWSF has the lowest soot yield of ~23 mg/g. It is reasonable as PL is composed of pyrolytic lignin macromolecules [52]. These macromolecules are rich in benzene rings and could readily react to form PAHs. Water-soluble fraction of bio-oil (represented by FWSF) mainly contains holocellulose decomposition products and water. During pyrolysis, most of the components crack into small gaseous species and do not directly give compound with benzene rings. The water could also react with these carbonaceous materials to reduce the soot yield. Thus making the soot yield of FWSF the lowest. When PL and FWSF are blended according to their contents in bio-oil. The soot yield of FB, which is the same as bio-oil, is ~31 mg/g.

Table 8-3. Soot yield during rapid pyrolysis of bio-oil and its fractions. Estimated soot yield is determined by calculation from individual parts <sup>a</sup> and <sup>b</sup> according to their contents in the mixture.

Samples	Experimental soot yield (mg/g)	Estimated soot yield (mg/g)	Percentage of experimental soot yield to estimated soot yield (%)
Bio-oil	$30.9\pm0.6$		
PL <sup>a</sup> + FWSF <sup>b</sup> (i.e. FB)	$30.5\pm0.8$	$32.3\pm1.1$	94.3
PL	$76.6\pm2.6$		
FWSF	$23.3\pm0.8$		
$(PL + FWSF-2)^{a} + water^{b}$ (i.e. FB-2)	$31.2\pm1.8$	$58.4\pm2.3$	53.5
FWSF-2	$45.6\pm0.8$		
$PL^{a} + FWSF-2^{b}$	$79.4\pm3.1$	$52.9\pm1.3$	150.1
			128   P a g e



Figure 8-1. PSDs of CM during rapid pyrolysis of bio-oil, FB, PL and FWSF at

1300 °C.



Figure 8-2. Micromorphology analysis of CM<sub>10</sub> samples during rapid pyrolysis at 1300 °C. (a)-(d): CM<sub>1</sub> (i.e. soot) samples from pyrolysis of bio-oil (a), FB (b), PL (c) and FWSF (d). (e)-(h): CM<sub>1-10</sub> sample from pyrolysis of bio-oil (e), FB (f), PL 129 | P a g e

#### (g) and FWSF (h).

### 8.3 Synergies among bio-oil fractions on soot yield during rapid pyrolysis at high temperatures

Table 8-3 further illustrates the comparison between estimated yield and measured yield during FB pyrolysis. When PL and FWSF are mixed for pyrolysis, the actual yield of soot is less than the estimated yield of soot calculated by PL and FWSF according to their contents in the mixture. The actual yield of soot is 94% of the estimated yields. It shows that there is a weak negative synergy between waterinsoluble fraction and water-soluble fraction in bio-oil during pyrolysis for soot formation. The main components of water-soluble fraction of bio-oil include organic matters and water. The synergy between organic matters in water-soluble fraction of bio-oil and PL is still unclear. Water could have a negative effect on soot formation through water-carbon interaction but this needs experimental verification. The successful formulation of water-soluble fraction of bio-oil (i.e. FWSF) provides a way to further analyse those synergies experimentally. Therefore, water was further separated out from FWSF. As levoglucosan and CaCl<sub>2</sub> are insoluble in FWSF without water, and their contents in FWSF are very low, levoglucosan and CaCl<sub>2</sub> were also removed. FB without levoglucosan and CaCl<sub>2</sub> (regarded as FB-2) was then prepared and pyrolyzed in DTF for verification of the ignorance of levoglucosan and CaCl<sub>2</sub>. The new mixture in which water, levoglucosan, and CaCl<sub>2</sub> removed from FWSF was termed as FWSF-2, it formulates the organics in water-soluble fraction of bio-oil.

Figure 8-3 further presents the PSDs of FB, FB-2, FWSF-2 and PL + FWSF-2,

accompanied with micromorphology analysis in Figure 8-4. The yield of soot is also included in Table 8-3. In Figure 8-3 and Table 8-3, no obvious difference was observed on PSDs and yield between soot from FB and FB-2. It indicates the ignorable effect of levoglucosan and CaCl<sub>2</sub> on soot formation in this study. Some reasons could explain this ignorable effect. Levoglucosan has high oxygen content and no benzene structure, which makes it hard to form soot and easy to be oxidised during pyrolysis. Besides, the contents of levoglucosan and especially CaCl<sub>2</sub> in bio-oil, are very low.



Figure 8-3. PSDs of CM from rapid pyrolysis of bio-oil fractions at 1300 °C.



Figure 8-4. Micromorphology analysis of CM<sub>10</sub> samples during rapid pyrolysis at 1300 °C. (a)-(c): CM<sub>1</sub> (i.e. soot) samples from pyrolysis of FWSF-2 (a), PL + FWSF-2 (b), FB-2 (c). (d)-(f): CM<sub>1-10</sub> sample from pyrolysis of FWSF-2 (d), PL + FWSF-2 (e), FB-2 (f).

PSDs from pyrolysis of FB-2 (same as FB), FWSF-2, PL + FWSF-2 display a unimodal distribution with a mode diameter at 0.077  $\mu$ m, 0.246  $\mu$ m and 0.246  $\mu$ m, respectively. The soot yield of FWSF-2 is ~46 mg/g, while after being mixed with PL, the soot yield increases to ~79 mg/g. PL and FSWF-2 have obviously positive synergies on soot formation during high temperature pyrolysis. The actual yield of soot sample is ~150 % to the estimated soot yield calculated by individuals according to their contents. It is reasonable because when PL and FWSF-2 mixture was fed into the furnace, the concentration of soot-forming carbonaceous materials

132 | P a g e

in gas phase was increased, these materials can more easily collide with each other for reaction, thus making PAHs as well as soot become more easily formed. Another reason is that large amount of small molecules like C<sub>2</sub>H<sub>2</sub> cracked from organics in FWSF could skip forming PAHs and soot precursors, and could directly collide with soot precursors formed from pyrolysis of PL for soot growth, as PL contains more benzene structures and readily forms PAHs and soot precursors.

When water was added into the mixture of PL and FWSF-2 according to its content in bio-oil, thus FB-2. The yield of soot from the mixture (i.e. FB-2) decreases sharply from ~79 mg/g to ~31 mg/g. In Table 8-3, the actual yield of soot is only ~53 % to the estimated soot yield comparing with the one without water. The carbon-water reaction could consume carbonaceous materials for soot formation as well as soot during pyrolysis. It clearly shows the water in bio-oil decreases the soot yield during high temperature pyrolysis and explains the negative synergies when PL and FWSF are mixed.

# 8.4 Characterization of soot clusters during rapid pyrolysis at high temperatures

It could be seen from morphology analysis in Figure 8-2 and Figure 8-4 that soot individual particles are very small, just tens of nanometers. Comparing the aerodynamic collection diameters in DLPI. Soot is largely collected and separated in DLPI in terms of soot clusters. Therefore, SMD was also applied here and it is calculated according to the contributions of soot clusters with certain aerodynamic diameters in Figure 8-1 and Figure 8-4. It reflects the degree of soot coagulation and agglomeration.

