Department of Chemical Engineering

Fuel Properties and Thermal Processing of Bio-oil and Its Derived Fuel Mixtures

Wenran Gao

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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: _Wenran GAo. 高雯然_

Date: _November, 2018_

To my beloved family

and friends

Abstract

Fossil fuel resources are depleting in reserve and are largely responsible for the environmental pollution due to carbon dioxide emission. Biomass, as a renewable energy resource, have been attracting much attentions because biomass is eco-friendly. However, biomass as a direct fuel suffers from low volumetric-energy-density and poor grindability due to its bulky and fibrous nature. Such fuel properties dictate that processes utilising biomass as a direct fuel must be of small scale and distributed nature. For large-scale applications, necessary pre-treatment is needed for achieving drastic volumetric energy densification of biomass in order to enable the biomass-derived fuels be suitable for transport. Fast pyrolysis is an attractive thermochemical technology to convert biomass into high-energy-density biofuels, i.e. bio-oil and biochar. Meanwhile, as a by-product of biodiesel industry, direct utilization of crude glycerol is also highly desired due to its huge surplus. Therefore, it is of critical importance to develop an innovative strategy for the co-utilization of fuel mixtures prepared from crude glycerol, bio-oil and/or biochar. An important application is the thermochemical processing of these fuels in fluidised-bed reactors (FBRs). As these fuel mixtures belong to a new class of fuels, understanding the properties of these fuels and the underlying physical chemistry during fuel processing in FBR becomes important. As pyrolysis is the first step of any fuel thermochemical processing, this thesis has a particular focus on bed agglomeration during the pyrolysis of these fuel mixtures in FBR.

The key objectives of this PhD thesis include 1) characterising the fuel properties and ageing of slurry fuels prepared from glycerol or crude glycerol, bio-oil, methanol and biochar; 2) experimentally determining the ignition temperatures of bio-oil and various bio-oil based fuel blends and slurry fuels; 3) understanding the cold flow behaviour of bio-oil and its derived fuel mixtures; and 4) investigating bed agglomeration during bio-oil fast pyrolysis in FBR at a range of temperature. These objectives have been successfully achieved, with the major research outcomes listed below.

Firstly, this PhD study has characterised the fuel properties and ageing behaviour of a series of bioslurry fuels prepared from glycerol/methanol/bio-oil (GMB) blend with

different biochar loading level (up to 16.7 wt %). The GMB/biochar (GMBB) bioslurry fuels generally exhibit non-Newtonian and thixotropic behaviour, especially those at high biochar to GMB blend ratios (2:20–4:20). An increase in biochar loading also increase the higher heating value (HHV), density and surface tension of the GMBB bioslurry fuels. Compared to the bio-oil/biochar (BB) bioslurry fuels at the same biochar loading level, the GMBB bioslurry fuels have much lower viscosity, water content and total acids number (TAN). Both the GMBB and BB bioslurry fuels have increasing viscosity, decreasing water content and TAN with increasing biochar to liquid ratio. Ageing results in decreases in the TAN and viscosity but an increase in water content of the GMBB slurry fuels. The leaching of alkali and alkaline earth metallic (AAEM) species from biochar in the GMBB bioslurry fuels increases with ageing. The presence of methanol and glycerol in the GMBB slurry fuels slow down the ageing and also leads to less leaching of AAEM species from biochar after accelerated ageing.

Secondly, this PhD thesis has investigated the rheological properties and ageing of bioslurry fuels prepared from crude glycerol/methanol/bio-oil (FCGMB) blend and biochar, benchmarking against the GMBB bioslurry for stationary combustion applications. Both FCGMB/biochar (FCGMBB) bioslurry and GMBB bioslurry fuels exhibit non-Newtonian and thixotropic behavior. The viscosities of FCGMBB bioslurry fuels are 222–268 mP.s which are lower than that of GMBB bioslurry due to the presence of water in formulated crude glycerol (FCG). Ageing leads to decreases in the TAN and viscosity but an increase in water content of both FCGMBB and GMBB bioslurry fuels due to various reactions. The changes of the water content (4.4–4.8%) and viscosity (6.0–11.7%) of FCGMBB, and the TAN (2.6% and 4.3%) of FCG1MBB/FCG3MBB bioslurry fuels before and after ageing are lower than that of GMBB bioslurry. This is due to the presence of soap and NaOH in FCGs. Overall, FCGMBB bioslurry fuels have better rheological property than GMBB bioslurry, and the presence of crude glycerol (CG) in the FCGMBB slurry fuels slows down the ageing.

Thirdly, this PhD study has determined the ignition temperatures of a series of bio-oil based fuel blends or slurry fuels prepared from bio-oil, bio-oil water-soluble fraction (WSF), CG and/or biochar via two different methods. One is

thermogravimetric analysis (TGA) method and the other is a modified method based on ASTM standard. Bio-oil has an ignition temperature of 506 °C while WSF has a slightly higher ignition temperature (511 °C) due to negative effect of water on ignition. Fuels with CG have lower ignition temperatures due to the presence of sodium salts in CGs. For example, the ignition temperatures of the CG/methanol/bio-oil/biochar (CGMBB) slurry range from 445 to 470 °C while that of the GMBB slurry is 510 °C. Although biochar has a lower ignition temperature (375 °C), slurry fuels have higher ignition temperatures than the respective blends. This is attributed to the formation of less volatile and more carbonaceous solid by the interactions between bio-oil components and biochar. The results show that the ASTM-based method measures ignition temperatures with emphasis on ignition of vapour phase but the TGA method provides that with emphasis on ignition of the solid residue after evaporation.

Fourthly, this PhD study has deployed differential scanning calorimetry (DSC) for investigating the cold flow behaviour of a series of fuel mixtures prepared from fast pyrolysis bio-oil, CG, methanol and/or biochar. Bio-oil alone has a melting peak temperature (T_{MP}) of −21.9 °C that may lead to difficulties in practical applications under extreme cold weather conditions. Bio-oil WSF is even more problematic as its T_{MP} is −8.7 °C. The results show that these problems can be alleviated or even eliminated by mixing various FCGs with bio-oil or WSF. The T_{MP} of FCGMB blends significantly decreased from −21.9 to −38.1 °C. Similar phenomena were also seen for the FCG/WSF (FCGWSF) blends, with decreases in T_{MP} from −8.7 to −32.0 °C. Water can worsen the cold flow properties of FCGMB and FCGWSF blends. However, other components in FCGs can lower the T_{MP} hence improve the cold flow properties of these fuel mixtures (with the effectiveness in the order of NaCl > NaOH > methanol > glycerol > soap due to solvation effect). The presence of biochar has a limited effect on the cold flow property of the slurry fuels, leading to a decrease of merely 4 °C in the T_{MP} at a 20% biochar loading level.

Fifthly, this PhD study has conducted a series of experiments to study bed agglomeration during fast pyrolysis of bio-oil in a FBR at 500–800 °C. The samples used include bio-oil, bio-oil WSF, bio-oil water-insoluble fraction (WIF) and

selected model compounds. Increasing pyrolysis temperature from 500 °C to 800 °C decreases the agglomeration yield of bio-oil, WSF and WIF from 40% to 15%, 26.2% to 11.6%, and 15.0% to 5.2% respectively. Investigation using model compounds suggests that the interactions between lignin-derived oligomers and sugar is mainly responsible for the high bed agglomeration yield of bio-oil and WSF, and such interactions weaken as pyrolysis temperature increases. Water has insignificant effect on bed agglomeration during bio-oil or WSF pyrolysis. The results also show that the bed agglomeration yield and the formation of tar (and/or coke) are in broad linear correlations, indicating that the tar (and/or coke) formed during fast pyrolysis contribute to the bed agglomeration of bio-oil. The linear correlation from the data of bio-oil has a steeper gradient compared to those of WSF and WIF, clearly indicating the synergy taken place between the WSF and WIF during fast pyrolysis in enhancing bed agglomeration.

Acknowledgement

Lastly, I would like to thank my late best friend, Ms Aijing Wang, who also wanted to join our research group, for her accompany at the beginning of my study. I miss you so much.

List of Publications from My PhD Study

Papers published in refereed journals:

1. Gao, W.; Zhang, M.; Wu, H., Bed Agglomeration during Bio-oil Fast Pyrolysis in a Fluidised-bed Reactor, Energy & Fuels, 2018, *32* (3), 3608-3613.
2. Gao, W.; Zhang, M.; Wu, H., Differential scanning calorimetry studies on the cold flow properties of fuel mixtures from bio-oil, crude glycerol, methanol, and/or biochar, Energy & Fuels, 2017, *31* (8), 8348-8355.
3. Gao, W.; Zhang, M.; Wu, H., Ignition temperatures of various bio-oil based fuel blends and slurry fuels. Fuel, 2017, *207*, 240-243.
4. Gao, W.; Zhang, M.; Wu, H., Fuel properties and ageing of bioslurry prepared from glycerol/methanol/bio-oil blend and biochar. Fuel 2016, *176*, 72-77.

Papers published in refereed conference proceedings:

1. Gao, W.; Zhang M., Wu, H., Rheological properties and ageing of bioslurry fuels prepared from crude glycerol/methanol/bio-oil blend and biochar for stationary combustion applications. The 11th Asia Pacific Conference on Combustion (ASPACC-11), 10-14th, December 2017, Sydney, Australia.
2. Feng, C.; Gao, W.; Wu, H., Combustion of bioslurry and its fractions: different contributions to PM10 emission. The 11th Asia Pacific Conference on Combustion (ASPACC-11), 10-14th, December 2017, Sydney, Australia.

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Chapter 1 Introduction

1.1 Background and Motive

The recent rapid growth in global economy has led to substantial increases in the world's energy consumption.[1-3] Fossil fuels as the main primary energy sources are finite and depleting.[4] The utilisation of fossil fuels is also known to be a key contributor to greenhouse gas emission that is responsible for global warming.[5, 6] Therefore, it is urgent and of significant importance to utilise renewable energy resources for future sustainable development.[7-9] Biomass is considered to be a promising alternative energy resource and is becoming increasingly important.[1, 2, 9]

However, biomass directly used as a fuel suffers from several undesired fuel properties, including low energy densities, poor grindability and high transport cost.[10] Fast pyrolysis is a thermochemical process that converts low-energy-density biomass to high-energy-density bio-oil and biochar.[3, 11-15] However, biochar powders are dusty and prone to spontaneous combustion.[16-19] Bio-oil also has some unfavourable properties including its acidity, instability and prone to ageing.[20-22] Therefore, extensive research has been carried out for biochar and bio-oil utlisation.[20, 21, 23-32] One strategy is to mix bio-oil with biochar, and also with the addition of other fuels (e.g. crude glycerol from biodiesel production process, see below).[17, 21] Such a strategy is favourable and has the potential to largely address the problems associated with biochar or bio-oil.[16, 18, 19, 33-36]

Biodiesel is another notable option for complementing petroleum diesel as it is renewable, non-toxic and biodegradable.[37-44] Crude glycerol is the major by-product along with the production of biodiesel, at ~10% by weight of the raw materials.[45-51]

The blooming biodiesel industry leads to huge feedstock of crude glycerol.[52-54] European Union, the biggest biodiesel producer in the world, generated 24.9 billion litres of biodiesel in 2016 which resulted in about 2.8 billion litres of crude glycerol.[49] Utilization of such extensive surplus by-product is of importance to the sustainable development of biodiesel industry.[45] Crude glycerol contains various impurities including water, methanol, soaps and salts while the purification of crude glycerol is too costly and cumbersome.[50] Therefore, it is essential to find utilization strategy of crude glycerol such as used as a boiler fuel to offer process heating.[55, 56] Unfortunately, direct combustion or gasification of crude glycerol in boilers is limited by its high viscosity.[55] This may be addressed by mixing crude glycerol with other fuels such as bio-oil. Fuel blends prepared by mixing crude glycerol, methanol and bio-oil or bio-oil water-soluble fraction (WSF) can significantly improve the fuel properties.[57-60] The fuel blends can further mixed with biochar to prepare slurry fuels. However, there is little knowledge on the fuel properties of such slurry fuels, especially the ignition behaviour and cold behaviour. Furthermore, how the biochar and impurities in crude glycerol affect the fuel properties are also largely unknown.

For fuel thermal processing such as pyrolysis, combustion or gasification, fluidised-bed reactors are extensively used due to its advantages in efficiency, convenience and versatility.[61-66] Bed agglomeration is a common but important operating issue which may cause defluidization of a fluidised-bed reactor.[67-71] There has been extensive research carried on the mechanism of bed agglomeration during combustion or gasification of biomass (driven by ash species).[61, 63-66, 72, 73] However, bed agglomeration during fuel pyrolysis in fluidised-bed is a new topic until recently when the mechanism of bed agglomeration during biomass fast pyrolysis (driven by organic matter which include all kinds of aromatic-ring system) were investigated.[62, 69-71] However, there is no investigation on fundamental mechanisms governing bed

agglomeration during fast pyrolysis of bio-oil and its derived fuel mixtures in fluidised-bed reactors.

1.2 Scope and Objectives

Therefore, this PhD thesis aims to carry out a systematic research on fuel properties and thermal processing of bio-oil and various bio-oil derived fuel mixtures. The fuel mixtures are prepared from bio-oil or its WSF, crude glycerol, and/or biochar. The specific objectives of this thesis are to:

- investigate fuel properties and ageing of slurry fuels prepared from glycerol or crude glycerol, bio-oil, methanol and biochar;

- carry out a systematic study into ignition behaviour of bio-oil based fuel blends and slurry fuels by thermogravimetric analysis (TGA) method and an ASTM-based method;

- conduct investigation into cold flow properties of bio-oil derived fuel mixtures via differential scanning calorimetry (DSC);

- reveal the fundamental mechanism related to bed agglomeration during fast pyrolysis of bio-oil under various temperatures in the fluidised-bed reactor.

1.3 Thesis Outline

This thesis contents 9 chapters (this chapter included) which are listed below, with the thesis map demonstrated in Figure 1-1.

- Chapter 1 Introduction

- Chapter 2 Literature review

- Chapter 3 Research methodology and analytical techniques

- Chapter 4 Fuel properties and ageing of bioslurry prepared from glycerol/methanol/bio-oil blend and biochar

- Chapter 5 Rheological properties and ageing of bioslurry fuels prepared from crude glycerol/methanol/bio-oil blend and biochar for stationary combustion applications

- Chapter 6 Ignition temperatures of various bio-oil based fuel blends and slurry fuels

- Chapter 7 Differential scanning calorimetry studies on the cold flow properties of fuel mixtures from bio-oil, crude glycerol, methanol and/or biochar

- Chapter 8 Bed agglomeration during bio-oil fast pyrolysis in a fluidised-bed reactor

- Chapter 9 Conclusions and recommendations

Chapter 1 Introduction
-Research background and motives
-Overall scope and objectives
-Thesis structure and map

Chapter 2 Literature Review
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-Research gaps and questions
-Specific objectives of this thesis

Chapter 3 Methodology and Analytical Techniques
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-Experimental procedures
-Analytical techniques

Objective 1 Fuel properties and aging of slurry fuels

Objective 2&3 Ignition behavior and cold flow behavior

Objective 4 Bed agglomeration and its mechanism

Chapter 4 Fuel properties and ageing of bioslurry prepared from glycerol/methanol/bio-oil blend and biochar
-Rheological and fuel properties
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-Leaching of AAEM species in slurry system

Chapter 6 Ignition temperatures of various bio-oil based fuel blends and slurry fuels
-Determination of ignition temperatures
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-Effect of crude glycerol and biochar

Chapter 8 Bed agglomeration during bio-oil fast pyrolysis in a fluidised-bed reactor
-Evidence of bed agglomeration
-Mechanism responsible for bed agglomeration

Chapter 5 Rheological properties and ageing of bioslurry fuels prepared from crude glycerol/methanol/bio-oil blend and biochar for stationary combustion applications
-Fuel properties and rheological properties
-Ageing of slurry fuels

Chapter 7 Differential scanning calorimetry studies on the cold flow properties of fuel mixtures from bio-oil, crude glycerol, methanol and/or biochar
-Determination of melting temperatures
-Effect of impurities in crude glycerol
-Effect of biochar particles

Chapter 9 Conclusions & Recommendations

Figure 1-1 Thesis map

Chapter 2 Literature Review

2.1 Introduction

With the rapid growth of global population and economy, energy shortage and environmental issues are becoming great challenges of our society.[74, 75] As the primary energy sources, the fossil fuels such as coal, oil and natural gas are expected to play a continuously-important role in the global energy mix. The use of fossil fuels are known to be major contributors to many environmental problems including greenhouse gas emissions.[9, 12, 76] Therefore, it is of critical importance to develop clean and renewable energy sources.[1, 7, 75] Recently, substantial research has been carried out on biofuels derived from biomass, such as bio-oil (derived from biomass pyrolysis)[1, 7, 31, 32, 77, 78] and biodiesel (derived from vegetable oil or fat transesterification)[43, 44, 79-82] which are considered as promising liquid fuel to partial substitute fossil fuel.[10, 23, 26, 46] It is extremely significant to utilize the by-products (biochar and crude glycerol) of bio-oil and biodiesel industry for their sustainable development.[3, 22, 52, 53, 83, 84] A prospective approach to utilize those by-products is to prepare bio-oil derived fuel mixtures.

The target of this chapter is to review the characterization and application of bio-oil, biochar and crude glycerol. The literature review begins with biomass fast pyrolysis to prepare bio-oil and biochar, followed by discussions on characterization and application of biochar and bio-oil as a fuel, especially cold flow behaviour and ignition behaviour of bio-oil, then moves to characterization and application of crude glycerol as a fuel. In addition, recent advancement in bio-oil derived fuel mixtures which contain crude glycerol, and/or biochar is outlined. A short summary is also given on thermal processing of bio-oil and its derived fuel mixtures. Finally, this

chapter concludes with identifying of research gaps and research objectives of this PhD study.

2.2 Biomass Fast Pyrolysis: Production of Bio-oil and Biochar

2.2.1 Advantages and disadvantages of biomass as a fuel

As prime energy sources, fossil fuels like petrol, coal and natural gas are expected to be depleted in the following 50 years.[85] Moreover, the utilization of fossil fuels also lead to environmental issues such as acid rain and global warming which are attributed to polluted gas emission (i.e. CO_2, CH_4, N_2O, and SO_2).[8, 74, 85-87] As a result, renewable and clean energy sources are attracting growing interest to reduce environmental pollution.[74, 85] Among all the alternative energies, biomass is considered as a promising renewable energy source for its advantages on carbon neutral as shown in Figure 2-1.[88-90]

$$CO_2 + H_2O + Light/Heat \underset{Combustion}{\overset{Photosynthesis}{\rightleftharpoons}} O_2 + Trees$$
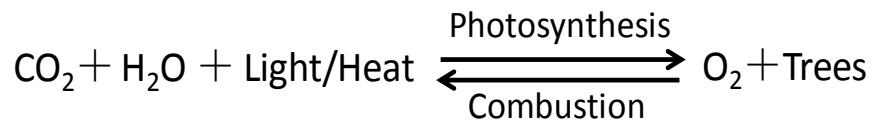
Figure 2-1 The biomass cycle.[89]

Biomass refers to any organic matters derived from plant and is mainly composed of hemicellulose, cellulose and lignin.[12, 89] Biomass has two broad categories: First is woody biomass such as wood from forest, crops, seaweed, agriculture residue and forestry residue; Second is non-woody biomass including animal wastes, human wastes and organic industrial wastes.[85, 89] As shown in Figure 2-1, the biomass energy initially comes from the sun and CO_2 is transformed into other carbon containing molecules in plants through photosynthesis.[85] During combustion process of biomass, carbon emissions are balanced by carbon stored by the trees growth.[85, 89]

As a result, carbon neutral or zero carbon emission is achieved which is the significant advantage of biomass as a fuel. Biomass as a fuel also has advantages in being renewable and cheap price compared to fossil fuels.[22]

However, biomass application suffering from its undesirable properties. Compared with fossil fuels, biomass has low energy density due to its inherent chemical composition and high moisture content.[22, 88] This means the value of the fuel can rapidly outweighed by fuel collection and transportation costs.[10] The bulky and fibrous nature of biomass lead to a poor grindability, thereby increase the milling cost as well as the difficulty of handling operations and feeding process.[91]
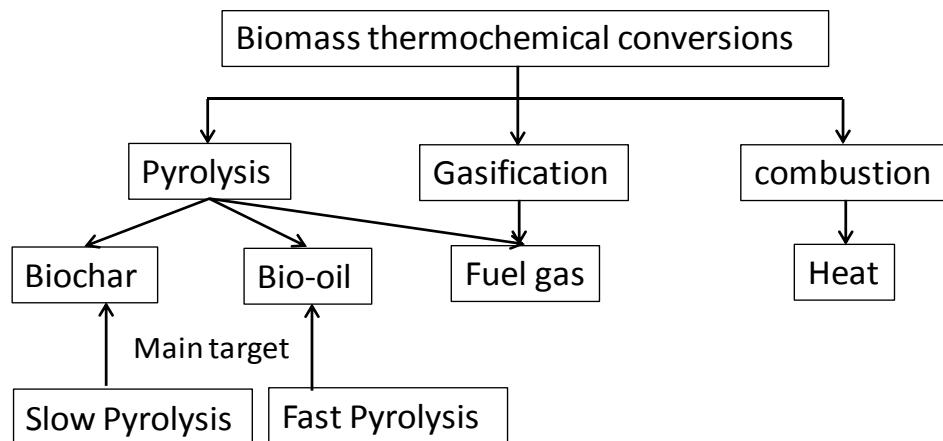
Figure 2-2 Biomass thermochemical conversions and its corresponding products.[7]

2.2.2   Biomass fast pyrolysis

To alleviate the undesirable features related to biomass application as a direct fuel, biomass could be converted to more useful biofuels through thermochemical or biochemical conversion routes.[90] Compared with biochemical conversion, thermochemical process of biomass has a shorter reaction time and better ability to decompose the organic structures of biomass.[92-94] As shown in Figure 2-2, there are three primary thermochemical conversion processes: pyrolysis, combustion and

gasification.[7, 12, 95] Combustion process of biomass generally aims to provide heat, while gasification process produces gaseous fuel for wide applications.[92, 94] Pyrolysis process can transform biomass to liquid (bio-oil), solid (biochar) and gaseous fuels through heating biomass at about 500 °C with the absence of oxygen, while slow pyrolysis and fast pyrolysis mainly target for production of biochar and bio-oil respectively.[9, 22, 74, 90]

Depending on biomass feedstocks, 60–75 wt% of liquid bio-oil, 15–20 wt% solid biochar and 10–20 wt% of noncondensable gases can be yielded through fast pyrolysis process.[96] Fast pyrolysis has following key characteristics:

- High heating rate and heat transfer rate at the interface of biomass particle.[7, 26] To obtain this objective, small biomass particles are required (typically < 3 mm) due to its low thermal conductivity.[9]

- Restrained pyrolysis temperature. To optimize the bio-oil yield for most biomass feedstock, the pyrolysis temperature generally being ~500 °C.[7, 26]

- Very short residence time for hot vapour. To reduce secondary reactions, the residence time of hot vapour are usually controlled within 2 s.[7, 12, 26]

- Rapid cooling of the pyrolysis vapours to get the condensed bio-oil.[7, 26]

Although any forms of biomass can be a candidate for fast pyrolysis, woody biomass is mostly used fast pyrolysis feedstock for its low ash content, high quality bio-oil produced, as well as its consistency and comparability between tests.[7, 8]

Reactor is the core for a fast pyrolysis process.[7, 26] There are several representative fast pyrolysis reactors such as fluidised-bed reactor, rotating cone reactor, ablative reactor, fixed bed reactor, vacuum reactor, augur reactor, and etc.[7, 26] The fluidised-bed reactor is most commonly used because it is simple in construction and easy in operation.[26, 97]

Table 2-1 Typical properties of bio-oil from wood pyrolysis and heavy fuel oil.[76]

Properties	Bio-oil	Heavy fuel oil
Water content, wt%	15–30	0.1
Ash	0–0.2	0.1
Solids, wt%	0.2–1	1
Distillation residue, wt%	< 50	1
Elemental analysis, wt%		
C	54–48	85
H	5.5–7.0	11
O	35–40	1.0
N	0–0.2	0.3
HHV, MJ/kg	16–19	40
pH	2.5	–
Viscosity, cP (@50 °C)	40–100	180

2.3 Application of Biochar from Biomass Fast Pyrolysis as a Fuel

The definition of biochar is "a solid material obtained from the carbonization of biomass", according to the International Biochar Initiative.[98] As mentioned before, biochar is a by-product of biomass fast pyrolysis with yields vary from 10 wt% to 25 wt%.[96] Biochar is composed of carbon (primary element), hydrogen, oxygen, ash, and a little amount of nitrogen and sulphur.[98-101] The properties of biochar (such as high surface area, pore fraction, and tailoring properties) enable the possibility of

being used as efficient catalyst for pyrolysis and gasification of biomass, biodiesel production, as well as bio-oil upgrading, or as adsorbent for water pollutants and air pollutants.[98, 100, 102, 103] It also has promising applications in environmental remediation like soil amendment due to its high cation exchange capacity as well as high surface area.[99, 101, 104, 105] Beside these applications, biochar obtained from biomass fast pyrolysis also can be utilized as a fuel for heat and power supplication due to its remarkable grindability and high energy density (~18 MJ/Kg).[106-108] This section states the challenges in application of biochar, a by-product of biomass fast pyrolysis, as a fuel.

The key challenge in biochar application as a fuel is related to the fine particle size distribution since it may lead to safety hazard during storage/transportation.[3, 19, 22, 106] Fine biochar powder is flammable which may cause spontaneous combustion when exposed to moisture and oxygen during transportation/storage.[3] High concentration of biochar particles in an open area is at risk of explosive.[3] In addition, surface utilization of biochar particles may lead to extensive particulate emissions which may bring undesired health risk for anyone who are exposed to biochar dust.[3]

Beside these safety and health issues, challenges in biochar utilized as a fuel also contain reactivity and emission characteristic during biochar combustion and gasification.[22] Inorganic matters in biomass, especially alkali and alkaline earth metallic (AAEM) species, are closely related to reactivity as well as ash-related conundrums.[106] Since biochar inherit most of the inorganic matters from biomass fast pyrolysis, it has extremely large concentration of AAEM species (6–7 times of that in biomass).[109, 110] The inorganic matters in biochar can act as catalyst for various reactions (i.e. pyrolysis, combustion and gasification).[22] It is reported that the forms of existence for inorganic matters (such as in organically bound structure and in salt form) affect its catalytic effect.[111, 112] The catalytic effect of K and Na species are

stronger than Ca species during biochar steam gasification.[112] Moreover, during pyrolysis, combustion and gasification, the inorganic matters in biochar may lead to a variety of ash-related problems, such as ash deposition,[113-115] particulate matter emission of fine inorganic,[116] fire-side corrosion,[117, 118] and bed agglomeration during operation of fluidised-bed. [119-122]

To solve the problems associated with biochar storage/transportation which are mentioned above, a promising approach is suspending biochar into bio-oil, WSF or bio-oil derived fuel blends to prepare slurry fuels (detailed discussion see section 2.7). This is also a scope of work in this thesis that studying the effect of biochar on fuel properties of slurry fuels including ignition behaviour and cold flow behaviour.

2.4 Characterization and Application of Bio-oil as a Fuel and Its Fractions

Bio-oil (also referred to as pyrolysis liquid/oil and bio-crude), a thick dark-brown and hydrogen-deficient liquid with a unique smoky odour, is usually produced from biomass fast pyrolysis with yield up to 70–80 wt%.[76, 123] It is a prospective substitute of petroleum oil although it has different fuel properties and composition compared to that of crude oil (see Table 2-1).[22] Fuel properties of bio-oil are closely related to its chemical composition,[31] so this section discusses the chemical composition of bio-oil and followed by its fuel properties. Although bio-oil can be utilized to recover chemicals,[13, 76] this section only focus on implications of bio-oil as a fuel to supply power and heat in boilers, gas turbines, diesel and stirling engines, or as a transportation fuel by upgrading.[77] This section also reviews bio-oil fractions since bio-oil can be separated to water-soluble fraction (WSF) and water-insoluble fraction (WIF) when water content higher than 30 wt%,[124, 125] and WSF also can be utilized as a fuel.