Figure 8-5 presents the SMD during pyrolysis of different samples. Similar to Chapter 5, Section 5.5. Soot concentration (Z) in flue gas was also applied here. Z reflects the average soot concentration in the furnace tube of DTF during rapid pyrolysis. It is an indicator of collision probability of soot particles during pyrolysis. Collision among soot particles is important as the precondition of coagulation and agglomeration for soot clusters formation. In Figure 8-5, PL has the smallest SMD as its Z is the lowest. When mixed with FWSF, the SMD of FB increases because of increasing of Z during pyrolysis. It is the same for the results when PL mixed with FWSF-2. When water is added into PL + FWSF-2, it significantly decreases the soot yield thus the Z in the reactor decreases, making SMD decreases. In general, Figure 8-5 shows that Z has a positive effect on SMD. It is reasonable because high Z means soot particles in the reactor are more likely to collide with each other for coagulation and agglomeration. However, there is an exception for FB (or FB-2) and FWSF-2, FWSF-2 has lower Z however higher SMD. One possible reason is the difference of coagulation and agglomeration. Coagulation is a collection with chemically-bond between soot particles, and it needs the essential supply carbonaceous radicals. However, agglomeration is just a loosely-connection among soot particles which caused by soot particle collision. The carbonaceous radicals are more reactant than soot and could easily react with water. The lack of carbonaceous radicals suppresses coagulations during soot particle collisions. Soot clusters formed through agglomeration are loosely connected and easily break [69]. Therefore, even though the chance of soot particle collision is higher for FB or FB-2, its SMD is smaller than that of FWSF-2.



Figure 8-5. SMD of soot samples from rapid pyrolysis of bio-oil and its fractions at 1300 °C.

#### 8.5 Conclusions

This chapter reports the rapid pyrolysis of bio-oil and its fractions in a DTF at 1300 °C. Soot formation and the synergies among fractions of bio-oil were studied. Formulated samples were successfully applied to represent the water-soluble fractions in bio-oil for soot formation. Pyrolyzed samples in  $CM_{10}$  are concentrated in  $CM_1$ , which are soot, while samples in  $CM_{1-10}$  are carbon cenospheres. Soot from bio-oil, PL and FWSF shows a unimodal distribution with a mode diameter of 0.077  $\mu$ m, 0.043  $\mu$ m and 0.077  $\mu$ m, respectively. PL has the higher soot yield of ~77 mg/g than that of ~23 mg/g for FWSF. When mixed, it shows negative synergy between PL and FWSF, the yield of mixture (i.e. bio-oil) is ~31 mg/g, which is ~94 % of the estimated soot yield calculated by individual fractions according to their contents in bio-oil. The organics in FWSF (i.e. FWSF-2) shows a unimodal distribution with a mode diameter at 0.246  $\mu$ m. The soot yield of it is ~150 % of the estimated with PL, the soot yield increases to 79 mg/g, which is ~150 % of the estimated

soot yield calculated by individuals. Water in bio-oil causes negative synergetic effects on soot formation during pyrolysis. In this study, the water in bio-oil could reduce the soot yield to  $\sim$ 53 % comparing with the one without water. Soot from pyrolysis of bio-oil and its fractions also has different average cluster sizes. The soot concentration has obvious effect on average soot cluster size as it increases the chance of collision. Water reduces average soot cluster size by reducing soot yield and avoiding soot coagulation.

### **CHAPTER 9 CONCLUSIONS AND RECOMMENDATIONS**

### 9.1 Introduction

This chapter summarizes the key research outcomes and provides some recommendations on future work according to the author's knowledge in this area. Overall, this thesis systematically studied the rapid pyrolysis of biomass, biomass model components and biomass derived products in a DTF at high temperature. The pyrolysis samples (mainly focused on soot) were characterized and discussed. We developed a novel sampling system and successfully characterized the size-segregated soot during pyrolysis. We then applied this system for pyrolysis products characterization after high temperature pyrolysis. The thesis reported the formation of soot, char and inorganic species during high temperature pyrolysis. Finally, based on the data and findings from the study and literature review, some recommendations are also proposed for future work in this area.

### 9.2 Conclusions

# 9.2.1 Characterization of Size-Segregated Soot from Pine Wood Pyrolysis in a DTF at 1300 °C

- DLPI could be applied for size-segregated collection of soot from pyrolysis, and the amount of feedstock should be optimized. (<150 mg for biomass).</li>
- CM<sub>10</sub> from pyrolysis of biomass is mainly CM<sub>1</sub> (>98%), CM<sub>1-10</sub> mainly consists of char fragments while CM<sub>1</sub> is soot.

- 3) Na, K and Cl are the major inorganic elements in soot.
- K is more likely to incorporate with soot to form organic bond than Na. Nonmature soot contains more Na and K than mature soot.
- 5) Water-soluble alkali species in soot could form ultrafine ash particle resultant from homogeneous condensation of alkali species, or deposit on the soot particles through heterogeneous condensation.

# 9.2.2 Mechanistic insights into effect of feeding rate on soot formation during rapid pyrolysis of biomass model components in a DTF at high temperature

- Feeding rate could significantly influence soot formation during rapid pyrolysis at high temperature.
- PSD: different feeding rate results in different PSDs from pyrolysis of Wcellulose and A-lignin. An increase in feeding rate results in an increase in the mode diameter of soot.
- 3) Soot yield and individual soot particle size: When feeding rate increases from 40 to 280 mg/min for W-cellulose and from 12 to 40 mg/min for A-lignin, both soot yield and individual soot particle size increase whereas the yield of nonmature soot decreases. As A-lignin feeding rate increases further above 40 mg/min, the soot yield remains unchanged, the diameters of individual soot particles decrease and the yield of non-mature soot increases.

4) The size of soot cluster: with the increase of feeding rate, the size of soot clusters increases substantially at soot concentration ≤ ~5 mg/min. However, at soot concentration > ~5 mg/min, the increase of soot cluster size with increasing soot concentration becomes considerably slower.

# 9.2.3 Differences in soot produced from rapid pyrolysis of xylan, cellulose and lignin under pulverized-fuel conditions

- 1) The  $CM_{10}$  samples collected are dominantly  $CM_1$  that is soot.
- 2) The yield of soot from lignin pyrolysis (~100.7 mg/g) is substantially higher than that from xylan pyrolysis (~7.0 mg/g) and cellulose pyrolysis (~11.6 mg/g).
- Fringe of soot from lignin soot is longer and straighter compared to that of cellulose soot and xylan soot.
- Soot from cellulose pyrolysis contains little inorganic species because of little ash content in cellulose. For xylan and lignin, Na, K, Cl and S could be found both in xylan soot and lignin soot.
- 5) Na and K salts could condense on soot through homogenous or heterogeneous condensation. They could also incorporate with soot and organically bind to soot. K is more likely to incorporate with soot compared to Na. Higher amounts of Na and K are incorporated in soot from pyrolysis of xylan compared to that from pyrolysis of lignin. Non-mature soot only takes a small ratio of soot. However, it contains higher contents of incorporated Na and K than mature soot.

# 9.2.4 Fundamental investigation into characteristics of particulate matter produced from rapid pyrolysis of biochar in a DTF at 1300 °C

- 1) The PSDs of  $PM_{10}$  for pyrolysis of LC500 and WC500 have a bimodal distribution with a fine mode diameter of 0.011 µm and a coarse mode diameter of 4.087 µm.
- 2) Na, K and Cl contribute to the majority of  $PM_1$ , Ca is the main inorganic in  $PM_{1-10}$ .
- 3)  $PM_{1-10}$  are fine char fragments generated during rapid pyrolysis.
- 4)  $PM_1$  contains dominantly inorganic species. Carbon only contributes to ~5.0 % and ~7.7% of  $PM_1$  produced from rapid pyrolysis of LC500 and WC500, respectively.

# 9.2.5 Soot formation and synergy study during rapid pyrolysis of bio-oil and its fractions in a DTF at 1300 $^{\circ}\mathrm{C}$

- Formulated samples were successfully applied to represent the water-soluble fractions in bio-oil for soot formation study.
- Pyrolyzed samples in CM<sub>10</sub> are concentrated in CM<sub>1</sub>, which are soot. While samples in CM<sub>1-10</sub> are carbon cenospheres.
- A negative synergy on soot formation between water-insoluble fraction of biooil and water-soluble fraction of bio-oil.

 Water in bio-oil causes negative synergetic effects on soot formation during pyrolysis.

#### 9.3 Recommendations

Based on literature reviews and the conclusions in the study, some recommendations are proposed here for future investigations.

- Bioslurry, a mixture of bio-oil and biochar, is also a potential fuel for biomass derived products for stationary utilization. The high temperature pyrolysis products of bio-oil and biochar are totally different as illustrated in the thesis. When mixed bio-oil and biochar is used for high temperature pyrolysis, the results should be very interesting and worth investigation.
- 2) In the thesis, we studied the high temperature rapid pyrolysis of biomass and biomass model components. However, the synergies between different biomass model components are still unknown. Future work is suggested to conduct experiments to clarify the synergies between different biomass model components on soot formation during high temperature pyrolysis.
- 3) The inorganics are known to have effects on soot and char formation. However, the studies of the effect of inorganic species on soot and char formation during biomass model components are not sufficient. Future work is suggested to study the effect of inorganic species on soot and char formation during biomass model components pyrolysis at high temperature.

- 4) In this thesis, we focused on the solid pyrolysis samples after high temperature pyrolysis. The gas, which is also very important pyrolysis product, needs to be characterized. Future work on gas products characterization is recommended.
- 5) Some factors like particle size and pyrolysis residence time could also influence soot formation and distribution during high temperature rapid pyrolysis. There is a lack of investigation on the effect of these factors. Future work of the effect of these factors on soot formation is recommended.
- 6) The phenomenon of soot oxidation is also common during stationary application. The incomplete combustion could also produce soot. Investigations of soot formation and oxidation during incomplete combustion are recommended.

### REFERENCES

- Bartle, J.R. and A. Abadi, Toward sustainable production of second generation bioenergy feedstocks. Energy & Fuels, 2009. 24(1): p. 2-9.
- Smeets, E.M., et al., A bottom-up assessment and review of global bio-energy potentials to 2050. Progress in energy and combustion science, 2007. 33(1):
   p. 56-106.
- 3. Global bioenergy statistics. Available from: https://worldbioenergy.org/global-bioenergy-statistics.
- 4. Zhang, Q., et al., Review of biomass pyrolysis oil properties and upgrading research. Energy conversion and management, 2007. **48**(1): p. 87-92.
- Yu, Y., et al., Mallee biomass as a key bioenergy source in Western Australia: importance of biomass supply chain. Energy & Fuels, 2009. 23(6): p. 3290-3299.
- Abdullah, H. and H. Wu, Biochar as a fuel: 1. Properties and grindability of biochars produced from the pyrolysis of mallee wood under slow-heating conditions. Energy & Fuels, 2009. 23(8): p. 4174-4181.
- Mohan, D., C.U. Pittman Jr, and P.H. Steele, Pyrolysis of wood/biomass for bio-oil: a critical review. Energy & Fuels, 2006. 20(3): p. 848-889.
- Cooper, D., G. Olsen, and J. Bartle, Capture of agricultural surplus water determines the productivity and scale of new low-rainfall woody crop industries. Australian Journal of Experimental Agriculture, 2006. 45(11): p. 1369-1388.
- Bartle, J., et al., Acacia species as large-scale crop plants in the Western Australian wheatbelt. Conservation Science Western Australia, 2002. 4(3).
- 10. Bartle, J., et al., Scale of biomass production from new woody crops for

salinity control in dryland agriculture in Australia. International journal of global energy issues, 2007. **27**(2): p. 115-137.

- Wu, H., et al., Production of mallee biomass in Western Australia: energy balance analysis. Energy & Fuels, 2008. 22(1): p. 190-198.
- Madadi, M. and A. Abbas, Lignin degradation by fungal pretreatment: a review. J. Plant Pathol. Microbiol, 2017. 8(2): p. 1-6.
- Turner, M.B., et al., Production of bioactive cellulose films reconstituted from ionic liquids. Biomacromolecules, 2004. 5(4): p. 1379-1384.
- Swatloski, R.P., et al., Dissolution of cellulose [correction of cellose] with ionic liquids. J Am Chem Soc, 2002. 124(18): p. 4974-5.
- 15. Rowell, R., The chemistry of solid wood. 1984.
- Runkel, R.O.H. and K.D. Wilke, Zur Kenntnis des thermoplastischen Verhaltens von Holz. Holz als Roh- und Werkstoff, 1951. 9(7): p. 260-270.
- Soltes, E. and T. Elder, Pyrolysis in organic chemicals from biomass. IS Goldstein. Florida, CRC Press, 1981.
- Glasser, W.G., R.A. Northey, and T.P. Schultz, Lignin: historical, biological, and materials perspectives. 1999: ACS Publications.
- Murphy, J. and K. McCarthy, Ethanol production from energy crops and wastes for use as a transport fuel in Ireland. Applied Energy, 2005. 82(2): p. 148-166.
- Fengel, D. and G. Wegener, Wood: chemistry, ultrastructure, reactions. 2011: Walter de Gruyter.
- 21. Nimz, H., Chemistry of potential chromophoric groups in beech lignin. 1973.
- 22. Vassilev, S.V., et al., An overview of the organic and inorganic phase composition of biomass. Fuel, 2012. **94**: p. 1-33.
- 23. Vassilev, S.V., C.G. Vassileva, and D. Baxter, Trace element concentrations

and associations in some biomass ashes. Fuel, 2014. 129: p. 292-313.