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2.4.1 Bio-oil as a fuel and its fuel properties

The fuel properties of bio-oil result from its chemical composition are highly rely on biomass type (i.e. leaf, wood and bark) or composition (such as cellulose, hemicellulose and lignin), biomass pre-treatment methods (i.e. particle size, moisture and ash content), pyrolysis parameters (i.e. pyrolysis temperature, residence time and heating rate), and post-treatment (i.e. condensation and filtration).[2, 8, 15]

2.4.1.1 *Physico-chemical properties of bio-oil*

Chemical composition

Bio-oil has a very complex chemical composition and mainly contains water, more than 400 organics and a little ash.[126] It is hard to analyse the chemical composition of bio-oil only by classical methods such as gas chromatography/mass selective detector (GC/MSD) and high performance liquid chromatography (HPLC), because of its low volatility leaded by high polarity and high molecular mass of the organic compounds in it.[1, 109] By solvent extraction, bio-oil can be separated to different fractions and this method can be combined with analytical techniques to analyse the primary composition of bio-oil.[13] Even though, there are still about 15% non-detectable compounds with high molar mass in bio-oil.[126] The chemical composition of a bio-oil from pine pyrolysis resulted from combination of solvent fraction and CG/MSD are shown in Table 2-2.

Table 2-2 Chemical composition of a bio-oil prepared from pine pyrolysis, combined results of solvent fraction and CG/MSD.[109]

	Wet (wt %)	Dry (wt %)
Water	23.9	0
Acids	4.3	5.6
Formic acid		1.5
Acetic acid		3.4
Propionic acid		0.2
Glycolic acid		0.6
Alcohols	2.2	2.9
Ethylene glycol		0.3
Methanol		0.6
Aldehydes, ketones, furans, pyrans	15.4	20.3
Nonaromatic Aldehydes		9.72
Aromatic Aldehydes		0.009
Nonaromatic ketones		5.36
Furans		3.37
Pyrans		1.10
Sugars	34.4	45.3
Anhydro-β-D-arabino-furanose,1,5-		0.27,
Anhydro-β-D-glucopyranose (Levoglucosen)		4.01
Dianhydro-α-D-glucopyranose,1,4,3,6-		0.17
Hydroxy, sugar acids		
Low-molecular mass lignin	13.4	17.7
Catechols		0.06
Lignin derived Phenols		0.09
Guaiacols (Methoxy phenols)		3.82
High-molecular mass lignin	1.95	2.6
Extractives	4.35	5.7
Fatty acids		
Triglycerides		
Resin acids		

*Analysed at the vTI (Germany)

Ultimate analysis

Bio-oil mainly contains C, H and O, and a trace amount of N, S and other metallic elements.[109] The oxygen content of bio-oil is 35–40% on dry basis which is embodied in variety of organic compounds and is considerably higher than that of hydrocarbon fuels.[109] The high oxygen content is considered as the main reason for the issues related with both handling and applications of bio-oil, such as the instability problem during storage which will be discussed next.[109] The CHN content of bio-oil can be determined via elemental analyser based on ASTM D 5291-92 and the sulphur content can be analysed by inductively coupled plasma (ICP) or by capillary electrophoresis technique based on ASTM D 4239.[127] Then the oxygen content (wet basis) could be estimated by difference according to equation.

Metals

Bio-oil has variety of inorganic elements (like Si, Al, Fe, Zn, Cu, Cr, Ni, Pb, N and Co) especially AAEM species which mainly are Na, K, Mg and Ca. These metals can cause unfavourable ash-related issues in thermochemical process[108] and also can act as catalysts for various reactions[15]. Recently, Wu et al. developed an evaporation-ashing-digestion-IC method to quantify the AAEM species in bio-oil and bio-oil derived fuel samples.[128] The new developed method has four steps: evaporation (convert sample to a solid-like residue), ashing (further convert the residue to ash), acid digestion (dissolve the ash into solution), and IC analysis to quantify the AAEM species in the obtained solution.[128] The evaporation process contains multiple slow heating and holding segments at temperatures of the boiling points of the main compounds in bio-oil to avoid the carry-over of biochar.[128]

Homogeneity

Bio-oil contains a huge range of chemical compounds with different chemical functionalities.[129] The homogeneity of bio-oil is related to the complex solubility and reactivity of these compounds in it.[129] Generally, bio-oil is considered as homogenous single-phase liquid with a small amount of solids (e.g., char particles).[129, 130] Microscopically, however, bio-oil has more than one phase and can be regarded as microemulsions.[129, 130] The multiphase character of bio-oil is due to the presence of char particles, waxy materials (such as fatty acids, fatty alcohols, sterols and aliphatic hydrocarbons), aqueous droplets and micelles made of heavy compounds.[130] The char particles and some heavy compounds in bio-oil sediment gradually on the bottom of containers during its storage because of density difference.[127, 129] As a result, homogenization of bio-oil is required before utilization/sampling.[127] The homogeneity of bio-oil can be detected by microscopic examination.[129]

Solubility

The solubility of bio-oil in an organic solvent is connected with its degree of polarity.[129] For highly polar bio-oil samples (e.g., wood bio-oils), alcohols with low molecular weight like methanol and ethanol are excellent solvents.[127, 129] These solvents can dissolve the whole bio-oil except char particles and some extractives.[127, 129] Another excellent solvent for wood pyrolysis bio-oils is acetone.[127, 129] Wood bio-oils cannot dissolved in hydrocarbons, such as hexane, diesel fuels and polyalfaolefines.[127, 129]

Acidity and material corrosion

Generally, the pH and total acid number (TAN) of bio-oil are 2–3 and 36–70 mg NaOH/g, respectively.[76, 127] The acidity of bio-oil can be attributed to the presence of volatile acids like acetic and formic acid.[127, 129] Moreover, phenolic compounds also contribute to the acidity of bio-oil.[127] Therefore, bio-oil heavily corrode many materials like aluminium, mild steel, copper and nickel, especially at high temperatures or in high water content.[131, 132] However, various plastics (such as polytetrafluoroethylene and polypropylene) and stainless steel are resistant to the corrosiveness of bio-oil that can be adopted to storage/handle bio-oil.[127, 133] The TAN of bio-oil can be determined by an acid-based titrator.

Stability

Chemically and thermally, bio-oil is less stable compares to fossil fuels which is attribute to the large amount of reactive oxygen-containing compounds with varying molecular weights.[127] Bio-oil is not a thermodynamic equilibrium product.[15, 134] Therefore, a wide range of chemical reactions may take place during long-term storage of bio-oil to get thermodynamic equilibrium which is also regarded as bio-oil "ageing".[15] Important possible reactions within different compounds in bio-oil are listed in Table 2-3.[15] As a result, the average molecular-weight distribution, water content and viscosity of bio-oil all increase.[15, 127, 129] Furthermore, higher temperatures promote the ageing effect.[129] For instance, the increase in viscosity of a bio-oil after being stored at 80 °C for 24h is equivalent to that after being stored for one year at room temperature.[127] It is better to store bio-oil at low temperature in a fridge. The presence of catalysts also elevate ageing effect[15] and biochar contains various inorganic species that can act as catalyst (see section 2.3). The influence of biochar on the ageing of bio-oil is in the scope of this thesis.

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Table 2-3 Important possible reactions within different compounds in bio-oil related to ageing.[15]

Compounds	Details	Reactions
Organic acids	With alcohols to form esters and water	Esterification and transesterification
	With olefins to form esters	
Aldehydes	React with each other to form polyacetal oligomers and polymers	Homopolymerization
	Aldehydes or ketones mixed with water react to form hydrates	Hydration
	With alcohols to form hemiacetals, or acetals and water	Hemiacetal formation, acetalization and transacetalization
	With phenolics to form resins and water	Phenol/Aldehyde reactions and formation of resins
	With proteins to form oligomers	Dimerization
Organic suffer	To form oligomers	
Unsaturated compounds	To form polyolefins	Olefinic condensation
olefins, ethers, ketones, nitrogen compounds, aldehydes, and organic acids	With air to form organic peroxides or hydroperoxides	Oxidation

2.4.1.2 *Fuel properties of bio-oil*

Water content

Typically, bio-oil has a considerably high water content (15–30 wt%).[28, 135] Water exists as a microemulsion or is dissolved in bio-oil.[127] Water is difficult to remove from bio-oil, and physical methods (e.g., centrifugation) cannot remove it.[129] Water influences other physical properties of bio-oil. With increase of water content, a decrease in the density, viscosity and heating value will be observed.[127] The increasing water content also promotes the stability of bio-oil until phase separation occurs when water content is up to 30%.[127] Phase separation of bio-oil due to water addition will be discussed in section 2.4.2. Moreover, water has both positive and negative effects on combustion applications of bio-oil.[127] The high water content leads to the low energy density of bio-oil and decreases both the local combustion temperatures and combustion reaction rate.[129] Besides, the high water content contributes to ignition problems, improves the ignition delay time, and deteriorates the cold flow behaviour of bio-oil.[129] The effect of water on ignition behaviour and cold flow behaviour is within the scope of this thesis. For the above reasons, the water content of bio-oil needs to be regulated and it can determined using Karl Fischer titration based on method ASTM E 203.[127, 129] Typically, moisture content of biomass is below 10% because it attributes to the water content of bio-oil.[135]

Solid content and ash content

In bio-oil collection process, cyclone systems are normally adopted to remove solids from hot pyrolysis vapors.[135] But bio-oil still contains a small amount of solids (< 0.5 wt %) with the average particle size being 5–10 μm due to the less efficiency of cyclones on removing small particles.[135] The solids in bio-oil mainly are char

particles and some other materials like fluidised-bed materials.[135] They have negative effects on fuel applications of bio-oil. Firstly, agglomeration and sedimentation of particles can occur during storage and char particles may accelerate ageing of bio-oil.[109, 129] Secondly, they can corrode and block the fuel injection and combustion devices such as pump and spray nozzles.[129] In addition, they increase particular emissions and ash content.[129] Ash content is identified as the amount of residues after bio-oil combustion at 775 °C and can be analysed by thermogravimetric analyser (TGA).[135] It is known that ash contribute to various issues during thermochemmical process, for example, corrosion and deposition.[91, 136] As a result, the presence of solids and ash are not desirable. Hot gas filtration and liquid filtration are possible methods to decrease both the solid and ash contents of bio-oil.[129]

Density, viscosity, surface tension, and the Ohnesorge number

In combustion, density, viscosity and surface tension are significant parameters due to they can influent the design of both the pump and pipeline.[129] More importantly, they can affect the atomization quality of the spray systems and then further affect both the combustion efficiency and emission efficiency.[129] To better evaluate the spray/atomization quality, Ohnesorge number is calculated based on the values of the three properties (detailed equation in section 3.4.5) to estimate the Sauter mean diameter (SMD) of a spray droplet.[137] A high Ohnesorge number of a fuel means bigger SMD after spray and subsequently predicts worse spray quality.[137-139]

The densities of bio-oils are in the range of 1.2–1.3 Kg/dm^3 which are higher than that of fossil fuels (0.8–1.0 Kg/dm^3) and they become higher with water content decreases.[127, 135] Viscosity of a bio-oil is a measure of its resistance to flow and can be determined as dynamic viscosity or kinematic viscosity using different viscometers.[127, 135] Newtonian fluids have constant viscosity at different shear rate

while non-Newtonian fluids have varying viscosity.[135] The majority of bio-oils are Newtonian fluids at low temperatures (< 80 °C).[135] Some bio-oils contain rich extractives may show non-Newtonian behaviour.[135] Typically, viscosities of bio-oils are 10–100 cP at 40 °C.[135] The surface tension of bio-oil is a measurement of its resistance to external force and generally is in the range of 28–40 mN/m at 25 °C.[129, 135] It is higher than that of fossil fuels (72 mN/m at 25 °C) which is attributed to the strong hydrogen bonding in bio-oil.[129] As the temperature increases, the surface tension becomes lower for most bio-oil.[135]

Heating value

The combustion heat of a fuel is the total amount of heat generated during the fuel completely combustion process.[109] There are two methods to define heating value, higher heating value (HHV, gross heat of combustion) and lower heating value (LHV, net combustion heat).[129] The difference between them is the water vaporisation heat generated during fuel burning.[129] The heating value of a bio-oil is related to its water content.[129] Typically, the LHV of bio-oils is 14–18 MJ/kg which is much less than that of fossil fuels because of its high oxygen content and water content.[135] However, due to the high density of bio-oil, its heating value based on volumetric can reach 50–60% of that of fossil fuels.[135] Commonly, bio-oils are measured for HHV.

2.4.2   Bio-oil water-soluble fraction and water-insoluble fraction

As mentioned before, phase separation of bio-oil occurs when water content reaches 30%.[140] After phase separation, bio-oil is separated into two fractions: water soluble fraction (WSF, top phase) and water insoluble fraction (WIF, bottom phase).[123, 141-148] There are two operation methods to separate bio-oil with extra water addition: add bio-oil to water and add water to bio-oil.[140] The former method with high water to

bio-oil ratio (usually >10:1) is suitable for obtain WIF or for analytical investigations.[140] While the latter one with low water to bio-oil ratio is suitable to collect WSF with relatively low water content. Cold water precipitation by adding water to bio-oil is an commonly used method to produce WSF and WIF.[149] It should be noted that there are many overlapped compounds which exist in both WSF and WIF if the water to bio-oil is very low (e.g., < 1:1).[109, 123, 150]
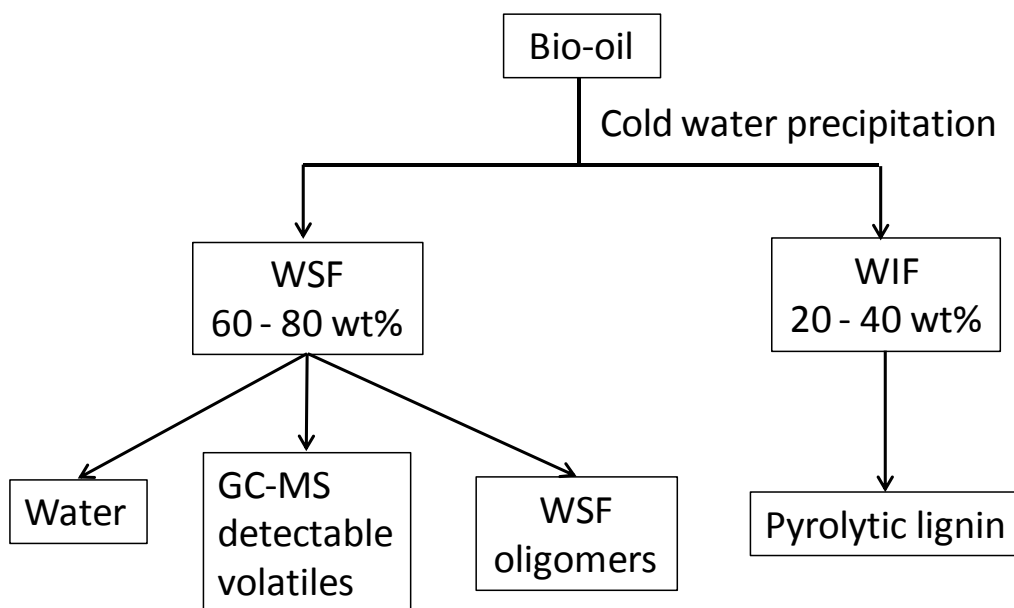
Figure 2-3 Bio-oil fractions and their main compositions.[123, 124, 150]

2.4.2.1 *Characterization and application of bio-oil water soluble fraction as a fuel*

As is shown in Figure 2-3, typically, the obtained WSF is yellow liquid with yield being 60–80 wt% of the bio-oil.[150] WSF mainly contains polar compounds which have low molecular weight, i.e. water, acids, alcohols, adehydes, ketones and saccharides.[123, 148] Garcia-Perez Manual et al. reported that WSF mainly composed of water, GC-MS detectable volatiles and WSF oligomers.[124] While WSF oligomers contain carbohydrates (slightly dehydrated sugars as well as furans), phenols, carbonyl groups (highly dehydrated structures), and carboxylic groups.[124] The water-rich carbohydrate-derived WSF could be applied as feedstock to produce

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hydrogen by steam reforming.[124, 151, 152] Due to WSF contains many chemicals, it can be utilized to extract value-added chemicals by innovated separation and refining technologies.[28, 153, 154]

Table 2-4 Fuel properties of WSF prepared from pine wood bio-oil with water to bio-oil ratio being 0.5:1 benchmarking against bio-oil.[58]

Samples	Bio-oil	WSF[a]
Elemental Analysis (wt %)[b]		
C	42.66	18.80
H	7.20	8.84
N	0.19	0.18
O[c]	49.95	72.18
Water content (wt %)	23.7	61.2
Viscosity (25℃, mPa s)	165.5	2.9
Surface tension (25℃, mN/m)	35.50	41.32
Density (25℃, g/cm^3)	1.21	1.07
HHV (MJ/Kg)[d]	18.65	13.03
TAN (mg NaOH/g)[e]	49.6	35.1

[a] WSF stands for bio-oil water soluble fraction obtained at a water/bio-oil ratio of 0.5;
[b] as-received basis;
[c] by difference;
[d] calculated high heating value;
[e] total acid number.

WSF also could be directly used as a fuel, especially when co-utilized with crude glycerol which can solve fuel application issues such as high viscosity.[58] Detailed advantages on WSF based fuels will be discussed in section 2.7. To reduce the water content in WSF, low water to bio-oil ratio (usually < 1:1) is adopted when preparing WSF.[58] Fuel properties of a WSF produced from pine wood bio-oil is shown in Table 2-4. Due to the addition of extra water during WSF preparation process, WSF has a considerable high water content which leads to a high oxygen content. As a result, WSF has a low HHV and viscosity compares to that of bio-oil. However, because of the dilution effect, the acidity of WSF decreases.[148] It is better to upgrade WSF such as co-utilize it with crude and/or biochar to obtain better fuel properties (see section 2.7).

2.4.2.2 *Characterization and application of bio-oil water insoluble fraction*

After phase separation, the brown and high viscous lignin-derived WIF (also referred to as pyrolytic lignin) containing high molecular compounds can be obtained with yield being 20–40 wt%.[150] Pyrolytic lignin significantly associated with the instability/ageing and coke formation issues during thermochemical process of bio-oil, particularly bio-oil ageing.[149, 155, 156] Therefore, to better understand bio-oil ageing, it is essential to investigate the composition and structure of WIF.[140] The WIF composition is associated with the feedstocks, pyrolysis conditions and extraction methods.[157] Typically, WIF mainly contains trimers and tetramers of hydroxyphenyl, guaiacyl, and syringyl compounds.[140, 157-160] The applications of WIF are focus on extraction of value-added chemicals, for example, utilization as a cost-effective phenol in phenol formaldehyde resins, and as an asphalt binder or binder modifier.[161-164]

2.5 Ignition Behaviour and Cold Flow Behaviour of Bio-oil

Ignition behaviour and cold flow behaviour are two important considerations for the handling, storage, transport and operation of a fuel.[165-167]

2.5.1   Ignition behaviour of bio-oil

Ignition behaviour is a significant parameter to safety handling, transportation and operation, as well as combustion performance during utilization of a bio-oil.[135] Bio-oils are difficult to ignite which is attributed to their chemical compositions especially water (due to its high vaporization heat).[135] Therefore, more energy is needed to ignite bio-oils compare to fossil fuels.[135] Unlike fossil fuels, bio-oils do not ignite spontaneously in a classic compression ignition engine.[127] So far, bio-oils are commonly ignited with the adding of ignition improvers, or by preheating the combustion chambers or air, or under assistance of pilot flames.[135] Usually, ignition behaviour of a bio-oil is described by flash point or ignition temperature.[127, 129, 135]

2.5.1.1 *Flash point*

The flash point of a fuel is described as the lowest temperature at which the vapour on the top of the fuel liquid can be ignited when revealed to a flame.[127, 135] It is the highest temperature for safety handling consideration to avoid fire hazard.[129] Despite this safety consideration, it is not important for performance of a bio-oil in an engine.[127] The flash point of a bio-oil can be measured according to ASTM D 93 by a close-cup tester with variation in the range of 40–70 °C or above 100 °C, which is related to the content of light organic volatiles.[127, 129, 135] However, it is hard to determine the flash point at 70–100 °C because the intense evaporation of water

inhibit the fuel vapour to ignite.[127, 135] Typically, the flash point for hardwood (e.g., oak-maple wood), softwood (e.g., pine wood), and straw bio-oils are 50–66 °C.[127]

2.5.1.2 *Ignition temperature*

The ignition temperature of a fuel can be described as the lowest temperature at which ignition occurs with specified test conditions. Unlike fossil fuels, bio-oils are non-flammable, non-distillable, have finite volatility, and only ignite at a relatively high temperature.[129] The poor ignition of bio-oils may attribute to the high water content and oxygen content with abundant nonvolatiles.[129] Generally, aromatic-rich bio-oils have higher ignition temperatures compare to paraffin-based bio-oils.[129] Classic test methods such as ASTM D 2699 to determine fossil fuels are not available for bio-oils due to strict high fuel qualities are required.[127] Therefore, appropriate development or modification of the test methods is necessary. TGA is a promising technique to study ignition temperatures of bio-oils. Thermogravimetry (TG) and differential thermogravimetry (DTG) curves are often used to identify the ignition temperature to provide fundamental understanding of ignition behaviour of bio-oils.[167-172]

2.5.2 Cold flow behaviour of bio-oil

Under cold weather, solidification or partial solidification may occur during bio-oil storage, transport and application which is an undesired issue.[166] For instance, partial solidification of a fuel may block the fuel injection systems and filters which further lead to engine ignition issues.[173] Generally, cold flow behaviour can be represented by pour point, cloud point, cold filter plugging point, and low temperature flow test. This section mainly focuses on pour point and cloud point. It also can be

characterized via differential scanning calorimetry (DSC) by determine melting process, i.e. determination of melting point.

2.5.2.1 *Pour point*

As a parameter to explain the fluidity of a fuel at low temperature, the pour point of fuels is defined as the lowest temperature at which the fuel can be pumped.[127, 135] The decrease of fluidity of a fuel mainly attributes to viscosity increase or crystallization of waxy materials.[135] The maximum limitation for pumpability is ~600 cSt.[174] Pour point can be measured based on ASTM D 97.[175] In this method, fuel samples should be preheated which aggravates fuel ageing and may leads to phase separation problem.[127] Typically, Wood pyrolysis bio-oils have a pour point of -12 – -33 °C. A bio-oil with low viscosity usually indicates it has a low pour point.[127] The pour point of other types of bio-oil may not in this range.[135]

2.5.2.2 *Cloud point*

Cloud point is another parameter to describe the cold flow behaviour of a fuel.[135] At low temperatures, paraffin compositions of mineral fuels may deposit as a wax which forms a cloud in fuels.[127] The cloud point is determined as the highest temperature at which a cloud of wax crystals first becomes visible.[127, 135] The cloud point of a fuel is higher compare to the pour point[176] and is associated with the feedstock, type, and boiling range of bio-oil.[127] Bio-oil containing more paraffin has a higher cloud point and is less suitable for low temperature application.[127] The method ASTM D 2500 can be used to determine the cloud point of fuels.[127] However, it is not suitable for bio-oils with dark colour due to the difficulty in observing the cloud.[135]

2.5.2.3 *Differential scanning calorimetry techniques to study cold flow behaviour*

The cold flow behaviour of a fuel also can be determined by DSC according to ASTM D 4419 or other methods.[175-183] Dunn et al. have proposed several empirical correlations to determine the values of pour point, cloud point, cold filter plugging point, and low temperature flow test from the characteristic temperatures obtained from DSC.[179, 181] In his work, DSC heating and cooling curves of methyl soyate, methyl tallowate, methyl soyate/ methyl tallowate admixtures, and winterized methyl soyate were analyzed.[181] The results show that both the DSC cooling curve and melting curve can be adopted to determine correlations with the cold flow behaviour while the cooling curve is slightly better.[181] Garcia-Perez et al. adopted DSC to evaluate the impact of different bio-oil to bio-diesel ratios on the cold flow behaviour of resulting bio-oil/biodiesel blends.[179] The results prove that DSC is a promising technique to quantify the effects of bio-oil derived molecules on cold flow behaviour of biodiesel.[179] DSC technique shows particular advantages for dark colour bio-oils because they are difficult to investigate the cold flow properties via ASTM methods.[179]

2.6 Bio-oil Upgrading Technologies

The undesired properties of bio-oils, such as high viscosity, high acidity, high water and oxygen content, and instability, inhibit their fuel applications.[20, 28, 31, 32, 184] As a result, it is essential to upgrade bio-oils before applied as fuels to supply heat or power.[184] There are substantial investigations on bio-oil upgrading study and various upgrading technologies, catalytically, chemically and physically, have been developed.[20, 21, 25, 28, 31, 184-189] This section will discusses several main upgrading technologies with emphasis on physical upgrading methods.

2.6.1 Physical upgrading of bio-oil

Improving of important properties of a bio-oil (such as oxygen content, solid content, viscosity and chemical instability) may positively affect their fuel performance.[26] Physical upgrading technology is considered as a relatively simple way for adapting bio-oil in diesel engines or turbines. There are three main physical upgrading methods: filtration, solvent addition, and emulsions/emulsification which are discussed below.

2.6.1.1 *Filtration*

The ash and alkali content of a bio-oil can be reduced by hot-vapour filtration to below 0.01% and 10 ppm, respectively.[26] The obtained bio-oils possess better quality with lower biochar particles.[26] However, catalytically active biochar particles may crack the vapour which reduces the bio-oil yield to below 20%, decreases the viscosity and the average molecular weight of bio-oil.[26] Liquid filtration also removes some big biochar particles. However, for the biochar particles below ~5 μm, it is hard to remove because the physico-chemical nature of bio-oils and high pressure drops and self-cleaning filters are needed.[26]

2.6.1.2 *Solvent addition*

Polar solvents, for example methanol, ethanol and furfural, are commonly used for years to homogenize and reduce viscosity of bio-oils.[26, 31] Decreasing of viscosity and increasing of heating value are the direct effects of the addition of those polar solvents.[31] The latter effect is due to the higher heating value of the solvents which is obvious.[31] The mechanisms for the reduction of viscosity are: (1) physical dilution which has no effect on chemical reaction rates; (2) decreasing the reaction rates via

molecular dilution or via changing the bio-oil microstructure; (3) preventing further chain growth by chemical reactions between solvents and chemical components in bio-oil.[31, 109] Moreover, solvent (particularly methanol) addition significantly improves the stability of bio-oils.[26]

2.6.1.3 *Emulsions/Emulsification*

Bio-oils are immiscible with hydrocarbon fuels, however, they can mix with other fuels like diesel fuels to prepare emulsions with or even without the addition of surfactants.[20, 26] Compared with other methods, emulsification is an easy and rapid method which can promote the heating value and stability while lower the viscosity of bio-oils.[20] There are two emulsification methods: stirring and ultrasonic emulsification.[20] The latter method can prepare emulsion droplets with super small diameter and narrow distribution effectively.[20] The prepared emulsion commonly shows acceptable dispersion and satisfied stability.[20] Span and Tween series are two commonly used emulsifiers.[20] Alcohols such as octanol may be used as the auxiliary emulsifier.[25] Many studies on emulsification of bio-oil and biodiesel or diesel were carried out.[25, 190-201] There are several parameters affect the stability of prepared emulsions: the emulsifier amount, the volume ratio of bio-oil to biodiesel/diesel, emulsifying temperature, and stirring intensity.[25, 200] Ikura et al.[202] have reported that the emulsions exhibit several desirable properties like acidity, viscosity and water content in comparison with unprocessed bio-oils. However, Chiaramonti et al. reported that the corrosion effect is promoted which is a issue in the internal combustion engine.[203]

2.6.2 Catalytic upgrading of bio-oil

Deoxygenation together with conventional refining are required to upgrade bio-oils used as conventional transport fuels, which can be achieved via catalytic cracking or hydrotreating.[26]

2.6.2.1 *Catalytic cracking*

Bio-oil upgrading by catalytic cracking is operated under normal pressure with temperature being 350–500 °C with utilization of catalysts.[204, 205] Deoxygenation is achieved by simultaneous reactions like dehydration, decarbonylation, and decarboxylation with formation of hydrocarbons, organics, water, CO, CO_2, and coke.[206] Zeolite catalysts with high acidity, high reactivity and regular porous structure (e.g., ZSM-5 and HZSM-5) are commonly used.[20] Although catalytic cracking improves the yield and quality of bio-oils, it exhibits several drawbacks, for instance, high coke yield, high water content, easy blockage of reactors, etc.