- 24. Leijenhorst, E.J., et al., Inorganic element transfer from biomass to fast pyrolysis oil: Review and experiments. Fuel Processing Technology, 2016.
  149: p. 96-111.
- Zhao, S., et al., Effects of organic and inorganic metal salts on thermogravimetric pyrolysis of biomass components. Korean Journal of Chemical Engineering, 2017. 34(12): p. 3077-3084.
- Czernik, S. and A. Bridgwater, Overview of applications of biomass fast pyrolysis oil. Energy & Fuels, 2004. 18(2): p. 590-598.
- Huber, G.W., S. Iborra, and A. Corma, Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. Chemical reviews, 2006.
  106(9): p. 4044-4098.
- Demirbas, A., Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues. Journal of analytical and applied pyrolysis, 2004. 72(2): p. 243-248.
- Bridgwater, A.V., Review of fast pyrolysis of biomass and product upgrading. Biomass and bioenergy, 2012. 38: p. 68-94.
- Churin, E. and B. Delmon, What can we do with pyrolysis oils. Pyrolysis and Gasification, London: Elsevier Applied Science, 1989: p. 326-333.
- Pütün, A.E., Biomass to bio-oil via fast pyrolysis of cotton straw and stalk. Energy Sources, 2002. 24(3): p. 275-285.
- Ahmad, M., et al., Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere, 2014. 99: p. 19-33.
- 33. Mohan, D., et al., Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent-a critical review. Bioresource technology, 2014. 160: p. 191-202.

- Shen, Y., Chars as carbonaceous adsorbents/catalysts for tar elimination during biomass pyrolysis or gasification. Renewable and Sustainable Energy Reviews, 2015. 43: p. 281-295.
- 35. Konwar, L.J., J. Boro, and D. Deka, Review on latest developments in biodiesel production using carbon-based catalysts. Renewable and Sustainable Energy Reviews, 2014. 29: p. 546-564.
- NAJAR, G.R., M.A. GANIE, and A. Tahir, Biochar for sustainable soil health: a review of prospects and concerns. Pedosphere, 2015. 25(5): p. 639-653.
- Yu, J., Y. Zhao, and Y. Li, Utilization of corn cob biochar in a direct carbon fuel cell. Journal of Power Sources, 2014. 270: p. 312-317.
- 38. Elleuch, A., et al., Experimental investigation of direct carbon fuel cell fueled by almond shell biochar: Part I. Physico-chemical characterization of the biochar fuel and cell performance examination. International journal of hydrogen energy, 2013. 38(36): p. 16590-16604.
- Gupta, R.K., et al., Biochar activated by oxygen plasma for supercapacitors.
   Journal of Power Sources, 2015. 274: p. 1300-1305.
- Jiang, J., et al., Highly ordered macroporous woody biochar with ultra-high carbon content as supercapacitor electrodes. Electrochimica Acta, 2013. 113: p. 481-489.
- 41. Duku, M.H., S. Gu, and E.B. Hagan, Biochar production potential in Ghana—a review. Renewable and Sustainable Energy Reviews, 2011. 15(8):
  p. 3539-3551.
- Kambo, H.S. and A. Dutta, A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. Renewable and Sustainable Energy Reviews, 2015. 45: p. 359-378.

- 43. Liu, N., et al., Characterization of biochars derived from agriculture wastes and their adsorptive removal of atrazine from aqueous solution: A comparative study. Bioresource technology, 2015. **198**: p. 55-62.
- 44. Inguanzo, M., et al., On the pyrolysis of sewage sludge: the influence of pyrolysis conditions on solid, liquid and gas fractions. Journal of Analytical and Applied Pyrolysis, 2002. 63(1): p. 209-222.
- Chen, G., et al., Biomass pyrolysis/gasification for product gas production: the overall investigation of parametric effects. Energy conversion and management, 2003. 44(11): p. 1875-1884.
- Al-Wabel, M.I., et al., Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes. Bioresource technology, 2013. 131: p. 374-379.
- 47. Zhang, J., J. Liu, and R. Liu, Effects of pyrolysis temperature and heating time on biochar obtained from the pyrolysis of straw and lignosulfonate. Bioresource Technology, 2015. 176: p. 288-291.
- 48. Lu, G., et al., Surface area development of sewage sludge during pyrolysis.Fuel, 1995. 74(3): p. 344-348.
- Bandosz, T.J. and K. Block, Effect of pyrolysis temperature and time on catalytic performance of sewage sludge/industrial sludge-based composite adsorbents. Applied Catalysis B: Environmental, 2006. 67(1-2): p. 77-85.
- 50. Peacocke, G., et al., Physical properties of flash pyrolysis liquids. Biomass and Bioenergy, 1994. 7(1-6): p. 169-177.
- Peacocke, G. and A. Bridgwater, Ablative plate pyrolysis of biomass for liquids. Biomass and Bioenergy, 1994. 7(1-6): p. 147-154.
- 52. Piskorz, J., D. Scott, and D. Radlein, Composition of oils obtained by fast pyrolysis of different woods. 1988, ACS Publications.

- 53. Oasmaa, A. and S. Czernik, Fuel oil quality of biomass pyrolysis oils state of the art for the end users. Energy & Fuels, 1999. **13**(4): p. 914-921.
- Amen-Chen, C., H. Pakdel, and C. Roy, Production of monomeric phenols by thermochemical conversion of biomass: a review. Bioresource technology, 2001. 79(3): p. 277-299.
- 55. Elliott, D.C., Analysis and comparison of biomass pyrolysis/gasification condensates. 1986, Pacific Northwest Lab., Richland, WA (USA).
- Viskanta, R., Overview of some radiative transfer issues in simulation of unwanted fires. International Journal of Thermal Sciences, 2008. 47(12): p. 1563-1570.
- 57. Murr, L. and K. Garza, Natural and anthropogenic environmental nanoparticulates: their microstructural characterization and respiratory health implications. Atmospheric Environment, 2009. **43**(17): p. 2683-2692.
- Bond, T.C., et al., Bounding the role of black carbon in the climate system: A scientific assessment. Journal of Geophysical Research: Atmospheres, 2013. 118(11): p. 5380-5552.
- Evans, R.J. and T.A. Milne, Molecular characterization of the pyrolysis of biomass. Energy & Fuels, 1987. 1(2): p. 123-137.
- Evans, R.J. and T.A. Milne, Molecular characterization of the pyrolysis of biomass. 2. Applications. Energy & Fuels, 1987. 1(4): p. 311-319.
- Khan, M. and B.L. Crynes, Survey of recent methane pyrolysis literature. Industrial & Engineering Chemistry, 1970. 62(10): p. 54-59.
- 62. Richter, H. and J.B. Howard, Formation of polycyclic aromatic hydrocarbons and their growth to soot—a review of chemical reaction pathways. Progress in Energy and Combustion science, 2000. 26(4-6): p. 565-608.
- 63. Frenklach, M. and H. Wang, Detailed mechanism and modeling of soot

particle formation, in Soot formation in combustion. 1994, Springer. p. 165-192.

- 64. Krestinin, A., et al., On the mechanism of soot particle formation. Kinetics and Catalysis, 2000. **41**(1): p. 90-98.
- D'alessio, A., et al., On the relevance of surface growth in soot formation in premixed flames. Proceedings of the Combustion Institute, 2000. 28(2): p. 2547-2554.
- 66. Kronholm, D.F. and J.B. Howard, Analysis of soot surface growth pathways using published plug-flow reactor data with new particle size distribution measurements and published premixed flame data. Proceedings of the Combustion Institute, 2000. 28(2): p. 2555-2561.
- Woods, I.T. and B.S. Haynes, Active sites in soot growth, in Soot Formation in Combustion. 1994, Springer. p. 275-289.
- 68. Frenklach, M. and H. Wang. Detailed modeling of soot particle nucleation and growth. in Symposium (International) on Combustion. 1991. Citeseer.
- Michelsen, H., Probing soot formation, chemical and physical evolution, and oxidation: A review of in situ diagnostic techniques and needs. Proceedings of the Combustion Institute, 2017. 36(1): p. 717-735.
- Williams, A., et al., Pollutants from the combustion of solid biomass fuels.Progress in Energy and Combustion Science, 2012. 38(2): p. 113-137.
- 71. Fitzpatrick, E., et al., Mechanistic aspects of soot formation from the combustion of pine wood. Energy & Fuels, 2008. **22**(6): p. 3771-3778.
- 72. Fitzpatrick, E., et al., Emission of oxygenated species from the combustion of pine wood and its relation to soot formation. Process safety and environmental protection, 2007. **85**(5): p. 430-440.
- 73. Palmer, H.B. and C.F. Cullis, The formation of carbon from gases. Chemistry

and physics of carbon, 1965. 1: p. 265-325.

- 74. Ciajolo, A., et al. Spectroscopic and compositional signatures of PAH-loaded mixtures in the soot inception region of a premixed ethylene flame. in Symposium (International) on Combustion. 1998. Elsevier.
- Russo, C., A. Tregrossi, and A. Ciajolo, Dehydrogenation and growth of soot in premixed flames. Proceedings of the Combustion Institute, 2015. 35(2): p. 1803-1809.
- 76. D'Alessio, A., et al. Precursor formation and soot inception in premixed ethylene flames. in Symposium (International) on Combustion. 1992. Elsevier.
- 77. Blevins, L.G., et al., The existence of young soot in the exhaust of inverse diffusion flames. Proceedings of the Combustion Institute, 2002. 29(2): p. 2325-2333.
- Dobbins, R.A. and H. Subramaniasivam, Soot precursor particles in flames, in Soot formation in combustion. 1994, Springer. p. 290-301.
- 79. Homann, K.H. and H.G. Wagner. Some new aspects of the mechanism of carbon formation in premixed flames. in Symposium (International) on Combustion. 1967. Elsevier.
- Harris, S.J. and A.M. Weiner, Chemical kinetics of soot particle growth.
   Annual Review of Physical Chemistry, 1985. 36(1): p. 31-52.
- Howard, J.B. Carbon addition and oxidation reactions in heterogeneous combustion and soot formation. in Symposium (International) on Combustion. 1991. Elsevier.
- Wang, H., Formation of nascent soot and other condensed-phase materials in flames. Proceedings of the Combustion Institute, 2011. 33(1): p. 41-67.
- 83. Öktem, B., et al., Chemical species associated with the early stage of soot

growth in a laminar premixed ethylene–oxygen–argon flame. Combustion and Flame, 2005. **142**(4): p. 364-373.

- Minutolo, P., et al., Spectroscopic characterisation of carbonaceous nanoparticles in premixed flames. Atmospheric Environment, 1999. 33(17): p. 2725-2732.
- Commodo, M., et al., Further details on particle inception and growth in premixed flames. Proceedings of the Combustion Institute, 2015. 35(2): p. 1795-1802.
- Commodo, M., et al., Characterization of combustion-generated carbonaceous nanoparticles by size-dependent ultraviolet laser photoionization. The Journal of Physical Chemistry A, 2013. 117(19): p. 3980-3989.
- Abid, A.D., et al., On evolution of particle size distribution functions of incipient soot in premixed ethylene–oxygen–argon flames. Combustion and Flame, 2008. 154(4): p. 775-788.
- 88. Grotheer, H.-H., et al., Mass spectrometry up to 1 million mass units for the simultaneous detection of primary soot and of soot precursors (nanoparticles) in flames. Chemosphere, 2004. 57(10): p. 1335-1342.
- Russo, C., et al., Probing structures of soot formed in premixed flames of methane, ethylene and benzene. Proceedings of the Combustion Institute, 2013. 34(1): p. 1885-1892.
- 90. Shaddix, C.R., et al., Flame structure of steady and pulsed sooting inverse jet diffusion flames. Proceedings of the Combustion Institute, 2005. 30(1): p. 1501-1508.
- 91. Apicella, B., et al., Soot nanostructure evolution in premixed flames by High Resolution Electron Transmission Microscopy (HRTEM). Proceedings of the

Combustion Institute, 2015. **35**(2): p. 1895-1902.

- 92. Alfè, M., et al., Structure–property relationship in nanostructures of young and mature soot in premixed flames. Proceedings of the Combustion Institute, 2009. 32(1): p. 697-704.
- 93. Herdman, J.D., et al., A comparison of Raman signatures and laser-induced incandescence with direct numerical simulation of soot growth in non-premixed ethylene/air flames. Carbon, 2011. 49(15): p. 5298-5311.
- Hayashida, K., S. Nagaoka, and H. Ishitani, Growth and oxidation of graphitic crystallites in soot particles within a laminar diffusion flame. Fuel, 2014. 128: p. 148-154.
- 95. Vander Wal, R.L., V.M. Bryg, and C.-H. Huang, Aircraft engine particulate matter: macro-micro-and nanostructure by HRTEM and chemistry by XPS. Combustion and Flame, 2014. 161(2): p. 602-611.
- 96. Vander Wal, R.L., V.M. Bryg, and C.-H. Huang, Insights into the combustion chemistry within a gas-turbine driven auxiliary power unit as a function of fuel type and power level using soot nanostructure as a tracer. Fuel, 2014.
  115: p. 282-287.
- 97. Dobbins, R. and C. Megaridis, Morphology of flame-generated soot as determined by thermophoretic sampling. Langmuir, 1987. **3**(2): p. 254-259.
- 98. Puri, R., et al., Aerosol dynamic processes of soot aggregates in a laminar ethene diffusion flame. Combustion and flame, 1993. 92(3): p. 320-333.
- 99. Lahaye, J. and G. Prado, Morphology and internal structure of soot and carbon blacks, in Particulate carbon. 1981, Springer. p. 33-55.
- Smekens, A., et al., The elemental composition and microstructure of soot emitted by different sources. Journal of aerosol science, 2000. 31: p. S917-S918.