2.6.2.2 *Catalytic hydrogenation/Hydrotreating*

In the catalytic hydrogenation (also referred to as hydrotreating) process of bio-oils in an autoclave, oxygenated compounds (e.g., organic acids and aldehydes) are removed by hydrogen under high pressure to promote its stability and combustion performance.[20] This process usually carried out at mild temperatures (i.e. 300–600 °C) in presence of catalysts such as sulfided CoMo or NiMo catalysts supported on alumina.[204, 205] Despite the requirement of huge amount of hydrogen and high pressure, there are still several issues of hydrotreating upgrading of bio-oil, such as high cost, demand for sophisticated equipments and superior techniques.[28]

2.6.3 Bio-oil upgrading by steam reforming

Steam reforming of bio-oils can generate hydrogen and synthesis gas in a sustainable and environmental friendly manner.[207, 208] Abundant studies have been performed on hydrogen generation by steam reforming of whole bio-oil or bio-oil WSF.[20] The produced synthesis gas is feedstock for alcohol or conventional hydrocarbon fuels.[31] While the produced hydrogen is commonly utilized as green energy source or as raw material in chemical industry.[20] Generally, steam reforming process of bio-oils is performed at high temperature (i.e. 600–800 °C) and uses noble metals and Nickel catalysts as catalysts.[31] Catalyst deactivation caused by coke formation is a main issue that limits the application of steam reforming of bio-oils.[31]

2.7 Recent Advancement in Bio-oil Derived Fuel Mixtures Containing Crude Glycerol and/or Biochar

As mentioned previously in section 2.6.1, utilizations of bio-oils in a diesel engine or turbine can be accomplished through physical upgrading of bio-oil to bio-oil/solvent fuel blends or emulsion fuels. It has been reported CG can be mixed with bio-oil directly or with the help of appropriate surfactant to prepare emulsion fuels.[209, 210] A homogeneous bio-oil and CG fuel blends can be achieved by further adding methanol.[57, 60] Since CG is miscible with water, it can directly mix with WSF to produce homogeneous fuel blends with a considerable high CG loading rate.[58] Another promising upgrading strategy is suspending biochar particles into bio-oil to prepare slurry fuels.[16, 18, 19, 22, 34-36, 128, 211] Therefore, this section mainly discusses the advancement in bio-oil derived fuel mixtures contain CG and/or biochar.

2.7.1   Characterization and application of crude glycerol as a fuel

Biodiesel is another potential alternative conventional transport fuel and CG is a main by-product of biodiesel industry with yield being ~10 wt% of that of biodiesel.[40, 46-48, 50, 51, 54, 83] Recently, the booming growth of biodiesel industry leads to a huge surplus of CG which arises the issue of its direct utilization due to purification of CG is costly.[54] Generally, CG contains less than 88 wt% of pure glycerol and the rest are impurities which mainly are catalysts, salts, methanol, water, methyl esters, soap, free fatty acids, and trace amount of ash.[47, 53] The chemical composition of CG commonly depends on the feedstock used to produce biodiesel, the production process and recovery process of biodiesel.[51] Using CG as an energy source is a potential approach due to it can accommodate CG directly without purification in a large scale.[83, 212] By further combination with biodiesel production, it may has further advancement in energy integration which reduces the transportation cost and the dependence on fossil fuels.[48]

However, direct combustion of CG may be problematic because of its poor fuel properties, for instance, high viscosity, high ignition temperature, and low heating value (16–26 MJ/kg).[55, 56] The inorganic species in CG may also lead to ash-related problems.[55] To address the above issues associated with direct combustion of CG, other fuels are mixed with CG to produce fuel blends or emulsions, such as yellow grease, gasoline bio-oil and bio-oil WSF.[57, 58, 60, 209, 212, 213] Detailed description of bio-oil derived fuel blends which contain CG are discussed in next section.

2.7.2   Bio-oil derived fuel blends and emulsion fuels contain crude glycerol

Recently, Wu et al. developed a fuel blend prepared from bio-oil and pure glycerol with addition of methanol as an additive to homogenize the blend.[60] Methanol also is a main impurity of CG from biodiesel industry.[51, 214] The prepared fuel blends possess improved fuel properties compared to that of bio-oil or glycerol alone as a fuel, for example, higher heating value, lower viscosity and surface tension, etc.[60] Based on safety considerations of storage and handling of a fuel together with potential glycerol to methanol ratio comes from biodiesel generation process, possible feasible compositions of the glycerol/methanol/bio-oil (GMB) blends (bio-oil $\geq$ 70 wt %, glycerol $\leq$ 20 wt %, and methanol $\leq$ 10 wt %) are suggested.[60] Like bio-oil, GMB fuel blends also suffering ageing problem during long-term storage which leads to an increase in the water content while a decrease in viscosity and acidity.[60] Further investigations on how the major impurities in CG affect the solubility and fuel properties of CG/methanol/bio-oil (CGMB) blends were carried out.[57] The results show that to some extent, all the studied impurities (i.e. water, soap, NaCl, and NaOH) deteriorate the solubility of glycerol in bio-oil.[57] However, fuel properties such as heating value, viscosity, surface tension, and density of the CGMB blends are little affected by those impurities, except the TAN is slightly decreased for fuel blends which contain NaOH.[57] In addition, the impurities in CG influence the ageing of CGMB fuel blends.[57] For example, the presence of NaOH and soap result in less changes in the fuel properties (i.e. viscosity, water content and TAN) during ageing process. [57]

Research on emulsifying bio-oil with CG to prepare emulsion fuels also have been performed.[209, 210] Wu et al.[209] proved that the temperature and surfactant have more significant effect on the stability of produced emulsions compare with stirring rate and time. To obtain a stable emulsion fuel, temperature above 45 °C and low Span

80 concentration (i.e. < 1%) is recommended.[209] The high stirring rate (> 3000 rpm) causes phase separation and is energy consuming, therefore is not preferred.[209] Extended ageing of emulsion fuels leads to a longer stable time (> 12 h).[209] Impurities in CG (except methanol) aggravate phase separation and drastic decrease the stable time of the emulsions to less than one hour.[209] With the content of methanol in CG being 10% and the content of other impurities being low (e.g., 5% for soap or water while 2% for NaCl or NaOH), stable time of 4–8 h for prepared emulsions can be achieved.[209] Wu et al.[210] further developed an approach to directly produce emulsions from bio-oil and CG without the introduction of surfactant via ultrasound and/or mechanical agitation. A higher ultrasound amplitude and a longer agitation time lead to improved stability of emulsions due to the increase in temperature caused by ultrasound process.[210] The maximum stable time of produced emulsions is up to 15 h under a recommended emulsification approach (ultrasound at 40% for 4 min and then mechanical agitated for 2 min) with the soap content in emulsion being ~1%.[210] The advantage in combining ultrasound and mechanical agitation is resulted from efficient droplet breakdown (by ultrasound agitation) and reduction in the possibility of droplet recoalescence (by mechanical stirring).[210] It has been proven that the prepared emulsions have equal or even improved fuel properties compared to bio-oil.[210]

Besides the whole bio-oil, bio-oil WSF also can be mixed with CG to prepare homogeneous CG/WSF (CGWSF) fuel blends at a high CG loading rate (50–70 wt %) without any additives.[58] The study shows that the WSF obtained from a water to bio-oil ratio of 0.5 has relatively higher solubility of CG in WSF compared to those obtained from water to bio-oil ratio of 0.2 and 0.4.[58] The prepared CGWSF fuel blends exhibit lower acidity and moisture while higher heating value and density compared to the WSF alone as a fuel.[58] Further adding biochar particles into CGWSF blends can produce CGWSF/biochar (CGWSFB) slurry fuels which have equal

energy density and possess even better fuel properties in terms of viscosity, Ohnesorge number and acidity.[58]

2.7.3 Bio-oil derived slurry fuels containing biochar

Through suspending biochar into bio-oil or WSF (as mentioned in section 2.7.2) to prepare slurry fuels is also an attractive approach to upgrade bio-oil for its near-term utilizations which also address the issues of biochar application (dusty or spontaneous combustion).[22] The concept of bio-oil/biochar (BB) slurry (also referred to as bioslurry) was initially developed by commercial developers.[215] Recently, Wu et al. had performed systematically investigations on the feasibility and fuel properties of BB slurry fuels.[16, 18, 19, 33-36, 128, 216]

Firstly, the economic feasibility of bioslurry-based supply chain for mallee biomass in Western Australia consists of the costs for biomass transportation, the introduction of distributed pyrolysers, and bioslurry transportation.[19] The results suggest that the bioenergy supply chain is economically feasible at large scales for dedicated bioenergy plants located in biomass production area while is highly economically competitive for coal-based power stations.[19] Further study on life-cycle evaluation on energy and carbon footprint of such a supply chain shows it has small energy and carbon footprints, which are less than 4% and 3% of the overall energy and carbon embedded in the delivered fuels.[19]

Following is the investigations on fuel and rheological properties of BB slurry fuels prepared with different biochar loading rates. The results demonstrate that the BB slurry fuels possess significant volumetric energy density (up to 23.2 GJ/m^3) and therefore are suitable for combustion and gasification utilizations.[36] The slurry fuels also possess low viscosity (< 453 mPa s) which indicates favourable pumpability,

and exhibit non-Newtonian with pseudo-plastic behaviour when biochar loading rates are 10–20 wt %.[36] Increase of biochar loading rate or decrease of temperature can lead to an increase in viscosity of slurry fuels.[36] Stability investigation of slurry fuels during storage shows that ageing effect leads to an increase in water content and reductions in acidity and viscosity.[16] Increasing biochar loading rate aggravates such ageing effect.[16] It is also proved that AAEM species can be leached from biochar into bio-oil phase due to the interactions between two phases which leads to undesired redistribution of inorganic species.[34] The leaching effect is mainly attributes to WSF of bio-oil, particularly the organic acids and water.[34]

Further spray characterization of slurry fuels were carried out by two types of atomizers: impact atomizer and twin-fluid atomizer.[33] The results indicate that increases in both viscosity and biochar loading rate can lead to an increase in droplet size distribution for both atomizers.[33] Compared to the impact atomizer, the twin-fluid atomizer is more applicable when the fuel flow rate is low, and a higher gas/fuel ratio resulted in a decrease in droplet sizes.[33]

In summary, slurry fuels show attractive economic feasibility, have small life-cycle energy and carbon footprints, possess good fuel and spray properties. Therefore, slurry fuels are suitable for stationary applications as substitution of fossil fuels. However, so far, no data are available in the open literature on the cold flow behaviour and ignition behaviour of bio-oil derived fuel mixtures. The fuel properties of slurry fuels prepared from biochar and bio-oil derived fuel blends also remain unknown. Such works are included in this PhD project.

2.8 Thermal Processing of Bio-oil

There are three types of main thermal processing for bio-oil: pyrolysis, combustion and gasification, while combustion and gasification are conventional bio-oil utilization technologies. This section mainly discusses the three types of thermal process of bio-oil with emphases on bed agglomeration phenomenon in a fluidised-bed reactor during pyrolysis or combustion process.

2.8.1   Pyrolysis

As aforementioned, pyrolysis is a significant process of biomass utilization (especially to produce bio-oil and biochar).[217] It is also the first step of subsequent combustion and gasification applications for both biomass and bio-oil. Therefore, it is important to investigate the pyrolysis process of bio-oil for fundamental understanding the combustion or gasification process of bio-oil. Thus far, little efforts have been put on bio-oil pyrolysis.

Recently, Li et al.[75, 217-220] carried out systemically studies on transformation of bio-oil during pyrolysis and reforming with emphases on formation of coke and aromatic structures during bio-oil pyrolysis. Heating up is the first stage of bio-oil chemical upgrading, combustion, or gasification/reforming.[217] Various types of reactions (e.g., thermal decomposition reactions) may undertaken when bio-oil is heated up due to bio-oil is extremely reactive at high temperature, which may restrict its utilization.[76] The formation of variety of large/complex aromatic ring systems is particularly significant. For instance, coke (solid carbonaceous materials) formation is an extremely severe issue for the upgrading or thermal processing of bio-oil.[221, 222] Because the formed coke may blocks the downstream equipment of gasification

systems or can deactivate the catalysts used in bio-oil upgrading.[223] Tar formation is a main issue in a gasifier for the utilization of gasification product gas.[224, 225]

Investigations on the evolution of aromatic ring structures during pyrolysis of bio-oil at temperature range of 350–800 °C were carried out. The results indicate that the tar yield reduces when temperature becomes higher due to the intensified decomposition of tar molecules at higher temperature.[218] At low temperature ($\leqslant$ 600 °C), trace amount of larger aromatic ring systems (with two or even more fused benzene rings or equivalent) were formed in the tar.[218] While at high temperatures ($\geqslant$ 700 °C), high concentrations of radicals were produced by pyrolysis reactions (e.g., Diels-Alder-type reactions) which would form larger aromatic ring systems.[218] To further study the reactions responsible for the formation and evolution of aromatic ring systems during bio-oil pyrolysis, lignin-derived oligomers and cellulose were also pyrolyzed under same conditions. The results show that at low temperature (around 350 °C), the radical combination reactions (polymerization is included) dominate upon the decomposition reactions while the latter reactions become more important when temperature increases.[218] As a result, a large amount of aromatic ring systems in bio-oil could polymerize into solids (not soluble in $CHCl_3$ + CH_3OH, also referred to as coke) during bio-oil pyrolysis at low temperatures.[218] Cellulose-/hemicellulose-derived species in bio-oil can intensify this process.[218]

Further investigations on coke formation during bio-oil, WSF and WIF pyrolysis at 250–800 °C in a two-stage fluidised-bed reactor were then carried out. The results indicate both WSF and WIF can form coke even at a low temperature.[217] The interactions among different components in bio-oil (i.e. species derived from cellulose/hemicellulose and lignin) are significant to coke formation. At low temperatures (250–400 °C), radical reactions between WSF and WIF are dominant reactions and change with temperature.[217] The recombination of produced radicals

leads to coke formation. However, at high temperature, thermal decompositions turn to dominant reactions which leads to reduction of coke formation.[217]

2.8.2 Combustion

As bio-oil is commonly used as a fuel in a boiler directly, it is significant to understand fundamentals of bio-oil combustion. Typically, the definition of combustion is a complex sequence of chemical reactions where a fuel reacts with oxygen at sufficiently high temperature, involving generation of heat and light.[62, 226] Because of the complicated nature of bio-oil, the combustion of bio-oil is particularly complex.[227]

Fundamental investigations on combustion of a bio-oil droplet found that it has following steps.[14, 129, 228] First is the evaporation of water, following is the heating of light compounds, with selective vaporisation and liquid-phase pyrolysis of heavy fractions.[14] At this step, bio-oil exhibits distinctive behaviour (i.e. swelling, shrinking, and microexplosions), with ejection of mass from bio-oil droplet.[14] The flame is blue then turns to yellow with increasing size.[14] When the flame is extinguished, the last step occurs which is the burnout of solid residue.[14] For bio-oil combustion in industrial scale, first step is the evaporation and combustion of light compounds followed by combustion of heavy compounds which is second step.[14] For stable combustion purpose, two steps need to be combined into one flame during industrial applications.[14]

Three main groups of burner technology are adopted for bio-oil combustion in a boiler: high pressure atomization, dual-block burner systems (with a separate air blower), and rotary cup atomization.[14] As mentioned before, to improve the atomization and combustion performance, moderate preheating of bio-oil and/or air

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maybe needed.[14] Another method is to blend it with additives such as methanol and ethanol.[14] It has been reported that due to the presence of fine char particles and volatile species in bio-oil, bio-oil combustion has particulate matter emission issue but considerably lower than that of fossil fuels.[229, 230]

2.8.3 Gasification

Gasification is defined as a thermol-chemical partial oxidation process.[231] By gasification, carbonaceous feedstock, such as biomass, coal and bio-oil, can be converted into gas with the presence of a gasifying agent (e.g., air, steam, oxygen, CO_2, or a combination of them).[231] Generally, the gasification process is performed at high temperature (800–1000 °C) and high pressure (up to 40 bar).[232] The fluidised-bed reactor and entrained-flow gasifier are commonly used for bio-oil gasification with or without catalysts.[233] The produced gas from bio-oil gasification typically consists of H_2, CO, CH_4, CO_2, and N_2 which is very similar to that from biomass gasification.[231, 232] After cleaning and conditioning, the gas can then be utilized to synthesize high-grade fuels (e.g., biohydrogen, methanol and dimethyl ether) or chemicals.[232-234]

2.8.4 Bed agglomeration in a fluidised-bed reactor

Due to the advancements of low process temperatures, fuel flexibility, and isothermal operation conditions, fluidised-bed reactors are widely used for combustion and gasification of fuels, especially biomass.[61, 63, 66] Bed agglomeration in a fluidised-bed reactor is one major issue that limit the application of fluidised-bed reactor because it reduces the fluidization quality and the heat-transfer in the bed.[64-66, 72, 73, 122, 235-237] As a result, the conversion efficiency becomes poor and the bed operational parameter cannot be controlled.[66] Most severely, bed agglomeration may lead to complete

defluidization resulting in suddenly plant shutdowns and high operational and maintenance expenditures.[61, 66]

It has been proven by substantial investigations that during biomass combustion or gasification, bed agglomeration is closely related to ash species.[61, 63, 66, 72, 122] Recently, Wu et al.[62, 67-71, 238] conducted systemically studies on bed agglomeration during biomass fast pyrolysis which is totally different. The results show that there exists two types of bed agglomerates, char-char and char-sand agglomerates, both of them are related to carbon-enriched necks.[71] The total agglomeration yield significantly decreases with pyrolysis temperature increases.[71] Holding time also affects bed agglomeration yield.[71] Two types of bed agglomeration were formed: one is driven by solvent-soluble organic matter which is the dominant one at high temperatures (> 450 °C); the other one is driven by solvent-insoluble organic matter which is the dominant one at low temperatures (< 400 °C). Agglomeration is driven by organic matter (contains various aromatic ring systems) acts as sticky agents which is formed during biomass pyrolysis reactions.[71]

Further studies on bed agglomeration behaviour of different biomass components (i.e. Mallee bark, leaf, and wood) suggest the ethanol-soluble extractive materials in biomass significantly affect the bed agglomeration behaviour.[69] By introducing sand loading as a new diagnostic factor, it proves that bed agglomeration phenomenon is not randomly but depends on biomass pyrolysis reactions taking place in the pyrolyser.[238] Bio-oil also can be processed in a fluidised-bed reactor for combustion, gasification, or upgrading. However, bed agglomeration behaviour of bio-oil fast pyrolysis in a fluidised-bed reactor is not investigated. Such work is included in this thesis.

2.9 Conclusion and Research Gaps

Based on the above literature review, it could be summarized that:

1) Fast pyrolysis is a prospective approach to convert bulky biomass to liquid bio-oil and solid biochar products with high energy density. However, bio-oil and biochar have some undesired properties which impede the expansion of their applications as a fuel.

2) Cold flow behaviour is a significant parameter for proper storage, transport and operation of bio-oil under cold weather. DSC is a promising technique to investigate cold flow properties of dark colour bio-oil as it is difficult to be determined by ASTM methods.

3) Ignition behaviour is a key factor to safety handling, transportation, operation, as well as combustion performance of bio-oil. It is difficult to ignite bio-oil due to its chemical components especially water. Ignition behaviour of bio-oil can be described by ignition temperature determined via TGA technology or ASTM standard.

4) Among bio-oil upgrading technologies, physical upgrading techniques are comparatively simple for applying bio-oil in a diesel engine or turbine. Three major physical upgrading methods are discussed such as filtration, solvent addition including methanol and ethanol addition, and emulsification of bio-oil with biodiesel or diesel to produce emulsions.

5) Bio-oil derived fuel mixtures containing CG and/or biochar are promising fuels as clean and sustainable energy sources that suitable for stationary applications. They also are promising substitutions for coal or fossil fuels

because of their proved advancements including low carbon footprints, good fuel properties adaptable to existing combustors.

6) Three types of thermal processing of bio-oil are reviewed including pyrolysis, combustion and gasification. Bed agglomeration limits the application of fluidised-bed reactor which is widely used for bio-oil combustion and gasification. There exists good understanding of agglomeration that occurs during biomass pyrolysis including the fundamental mechanism governing bed agglomeration. However, it remains unknown if bed agglomeration occurs during bio-oil pyrolysis and its mechanism is unclear.

Therefore, further research and development should be carried out in the above research area, including:

1) Preparation and properties of slurry fuels produced from GMB or CGMB blends and biochar. Such slurry fuels may possess better fuel properties than that of the corresponding blend fuels and may suitable for stationary applications. It is significant to perform subsequent research on the effect of CG and methanol on fuel properties, ageing and redistribution of AAEM species.

2) Studying on the cold flow properties of bio-oil and its derived fuel mixtures. It is of great value to investigate how the impurities in CG and biochar affect the cold flow properties of those fuel mixtures. The outcomes can provide guidance for handling, transportation and operation of those fuel mixtures under cold weather.

3) Studying on the ignition temperatures of bio-oil and its derived fuel mixtures. Further understanding the influence of the impurities in CG and biochar on

ignition temperature of a fuel. Such data is significant to evaluate the combustion performance of those fuel mixtures.

4) Understanding of the fundamental mechanism of bed agglomeration during bio-oil fast pyrolysis in a fluidised-bed reactor. Further investigate bed agglomeration of pyrolysis of bio-oil derived fuel mixtures to determine the effect of the addition of CG and biochar on bed agglomeration.

5) Combustion/gasification of bio-oil derived fuel mixtures. Such research is of great significance to understand the combustion or gasification behaviour of those fuels in practice.

6) Preparation of bio-oil derived fuels containing industrial CG. The outcomes can integrate production process of bio-oil derived fuels with biodiesel, thereby improving the economic value chain of biodiesel industry.

2.10   Study Objectives of the Present Study

As identified by previous literature review and discussion, there are several research gaps in the research field. However, it is unlikely to fulfil all the research gaps during the limited time of this PhD study. Therefore, this research will mainly focuses on the below objectives:

1) To prepare slurry fuels from glycerol/methanol/bio-oil (GMB) or crude glycerol/methanol/bio-oil (CGMB) fuel blends and biochar, then further investigate the fuel properties and ageing of slurry fuels benchmarking against that of GMB or CGMB fuel blends as a fuel.

2) To investigate the ignition behaviour of bio-oil and various bio-oil derived fuel mixtures by two methods: a TGA-based method and a modified method based on ASTM standard.

3) To investigate the cold flow behaviour of bio-oil and various bio-oil derived fuel mixtures by DSC (melting process), focusing on the influence of CG and biochar.

4) To investigate bed agglomeration during fast pyrolysis of bio-oil in a fluidised-bed reactor and explain the fundamental mechanisms responsible for bed agglomeration.

Chapter 3 Research Methodology and Analytical Techniques

3.1 Introduction

This chapter presents the research methodologies applied for the study targeting at the objectives outlined in Chapter 2. The experimental and analytical techniques are detailed in the following sections.

3.2 Methodology

Considering the targets of this thesis, twelve fuel samples are involved to study the fuel properties and thermal processing, including bio-oil and water soluble fraction (WSF), and other ten bio-oil derived fuel mixtures, such as bio-oil/biochar fuel slurry, WSF/biochar fuel slurry, glycerol/methanol/bio-oil fuel blend, crude glycerol/methanol/bio-oil fuel blend, glycerol/WSF fuel blend, crude glycerol/WSF fuel blend, glycerol/methanol/bio-oil/biochar slurry fuel, crude glycerol/methanol/bio-oil/biochar slurry fuel, glycerol/WSF/biochar slurry fuel, and crude glycerol/WSF/biochar slurry fuel, hereafter referred to as "BB", "WSFB", "GMB", "CGMB", "GWSF", "CGWSF", "GMBB", "CGMBB", "GWSFB" and "CGWSFB", respectively (G and CG refers to glycerol and crude glycerol). A series of systematic experiments were thus performed, including:

1) Biomass pyrolysis in a drop-tube/fixed-bed reactor to prepare biochar for the preparation of slurry fuels while bio-oil was separated via cold-water precipitation to obtain WSF.

2) Preparation of bio-oil derived fuel mixtures by adding G or CG, and/or biochar to bio-oil or WSF with different compositions.

3) Fuel properties characterizations. Ageing experiments were conducted by storing the fuel samples in an oven at 80 ℃ for 24 h. The fuel samples were analysed by a series of instruments to acquire fuel properties, i.e., rheological properties, water content, total acid number (TAN), density, Proximate and Ultimate analysis, and surface tension, etc.

4) Ignition temperatures of bio-oil and its derived fuel mixtures were carried out via thermogravimetric analysis (hereafter referred to as TGA) method and modified ASTM method.

5) Cold flow properties of bio-oil and its derived fuel mixtures were performed via differential scanning calorimetry (hereafter referred to as DSC).

6) Bio-oil fast pyrolysis was conducted in a fluidised-bed reactor to investigate the bed agglomeration phenomenon.

All the experiments were conducted duplicate to make sure the reproducibility of the experiment results. Figure 3-1 presents the overall research methodology with the methodology description of each research objective detailed below.
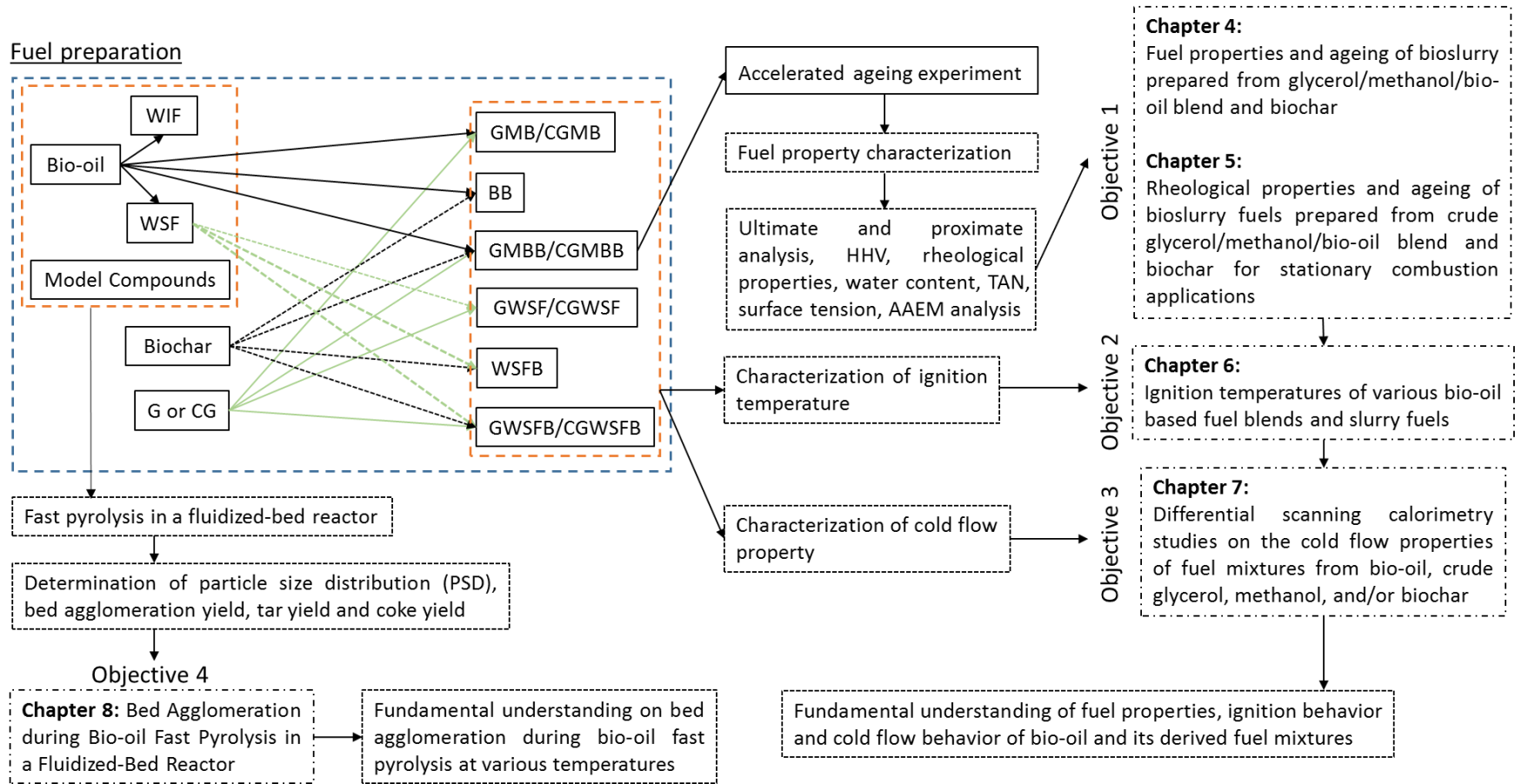
Figure 3-1 Research methodology

3.2.1   Fuel properties and ageing of GMBB and CGMBB slurry fuels

The biochar samples were prepared by pine wood fast pyrolysis at 500 ℃ in a fluidised-bed reactor (see section 3.3.1). The GMB fuel blend was produced by adding glycerol and methanol into bio-oil (see section 3.3.1). A range of BB, GMBB and CGMBB slurry fuels with different biochar loading rate were prepared from produced biochar and bio-oil (see section 3.3.1). Selected fuel samples were then subjected to ageing followed a method detailed in section 3.3.2. The proximate and ultimate analysis of bio-oil and biochar samples were carried out by methods described elsewhere (see section 3.4.1). Fuel properties of all the fuel samples were also analysed, such as rheology (section 3.4.4), total acid number (TAN), water content and higher heating value (HHV) (section 3.4.2 and 3.4.5). The Alkali and Alkaline Earth Metallic (AAEM) species in the fuel samples were quantified using an evaporation−ashing−digestion−ion chromatography (IC) method (section 3.4.3). The results and discussions of this work are detailed in chapter 4 and 5.

3.2.2   Ignition temperatures of various bio-oil based fuel blends and slurry fuels

The used bio-oil and biochar samples were produced accordingly (see section 3.3.1). WSF was prepared by adding water into bio-oil (see section 3.3.1). A range of bio-oil based fuel blends and slurry fuels were then prepared from bio-oil and WSF (see section 3.3.1). It was reported that ignition behaviour plays an important role in the storage and transport of a fuel. The ignition temperatures of those fuel samples were then tested by two methods, a TGA method and a modified method based on ASTM standard E659 (see section 3.3.3). Chapter 6 describes the results and discussions of this work.

3.2.3   Differential scanning calorimetry studies on the cold flow properties of fuel mixtures from bio-oil, crude glycerol, methanol, and/or biochar

The Bio-oil, biochar and WSF samples were produced respectively (see section 3.3.1). A set of fuel mixtures were prepared via mixing bio-oil or WSF, G or CG and/or biochar using magnetic stirring at room temperature (see section 3.3.1). The cold flow property of the fuel samples was investigated by determine the meting peak temperatures. All the fuel samples were then introduced into DSC analysis to achieve the melting peak temperature following a method reported elsewhere[239] (see section 3.3.4). Chapter 7 clarifies the results and discussions about this work.

3.2.4   Bed agglomeration during bio-oil fast pyrolysis in a fluidised-bed reactor

To investigate the bed agglomeration during fast pyrolysis of bio-oil in a fluidised-bed reactor at temperatures of 500−800 °C, the bio-oil, WSF, WIF, and selected model compounds were prepared and sent to the furnace for fast pyrolysis to collect bed materials (see section 3.3.5). Via the comparison of the bed agglomeration yields of bio-oil, bio-oil fractions (i.e. WSF and WIF) and model compounds, the interactions between lignin-derived oligomers and sugar are revealed to be responsible for bed agglomeration during fast pyrolysis of bio-oil. Tar yield and coke yield also studied to investigate its correlations with bed agglomeration (see section 3.4.6). The results and discussions about this work are presented in chapter 8.

3.3 Experimental Section

3.3.1   Sample preparation

Bio-oil (see Chapter 4−8). The bio-oil sample used in this thesis was provided by an anonymous company and was produced by pine wood fast pyrolysis at 500 ℃ in a fluidised-bed reactor. The obtained bio-oil sample was stored at ~4 ℃ before used for experiment.

Biochar (see Chapter 4-7). The pine wood chips were received from WA&J King Pty Ltd (Western Australia) and then dried in an oven. It was cut and sieved into size fraction of 1−2 mm and then stored in a fridge at ~4 ℃ before usage. Biochar sample was prepared from the fast pyrolysis of pine wood biomass at 500 ℃ in a drop-tube/fixed-bed reactor according to a previous method.[34] The collected biochar was then ground (using a ball mill, Retsch MM400) for 8 min with frequency being 15 Hz and sieved to the size fraction of < 75 μm for subsequent slurry fuels preparation.

WSF and WIF (see Chapter 6, 7 and 8). The bio-oil WSF and WIF samples were achieved by cold-water precipitation method. In brief, cold water was added into bio-oil with the mass ratio of water to bio-oil being 0.5:1, which is known to produce optimal bio-oil WSF that is suitable for preparing stable fuel mixture with crude glycerol and has a relatively low water content [58]. The WSF (the upper fraction, with additional water) and WIF (the bottom fraction) were then produced after phase separation. The achieved WSF was used without further retreatment, while the WIF sample was dried at 35 ℃ in an oven and then redissolved in ethanol to the equal percentage as it is in bio-oil. Excluding the extra water added, the yields of WSF and

WIF samples are 45.0 wt% and 27.3 wt%, respectively, with the rest 27.7% being water and other light compounds lost during the WIF drying process.

Mixed solvent (hereafter denoted as MS) (see Chapter 8). A MS with the mass ratios being 33.3% of acetic acid, 33.3% of hydroxyactone, 13.3% of phenol, 13.3% of furfural and 6.8% of methanol was prepared,[240] all chemicals were supplied by Sigma-Aldrich. A series of formulated systems based on bio-oil fractions and model compounds, including Sugar/MS, Water/Sugar/MS, WIF/MS, WIF/Sugar/MS and WIF/Water/Sugar/MS mixtures, were also prepared by adding levoglucosan (used as model compound to represent the sugars contained in bio-oil[240], purchased from Novachem), WIF and/or water into MS. The compositions of these formulated systems are listed in Table 3-1.

Table 3-1 Compositions of a series of model compounds prepared in this study (wt%, MS: mixed solvent, WIF: water-insoluble fraction).

	Model compounds	Sugar [a]	WIF	Water	MS
Formulated WSF without water	Sugar/MS	7.0			93.0
Formulated WSF with water	Water/Sugar/MS	7.0		60.0	33.0
	WIF/MS		27.3		72.7
Formulated bio-oil without water	WIF/Sugar/MS	7.0	27.3		65.7
Formulated bio-oil with water	WIF/Water/Sugar/MS	7.0	27.3	23.5	42.2

[a] Sugar is represented by levoglucosan.

CG (see Chapter 5–7). Different types of CG were formulated based on the compositions of practical crude glycerol,[60] via mixing pure glycerol (G5516, analytical grade, Sigma-Aldrich) with other impurities, such as sodium oleate (26125, represents soap, Sigma-Aldrich), sodium chloride (NaCl, analytical grade, Chem-Supply), methanol (analytical grade, Chem-Supply), sodium hydroxide (NaOH, analytical grade, Chem-Supply) and deionized water. The formulated CG compositions could be found in chapter 5–7.

Fuel blends (see Chapter 4‒7). The GMB and CGMB fuel blends were prepared by adding G or CG, and methanol to bio-oil with detailed compositions elsewhere (see chapter 4–7). The GWSF and CGWSF fuel blends were produced by mixing G or CG with WSF and the compositions were presented in chapter 6 and chapter 7.

Slurry fuels (see Chapter 4‒7). The slurry fuels were manufactured via suspending fine biochar particles into bio-oil, WSF or other fuel blends with various biochar loading levels (i.e. 5%, 10%, 15% and 20%). All fuel mixtures were prepared via mixing using magnetic stirring at room temperature.
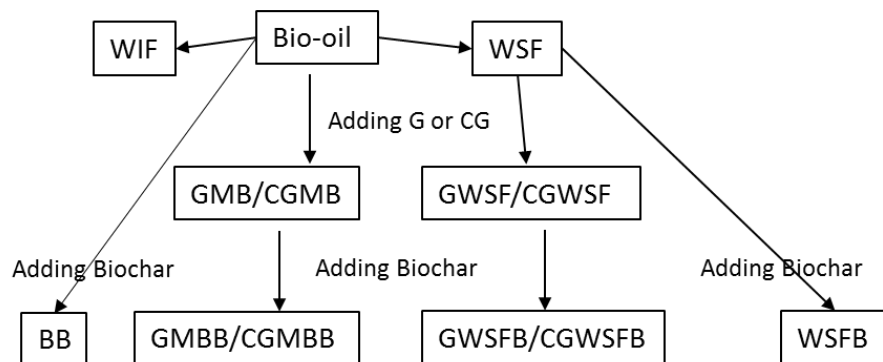
Figure 3-2 Allocation of bio-oil and its derived fuel mixtures.

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3.3.2   Accelerated ageing experiment

Ageing experiment of slurry fuels was conducted according to a procedure described previously [241, 242]. Briefly, selected samples were sealed in a glass container and then stored in an oven at 80 ℃ for 24h – a condition equivalent to ageing at room temperature for a year [133]. Upon the completion of an ageing experiment, the samples were cooled rapidly in an ice bath for collection. The weight of those fuel samples before and after ageing were recorded to make sure insignificant volatile loss during heating process. Both the aged samples and the corresponding control samples were conducted to fuel analysis, such as viscosity, water content, density, surface tension, and total acid number (TAN).

3.3.3   Characterization of ignition temperature

The ignition temperatures of bio-oil based fuel samples were determined using a TGA (Mettler TGA/DSC 1 STAR). In each run, 15–20 mg of sample was put into a platinum pan. Air was used as purge gas with a flow rate of 100 mL/min. In the TGA, the sample was hated from 40 to 1000 °C at 10 °C/min. All experiments were carried out at least in duplicate. The ignition temperature of fuel samples was defined following an intersection method [170, 243]. Briefly, two points on a TGA curve are firstly identified through DTG curve. One is the point at which a vertical line from the first DTG peak after 200 ℃ (DTG peak before 200 ℃ is considered to be related to the removal of water and some light volatiles [243-245]) crosses the TGA curve. The other one is the point at which a vertical line from the beginning/onset of this DTG peak crosses the TGA curve. Then two tangents at these two points on TGA curve are drawn and the corresponding temperature of their intersection is identified as the ignition temperature. The standard deviations of ignition temperatures determined by the TGA method is within 3 ℃. A modified test method based on ASTM standard

E659 (hereafter referred to as ASTM-based method) was also deployed. Briefly, a portion of fuel sample is placed in a muffle furnace at known temperatures and observed inside the furnace over a ten minute period to determine whether ignition occurs. Auto ignition is evidenced by the sudden appearance of a flame inside the vessel. If ignition is not observed, the temperature of furnace will be raised by a 20 °C interval until ignition is observed. All tests were carried out at least in duplicates.

3.3.4 Characterization of cold flow property

The cold flow property of the fuel samples was studied using a DSC (Perkin Elmer DSC 6000). Briefly, in an analysis, 10±0.5 mg of a fuel sample was loaded into a 40 μL sealed aluminium pan which is then subjected to DSC analysis with nitrogen as the purge gas at 50 mL/min. The fuel sample was first cooled to −100 °C and then kept at the temperature 5 min. The system was then heated to 30 °C at a heating rate of 5 °C /min, followed by cooled to −100 °C again at a cooling rate of 5 °C /min. For methanol, it was holding at −150 °C for 5 min firstly, then heated to 20 °C at a heating rate of 5 °C /min, finally cooled to −150 °C at same cooling rate. All experiments were performed at least in duplicate. In this study, the melting peak temperature (T_{MP}) is used as melting point instead of the onset temperature to study the cold flow property of fuel samples for several reasons. First, based on standard method of ASTM-E794, T_{MP} should be reported as the melting point of mixtures. Bio-oil and bio-oil based fuels are known to be complex mixture of various chemical compounds. Second, the onset temperature is known to have poor repeatability for such mixtures.[246] On the contrary, T_{MP} has good repeatability for mixtures, with standard deviations of T_{MP} determined by DSC being < 1 °C in this study. For methanol, the onset temperature based on the ending edge is taken as the melting point.[239]

3.3.5 Fast pyrolysis experiments

Fast pyrolysis experiments were carried out in a laboratory-scale fluidised-bed quartz reactor equipped with an atomization system (see Figure 3-3) at 500–800 °C. Silica sand (35 g, 125–250 μm) was loaded into the reactor as bed material with bed height being ~4.2 cm. The reactor was housed in an electrically heated furnace and preheated to the desired pyrolysis temperature, with 0.8–2.4 L/min argon gas as fluidisation gas. An air-assist nozzle set (model: VLA-3, VLT-1 and VLB, Paasche Airbrush) was used for atomization of bio-oil samples with argon gas (3 L/min) as atomization gas. The nozzle set was under both water-cooled and gas-cooled (argon gas, 1 L/min) conditions to maintain the temperature of the outlet of the nozzle below 70 °C. The total gas flow rate was 4.8–6.4 L/min which adjusts the residence time to be 2 s in all experiments at different temperatures. The bio-oil sample was fed by a stainless steel syringe powered by a syringe pump (model: KDS LEGATO 210) at a feeding rate of 0.12 g/min for 10 min. For the purpose of comparison, the amount of bio-oil fraction (WIF or WSF) and model compounds fed into the reactor were kept equivalent to the respective amount in 1.2 g bio-oil, by adjusting the feeding rate. The reactor was further held for 15 min at desired pyrolysis temperature before it was lifted out of furnace to cool down to below 50 °C with argon gas continuously flowing through the reactor. All samples in the bed were collected for further analysis.
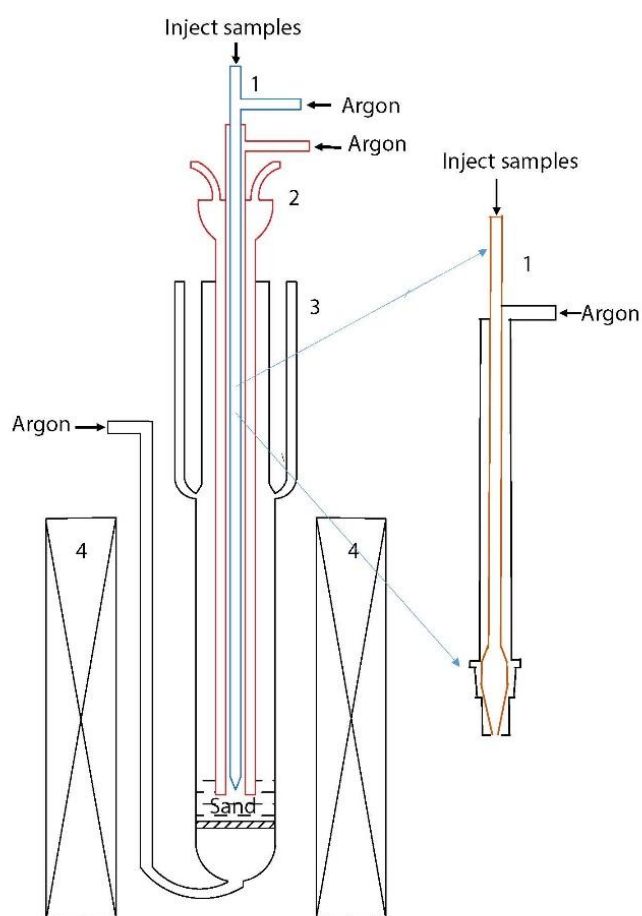
Figure 3-3 Schematic diagram of the fluidised-bed reactor system: 1, samples feeding and spray system; 2, water cooling tube; 3, quartz reactor; 4, furnace.

3.4 Instruments and Analytical Techniques

3.4.1   Ultimate and proximate analysis

The biochar and bio-oil samples were subjected to ultimate analysis using an elemental analyzer (Perkin-Elmer 2400 Series II model) based on AS 1038.6.1-1997 (R2013).[247] The proximate analysis of biochar was also carried out via thermogravimetric analysis (TGA; Mettler TGA/DSC 1 STAR model) according to the procedure detailed in ASTM E870-82.

3.4.2 Higher heating value

The higher heating value (HHV) of the bio-oil and bio-oil derived fuel samples were calculated following a method reported previously based on the elemental composition [248], in details:

$$\text{HHV (MJ/kg)} = -1.3675 + 0.3137C + 0.7009H + 0.0318O \qquad (3\text{-}1)$$

3.4.3 Quantification of inorganic species

The inorganic (mainly AAEM) species in biochar was quantified via a previous method [112], based on which a method was recently developed [128] for determining the concentration of AAEM species in bio-oil, fuel blends and bioslurry samples. In this study, the liquid phases of the GMBB and BB bioslurry samples were also obtained via the filtration of the corresponding bioslurry samples using a 0.45 μm polyvinylidene difluoride (PVDF) syringe filter and subjected to the analysis of AAEM species via the same method. Briefly, a solid, liquid or slurry sample was ashed using a carefully-devised temperature-time program (including an initial evaporation step for liquid or slurry sample). The ash was then digested using a mixture of nitric acid and hydrofluoric acid (1:1, v:v). The residues after excessive acid evaporation were dissolved in 0.02 M methanesulfonic acid solution for analysis by ion chromatography (IC, model DIONEX ICS-3000).

3.4.4 Rheological properties

The rheological properties of fuel samples were measured using a rheometer (model Haake Mars II) equipped with a proper sensor system and a Thermocontroller (Haake TC501). For bio-oil, WSF and other fuel blend samples, a cone-plate (C35/4

Ti) sensor system and a sample size of 0.8 mL were used. For slurry fuel samples, a Z20 cylinder sensor system and a sample volume of 8.1 mL were used. Steady shear tests were determined to study the flow behaviour and thixotropy behaviour of fuel samples. In brief, the shear rate was increased to 1000 s^{-1} from 0 s^{-1} and then held for 30 s before decreasing to 0 s^{-1}. The viscosity of bio-oil and GMB blend were obtained by averaging at least 50 data points from 100 s^{-1} to 1000 s^{-1} where the samples show Newtonian behaviour, while for slurry samples, the viscosity at the 100 s^{-1} were used.

3.4.5   Water content, acidity, surface tension, density and Ohnesorge number

The water content and total acid number (TAN) of fuel samples were determined by a Karl Fisher titrator (Metter V30) and an acid-base titrator (MEP Oil Titrino plus 848), respectively, according to the previous methods [16]. The surface tension of fuel samples were measured following Wilhelmy method using a surface tensiometer (KSV Sigma 701) with a round platinum rod (diameter of 1 mm). The fuel density was determined by measuring the mass of the fuel at a constant volume using a 5 mL volumetric flask. Both bulk density and surface tension were determined at room temperature (about 25 ℃). The standard deviations of density and surface tension are less than 1% and 5%, respectively.

The Ohnesorge number of selected fuel samples were estimated by previous reported method[35, 137-139] based on viscosity, surface tension and density, via following equation:

$$\text{Ohnesorge number} \equiv \eta_F / (\sigma_L \rho_F D_F)^{0.5} \qquad (3\text{-}2)$$

Where η_F, σ_L and ρ_F are the viscosity, surface tension and density of the fuel sample respectively, and D_F is the diameter of fuel passage.[137, 139]

3.4.6   Determination of particle size distribution (PSD), bed agglomeration yield, tar yield and coke yield

The bed samples collected after pyrolysis experiments were sieved into a series of size fractions (i.e. 125–250 μm, 250–355 μm, 355–500 μm, 0.5–1 mm, 1–2 mm, 2–3 mm and > 3 mm) using a vibratory sieve shaker (Retsch, AS 200 digit) sieving for 30 min with amplitude set to about 30%. The mass of each fraction was determined and the data were used to calculate the PSD of the bed samples collected after the pyrolysis of bio-oil, WSF, WIF or model compounds.

The bed agglomerates were also washed by a chloroform and methanol mixture (4:1 by volume) according to previous method[71] for quantifying the yield of solvent-soluble organic matter (termed as tar) and solvent-insoluble organic matter (termed as coke) in bed agglomerates. In brief, a flask was used to put the bed agglomerates, then twice the weight of a chloroform and methanol mixture was added in, followed by manual shaking for about 30 min. After this, the solution and the solids were separated via filtration. The collected solution was dried in an oven at 35 ℃, and the yield of the solid residue after evaporation normalised to the total mass of bio-oil fed into the fluidised-bed reactor is considered to be the tar yield. The collected solids were first dried in an oven at 35 ℃, then combusted in a quartz reactor at 600 ℃ with air flow rate being 1 L/min for 30 min. The weight loss after combustion normalised to the total mass of bio-oil fed into the fluidised-bed reactor was considered to be the coke yield.

Because the bed material (i.e. silica sand) has a size of 125–250 μm, after pyrolysis experiments any particles in the bed sample having sizes >250 μm are deemed to be bed agglomerates. Therefore, this study uses a parameter called agglomeration yield, calculated as the mass of the total particles with sizes >250 μm in the bed sample

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divided by the total mass of bed sample collected after a pyrolysis experiment. Both the agglomerate yield before and after solvent washing were determined accordingly.

3.4.7   Optical imaging

Optical images of selected bed materials were acquired using an optical microscope (Olympus SL 60/61) connected with a camera.

3.5 Summary

Bio-oil and biochar are produced from pine wood biomass fast pyrolysis, while WSF was obtained from bio-oil cold-water precipitation. Bio-oil derived fuel mixtures were further prepared from bio-oil or WSF, G or CG, and/or biochar. Fuel properties and ageing of GMBB and CGMBB slurry fuels were investigated according to the analytical techniques presented in section 3.4, such as viscosity, TAN, water content, surface tension and density etc. The AAEM species of those slurry fuels were also quantified using method described in section 3.4.3. Moreover, the ignition temperatures of bio-oil and a range of bio-oil based fuels were carried out via TGA method and ASTM-based method to investigate their ignition behaviour. Melting temperatures of bio-oil and its derived fuel mixtures were determined by DSC to study their cold flow behaviour with emphasis on the effect of CG and biochar. In addition, bed agglomerate during fast pyrolysis of bio-oil and its fractions (WSF and WIF) were explored by determine the bed agglomeration yields. Fast pyrolysis of selected model compounds were also performed to explain the fundamental mechanisms relevant to bed agglomeration.

Chapter 4 Fuel Properties and Ageing of Bioslurry Prepared from Glycerol/Methanol/Bio-oil Blend and Biochar

4.1 Introduction

Fast biomass pyrolysis, which is typically of small scales for distributed applications, is a promising thermochemical technology for producing bio-oil that can be future refined to liquid transport fuels and biochar as a high-energy-density solid by-product [6, 12, 204, 249-251]. Applications of the fine and combustible biochar particles may lead to potential environmental hazard during transportation (e.g., dusty [252] or spontaneous combustion [19]). Therefore, bio-oil/biochar bioslurry (hereafter referred to as "BB bioslurry") via suspending fine biochar particles into bio-oil has been considered as an important strategy for biomass-derived fuels penetrating into the existing energy markets in the near term. Such concept was initially attempted by commercial developers (e.g., Karlsruhe [253]) and also attracted systematic investigations into its preparation, fuel properties, performance and applications [16, 17, 19, 254-257]. It was demonstrated that bioslurry has suitable fuel and rheological properties for combustion and gasification in stationary applications [254]. However, during bioslurry storage, there is undesired migration of inorganic (especially alkali and alkaline earth metallic, i.e. AAEM) species from biochar to bio-oil phase [16]. Such migration of inorganic species is due to the acidic compounds and water in bio-oil and may be hindered in presence of organic solvents such as methanol [255].

On the other hand, the biodiesel industry produces a large quantity of surplus glycerol as a by-product (~19 million in 2015) and also abundant low-grade methanol [51, 258-260]. Glycerol is usually disposed of as waste stream which is neither economically nor environmentally friendly and the recovery and purification of

low-grade methanol can also be energy intensive. Recent studies showed that blending glycerol, methanol and bio-oil may produce glycerol/menthol/bio-oil fuel blends that have synergistically improved the blended fuel properties in terms of viscosity, water content, acid number and stability [57, 60]. Therefore, it is plausible to further explore the production of bioslurry (hereafter referred to as "GMBB bioslurry") via suspending fine biochar particles into glycerol/methanol/bio-oil blends (hereafter referred to as "GMB blends") for stationary applications. The production of GMBB slurry fuels may benefit both bio-oil and biodiesel industries as it helps effective by-products (i.e. biochar and glycerol) utilisation. It addresses not only the dust and spontaneous combustion issues associated with biochar but also resolves the high-viscosity issue associated with glycerol when either biochar or glycerol is utilized alone. Compared to BB bioslurry, GMBB bioslurry may also be advantageous as it can potentially have better/synergistic rheological properties and also dilute the inorganic species in the bioslurry fuel hence potentially reduce particulate matter emission during bioslurry combustion/gasification.

Unfortunately, based on the knowledge of these authors, thus far, there have been no investigations into GMBB bioslurry fuels in the literature. Therefore, the objective of this study is to carry out a systematic study on fuel properties and ageing of GMBB slurries prepared from biochar and GMB blends. A series of GMBB slurry samples with different biochar loading levels were prepared for various characterization and analysis, in comparison to the BB bioslurry samples prepared from the same biochar and bio-oil.