- 101. Wu, J., Soot abatement using oxygenated additives. 2004.
- 102. Ishiguro, T., Y. Takatori, and K. Akihama, Microstructure of diesel soot particles probed by electron microscopy: first observation of inner core and outer shell. Combustion and flame, 1997. 108(1-2).
- Septien Stringel, S., High temperature gasification of millimetric wood particles between 800 C and 1400 C. 2011, INPT.
- Glassman, I. Soot formation in combustion processes. in Symposium (international) on combustion. 1989. Elsevier.
- 105. Wang, X., et al., Soot formation during biomass pyrolysis: Effects of temperature, water-leaching, and gas-phase residence time. Journal of Analytical and Applied Pyrolysis, 2018. 134: p. 484-494.
- 106. Ruiz, M., et al., Influence of the temperature on the properties of the soot formed from C 2 H 2 pyrolysis. Chemical Engineering Journal, 2007. 127(1):
  p. 1-9.
- 107. Vander Wal, R.L. and A.J. Tomasek, Soot nanostructure: dependence upon synthesis conditions. Combustion and Flame, 2004. **136**(1): p. 129-140.
- Tree, D.R. and K.I. Svensson, Soot processes in compression ignition engines. Progress in Energy and Combustion Science, 2007. 33(3): p. 272-309.
- Barry, E., et al., Heavy-Duty Diesel Engine/Fuels Combustion Performance and Emissions—A Cooperative Research Program. SAE transactions, 1985: p. 503-525.
- Calcote, H. and D. Manos, Effect of molecular structure on incipient soot formation. Combustion and Flame, 1983. 49(1-3): p. 289-304.
- 111. Trubetskaya, A., et al., Potassium and soot interaction in fast biomass pyrolysis at high temperatures. Fuel, 2018. 225: p. 89-94.

- 112. Qin, K., et al., Characterization of residual particulates from biomass entrained flow gasification. Energy & Fuels, 2012. **27**(1): p. 262-270.
- 113. Trubetskaya, A., et al., Effects of several types of biomass fuels on the yield, nanostructure and reactivity of soot from fast pyrolysis at high temperatures.
   Applied energy, 2016. 171: p. 468-482.
- 114. Yu, Y., X. Lou, and H. Wu, Some recent advances in hydrolysis of biomass in hot-compressed water and its comparisons with other hydrolysis methods. Energy & Fuels, 2008. 22(1): p. 46-60.
- 115. Zhang, M. and H. Wu, Pyrolytic lignin from fast pyrolysis bio-oil via cold-water precipitation: Optimal separation conditions and properties. Fuel, 2019.
  242: p. 580-586.
- Oasmaa, A., E. Kuoppala, and Y. Solantausta, Fast pyrolysis of forestry residue.
   Physicochemical composition of product liquid. Energy & Fuels, 2003. 17(2): p. 433-443.
- 117. Li, M., et al., Ternary System of Pyrolytic Lignin, Mixed Solvent, and Water:Phase Diagram and Implications. Energy & Fuels, 2017. 32(1): p. 465-474.
- Chen, X. and H. Wu, Transformation and release of phosphorus during rice bran pyrolysis: Effect of reactor configurations under various conditions. Fuel, 2019. 255: p. 115755.
- 119. Ghezelchi, M.H., M. Garcia-Perez, and H. Wu, Bioslurry as a Fuel. 7: Spray Characteristics of Bio-oil and Bioslurry via Impact and Twin-Fluid Atomizers. Energy & Fuels, 2015. 29(12): p. 8058-8065.
- 120. Oasmaa, A., et al., Physical characterisation of biomass-based pyrolysis liquids: application of standard fuel oil analyses. VTT publications, 1997.
- 121. Gao, X. and H. Wu, Effect of sampling temperature on the properties of inorganic particulate matter collected from biomass combustion in a drop-

tube furnace. Energy & Fuels, 2010. 24(8): p. 4571-4580.

- 122. ASTM International. E871-82(2019) Standard Test Method for Moisture Analysis of Particulate Wood Fuels. West Conshohocken, PA; ASTM International, 2019. doi: https://doi.org/10.1520/E0871-82R19.
- 123. Zhang, M., X. Gao, and H. Wu, A Method for the Quantification of Alkali and Alkaline Earth Metallic Species in Bioslurry Fuels. Energy & Fuels, 2013. 27(11): p. 6823-6830.
- 124. Standard, A., AS 1038.6.1—1997 (2013). Coal and Coke—Analysis and Testing. Part 6.1: Higher Rank Coal and Coke—Ultimate Analysis—Carbon and Hydrogen. In Standard Australia: Sydney, Australia, 2013.
- 125. Rahim, M.U., X. Gao, and H. Wu, Determination of chlorine in solid fuels using an improved Eschka method. Fuel, 2014. 129: p. 314-317.
- 126. Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D. Determination of Sugars, Byproducts and Degradation Products in Liquid Fraction Process Sample; National Renewable Energy Laboratory (NREL): Golden, CO, 2008; Laboratory Analytical Procedure (LAP), Technical Report NREL/TP-510-42623.
- 127. Liaw, S.B., et al., Differences in Leaching Characteristics of Mg and Ca from Various Biomass Components of Mallee Tree in Hot-Compressed Water. Energy & Fuels, 2016. **30**(10): p. 7851-7857.
- 128. Fitzpatrick, E., et al., The mechanism of the formation of soot and other pollutants during the co-firing of coal and pine wood in a fixed bed combustor. Fuel, 2009. 88(12): p. 2409-2417.
- 129. Wilson, J., et al., Soot formation from the combustion of biomass pyrolysis products and a hydrocarbon fuel, n-decane: an aerosol time of flight mass spectrometer (ATOFMS) study. Energy & Fuels, 2013. 27(3): p. 1668-1678.