Table 4-1 Fuel Properties of Bio-oil, Glycerol, Methanol and Biochar used in this study.

samples	bio-oil	glycerol	methanol	biochar
Proximate Analysis				
water content (wt %, ar[a], db[b])	23.7	nd[c]	nd[c]	2.4
ash (wt %, ar[a], db[b])	nd[c]	nd[c]	nd[c]	2.3
volatile matter (wt %, ar[a])	nd[c]	nd[c]	nd[c]	19.0
fixed carbon (wt %, ar[a])	nd[c]	nd[c]	nd[c]	76.3
Elemental Analysis (wt %)				
$C^{a,d}$	42.39	39.13	37.50	82.18
$H^{a,d}$	7.53	8.70	12.5	2.95
$N^{a,d}$	0.06	-	-	0.11
O^{e}	50.02	52.17	50.00	14.76
$Na^{a,b}$	0.0002	nd[c]	nd[c]	0.0125
$K^{a,b}$	0.0014	nd[c]	nd[c]	0.3109
$Mg^{a,b}$	0.0003	nd[c]	nd[c]	0.1113
$Ca^{a,b}$	0.0015	nd[c]	nd[c]	0.3146
Viscosity (25℃, mPa s)	198.6	694.4[f]	0.8[f]	nd[c]
Surface tension (25℃, mN/m)	35.2	63.0	22.35[g]	nd[c]
density (25℃, g/cm^3)	1.21	1.26[f]	0.78[g]	nd[c]
HHV (MJ/Kg)	18.8[h]	18.7	20.8	27.0[h]
TAN (mg NaOH/g)[i]	49.4	nd[c]	nd[c]	nd[c]

[a] as-received basis for bio-oil; [b] dry basis for biochar; [c] not determined; [d] dry and ash free basis for biochar, calculated for glycerol and methanol; [e] by difference; [f] value reported in ref [261]; [g] value reported in ref [262]; [h] calculated high heating; [i] total acid number.
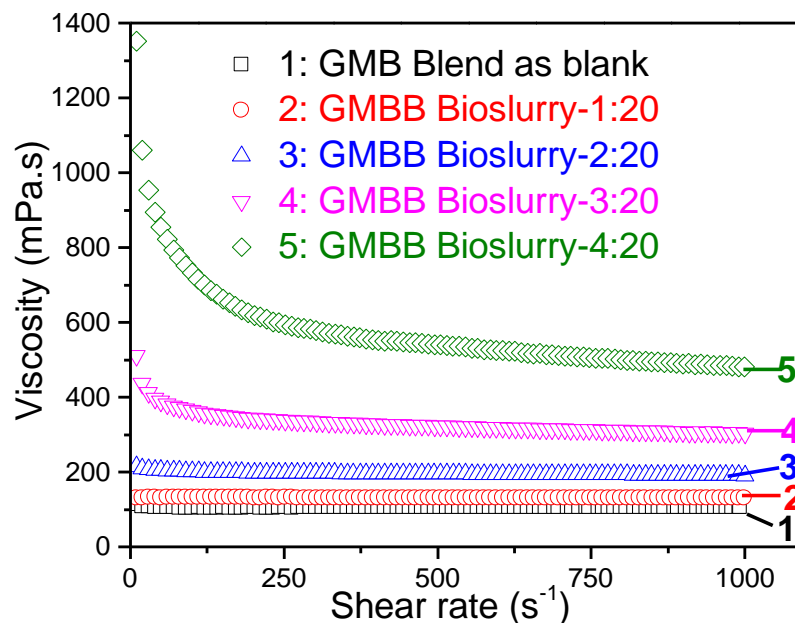
Figure 4-1 Viscosity of GMB blend and GMBB bioslurry fuels as a function of shear rate (at 25 °C). GMB blend stands for Glycerol/Methanol/Bio-oil blend; GMBB bioslurry-x:20 (x can be 1 to 4) stands for bioslurry fuels prepared from GMB blend and biochar at biochar to GMB blend ratio of x:20.

4.2 Rheological and Fuel Properties of GMBB Bioslurry Fuels

Figure 4-1 and Figure 4-2 present the viscosity and shear stress of GMBB bioslurry fuels and GMB blends as a function of shear rate. It is clear seen in Figure 4-1 that the GMBB bioslurry fuels generally exhibit non-Newtonian behaviour, especially those at high biochar to GMB blend ratios (2:20–4:20). At a low biochar loading level (e.g., biochar to GMB blend ratio of 1:20 and the GMB blend), Newtonian behaviour is predominant, although slight shear thinning is evident at low shear rates (less than 50 S^{-1}). This is consistent with our previous findings on bio-oil and BB bioslurries [36]. In addition, the GMBB bioslurry fuels prepared at high mass ratios of biochar to GMB blend (e.g., 3:20 and 4:20) also clearly show thixotropic behaviour as characterized by the hysteris loop in Figure 4-3. The area of hysteresis loop

increases as an increased amount of biochar presented in the GMBB bioslurry. As discussed previously on BB bioslurry [36], this is most likely due to the agglomerated char in the bioslurry being broken by shearing effect along the upward ramp.
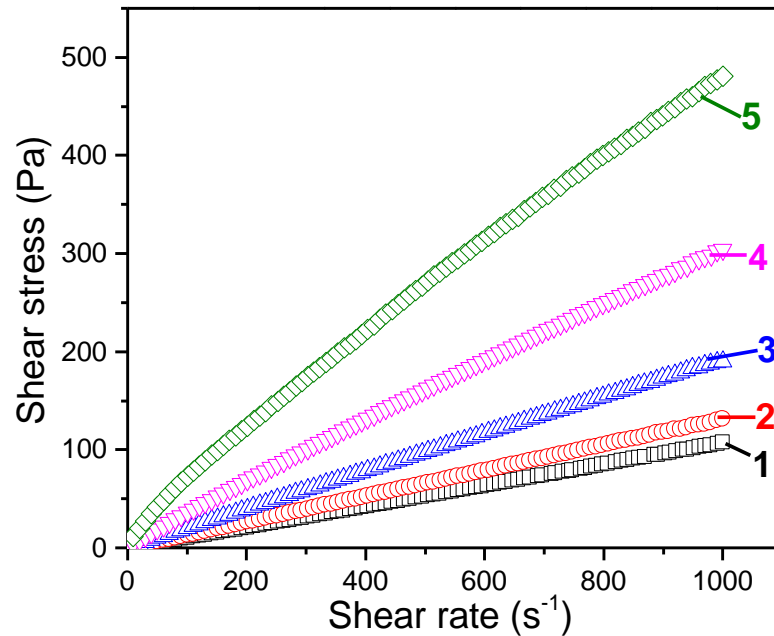
Figure 4-2 Shear stress of GMB blend and GMBB bioslurry fuels as a function of shear rate (at 25 °C). GMB blend stands for Glycerol/Methanol/Bio-oil blend; GMBB bioslurry-x:20 (x can be 1 to 4) stands for bioslurry fuels prepared from GMB blend and biochar at biochar to GMB blend ratio of x:20.

Table 4-2 presents the data on the elemental analysis, heating value, viscosity, density and surface tension of GMBB bioslurry fuels, benchmarking against GBM blends. Apparently, the addition of biochar into GMB blends increases the HHV of the GMBB bioslurry fuels slightly due to the low loading levels. The viscosity of the GMBB bioslurry fuels also increases with an increasing biochar loading level (see Figure 4-2). It is known that for slurry fuels, the density and surface tension play important roles in combustion [60, 254]. As is shown in Table 4-2, similar to those of BB

Table 4-2 Fuel properties of glycerol/methanol/bio-oil (GMB) blend and glycerol/methanol/bio-oil/biochar (GMBB) bioslurry fuels.

Fuels	Elemental analysis (wt %)[b]				Heating value	Viscosity	Density	Surface tension	Ohnesorge number
	C	H	O[a]	N	HHV (MJ/Kg)[b]	(mPa s, at 25℃)	(25 ℃, ton/m^3)	(25 ℃, mN/m)	(dimensionless)
GMB Blend	41.76	7.98	50.21	0.05	18.92	105.6	1.18	33.4	2.4
Bioslurry-20:1 [c]	43.69	7.74	48.52	0.05	19.31	132.6	1.18	33.9	2.5
Bioslurry-20:2 [c]	45.44	7.52	46.98	0.06	19.65	200.1	1.19	35.6	3.7
Bioslurry-20:3 [c]	47.03	7.32	45.58	0.06	19.97	353.1	1.20	38.3	6.2
Bioslurry-20:4 [c]	48.50	7.14	44.30	0.06	20.26	668.6	1.21	40.8	11.4

[a] by difference; [b] calculated value; [c] Bioslurry-x:20 (x can be 1 to 4) stands for GMBB bioslurry fuels prepared from GMB blend and biochar at biochar to GMB blend ratio of x:20.

bioslurry fuels reported previously [254], both the density and surface tension of GMBB bioslurry fuels increase with increased biochar loading level. The Ohnesorge number, which is correlated to slurry fuel properties including surface tension, density and viscosity, is commonly used for predicting the Sauter mean diameter (SMD) of the spray droplets produced from atomization [60, 254]. It can be seen that the Ohnesorge numbers of GMBB bioslurry fuels increase with increasing biochar loading level, which means the atomisation of a GMBB bioslurry fuels with more biochar loading produces spray droplets of a larger higher SMD.
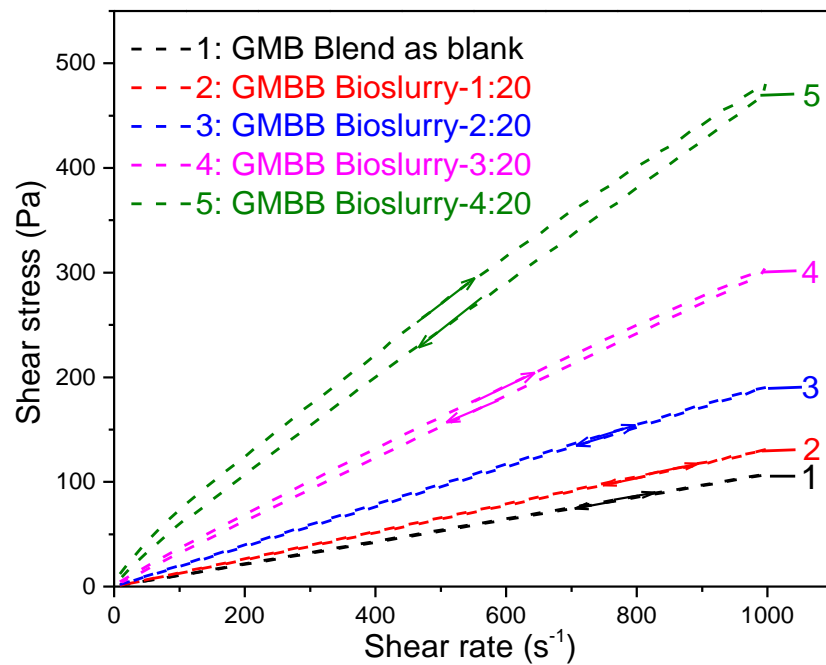
Figure 4-3 Thixotropic behaviour of GMB blend and GMBB bioslurry fuels as a function of shear rate (at 25 °C). GMB blend stands for Glycerol/Methanol/Bio-oil blend; GMBB bioslurry-x:20 (x can be 1 to 4) stands for bioslurry fuels prepared from GMB blend and biochar at biochar to GMB blend ratio of x:20.

Figure 4-4 Water content of bioslurry samples before and after ageing as a function of the biochar to liquid ratio (on the basis of weight). Ageing test was conducted at 80 °C for 24 h. Biochar to liquid ratio of 0 represents the GMB blend or bio-oil blank. GMB blend stands for Glycerol/Methanol/Bio-oil blend; GMBB bioslurry stands for bioslurry fuels prepared from GMB blend and biochar at various biochar to GMB blend ratios. BB bioslurry stands for bioslurry samples prepared from biochar and bio-oil at the same solid to liquid ratios for comparison.

4.3 Ageing of GMBB Bioslurry

Ageing of GMBB bioslurry was characterized by changes in viscosity, water content and TAN, benchmarking against the ageing of the BB slurry prepared from the same bio-oil and biochar. It is interesting to note that, however, phase separation of the BB slurry fuel occurred after accelerated ageing so that only the properties of BB slurry before ageing are presented. This in turn suggests that glycerol and methanol play important roles in slowing down the ageing rate of the GMBB slurry fuels. As shown in Figure 4-4 and Figure 4-5, both GMBB slurry fuels and BB slurry fuels have

decreasing water content and TAN with increasing biochar to liquid ratio. The water content and TAN of the GMBB slurry fuels are much lower than those of the BB slurry fuel. This is understandable as bio-oil is the main source of the water and acids in the mixtures. As the biochar loading level increases, the fraction of bio-oil in the mixture decreases, leading to the proportion of bio-oil in a GMBB slurry being lower than that in a BB slurry at the same biochar to liquid ratio.
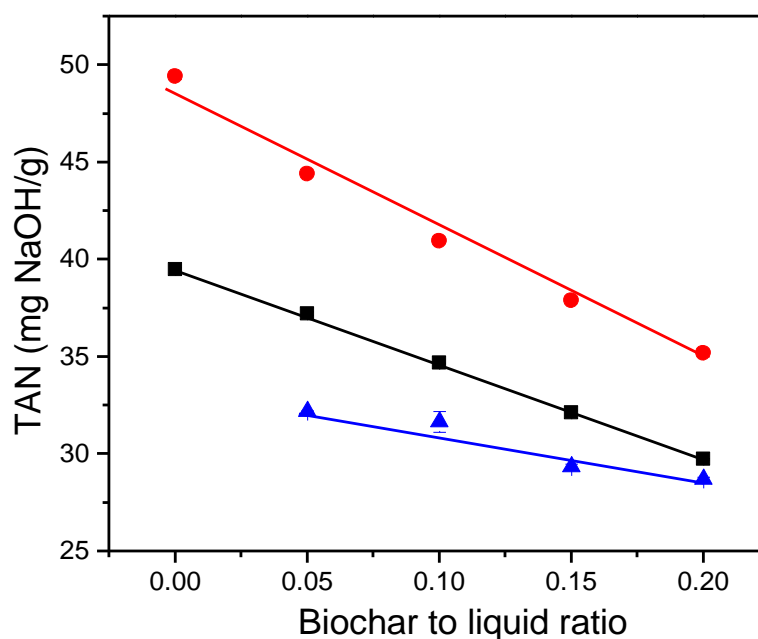
Figure 4-5 TAN of bioslurry samples before and after ageing as a function of the biochar to liquid ratio (on the basis of weight). Ageing test was conducted at 80 °C for 24 h. Biochar to liquid ratio of 0 represents the GMB blend or bio-oil blank. GMB blend stands for Glycerol/Methanol/Bio-oil blend; GMBB bioslurry stands for bioslurry fuels prepared from GMB blend and biochar at various biochar to GMB blend ratios. BB bioslurry stands for bioslurry samples prepared from biochar and bio-oil at the same solid to liquid ratios for comparison.

Another observation from Figure 4-4 and Figure 4-5 is that after ageing the water content of GMBB slurries increased while the TAN decreased. This is similar to the previous reports [16, 60] from the ageing of GMB blend and the BB bioslurry fuels that were prepared from bio-oil and biochar. The decrease in TAN can be attributed to the esterification reactions between acidic compounds in bio-oil and glycerol/methanol or biochar, while the increase in water content can be a result of esterification, acetalization and/or polycondensation reactions. It is interesting to note that the increase in the water content of the GMBB slurry fuels at all biochar loading levels are similar (1.1 %), in contrast to a significant difference in TAN of the GMBB slurry fuels before and after ageing from 5.0 to 1.0 mg NaOH/g as the biochar to liquid ratio increases.

This results suggest that as the biochar to liquid ratio increases from 0.05 to 0.2, the acetalization and/or polycondensation reactions dominates the water formation but the reactive acids in bio-oil becomes the limiting factor for further TAN reduction. The results suggest that an increase in biochar loading level provides more available catalysts for acetalization and/or polycondensation reactions. It is noteworthy that at the same biochar to liquid ratio, the water contents of GMBB bioslurry fuels after ageing are much lower than those of the BB bioslurry fuel, although ageing does result in increasing water contents. This again demonstrates that the GMBB bioslurry fuels prepared from GMB blend and biochar have better ageing properties than the BB bioslurry fuels prepared from bio-oil and biochar.
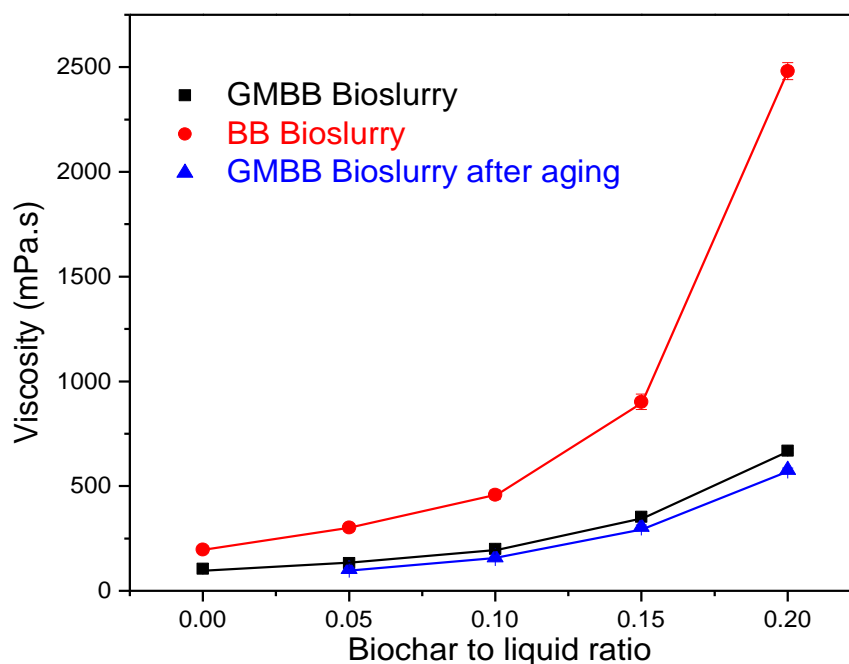
Figure 4-6 Viscosity of bioslurry samples before and after ageing as a function of the biochar to liquid ratio (on the basis of weight). Ageing test was conducted at 80 °C for 24 h. Biochar to liquid ratio of 0 represents the GMB blend or bio-oil blank. GMB blend stands for Glycerol/Methanol/Bio-oil blend; GMBB bioslurry stands for bioslurry fuels prepared from GMB blend and biochar at various biochar to GMB blend ratios. BB bioslurry stands for bioslurry samples prepared from biochar and bio-oil at the same solid to liquid ratios for comparison.

Figure 4-6 shows that the viscosity of both the GMBB and BB bioslurry fuels increase with increasing biochar to liquid ratio. However, the GMBB bioslurry fuels have considerably lower viscosity than the BB slurry, especially at a high biochar loading level. For example, when the biochar to liquid ratio is 0.2, the viscosity of the GMBB bioslurry is only 26.9 % of that of the BB bioslurry. The results again suggest that synergistic effect of preparing the GMBB bioslurry fuels from the GMB blend and biochar (especially the positive effect of the methanol present in the GMB blend in the reduction of viscosity [60, 109, 110, 134, 263]). It is also noted that after ageing,

there are slight decreases in the viscosity of the GMBB bioslurry fuels, most likely due to the increases in the water contents (see Figure 4-4).
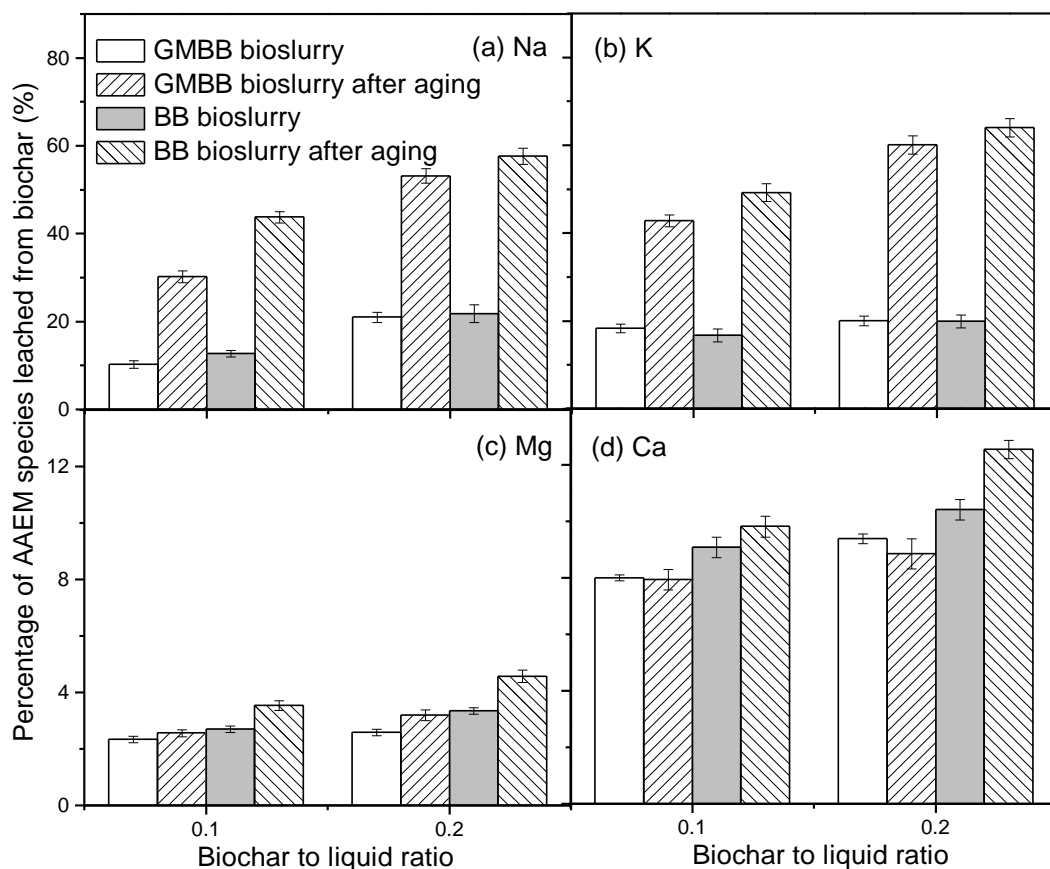
Figure 4-7 Percentage of AAEM species leached from biochar to bio-oil phase of the GMBB and BB bioslurry fuels with biochar to liquid ratio of 0.1 and 0.2 (on the basis of weight). Ageing test was conducted at 80 °C for 24 h. GMB blend stands for Glycerol/Methanol/Bio-oil blend; GMBB bioslurry stands for bioslurry fuels prepared from GMB blend and biochar at various biochar to GMB blend ratios and stored at room tem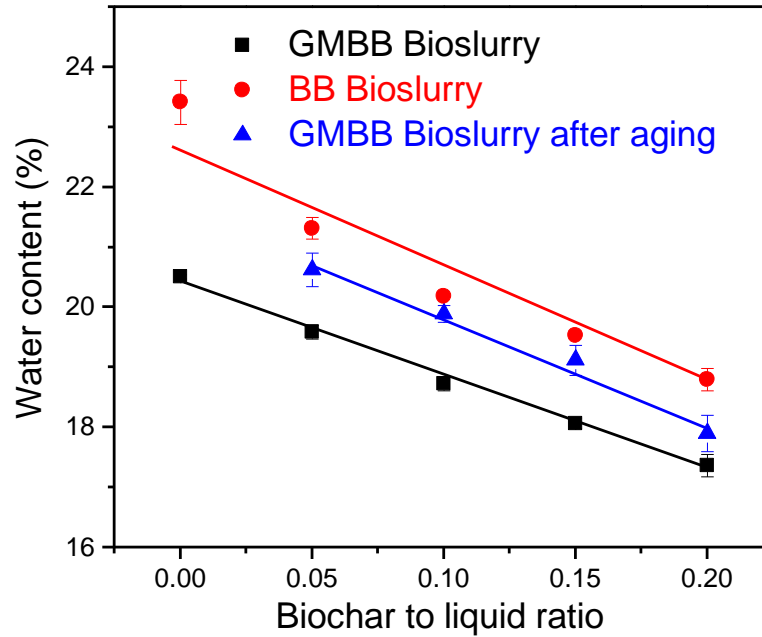perature for 7 days before accelerated ageing at 80 °C. BB bioslurry stands for bioslurry samples prepared from biochar and bio-oil at the same solid to liquid ratios and also stored at room temperature for 7 days for comparison.

4.4 Leaching Characteristics of AAEM Species in the GMBB Bioslurry System

It is known that a proportion of the AAEM species in biochar can be leached out by the acidic bio-oil for the BB bioslurry fuels prepared from biochar and bio-oil [16]. The key question is how the leaching of the AAEM species in biochar would be influenced by the GMB blend for the GMBB bioslurry fuels. Figure 4-7 presents the leaching characteristics of AAEM species in the GMBB bioslurry fuels at biochar to liquid ratio of 0.1 and 0.2, benchmarking against that in the BB bioslurry fuels at the same biochar to liquid ratios. The leaching of the AAEM species from the biochar increases with increasing biochar to liquid ratio for both the GMBB and BB bioslurry fuels. The effect of ageing on the leaching of AAEM species follows similar trends for the GMBB bioslurry fuels at different biochar to liquid ratios.

Figure 4-7 shows that even after ageing for 7 days at room temperature, the leaching of AAEM species from biochar continues to increase in both the GMBB and BB slurry systems. It appears that the leaching of AAEM species from biochar into liquid phase has not reached equilibrium after 7 days. While the increase in the amount of Na and K species leached from biochar is more than doubled after ageing for 7 days, which of Mg and Ca species is less than 35 %. It is known that Na and K species in biochar are mainly present in ionic forms while Mg and Ca species are more in organically-bound form [57]. The significant increase in the leaching of Na and K after ageing indicates an increase in the dissolution of ionic compounds in the liquid phase as a result of increased amount of water in the GMBB slurry samples after ageing (see Section 4.3).

In addition, the amount of AAEM species leached by bio-oil in the BB bioslurry fuel is only slightly higher than that by GMB blend in the GMBB bioslurry fuels after ageing for 7 days at room temperature. However, after accelerated ageing at 80 ℃

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for 24h (equivalent to ageing at room temperature for a year [16, 133]), the difference in the leaching of AAEM species from biochar in the BB bioslurry and GMBB bioslurry systems became considerably larger. The results suggest that the ability of the GMB blend in the GMBB bioslurry systems becomes the limiting factor in the leaching process after long-term storage.

There are at least three possible reasons for the less capability of the GMB blend in leaching the AAEM species from biochar, in comparison to that of bio-oil. First, compared to on the same mass basis, bio-oil contains more water and acids (which are known to be responsible for the leaching of AAEM species from biochar [60]) than the GMB blend (23.5 % vs. 20.8 % for water content and 49.1 vs. 41.5 mg NaOH/g for TAN). Second, methanol was reported to be ineffective for leaching the AAEM species from biochar [57]. The leaching of AAEM species from biochar by glycerol is also insignificant, with only 0.0, 2.4, 0.06 and 0.45% of Na, K, Mg and Ca being leached from the biochar by glycerol. Third and the last, it was previously reported [57] that the presence of methanol reduces the leaching of AAEM species from biochar by solvent–water/acid system because methanol decreases the solubility of ionic compounds in the liquid phase. Therefore, the presence of methanol and/or glycerol in the GMBB bioslurry fuels might reduce the leaching capability of water and/or acidic compounds in the mixture.

4.5 Conclusions

This study reports the fuel properties (heating value, density, surface tension, viscosity, water content, TAN, and etc.) of bioslurry fuels prepared from GMB blend at different biochar loading levels. The results show that biochar loading level is an important parameter in determining the fuel properties of both the GMBB and BB bioslurry fuels. An increasing biochar loading level decreases the water content and

TAN but increases the viscosity of the bioslurry fuels. In presence of methanol and glycerol, the GMBB bioslurry fuels have lower viscosity, water content and TAN than the BB bioslurry prepared from biochar and bio-oil only. Ageing of the GMBB and BB bioslurry fuels leads to reductions in the viscosity and TAN but an increase in the water content of the bioslurry fuels. The addition of methanol and glycerol slows down the ageing process hence reduce the leaching of the AAEM species in biochar by the liquid phase in the GMBB bioslurry fuels.

Chapter 5 Rheological Properties and Ageing of Bioslurry Fuels Prepared from Crude Glycerol/Methanol/Bio-oil Blend and Biochar for Stationary Combustion Applications

5.1 Introduction

Crude glycerol is a major by-product of biodiesel industry and its utilization is of great importance to both economic and environmental performance of a biodiesel plant [51, 54, 57, 58, 214]. Direct utilization of crude glycerol is highly desired because of the large amount of glycerol surplus and the high cost associated with crude glycerol purification [54, 214, 260]. Recently, Wu et al. [264] developed a plausible way for crude glycerol direct utilization via mixing formulated crude glycerol (FCG) with fast pyrolysis bio-oil (with the addition of methanol) to produce FCG/methanol/bio-oil (i.e. FCGMB) blend and also mixing the resultant FCGMB blend with biochar to prepare FCGMB/biochar (FCGMBB) bioslurry fuels. Those blend and bioslurry fuels meet the specifications for stationary combustion applications [264]. Such strategies for producing FCGMBB bioslurry fuels not only help the effective utilization of by-products (e.g., biochar from fast pyrolysis bio-oil production and crude glycerol from biodiesel production) but also address issues associated with those by-products (e.g., biochar being dusty and prone to spontaneous combustion and crude glycerol being of high viscosity) [19, 265]. However, little is reported on the rheological properties and ageing of FCGMBB bioslurry fuels in the open literature. These are the objectives of this study, i.e. to determine the rheological properties and ageing of FCGMBB bioslurry fuels.

Table 5-1 Compositions of different types of formulated crude glycerol (FCG) samples in this study (wt %).

FCG	Glycerol	Soap	Water	NaOH	NaCl
FCG1	83.3	10.4	4.2	2.1	
FCG2	81.2		14.6		4.2
FCG3	66.7	10.4	20.8	2.1	

Figure 5-1 Viscosity of FCGMBB bioslurry fuels benchmarking against GMBB bioslurry as a function of shear rate (at 25 °C). GMBB bioslurry stands for glycerol/methanol/bio-oil/biochar bioslurry; FCG1–3MBB bioslurry stands for FCG1–3/methanol/bio-oil/biochar bioslurry; FCG stands for formulated crude glycerol.

Table 5-2 Fuel properties of CGMB blend and CGMBB bioslurry fuels benchmarking against the biochar, bio-oil, GMB blend, BB and GMBB bioslurry.

	Elemental Analysis (wt%)[a]				HHV[c]	Water Content	TAN[d]	Viscosity	Surface Tension	Density	Ohnesorge Number
	C	H	N	O[b]	MJ/Kg	wt%	mgNaOH/ g	mP.s, @25 ℃	mN/m, @25 ℃	g/cm³, @25℃	dimensionless
Biochar	82.14	3.17	0.11	14.28	27.17	2.3	nd[e]	nd[e]	nd[e]	nd[e]	nd[e]
Bio-oil	42.50	7.10	0.06	50.34	18.54	23.6	49.42	174.2	36.5	1.20	3.15
GMB blend [f]	41.96	7.59	0.05	50.40	18.71	20.78	43.08	88.09	35.4	1.17	1.64
CG1MB blend [g]	42.00	7.54	0.05	50.26	18.69	21.65	42.69	86.57	33.1	1.17	1.66
CG2MB blend [g]	41.59	7.58	0.05	50.57	18.60	21.70	42.99	82.88	34.8	1.17	1.55
CG3MB blend [g]	41.67	7.61	0.05	50.57	18.65	21.72	42.13	82.39	33.1	1.17	1.58
BB bioslurry [h]	46.49	6.71	0.07	46.73	19.41	21.18	42.14	656.0	37.0	1.21	11.72
GMBB bioslurry [i]	46.00	7.14	0.06	46.79	19.56	19.44	36.34	288.1	35.7	1.19	5.28
CG1MBB bioslurry [j]	46.04	7.11	0.06	46.66	19.54	19.78	35.90	268.2	33.5	1.19	5.07
CG2MBB bioslurry [j]	45.67	7.14	0.06	46.94	19.46	20.04	36.13	233.7	35.5	1.19	4.29
CG3MBB bioslurry [j]	45.75	7.17	0.06	46.94	19.50	20.31	35.94	222.1	33.6	1.19	4.20

[a] measured value for biochar and bio-oil, calculated value for others; [b] by difference; [c] calculated high heating value, HHV stands for higher heating value; [d] total acid number; [e] not determined; [f] GMB blend stands for glycerol/methanol/bio-oil blend; [g] CG1–3MB blend stands for CG1–3/methanol/bio-oil blend; [h] BB bioslurry stands for bio-oil/biochar bioslurry; [i] GMBB bioslurry stands for glycerol/methanol/bio-oil/biochar bioslurry; [j] CG1–3MBB bioslurry stands for CG1–3/methanol/bio-oil/biochar bioslurry; CG stands for crude glycerol.

5.2 Fuel and Rheological Properties of FCGMBB Bioslurry Fuels

Table 5-2 presents the data on fuel properties of the FCGMB blend and FCGMB/biochar (FCGMBB) bioslurry fuels benchmarking against biochar, bio-oil, glycerol/methanol/bio-oil (GMB) blend, bio-oil/biochar (BB) bioslurry and glycerol/methanol/bio-oil/biochar (GMBB) bioslurry. FCGMBB bioslurry fuels have a slightly higher HHV (19.46–19.54 MJ/Kg), lower water content (19.78–20.31%) and TAN (35.90–36.13 mgNaOH/g) in comparison to those of FCGMB blends (18.60–18.69 MJ/Kg, 21.65–21.72% and 42.13–42.99 mgNaOH/g, respectively). The viscosity, surface tension and density of FCGMBB bioslurry are 222–268 mP.s, 33.5–35.5 mN/m and 1.19 g/cm^3 respectively. Due to the addition of biochar particles, these are higher than those of FCGMB blend which being 82.4–86.6 mP.s, 33.1–34.8 mN/m and 1.17 g/cm^3 respectively. To predict the spray quality during atomization, the Ohnesorge number of bioslurry samples were also calculated based on viscosity, surface tension and density. It can be seen that the Ohnesorge number of FCGMBB bioslurry fuels (4.20–5.07) are much higher than that of FCGMB blend (1.55–1.66). Such observations are consistent with those on GMB blends and GMBB bioslurries [265], as well as bio-oil and BB bioslurry[36].

In addition, FCGMBB bioslurry samples containing different types of FCG also have similar fuel properties except viscosity. Furthermore, compares to GMBB slurry sample, FCGMBB slurry fuels have same density and similar HHV, water content, TAN and surface tension, while a slightly lower viscosity and Ohnesorge number. These findings demonstrate that the impurities in CG have limited influence on the fuel properties FCGMBB slurry fuels which are consistent with our previous studies on FCGMB blends and FCG/WSF blends.[57, 58] Overall, fuel properties of FCGMBB slurry fuels are equivalent to or even better compared with that of GMBB slurry or FCGMB blend.
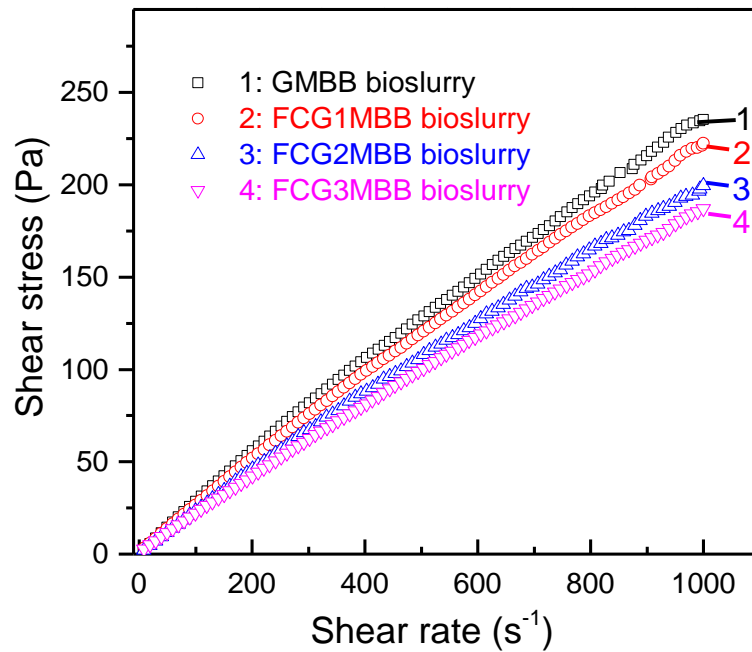
Figure 5-2 Shear stress of FCGMBB bioslurry fuels benchmarking against GMBB bioslurry as a function of shear rate (at 25 °C). GMBB bioslurry stands for glycerol/methanol/bio-oil/biochar bioslurry; FCG1–3MBB bioslurry stands for FCG1–3/methanol/bio-oil/biochar bioslurry; FCG stands for formulated crude glycerol.

Figure 5-1 and Figure 5-2 present the viscosity and shear stress as a function of shear rate for FCGMBB bioslurry fuels, benchmarking against GMBB bioslurry fuels. It is clear to see from Figure 5-1 that both FCGMBB and GMBB bioslurry fuels exhibit non-Newtonian behaviour. Figure 5-2 shows that compared to GMBB bioslurry, FCGMBB bioslurry samples have lower viscosities. The variances in the viscosity of bioslurry fuels are mainly attributed to the differences in water contents (see Table 5-2). FCGMBB bioslurry fuels also show thixotropic behavior which is characterized by the hysteresis loop (see Figure 5-3). The pseudo-plastic behavior is attributed to the breakdown of agglomerated char particles along the upward ramp [36]. Such findings are consistent with those on BB and GMBB bioslurry fuels [35, 36, 265]. It is worth noting that the area of hysteresis loop of FCGMBB bioslurry fuels are smaller than that of GMBB bioslurry, which also attributed to high water contents in FCGs.

Overall, the FCGMBB bioslurry fuels have better rheological properties than the GMBB bioslurry fuel.
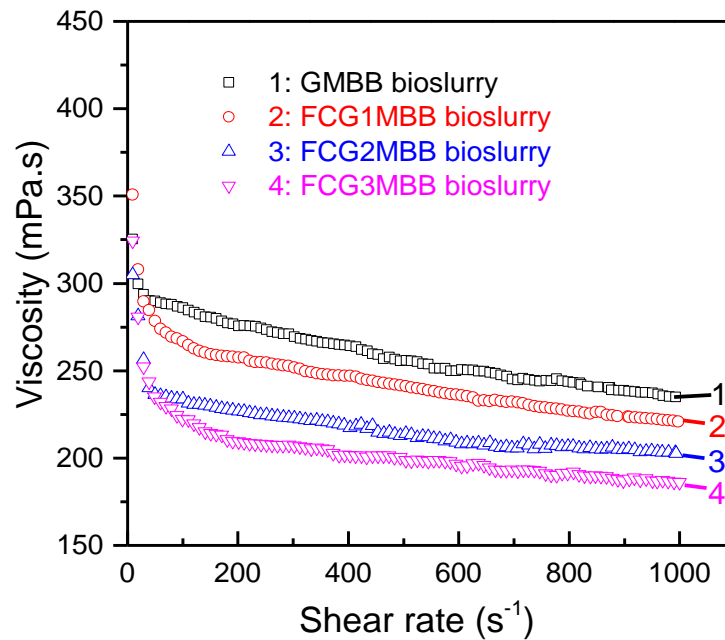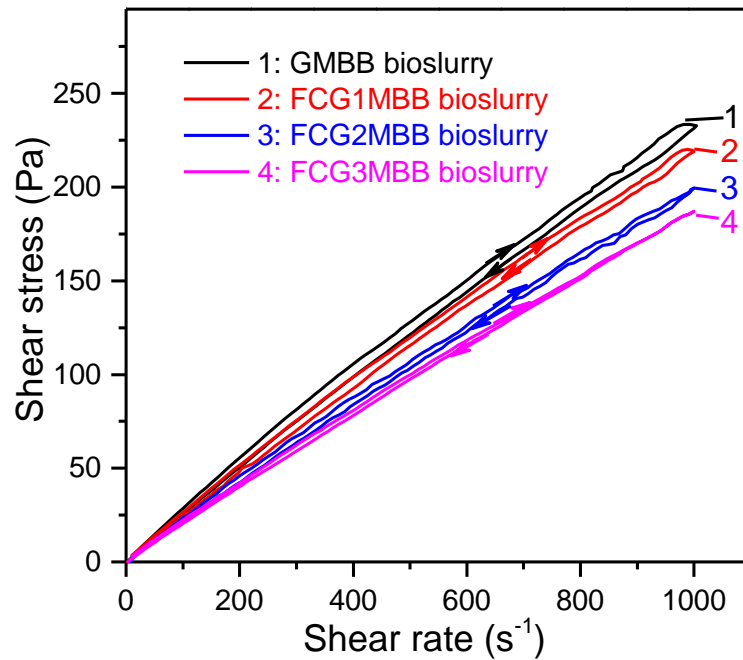

Figure 5-3 Thixotropic behavior (c) of FCGMBB bioslurry fuels benchmarking against GMBB bioslurry as a function of shear rate (at 25 °C). GMBB bioslurry stands for glycerol/methanol/bio-oil/biochar bioslurry; FCG1–3MBB bioslurry stands for FCG1–3/methanol/bio-oil/biochar bioslurry; FCG stands for formulated crude glycerol.
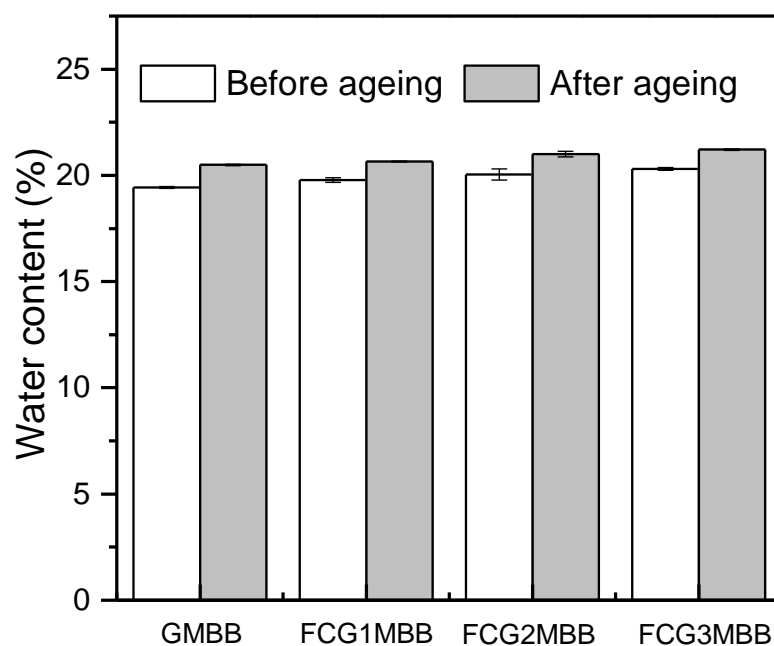
Figure 5-4 Water content of FCGMBB bioslurry samples benchmarking against GMBB bioslurry before and after ageing. GMBB bioslurry stands for glycerol/methanol/bio-oil/biochar bioslurry; FCG1–3MBB bioslurry stands for FCG1–3/methanol/bio-oil/biochar bioslurry; FCG stands for formulated crude glycerol.

5.3 Ageing of FCGMBB Bioslurry Fuels

The ageing of FCGMBB bioslurry fuels was investigated via changes in water content, TAN and viscosity, benchmarking against the ageing of GMBB bioslurry fuel. As is shown in Figure 5-4 to Figure 5-6, after ageing, the water contents of FCGMBB bioslurry samples increase while the TAN and viscosity decrease. This can be attributed to the previously-reported reactions taken place during ageing, such as esterification, acetalization and/or polycondensation reactions [16]. Such a trend is also consistent with those of GMBB and BB bioslurry fuels reported earlier [16, 265].
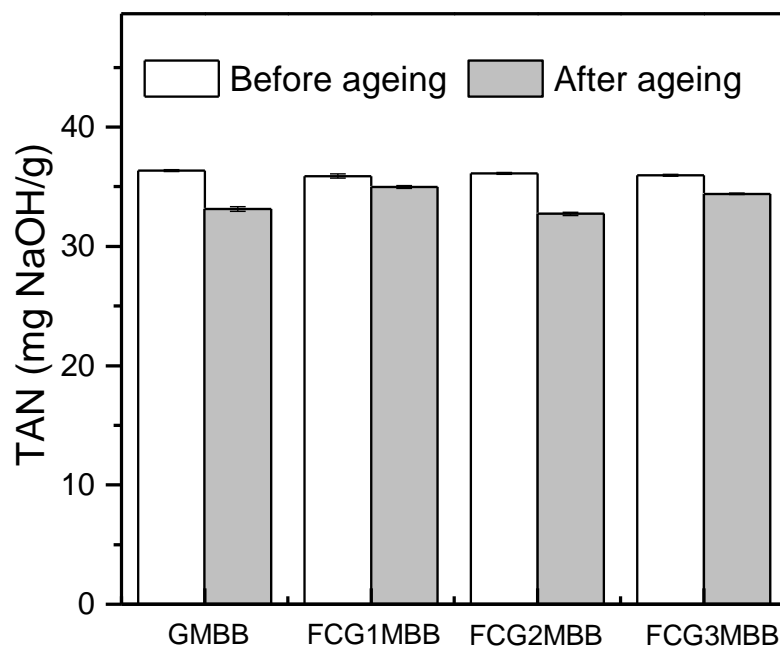
Figure 5-5 TAN of FCGMBB bioslurry samples benchmarking against GMBB bioslurry before and after ageing. GMBB bioslurry stands for glycerol/methanol/bio-oil/biochar bioslurry; FCG1–3MBB bioslurry stands for FCG1–3/methanol/bio-oil/biochar bioslurry; FCG stands for formulated crude glycerol.

It is also worth noting that the changes of the water content (4.4–4.8%) and viscosity (6.0–11.7%) of FCGMBB bioslurry fuels before and after ageing are reduced than that of GMBB bioslurry fuel (5.4% and 24.0%, respectively). This is likely attributed to the presence of soap and NaOH in FCGs which affect the acid-base reactions during ageing or even before ageing [57]. The reductions in the TAN for the FCG1MBB and FCG3MBB bioslurry fuels before and after ageing are 2.6% and 4.3% respectively. These are considerably lower than that of GMBB bioslurry (8.8%) due to sodium salts (e.g., soap and NaOH) addition. Such observations are consistent with previous findings on GMB and FCGMB fuel blends.[57] Overall, the presence of crude glycerol in FCGMBB bioslurry fuels slows down the ageing.
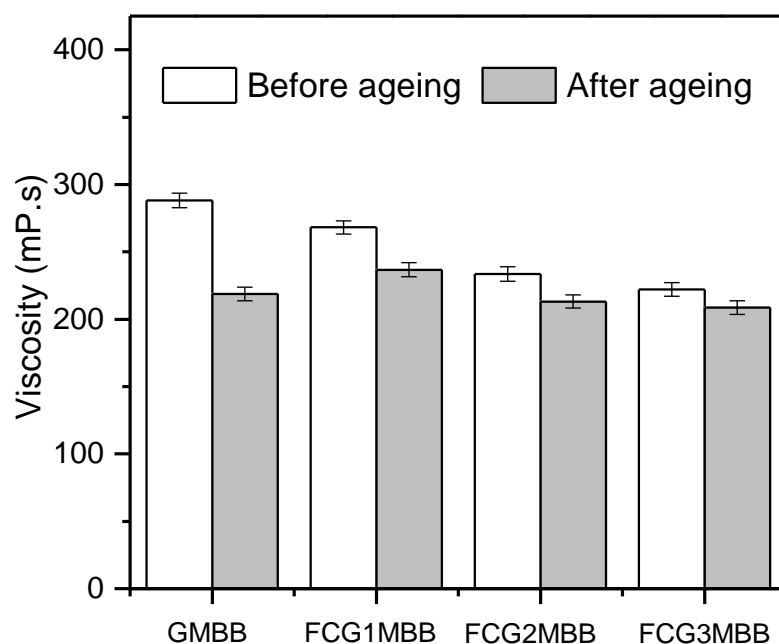
Figure 5-6 Water content (a), TAN (b) and viscosity (c) of FCGMBB bioslurry samples benchmarking against GMBB bioslurry before and after ageing. GMBB bioslurry stands for glycerol/methanol/bio-oil/biochar bioslurry; FCG1–3MBB bioslurry stands for FCG1–3/methanol/bio-oil/biochar bioslurry; FCG stands for formulated crude glycerol.

5.4 Conclusions

This study reports the fuel properties (especially the rheological properties) and ageing of FCGMBB bioslurry fuels prepared from FCGMB blends and biochar for stationary combustion applications. The results show that compare to those of FCGMB blends, FCGMBB slurry fuels have slightly higher HHV, surface tension and density, while have lower water content and TAN. It also reveals that FCGMBB bioslurry samples have lower viscosities than the GMBB bioslurry and exhibit non-Newtonian and thixotropic behavior. After ageing, the water contents of FCGMBB bioslurry samples increase while the TAN and viscosity decrease. In

comparison to the GMBB bioslurry fuel, the ageing of FCGMBB bioslurry fuels slows down due to the presence of soap and NaOH in crude glycerol.

Chapter 6 Ignition Temperatures of Various Bio-oil Based Fuel Blends and Slurry Fuels

6.1 Introduction

Utilisation of crude glycerol is challenging but of critical importance to the economic and environmental performance of biodiesel production plants [51, 54, 57, 58, 214]. Recent studies [16, 34, 57, 58, 60, 265] indicated that crude glycerol can be mixed with fast pyrolysis bio-oil or its water soluble fraction (WSF), with or without the introduction of fine biochar particles, to prepare new classes of bio-oil-based fuel blends or slurry fuels. The reported fuel properties of these fuel blends or slurry fuels meet the specifications on various aspects for stationary applications (e.g., combustion in boilers) [58, 60, 265]. Ignition behaviour is an important consideration for safety during fuel storage and transport as well as combustion performance during applications [167]. The glycerol was reported to have an ignition temperature of 370 °C [56, 261]. However, little is known on the ignition behaviour of the fuel blends and slurry fuels prepared from bio-oil (or bio-oil WSF) and glycerol, with or without biochar addition. Therefore, the objective of this study is to investigate the ignition temperatures of these bio-oil-based fuel blends or slurry fuels. The ignition temperature was determined via two methods, ie. thermogravimetric analysis (TGA)[171] and an ASTM-based method modified from ASTM standard E659.

Table 6-1 Compositions of different types of formulated crude glycerol samples for use in this study (wt %).

Crude glycerol	Glycerol	Soap	Water	NaOH	NaCl	Methanol
CG1	83.3	10.4	4.2	2.1		
CG2	81.2		14.6		4.2	
CG3	66.7	10.4	20.8	2.1		
CG4	80.0	10.0	4.0	2.0		4.0
CG5	78.0		14.0		4.0	4.0
CG6	64.0	10.0	20.0	2.0		4.0
CG7	76.2		23.8			
CG8	72.7		22.7			4.6

CG: crude glycerol;

6.2 Ignition Temperatures of Biochar, Bio-oil and Bio-oil Based Fuel Blends and Slurry Fuels Measured by TGA Method

Table 6-1 shows the compositions of different types of CG used in this study. CG1–3 are used to prepare CG/methanol/bio-oil (hereafter referred to as CGMB) blends while CG4–6 are used to prepare CG/WSF (hereafter referred to as CGWSF) blends. CG7 and CG8 were also prepared to study the effect of sodium salts. Table 6-2 demonstrates the fuel properties of bio-oil, bio-oil WSF and biochar used in this study.

Table 6-2 Fuel properties of bio-oil, bio-oil WSF and biochar used in this study.

Samples	Bio-oil	Biochar	WSF
Proximate analysis			
water content (wt %, ar [a], db [b])	23.4	2.3	61.5
ash (wt %, ar [a], db [b])	nd [c]	2.5	nd [c]
volatile matter (wt %, ar [a])	nd [c]	19.4	nd [c]
fixed carbon (wt %, ar [a])	nd [c]	75.8	nd [c]
Elemental analysis (wt %)			
C [a,d]	42.49	82.42	18.60
H [a,d]	7.10	3.17	8.91
N [a,d]	0.06	0.11	0.17
O [e]	50.35	14.30	72.32
Viscosity (25 °C, mPa s)	175.3	nd [c]	3.1
HHV (MJ/Kg) [f]	18.5	27.2	13.0
TAN (mg NaOH/g) [g]	48.6	nd [c]	35.1

[a] as-received basis for bio-oil; [b] dry basis for biochar; [c] not determined; [d] dry and ash free basis for biochar, calculated for glycerol and methanol; [e] by difference; [f] calculated higher heating value; [g] total acid number.

Table 6-3 Ignition temperatures of biochar, bio-oil and bio-oil based fuel blends and slurry fuels measured by TGA method.

	Ignition temperature (°C)		Ignition temperature (°C)
Biochar	375	Biochar	375
Bio-oil	506	WSF [f]	511
GMB blend [a]	505	GWSF blend [g]	nd [h]
CG1MB blend [b]	445	CG4WSF blend [i]	nd [h]
CG2MB blend [b]	453	CG5WSF blend [i]	nd [h]
CG3MB blend [b]	433	CG6WSF blend [i]	nd [h]
BB slurry [c]	497	WSFB slurry [j]	454
GMBB slurry [d]	510	GWSFB slurry [k]	456
CG1MBB slurry [e]	460	CG4WSFB slurry [l]	424
CG2MBB slurry [e]	468	CG5WSFB slurry [l]	433
CG3MBB slurry [e]	447	CG6WSFB slurry [l]	443

[a] GMB blend stands for glycerol/methanol/bio-oil blend; [b] CG1–3MB blend stands for CG1–3/methanol/bio-oil blend; [c] BB slurry stands for bio-oil/biochar slurry; [d] GMBB slurry stands for glycerol/methanol/bio-oil/biochar slurry; [e] CG1–3MBB slurry stands for CG1-3/methanol/bio-oil/biochar slurry; [f] WSF stands for water soluble fraction; [g] GWSF blend stands for glycerol/WSF blend; [h] not determined; [i] CG4–6WSF blend stands for CG4–6/WSF blend; [j] WSFB slurry stands for WSF/biochar slurry; [k] GWSFB slurry stands for stands for glycerol/WSF/biochar slurry; [l] CG4–6WSFB slurry stands for stands for CG4–6/WSF/biochar slurry; CG stands for crude glycerol.

Table 6-3 shows the ignition temperatures of the bio-oil based blend and slurry fuels measured by TGA method. First, the results show that bio-oil or WSF alone has high ignition temperature being 506 and 511 °C, respectively. The difficulty in the ignition of bio-oil or WSF is likely due to the formation of carbonaceous solid by cracking reactions at high temperature (such residue solid is known to be hard to ignite [243]). The slightly higher ignition temperature of WSF in comparison to bio-oil can be attribute to the negative effect of higher water content in WSF.

Second, ignition temperatures of the slurry fuels containing CG are lower compared to those slurries with only bio-oil, WSF or glycerol. For example, CGMB/biochar (CGMBB) slurry fuels have ignition temperatures in a range of 445–470 °C while bio-oil/biochar (hereafter referred to as BB) and glycerol/methanol/bio-oil/biochar (hereafter referred to as GMBB) slurry ignited at 497 and 510 °C, respectively. Third, the ignition temperatures of CGWSF/biochar (CGWSFB) slurry fuels (424–445 °C) tested by TGA method are lower than that of glycerol/WSF/biochar (GWSFB) slurry (456 °C). This is attributed to the presence of sodium salt in CGs which may has catalytic effect on ignition. It was known that inorganic species decreases the ignition temperatures of solid fuels [266]. To prove this point for these liquid/slurry fuels, further experiments were undertaken to measure the ignition temperatures of fuels prepared from CGs without sodium salts. It was found that the ignition temperatures are 502 and 469 °C for CG7MBB slurry and CG8WSFB slurry, respectively. Such ignition temperatures are considerably higher than the corresponding fuels prepared from CGs with sodium salts, i.e. 447 and 443 °C for CG3MBB slurry and CG6WSFB slurry, respectively.

Last, GMBB or CGMBB slurry fuels demonstrate higher ignition temperatures compared with their corresponding blends. Although biochar has an ignition

temperature of 375 °C, lower than that of the GMB or CGMB blends, the addition of biochar has increased the ignition temperature. This is probably due to the evaporation of some fuel components during TGA analysis before ignition takes place, resulting in less volatile and more carbonaceous solid (due to the interactions between bio-oil components and biochar [16, 34, 265]). In the cases of CGWSF and GWSF blend fuels, these blends have very high weight losses (over 80%, caused by the evaporation of volatile components) in the temperature range of 35–300 °C so that the ignition temperatures cannot even be determined by the TGA method. This suggests the limitation of the TGA method that effectively measures the ignition temperature of the solid residue after at least some evaporation.