- Wu, H., et al., An experimental study on the effect of system pressure on char structure of an Australian bituminous coal. Energy & Fuels, 2000. 14(2): p. 282-290.
- Werkelin, J., et al., Chemical forms of ash-forming elements in woody biomass fuels. Fuel, 2010. 89(2): p. 481-493.
- 132. Gao, X. and H. Wu, Combustion of volatiles produced in situ from the fast pyrolysis of woody biomass: direct evidence on its substantial contribution to submicrometer particle (PM1) emission. Energy & Fuels, 2011. 25(9): p. 4172-4181.
- Johansen, J.M., et al., Release of K, Cl, and S during pyrolysis and combustion of high-chlorine biomass. Energy & Fuels, 2011. 25(11): p. 4961-4971.
- 134. Gao, X. and H. Wu, Biochar as a fuel: 4. Emission behavior and characteristics of PM1 and PM10 from the combustion of pulverized biochar in a drop-tube furnace. Energy & Fuels, 2011. 25(6): p. 2702-2710.
- 135. Chen, X., S.B. Liaw, and H. Wu, Important role of volatile–char interactions in enhancing PM 1 emission during the combustion of volatiles from biosolid. Combustion and Flame, 2017. 182: p. 90-101.
- Lindström, E., et al., Slagging characteristics during combustion of cereal grains rich in phosphorus. Energy & Fuels, 2007. 21(2): p. 710-717.
- Wigmans, T., H. Haringa, and J.A. Moulijn, Nature, activity and stability of active sites during alkali metal carbonate-catalysed gasification reactions of coal char. Fuel, 1983. 62(2): p. 185-189.
- 138. Rahim, M.U., et al., Release of chlorine during mallee bark pyrolysis. Energy & Fuels, 2012. 27(1): p. 310-317.
- 139. Wornat, M.J., et al., Structural and compositional transformations of biomass
chars during combustion. Combustion and Flame, 1995. 100(1-2): p. 131-143.

- Haynes, B.S. and H.G. Wagner, Soot formation. Progress in energy and combustion science, 1981. 7(4): p. 229-273.
- Burnham, A.K., X. Zhou, and L.J. Broadbelt, Critical review of the global chemical kinetics of cellulose thermal decomposition. Energy & Fuels, 2015.
   29(5): p. 2906-2918.
- Yang, X., et al., Unveiling the Pyrolysis Mechanisms of Hemicellulose:
  Experimental and Theoretical Studies. Energy & Fuels, 2019. 33(5): p. 4352-4360.
- 143. Li, C., et al., Catalytic transformation of lignin for the production of chemicals and fuels. Chemical reviews, 2015. **115**(21): p. 11559-11624.
- 144. Yanez, A.J., et al., Coupled structural and kinetic model of lignin fast pyrolysis. Energy & Fuels, 2018. 32(2): p. 1822-1830.
- 145. Köylü, Ü.Ö., et al., Fractal and projected structure properties of soot aggregates. Combustion and Flame, 1995. **100**(4): p. 621-633.
- 146. Tian, K., et al., Determination of the morphology of soot aggregates using the relative optical density method for the analysis of TEM images. Combustion and Flame, 2006. 144(4): p. 782-791.
- 147. Castoldi, L., et al., Effect of potassium on a model soot combustion: Raman and HRTEM evidences. Aerosol Science and Technology, 2016. 50(4): p. 405-415.
- Xiao, Z., et al., Effect of the interaction between sodium and soot on fine particle formation in the early stage of coal combustion. Fuel, 2017. 206: p. 546-554.
- 149. Simonsson, J., et al., Influence of potassium and iron chloride on the early

stages of soot formation studied using imaging LII/ELS and TEM techniques. Proceedings of the Combustion Institute, 2017. **36**(1): p. 853-860.

- Ruiz, M.P., et al., Influence of different operation conditions on soot formation from C2H2 pyrolysis. Industrial & Engineering Chemistry Research, 2007. 46(23): p. 7550-7560.
- 151. Karataş, A.E. and Ö.L. Gülder, Soot formation in high pressure laminar diffusion flames. Progress in Energy and Combustion Science, 2012. 38(6):
  p. 818-845.
- Trubetskaya, A., et al., Characterization and reactivity of soot from fast pyrolysis of lignocellulosic compounds and monolignols. Applied Energy, 2018. 212: p. 1489-1500.
- Vander Wal, R.L. and A.J. Tomasek, Soot nanostructure: dependence upon synthesis conditions. Combustion and Flame, 2004. 136(1-2): p. 129-140.
- 154. Liaw, S.B. and H. Wu, A new method for direct determination of char yield during solid fuel pyrolysis in drop-tube furnace at high temperature and its comparison with ash tracer method. Energy & Fuels, 2018. 33(2): p. 1509-1517.
- Quann, R. and A. Sarofim. Vaporization of refractory oxides during pulverized coal combustion. in Symposium (international) on combustion.
   1982. Elsevier.
- 156. Gryglewicz, G. and S. Jasieńko, The behaviour of sulphur forms during pyrolysis of low-rank coal. Fuel, 1992. 71(11): p. 1225-1229.
- 157. Attar, A. and L.R. Messenger, The desulfurization of organic sulfur and the transformations of organic sulfur functional groups in coal pyrolysis. Chemical Engineering Communications, 1983. 20(1-2): p. 53-62.
- 158. Liaw, S.B. and H. Wu, High-Phosphorus Fuel Combustion: Effect of Oxyfuel

Conditions on PM10 Emission from Homo-and Heterogeneous Phases. Energy & Fuels, 2016. **31**(3): p. 2317-2323.

- 159. Trubetskaya, A., et al., Characterization and reactivity of soot from fast pyrolysis of lignocellulosic compounds and monolignols. Applied Energy, 2018. 212: p. 1489-1500.
- Li, Y., et al., Characteristics and Mechanism of Soot Formation during the Fast Pyrolysis of Biomass in an Entrained Flow Reactor. Energy & Fuels, 2018. 32(11): p. 11477-11488.

## **APPENDIX I: COPYRIGHT PERMISSION STATEMENTS**

A. Chapter 4, reprinted with permission from (Changya Deng, Sui Boon Liaw, and Hongwei Wu, Characterization of Size-Segregated Soot from Pine Wood Pyrolysis in a Drop Tube Furnace at 1300 °C, Energy & Fuels, 2019. 33(3): p. 2293-2300.)

Clearance Center	tsLink®	A Home	? Help	Email Support	Sign in	Create Account	
	Characterizati Pyrolysis in a I	on of Size Drop Tube	-Segreg Furna	ated Soot fro ce at 1300 °C	m Pine V	Vood	
	Author: Changya D	eng, Sui Booi	n Liaw, Ho	ongwei Wu			
ACS Publications	Publication: Energ	y & Fuels					
<ul> <li>Most Trusted. Most Cited. Most Read.</li> </ul>	Publisher: America	n Chemical S	ociety				
	Date: Mar 1, 2019						
	Copyright © 2019, American Chemical Society						
ERMISSION/LICENSE IS	GRANTED FOR YO	UR ORDER	AT NO C & Conditi	HARGE	ı because n	o fee is being	
harged for your order. Pleas	e note the following:					-	
Permission is granted for yo	our request in both p	rint and elect	ronic forr	nats, and translati	ions.		
If figures and/or tables were	e requested, they ma	y be adapted	or used i	n part.			
Appropriate credit for the re om (COMPLETE REFERENCE) formation in place of the ca	our records and send equested material sh CITATION). Copyrigh pitalized words.	ould be given t (YEAR) Ame	o your pu n as follow erican Che	s: "Reprinted (ada mical Society." Ins	school. apted) with sert approp	permission riate	
One-time permission is grar erivative works or other edi	ted only for the use tions). For any other	specified in y uses, please s	our reque submit a i	est. No additional new request.	uses are gr	anted (such as	

© 2020 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions Comments? We would like to hear from you. E-mail us at customercare@copyright.com B. Chapter 5, reprinted with permission from (Deng, C. and H. Wu, Mechanistic insights into effect of feeding rate on soot formation during rapid pyrolysis of biomass model components in a drop-tube furnace at high temperature. Proceedings of the Combustion Institute, 2021. 38(4): p. 5191-5199.)