6.3 Ignition Temperature of Selected Bio-oil Based Fuels Tested by ASTM-based Method and TGA Method

Consequently, selected fuel samples were subjected to external analysis of ignition temperature using an ASTM-based method, with the results presented in Figure 6-1 that also include the results from the TGA method for benchmarking. The results show that both CGMBB slurry and CGWSFB slurry fuels have higher ignition temperatures than the corresponding blends. Such results are consistent with the TGA results. In addition, the ignition temperature of WSF is much higher than the WSF based blend and slurry fuels. Therefore, these results indicates the positive effects of CG and/or biochar addition on WSF ignition.
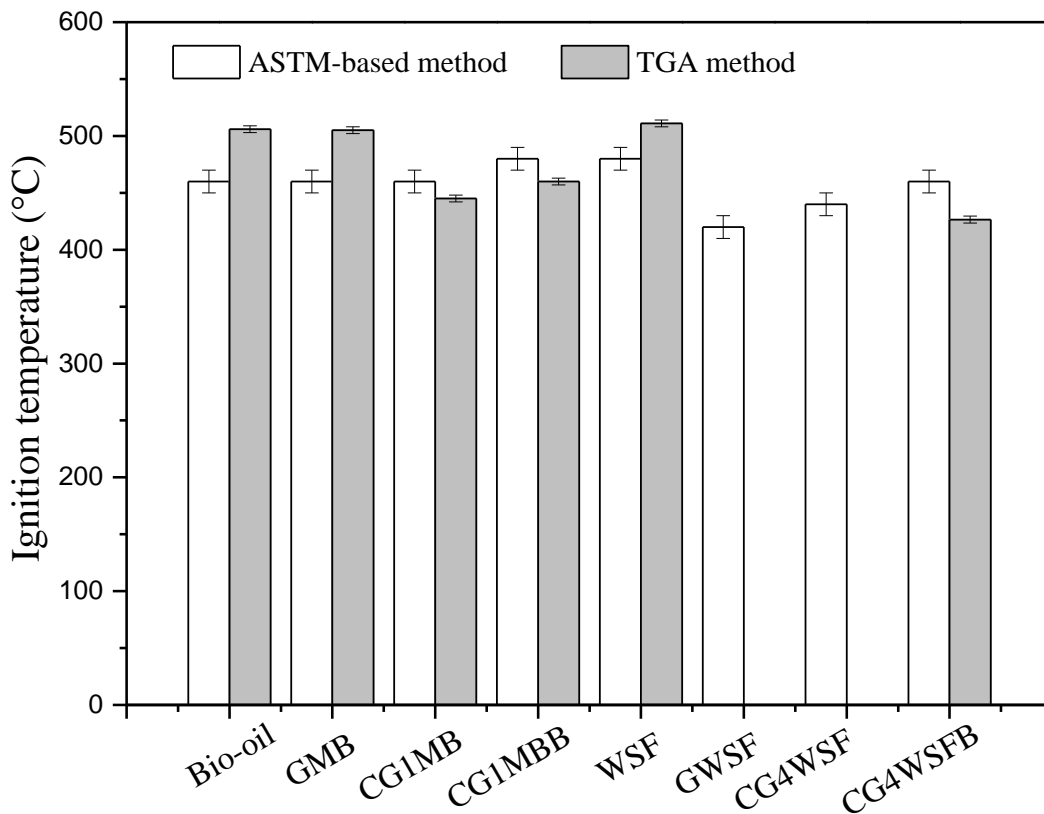
Figure 6-1 Ignition temperature of selected bio-oil based fuels tested by ASTM-based method and TGA method. TGA stands for thermogravimetric analysis; GMB stands for glycerol/methanol/bio-oil blend; CG1MB stands for CG1/methanol/bio-oil blend; CG1MBB stands for CG1/methanol/bio-oil/biochar slurry; WSF stands for water soluble fraction; GWSF stands for glycerol/WSF blend; CG4WSF stands for CG4/WSF blend; CG4WSFB stands for CG4/WSF/biochar slurry; CG stands for crude glycerol.

However, the ignition temperatures of bio-oil or WSF obtained from ASTM-based method are much lower than those from TGA method, while those of bio-oil, GMB and CGMB blends measured by the two methods are similar. It is worth noting that rather than being swept away by carrier gas in TGA test, the evaporated volatiles of the fuel samples were largely retained in the furnace in the ASTM-based method. This means ignition of vapour phase is the dominating factor in measurement by the

ASTM-based method, while TGA method is more emphasized on ignition of the solid residue after evaporation. The high ignition temperature of WSF compared to that of the bio-oil tested by the ASTM-based method indicates the negative effect of water on vapour phase ignition. The significant reductions in ignition temperatures of the GWSF or CGWSF blends compared to that of WSF tested by ASTM-based method are also likely due to the significant decrease in water content of the blends. The ASTM-based method is applicable for determining ignition temperatures of volatile fuels but is time consuming and labour intensive especially when increasing temperature in small intervals to observe ignition. Conversely, TGA method is easy to operate and the accuracy of ignition temperature measurement is within 3 °C.

Although emphasising more on ignition of the solid residue, the TGA method can provide information on evaporation profile and comparison of the ignition difficulty of different samples. Combining the information given by these two methods, it can be concluded that glycerol or crude glycerol at high proportion in CGWSF based fuels can significantly improve the ignition behaviour in vapour phase. The results further suggest that biochar and salts in CG can affect the ignition temperatures via changing the compositions of vapour and solid residue or introducing catalytic effect. Compared with bio-oil or WSF alone as liquid fuels or together with biochar as slurry fuels, addition of crude glycerol into these fuels produce blends or slurries with better ignition property.

6.4 Conclusion

This study reports the ignition temperature of a series of bio-oil based fuel blends and slurry fuels by two methods. The results show that bio-oil has a high ignition temperature because the formed carbonaceous solid is hard to decompose. Sodium salt in CGs have positive effect on bio-oil based fuels ignition while water have

negative effect. Biochar has a very low ignition temperature, however, slurry fuels have higher ignition temperature than their corresponding blends, and the possible reason is less volatile and more carbonaceous solid were formed during combustion. The two methods have different emphasis, the ASTM-based method emphasized on ignition of vapour phase while TGA method more emphasized on ignition of the solid residue after evaporation.

Chapter 7 Differential Scanning Calorimetry Studies on the Cold Flow Properties of Fuel Mixtures from Bio-oil, Crude Glycerol, Methanol and/or Biochar

7.1 Introduction

Biodiesel can be used as a liquid fuel or mixed with other fuels in various applications.[25, 79, 267] The rapid-growing biodiesel industry produces a large surplus of glycerol as by-product in the market.[54, 214, 268] Utilisation of crude glycerol is a key concern for the industry's economic and environmental performance[54, 268, 269] and direct utilization of crude glycerol is highly desired. One attractive option[16, 34, 57, 58, 60, 265] is to mix crude glycerol with fast pyrolysis bio-oil, methanol and/or biochar to prepare bio-oil based fuel mixtures for stationary combustion applications (e.g., combustion in boilers). It was reported that these mixtures have fuel properties that are equivalent to or even better than that of bio-oil, including heating value, surface tension, density, total acid number (TAN), viscosity, and water content.[34, 57, 58, 60]

Under cold climate conditions, cold flow property is an important consideration of a fuel[42, 173] because problematic solidification or even partial solidification may take place during fuel handling, operation and transport.[165, 166] However, the cold flow property of these bio-oil based fuel mixtures is seldom reported in the open literature. Furthermore, evaluating cold flow properties of bio-oil via conventional parameters (e.g., cloud point and pour point[41, 181, 267]) is known to be laborious and time consuming especially when testing pour point which need to preheat samples (which may also lead to water separation on sample's surface).[41] It is even difficult to observe the cloud point of bio-oil due to its dark colour.[127, 270] Fortunately, cold flow properties can be associated with the melting point of each fuel component and

its solubility in the fuel[86, 173] so that it is possible to examine the melting process using differential scanning calorimetry (DSC).[79, 179, 181]

The cold flow property of the fuel mixtures of bio-oil, crude glycerol, methanol and/or biochar may be difficult to predict due to the complicated compositions of these fuels. For example, bio-oil or its water soluble fraction (WSF) have high water contents[58] that can significantly influence the fuel melting temperatures. While glycerol has a melting point of 17.8 ℃, supercooling of glycerol is known to take place.[271, 272] Therefore, when mixing with bio-oil or WSF, the effect of glycerol or crude glycerol on melting process of the mixtures are largely unknown. In addition, the presence of biochar in such fuel mixtures may affect the melting process. For example, solid particles can act as nucleation sites for enhancing the crystallization or melting process.[273] Therefore, it is the objective of this study to carry out a systematic set of experimental investigation into the cold flow property (melting process) of fuel mixtures prepared from bio-oil, bio-oil WSF, crude glycerol and/or biochar, focusing on the effect of crude glycerol and biochar.

Table 7-1 Fuel compositions of different types of formulated crude glycerol used in this study (wt %).

crude glycerol	glycerol	soap	water	NaOH	NaCl	methanol
FCG1	83.3	10.4	4.2	2.1		
FCG2	79.1		16.7		4.2	
FCG3	66.7	10.4	20.8	2.1		
FCG4 [a]	80.0	10.0	4.0	2.0		4.0
FCG5	76.0		16.0		4.0	4.0
FCG6 [a]	64.0	10.0	20.0	2.0		4.0

[a] FCG4 and FCG6 were used in a previous study;[58] FCG: formulated crude glycerol;

Table 7-2 Fuel compositions of different types of formulated crude glycerol used in this study (wt %).

Samples	Bio-oil	Biochar	WSF
Proximate analysis			
water content (wt %, ar [a], db [b])	23.5	2.3	61.6
ash (wt %, ar [a], db [b])	nd [c]	2.5	nd [c]
volatile matter (wt %, ar [a])	nd [c]	19.3	nd [c]
fixed carbon (wt %, ar [a])	nd [c]	75.9	nd [c]
Elemental analysis (wt %)			
C [a,d]	42.50	82.44	18.59
H [a,d]	7.10	3.17	8.92
N [a,d]	0.06	0.11	0.17
O [e]	50.34	14.28	72.32
Viscosity (25 °C, mPa s)	174.2	nd [c]	3.1
HHV (MJ/Kg) [f]	18.5	27.2	13.0
TAN (mg NaOH/g) [g]	48.6	nd [c]	35.1

[a] as-received basis for bio-oil; [b] dry basis for biochar; [c] not determined; [d] dry and ash free basis for biochar, calculated for glycerol and methanol; [e] by difference; [f] calculated higher heating value; [g] total acid number.

7.2 Cold Flow Properties of Individual Components for Preparing Fuel Blends

Individual components of the fuel blends including bio-oil, bio-oil WSF, methanol, glycerol and FCGs were firstly subjected to DSC analysis. Figure 7-1 shows that there are clearly two regions for bio-oil during heating process. One is recognized as melting region between −50 and −19 °C, with a T_{MP} of −21.9 °C; the other one is attributed to a cold crystallization region between −90 and −50 °C. On the cooling curve of the bio-oil, there is a small exothermic peak centring at −64.5 °C. Considering the peak intensity and signal to noise ratio,[274] the heating curve is used for subsequent DSC analysis of all fuel samples hereafter.
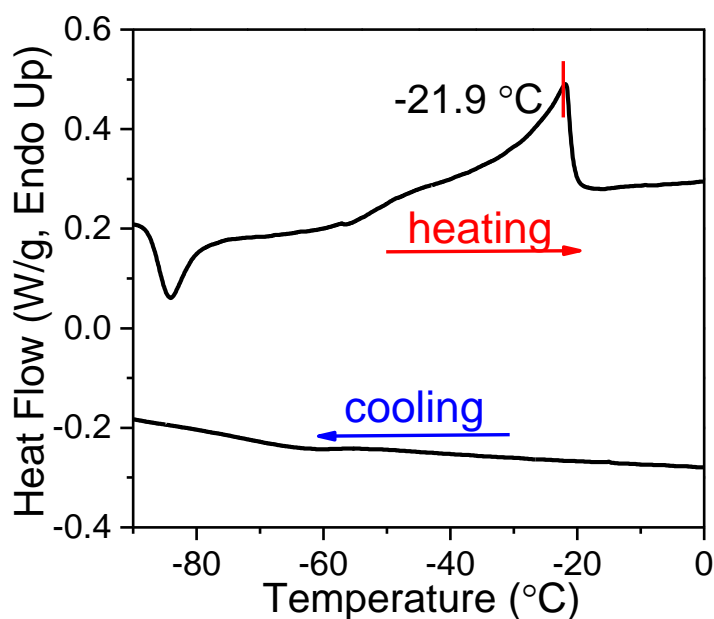
Figure 7-1 DSC curves of bio-oil.
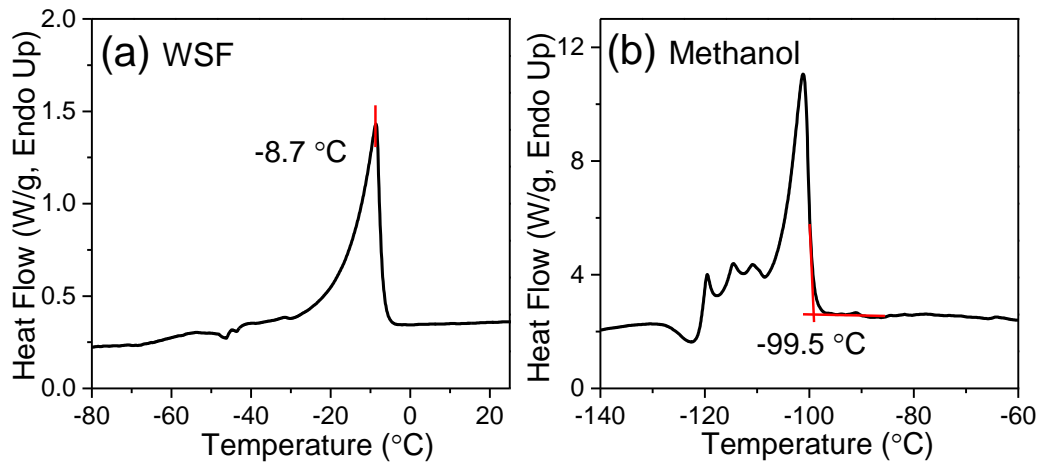
Figure 7-2 DSC curves of (a) WSF and (b) methanol.

Figure 7-2a shows that bio-oil WSF has a T_{MP} at −8.7 °C which is considerably higher than that of bio-oil, most likely due to the much higher water content of WSF (61.6%) than that of the bio-oil (23.5%, see Table 7-2). Such high T_{MP} foresees issues associated with direct application of WSF under cold weather conditions. As to glycerol or FCGs, no peak was found most likely due to supercooling of glycerol[261, 271]. For methanol, the DSC curve (see Figure 7-2b) is similar to those reported in literature[239], and the melting temperature of methanol obtained in this study is −99.5 °C which is in good agreement with reported value (−97.6 °C).
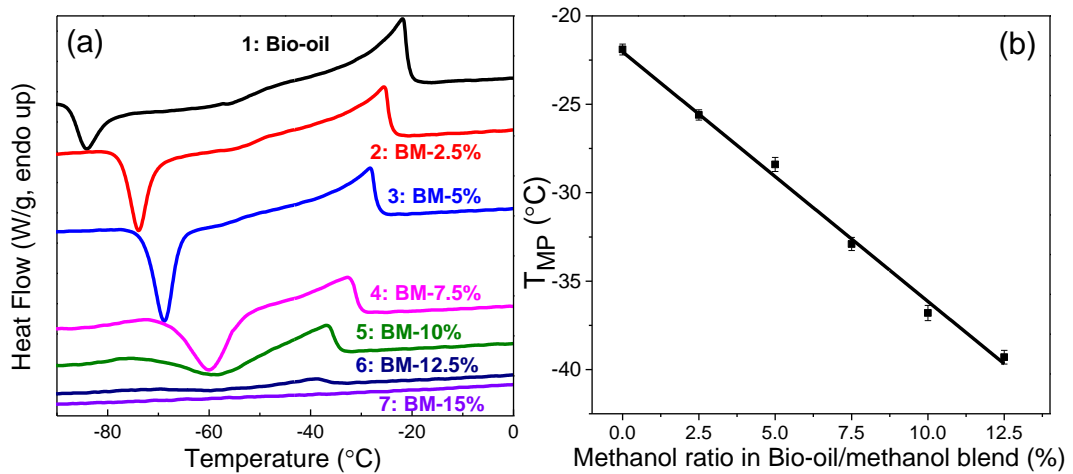
Figure 7-3 (a) DSC curves of BM blends with methanol mass ratio from 0% to 15% in blends, (b) T_{MP} of BM blends as a function of methanol mass ratio in BM blends, T_{MP} stands for the melting peak temperature; BM stands for bio-oil/methanol blend.

7.3 Effects of Individual Components in FCG on Cold Flow Properties of Bio-oil and WSF

Crude glycerol consists of various components include methanol, water, glycerol, NaCl, NaOH, and soap. Considering the low melting temperature of methanol and its good dispersion in bio-oil, methanol is expected to reduce the T_{MP} of fuel mixtures compare to that of bio-oil. This is proved via the DSC analysis of a set of bio-oil/methanol (BM) mixtures. Figure 7-3a shows that an increase in methanol addition in the BM mixture leads to a substantial decrease in the T_{MP} of the fuel mixture. The melting peak of BM mixture finally disappears as the concentration of methanol in BM mixtures reaches 15%. Figure 7-3b shows that the T_{MP} of BM blends decrease almost linearly with the increase in concentration of methanol in the fuel.
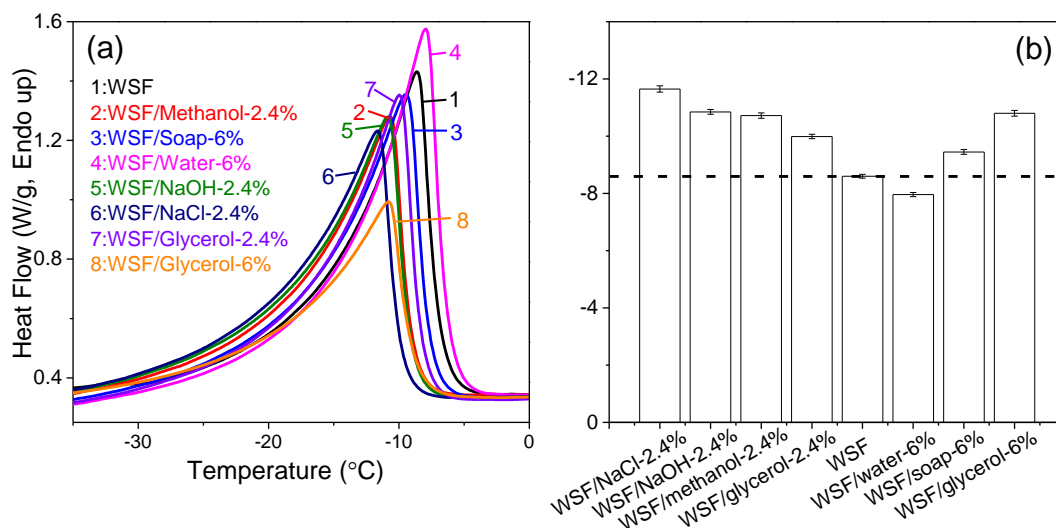
Figure 7-4 (a) DSC curves of WSF and WSF with major impurities in crude glycerol blends; and (b) T_{MP} of WSF and WSF with major impurities in crude glycerol blends. T_{MP} stands for the melting peak temperature; WSF stands for water soluble fraction.

The effects of other components in FCG on the cold flow properties were investigated via the DSC analysis of a set of WSF/impurities mixtures. The concentrations of these components in the fuel mixtures were selected based on those in FCGWSF blend with 60% of FCG. Figure 7-4 shows that increasing water content can worsen the cold flow properties of WSF due to the high freezing point of water but other major components in crude glycerol all decrease the T_{MP} of WSF. It can be seen in Figure 7-4 that the abilities of these components in reducing the T_{MP} are in the order of NaCl > NaOH > methanol > glycerol > soap. Such effect on T_{MP} may be explained by the solvation theory.[275, 276] In the WSF system, water is the major component responsible for the high T_{MP}. The impurities (e.g., NaCl, NaOH and methanol) can bind/occupy part of the water via solvation so that the T_{MP} are decreased.[277] The effect of ionic compounds is more than organic compounds (methanol and glycerol) due to the stronger solvation force (i.e. electrostatic interaction between ionic compounds and water).[278, 279] The reason for the superiority of methanol over glycerol can be attributed to the better dispersion of methanol in the

bio-oil system[60, 86]. For soap, its effect is insignificant because its fatty acid carbon chain is known to have high T_{MP}.[183]
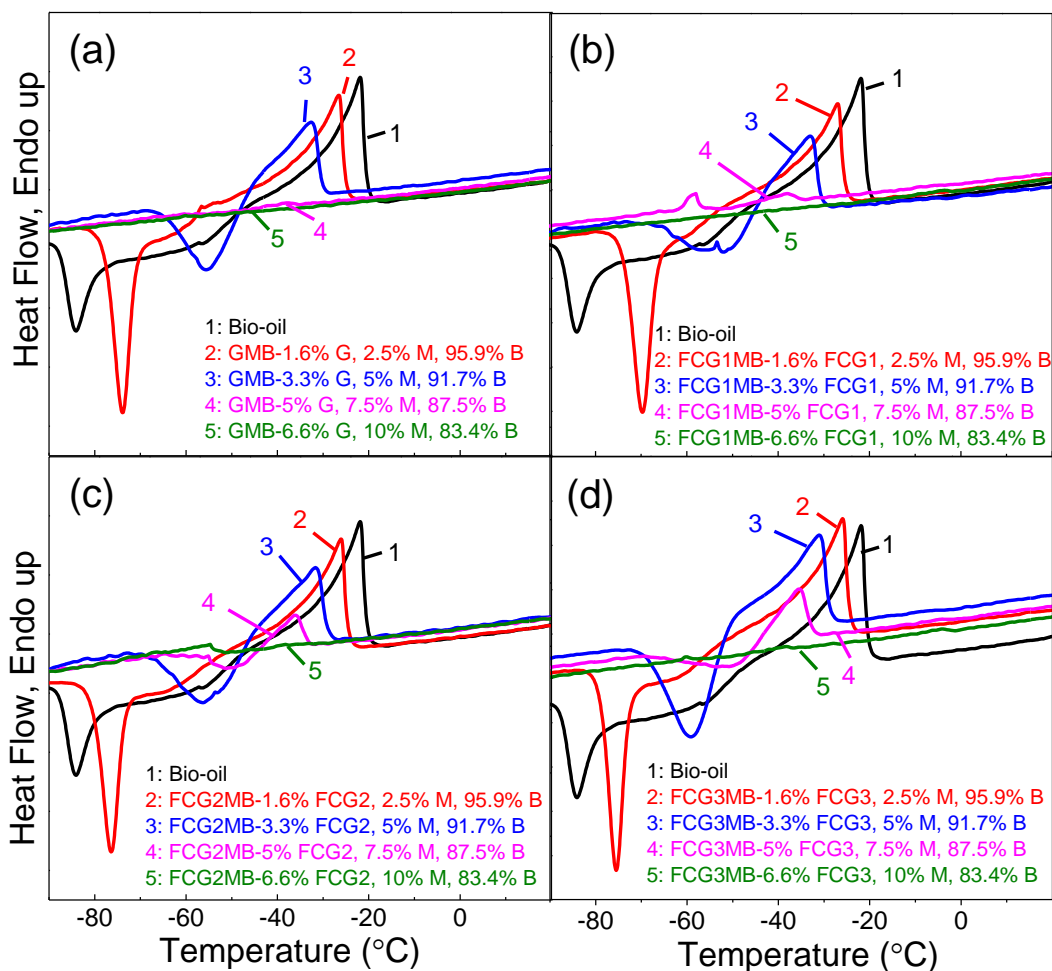
Figure 7-5 DSC curves of selected (a) GMB blends, (b−d) FCG1−3MB blends benchmarking against bio-oil, the concentration after hyphen represents the content of G or FCG, M and B in the mixture before the hyphen. GMB blend stands for glycerol/methanol/bio-oil blend; FCG1−3MB blend stands for FCG1−3/methanol/bio-oil blend; G: glycerol; FCG: formulated crude glycerol; M: methanol; B: bio-oil.

7.4 Cold Flow Properties of FCGMB Fuel Blends Prepared From FCG, Methanol and Bio-oil

Figure 7-5 shows that the cold flow properties of FCGMB blends benchmarking with the glycerol/methanol/bio-oil (GMB) blend. As the addition of FCG1−3 and methanol into the fuel blend increase, there is a significant shift of the T_{MP} to a lower temperature region. The melting peak virtually disappears when the contents of FCGs and methanol have been increased to 6.6% and 10%, respectively. For the GMB blends with the absence of impurities, the melting peak disappears at even lower glycerol or methanol concentrations (5% and 7.5%, respectively). This proves that not only methanol but also glycerol/FCGs indeed can improve the cold flow properties of such bio-oil based fuel mixtures, and also suggests that the improve extent of glycerol is higher than FCGs.