Clearance Clearer	RightsLink®	A Home	? Help	Email Support	Sign in	Create Account
<b>X</b> (2)	Mechanistic insights into effect of feeding model components in a drop-tube furnace	rate on soot formation	n durin;	g rapid pyroly	sis of bi	omass
PROCEEDINGS OF THE COMBUSTION INSTITUTE	Author: Changya Deng, Hongwei Wu					
	Publication: Proceedings of the Combustion Institute					
	Publisher: Elsevier					
	Date: 2021					
	© 2020 The Combustion Institute. Published by Elsevier Inc. All rig	ghts reserved.				
ournal Auth Please note tha Permission is n ights, please v	or Rights at, as the author of this Elsevier article, you retain the right to to required, but please ensure that you reference the journ. isit: https://www.elsevier.com/about/our-business/policies/o	p include it in a thesis or disser al as the original source. For m copyright#Author-rights	rtation, pr nore infor	ovided it is not pu mation on this an	ublished co d on your c	mmercially. ther retained
					CLO	

C. Chapter 6, reprinted with permission from (Changya Deng, Sui Boon Liaw, Xiangpeng Gao, and Hongwei Wu, Differences in soot produced from rapid pyrolysis of xylan, cellulose and lignin under pulverized-fuel conditions. Fuel, 2020. 265: p. 116991.)



© 2020 Copyright - All Rights Reserved | Copyright Clearance Center, Inc. | Privacy statement | Terms and Conditions Comments? We would like to hear from you. E-mail us at customercare@copyright.com D. Chapter 7, reprinted with permission from (Deng, C., S.B. Liaw, and H. Wu, Fundamental investigation into characteristics of particulate matter produced from rapid pyrolysis of biochar in a drop-tube furnace at 1300 °C. Proceedings of the Combustion Institute, 2021. 38(4): p. 5229-5236.)

Copyright Clearance Center	RightsLink®	A Home	? Help	Email Support	Sign in	Create Account
	Fundamental investigation into characteristics of biochar in a drop-tube furnace at 1300 °C Author: Changya Deng,Sui Boon Liaw,Hongwei Wu Publication: Proceedings of the Combustion Institute Publisher: Elsevier Date: 2021 © 2020 The Combustion Institute. Published by Elsevier Inc. All rights rese	of particulate ma	tter pr	oduced from ı	rapid pyr	olysis of
Journal Author Please note tha Permission is n rights, please vi BACK	or Rights it, as the author of this Elsevier article, you retain the right to includ or required, but please ensure that you reference the journal as the isit: https://www.elsevier.com/about/our-business/policies/copyrigh	e it in a thesis or disse original source. For m t#Author-rights	rtation, pi nore infor	rovided it is not pu mation on this and	iblished cor d on your o CLOS	nmercially. ther retained SE WINDOW

## **APPENDIX Π: ATTRIBUTION TABLES**

[1] Deng, C. and H. Wu, Mechanistic insights into effect of feeding rate on soot formation during rapid pyrolysis of biomass model components in a drop-tube furnace at high temperature. Proceedings of the Combustion Institute, 2021. 38(4): p. 5191-5199.

Authors	Concepti- on and design	Experime- nts conducti- on & data acquisiti- on	Data processi- ng & analysis	Interpret- ation & discussio- n	Manuscri- pt writing, revision and finalisati- on	Final Approval		
Hongwei Wu	х		х	х	х	x		
I acknowledge that these represent my contribution to the above research output and agree that this paper could be incorporated as part of Changya Deng's thesis. Sign:								

[2] Changya Deng, Sui Boon Liaw, and Hongwei Wu, Fundamental investigation into characteristics of particulate matter produced from rapid pyrolysis of biochar in a drop-tube furnace at 1300° C. Proceedings of the Combustion Institute, 2020.

Authors	Concepti- on and design	Experime- nts conducti- on & data acquisiti on	Data processi- ng & analysis	Interpret- ation & discussio- n	Manuscri- pt writing, revision and finalisati- on	Final Approval	
Sui Boon Liaw	х		х	х	х		
I acknowledge that these represent my contribution to the above research output and agree that this paper could be incorporated as part of Changya Deng's thesis. Sign:							
Hongwei Wu	x		x	х	х	х	
I acknowledge th and agree that t Sign:	hat these rep his paper co	present my o uld be incor	contribution porated as p	to the abov part of Chang	e research o gya Deng's tl	utput nesis.	

[3] Changya Deng, Sui Boon Liaw, Xiangpeng Gao, and Hongwei Wu, Differences in soot produced from rapid pyrolysis of xylan, cellulose and lignin under pulverized-fuel conditions. Fuel, 2020. 265: p. 116991.

Authors	Concepti- on and design	Experime- nts conducti- on & data acquisiti- on	Data processi- ng & analysis	Interpret- ation & discussio- n	Manuscri- pt writing, revision and finalisati- on	Final Approval	
Sui Boon Liaw	x		x	x	x		
I acknowledge that these represent my contribution to the above research output and agree that this paper could be incorporated as part of Changya Deng's thesis. Sign:							
Xiangpeng Gao			x	x	x		
I acknowledge that these represent my contribution to the above research output and agree that this paper could be incorporated as part of Changya Deng's thesis. Sign							
Hongwei Wu	x		x	x	x	x	
I acknowledge that these represent my contribution to the above research output and agree that this paper could be incorporated as part of Changya Deng's thesis. Sign:							

[4] Changya Deng, Sui Boon Liaw, and Hongwei Wu, Characterization of Size-Segregated Soot from Pine Wood Pyrolysis in a Drop Tube Furnace at 1300 °C.Energy & Fuels, 2019. 33(3): p. 2293-2300.

Authors	Concepti- on and design	Experime- nts conducti- on & data acquisiti- on	Data processi- ng & analysis	Interpret- ation & discussio- n	Manuscri- pt writing, revision and finalisati- on	Final Approval		
Sui Boon Liaw	x		x	x	x			
I acknowledge that these represent my contribution to the above research output and agree that this paper could be incorporated as part of Changya Deng's thesis. Sign:								
Hongwei Wu	x		x	x	x	x		
I acknowledge t and agree that t Sign:	hat these rep his paper co	present my o uld be incor	contribution porated as p	to the abov part of Chang	e research o gya Deng's tl	utput nesis.		