To further investigate the influence of FCG or glycerol, methanol concentration was kept constant at 5% while increasing the FCG or glycerol ratio in the mixture as is shown in Figure 7-6. With increasing amount (up to 3%, based on detailed discussion on solubility of FCGs in FCGMB system previously[57, 60]) of glycerol and FCG1−3, the T_{MP} of the mixtures become lower (from −28.3 to −31.7, −31.2, −30.5 and −29.6 °C for BM5-G and BM5-FCG1−3 respectively). In addition, the T_{MP} of BM5-G and BM5-FCG blends with same concentration of G/FCGs follows the trend of BM5-G < BM5-FCG1 < BM5-FCG2 < BM5-FCG3, as is shown in figure 7-7. This indicates the influence on T_{MP} decrease follows the sequence of glycerol > FCG1 > FCG2 > FCG3. The observed difference in the effect of glycerol and FCGs can be mainly attributed to the effect of water that is presented in the FCGs. Because of the negative effect of water on cold flow properties (see section 7.2), glycerol has a better performance than FCGs in decreasing the T_{MP} of the fuel blends. For the same

reason, FCG1 is more effective than FCG2 and FCG3 in lowering the T_{MP} of the fuel mixtures due to its considerably low water content.
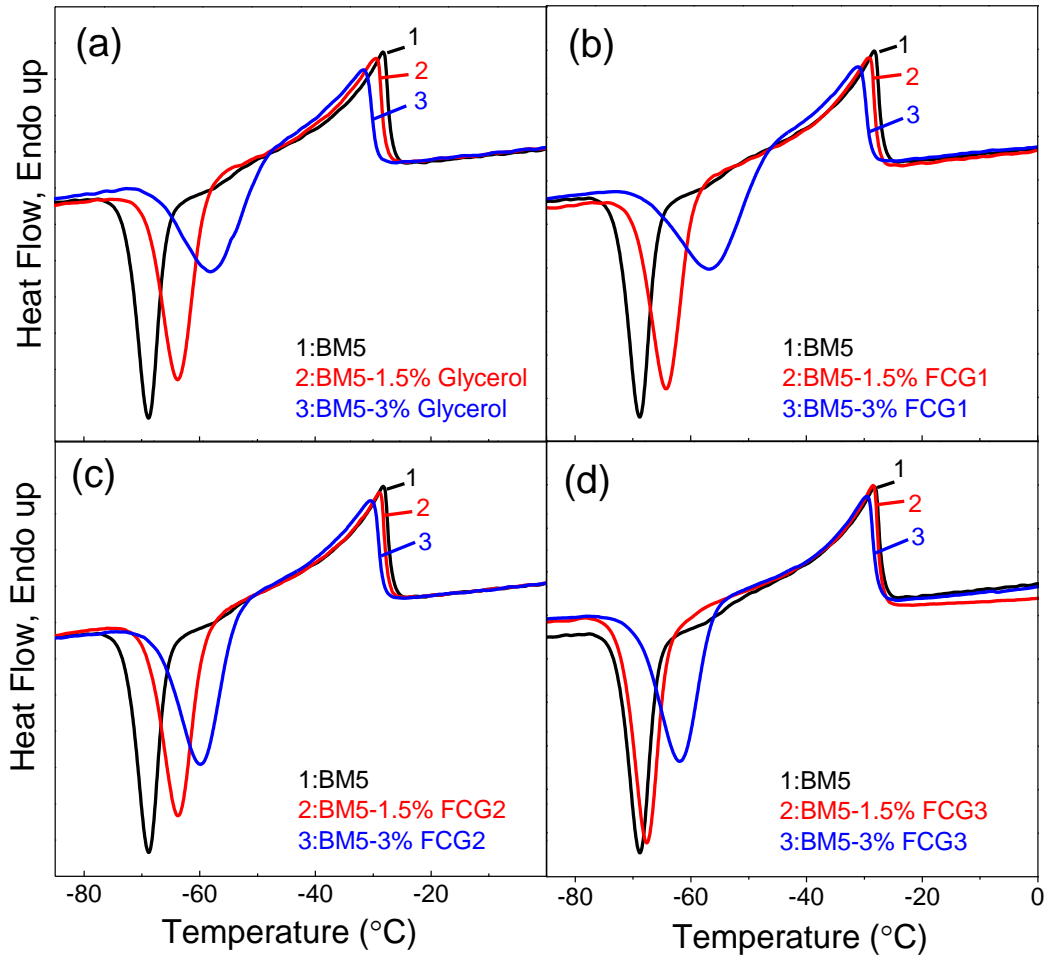
Figure 7-6 DSC curves of selected (a–d) BM5-G and BM5-FCG1–3 blends with methanol content fixing at 5% in BM blend and G or FCG1–3 content being 1.5% and 3% in the whole blend benchmarking against BM5 blend. BM5 stands for bio-oil/methanol blend with methanol ratio of 5%; G: glycerol; FCG: formulated crude glycerol; M: methanol; B: bio-oil.
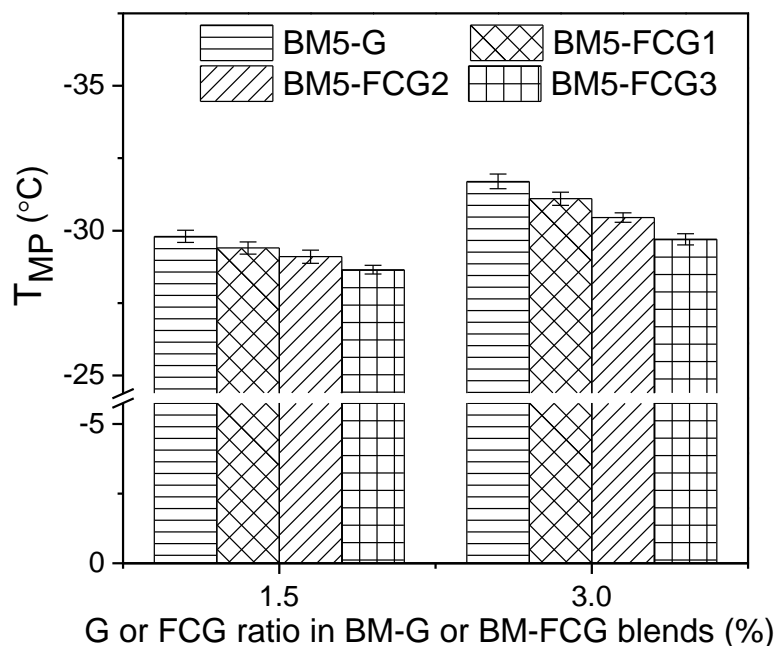
Figure 7-7 T_{MP} of BM blends as a function of G or FCG1–3 mass ratio in BM blends. T_{MP} stands for the melting peak temperature; BM blend stands for bio-oil/methanol blend; BM5 stands for bio-oil/methanol blend with methanol ratio of 5%; G stands for glycerol; FCG stands for formulated crude glycerol.

7.5 Cold Flow Properties of FCGWSF Fuel Blends Prepared from FCG and Bio-oil WSF

As seen in Figure 7-8, the addition of FCGs to prepare the FCGWSF or Glycerol/WSF (GWSF) blends lead to substantial decreases in the T_{MP} of the fuel blends (from −8.7 to −32.0 °C). The melting peak almost disappears at high mass concentrations of FCG or glycerol (e.g., ~60% for FCG4−5 or glycerol and >70% for FCG6, respectively). Further calculation shows that at such FCG or glycerol concentrations, the contents of water and glycerol in these fuel blends is below 35% and more than 45%, respectively. Figure 9 shows that the effect of glycerol and FCGs in reducing the T_{MP} of the FCGWSF blends follows the order of glycerol > FCG4 > FCG5 > FCG6. This is consistent with the trend observed for the FCGMB

system and the reason is the difference in water content of FCGs (see section 7.3). Figure 7-8 also shows that the cold crystallization peak appears when the concentrations of glycerol, FCG4 and FCG5 reach 40% or the concentration of FCG6 reaches 60%.
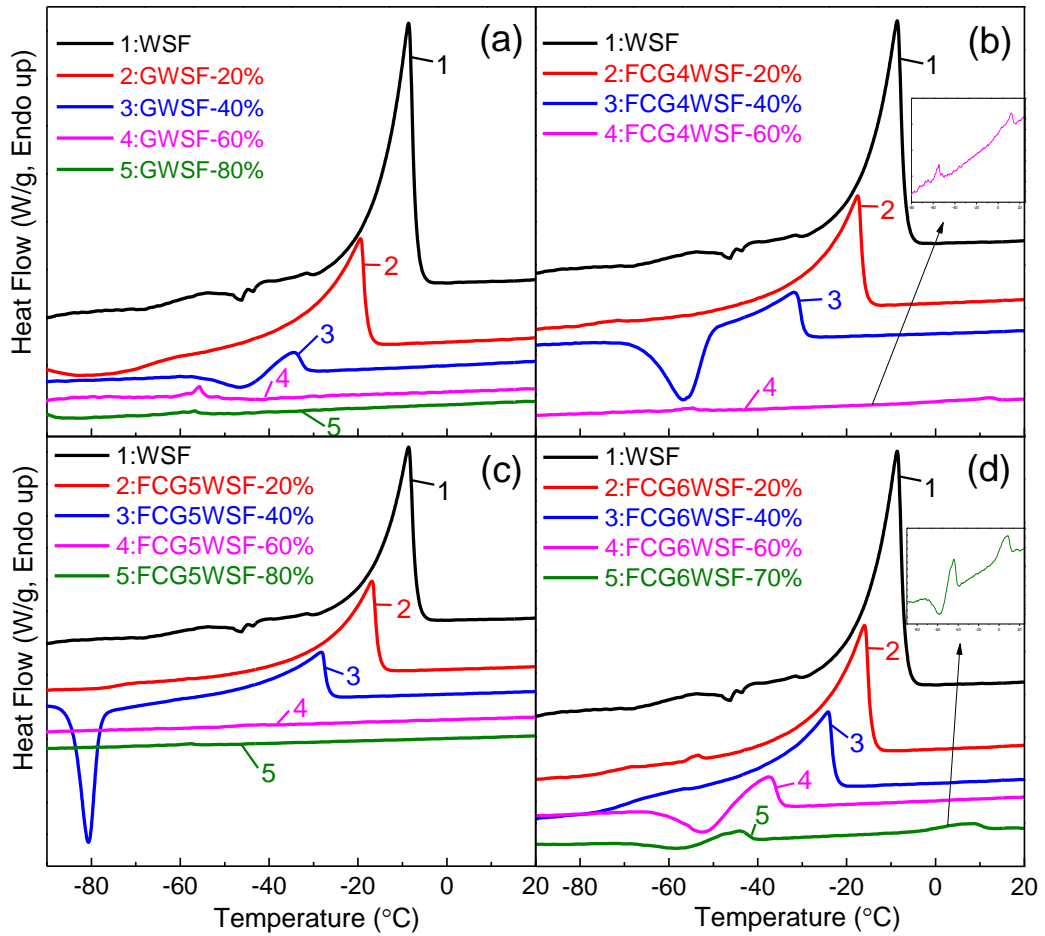
Figure 7-8 DSC curves of (a–d) GWSF and (b–d) FCG4–6WSF blends with glycerol or FCG4–6 ratio varying from 20% to 80%. GWSF stands for G/WSF blends; FCG4–6WSF stands for FCG4–6WSF blends; G stands for glycerol; FCG stands for formulated crude glycerol; WSF stands for water soluble fraction.

The results clearly show that the additions of FCG or glycerol can substantially improve cold flow properties of bio-oil based fuels. The approach of preparing FCGWSF fuel blends from bio-oil WSF and crude glycerol is an attractive technical option for crude glycerol utilisation due to the very high glycerol uptake and favourable cold flow properties. Furthermore, the results also demonstrate that water plays an important role in influencing the T_{MP} of the fuels. It should be noted that for FCG4WSF with 60% FCG4 and FCG6WSF with 70% FCG6, there are small peaks at around 7 °C. These can be attributed to the formation of fatty acid esters due to the reaction between fatty acids (formed from soap react with acids) and alcohols,[58, 179, 181] leading to the FCG4WSF and FCG6WSF blend fuels being gel- or jelly-like instead of clear solution when stored at 4 °C.
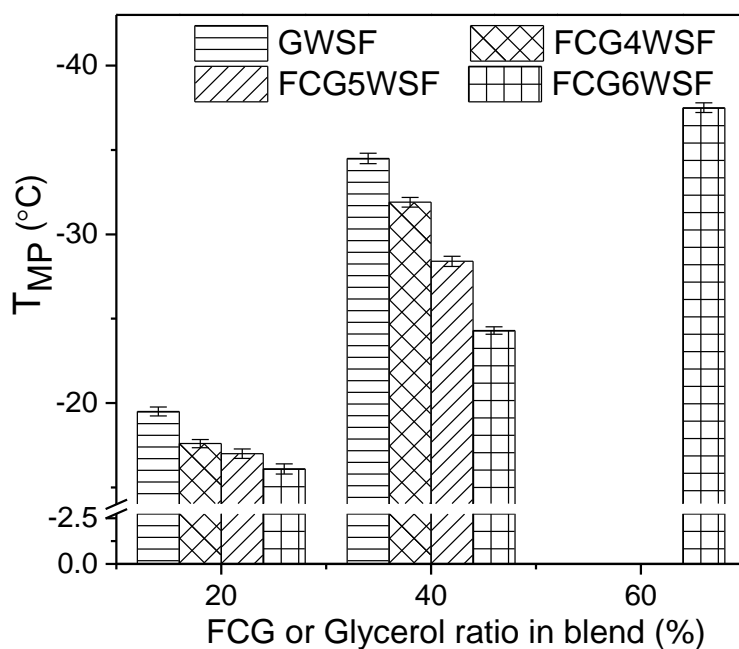
Figure 7-9 T_{MP} of GWSF and FCG4–6WSF blends as a function of G or FCG4–6 mass ratio in blends. T_{MP} stands for the melting peak temperature; GWSF stands for G/WSF blends; FCG4–6WSF stands for FCG4–6WSF blends; G stands for glycerol; FCG stands for formulated crude glycerol; WSF stands for water soluble fraction.
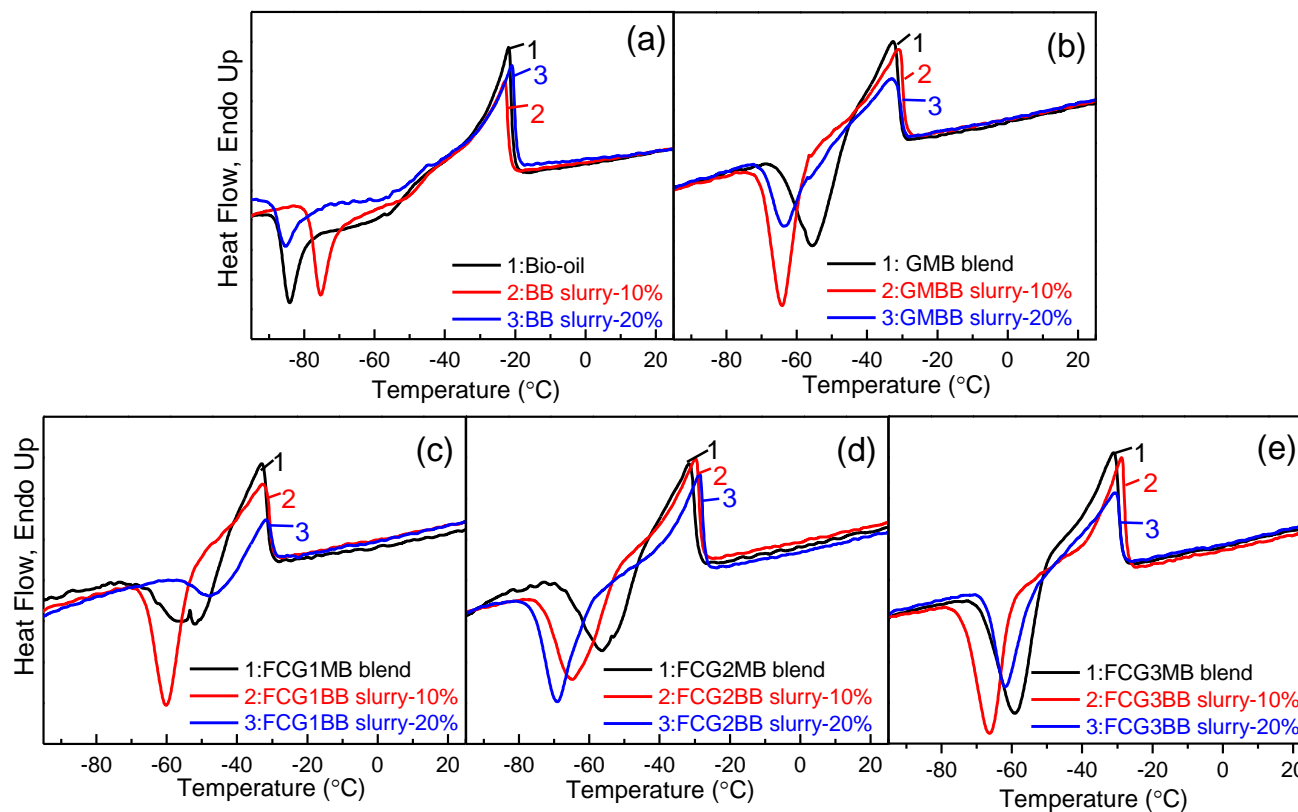
Figure 7-10 DSC curves of (a) BB slurry fuels, (b) GMBB slurry fuels, (c–e) FCG1–3MBB slurry fuels. BB, GMBB, FCGMBB, WSFB, GWSFB, FCGWSFB slurry fuels were prepared from biochar (10% or 20%) and corresponding bio-oil, GMB and FCGMB fuel blends. GMB or FCGMB are blends prepared using 3.3% glycerol (or FCG), 5% methanol and 91.7% bio-oil. BB stands for bio-oil/biochar slurry; GMBB stands for glycerol/methanol/bio-oil/biochar slurry; FCGMBB stand for crude glycerol/methanol/bio-oil/biochar slurry; FCG stands for formulated crude glycerol.
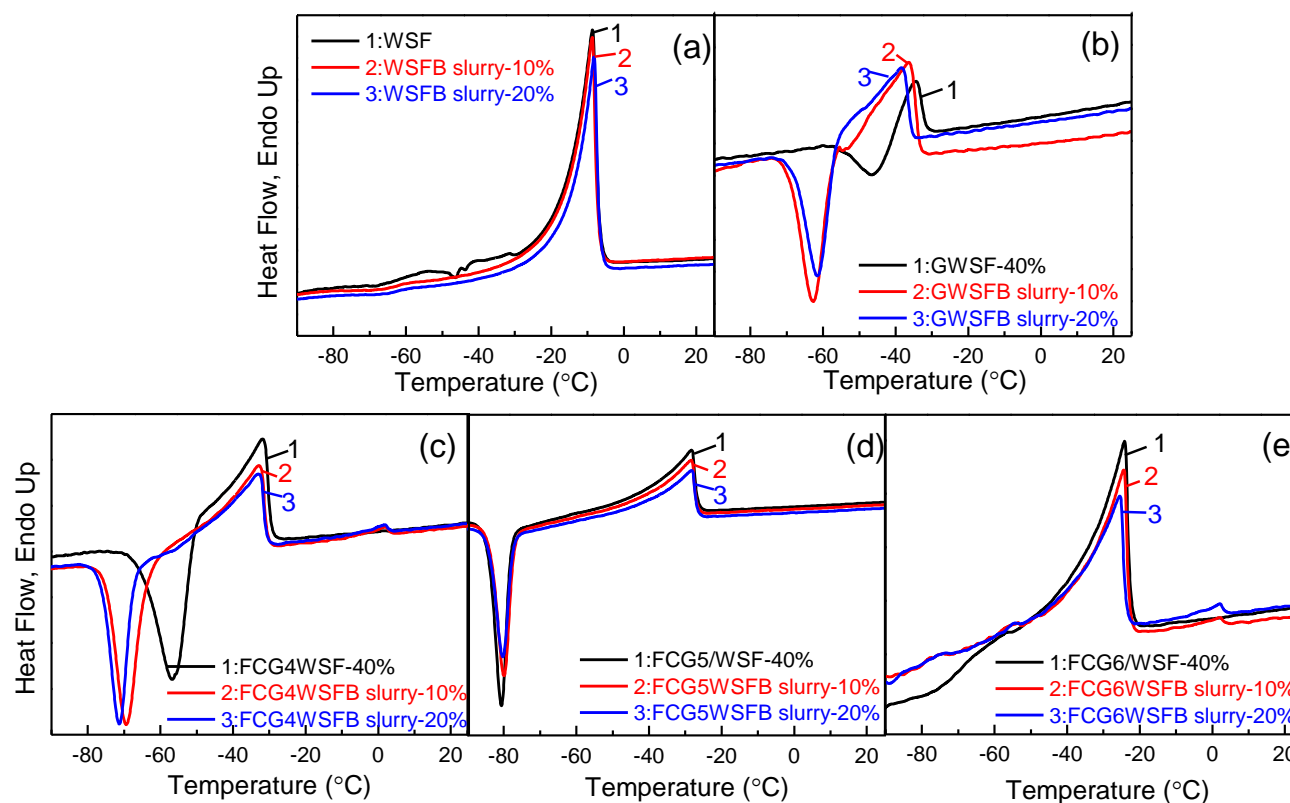
Figure 7-11 DSC curves of (a) WSFB slurry fuels, (b) GWSFB slurry fuels, and (c–e) FCG4–6WSFB slurry fuels. BB, GMBB, FCGMBB, WSFB, GWSFB, FCGWSFB slurry fuels were prepared from biochar (10% or 20%) and corresponding WSF, GWSF and FCGWSF fuel blends. GWSF and FCGWSF are blends prepared using 40% glycerol (or FCG) and 60% WSF. WSFB stands for WSF/biochar slurry; GWSFB stands for glycerol/WSF/biochar slurry; FCGWSFB stands for stands for crude glycerol/WSF/biochar slurry; WSF stands for water soluble fraction; FCG stands for formulated crude glycerol.

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7.6 Cold Flow Properties of FCGMB/Biochar (FCGMBB) and FCGWSF/Biochar (FCGWSFB) Slurry Fuels

Figure 7-10 presents the DSC curves for bioslurry fuels prepared from FCGMB or FCGWSF blends with the additions of biochar. Even at 20% biochar loading level, the T_{MP} of the slurry fuels are still very similar to the respective blends, with very slight increases (< 4 °C). This means the presence of fine biochar particles in the fuel mixtures has very little effect on the T_{MP} of these bio-oil based fuels.

However, it appears that the cold crystallization peak can be affected by presence of biochar. Figure 7-10 and Figure 7-11 show that the cold crystallization peaks of most slurries studied shift to lower temperatures than those of the respective blends. In addition, the presence of biochar particles in the fuel mixtures also shift the small melting peaks at 7 °C for FCG4WSF and FCG6WSF blends (see section 7.3) to ~2 °C, with increased intensities. While the exact reasons are unknown at present, there are two possible reasons for such an observation. One is that the biochar particles in the fuel mixtures can act as nucleation agents for the crystallization of slurry fuels hence enhancing this process. Similar observations were reported in a previous study on the role of calcium carbonate ($CaCO_3$) particles in the cold crystallization behaviour of poly(ethylene terephthalate).[273] The other is the possible changes in the properties and compositions of bio-oil components in a bioslurry system, as a result of interactions between bio-oil and biochar particles.[16, 265] Nevertheless, the results clearly show that FCG with low water content can produce bio-oil/FCG and WSF/FCG blends with better cold flow properties. The results also show that with the presence of biochar, FCG containing high content of soap (e.g., 10%) may cause some solidification issues when mixing with WSF at a high concentration (above 40%) in the fuel mixture.

7.7 Conclusion

This study investigates the cold flow properties of various fuel mixtures from bio-oil, crude glycerol, methanol and/or biochar by determine T_{MP} using DSC. The results show that bio-oil and WSF have a T_{MP} of -21.9 and -8.7 °C which may problematic when direct utilization under cold weather conditions. The addition of FCG can significantly improve cold flow properties of both FCGMB and FCGWSF fuel blends, which can alleviate or even eliminate those issues. Except water that increases the T_{MP}, all other components in FCGs decrease the T_{MP} due to the solvation effect hence improve the cold flow properties of the fuel mixtures, with the order of improvements of NaCl > NaOH > Methanol > Glycerol > Soap. Suspended biochar particles in the slurry fuels have very limited effect on the cold flow properties of slurry fuels. The presence of biochar particles only slightly affect the solidification of FCGWSFB slurry fuels when the FCG has a high soap content (e.g., 10%) and its loading level is over 40% in the slurry fuels.

Chapter 8 Bed Agglomeration during Bio-oil Fast Pyrolysis in a Fluidised-Bed Reactor

8.1 Introduction

Biomass as a solid fuel has undesired properties such as low energy density, poor grindability, bulky, fibrous and widely dispersed and is not suitable for long distance transport.[18, 19, 35, 36] Fast pyrolysis of biomass,[5, 7, 9, 109, 280-282] as a thermochemical technology, is an attractive approach to produce high-energy-density bio-oil which is suitable for transport for centralised processing and biochar that can be applied locally for soil amendment and carbon sequestration.[4, 8, 14, 109, 283, 284] Depending on the destination of bio-oil subsequent centralised applications, bio-oil may be upgraded and/or refined for producing liquid transport fuels through further thermochemical processing.

Fluidised-bed reactors are widely adopted in various thermochemical processing (e.g., pyrolysis, combustion and gasification) of various fuels due to its advantages in isothermal operation condition, fuel flexibility and low operating temperature.[13, 61, 64, 285-287] One key operational issue is bed agglomeration that may lead to defluidisation, leading to detrimental effect on the durable operations of a fluidised-bed reactor.[63, 65, 66, 73] It is noted that bed agglomeration during biomass combustion/gasification is driven by ash species and has been extensively investigated.[61, 63-66, 72, 73, 288] However, as shown in a series of recent experimental studies by Wu et al.,[67-71, 238] bed agglomeration during biomass pyrolysis is completely different and driven by organic matter that contains various aromatic-ring systems. Bio-oil, as a product of biomass pyrolysis, is known to contain various aromatic compounds,[58, 211, 218] and it may be used as a direct feedstock in fluidised-bed for various thermochemical processing. Therefore, it is plausible to investigate bed agglomeration phenomena

during bio-oil pyrolysis under various conditions. In addition, apart from aromatic compounds, bio-oil also contains various other chemicals such as alcohols, ketones, sugars, and carboxylic acids etc.[4, 240] However, it is largely unknown if other components in the bio-oil are also important and may play synergistic effect on bed agglomeration during pyrolysis. Therefore, it is reasonable to further investigate the fundamental mechanism responsible for bed agglomeration during bio-oil fast pyrolysis in fluidised-bed reactor.

Therefore, this paper aims to systematically investigate bed agglomeration during the pyrolysis of bio-oil in a fluidised-bed reactor at 500–800 °C. In addition to bio-oil, bio-oil fractions (water-soluble fraction or water-insoluble fraction) and model compounds were also investigated to reveal the fundamental mechanisms responsible for bed agglomeration.

Table 8-1 Fuel properties of bio-oil, bio-oil WSF and WIF used in this study.

	Elemental analysis (wt%)[a]				Water content	Density	Viscosity	HHV[d]
	C^a	H^a	N^a	O^b	wt%, ar[c]	g/mL, ar[c]	mPa s, 25 °C	MJ/kg
Bio-oil	55.90	5.92	0.09	38.09	23.50	1.20	178.4	18.64
WSF[e]	48.20	4.85	0.44	46.52	61.10	1.07	3.0	12.89
WIF[f]	66.13	6.74	0.07	27.06	nd[g]	0.81	6.3	24.26

[a] dry basis; [b] by difference; [c] as-received basis; [d] calculated HHV (higher heating value); [e] water-soluble fraction; [f] water-insoluble fraction in ethanol at a concentration of 27.3%; [g] not determined.
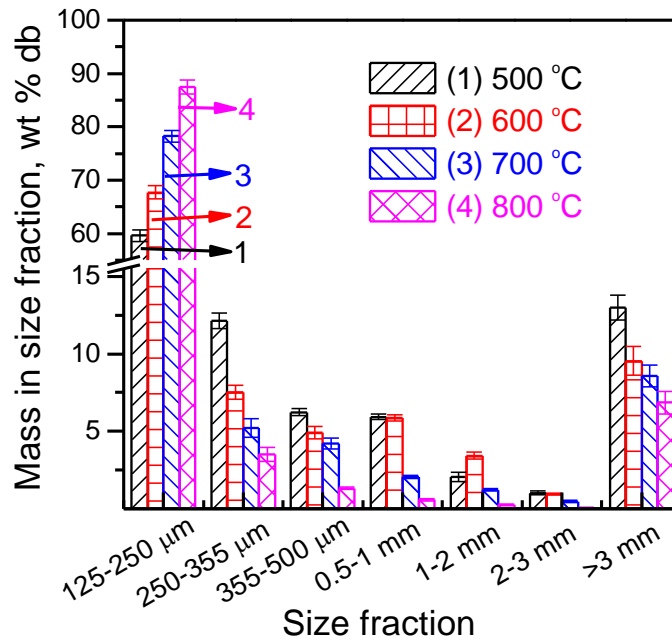
Figure 8-1 Particle size distribution of the bed samples collected from the fast pyrolysis of bio-oil in a fluidised-bed pyrolysis reactor at 500–800 °C.

8.2 Evidence and Extent of Bed Agglomeration during Fast Pyrolysis of Bio-oil in a Fluidised-Bed Reactor

Figure 8-1 presents the PSD of the bed samples collected after bio-oil fast pyrolysis at 500–800 °C. Because the silica sand particles as bed material have a size of 125−250 µm, any particles > 250 µm collected after pyrolysis can be safely considered to bed agglomerates. Figure 8-1 shows that depending on pyrolysis temperature, the bed agglomerates (i.e. the materials > 250 µm) contribute to 12.6 to 40.4% of the total mass of the bed samples. The bed agglomerates distributed in the size fractions of 250−355 µm, 355−500 µm, 0.5−1.0 mm, 1.0–3.0 mm and > 3 mm account for 3.5−12.1%, 1.3−6.2%, 0.6−5.9%, 0.3−4.4% and 6.9−13.0% of the total bed agglomerates, respectively.
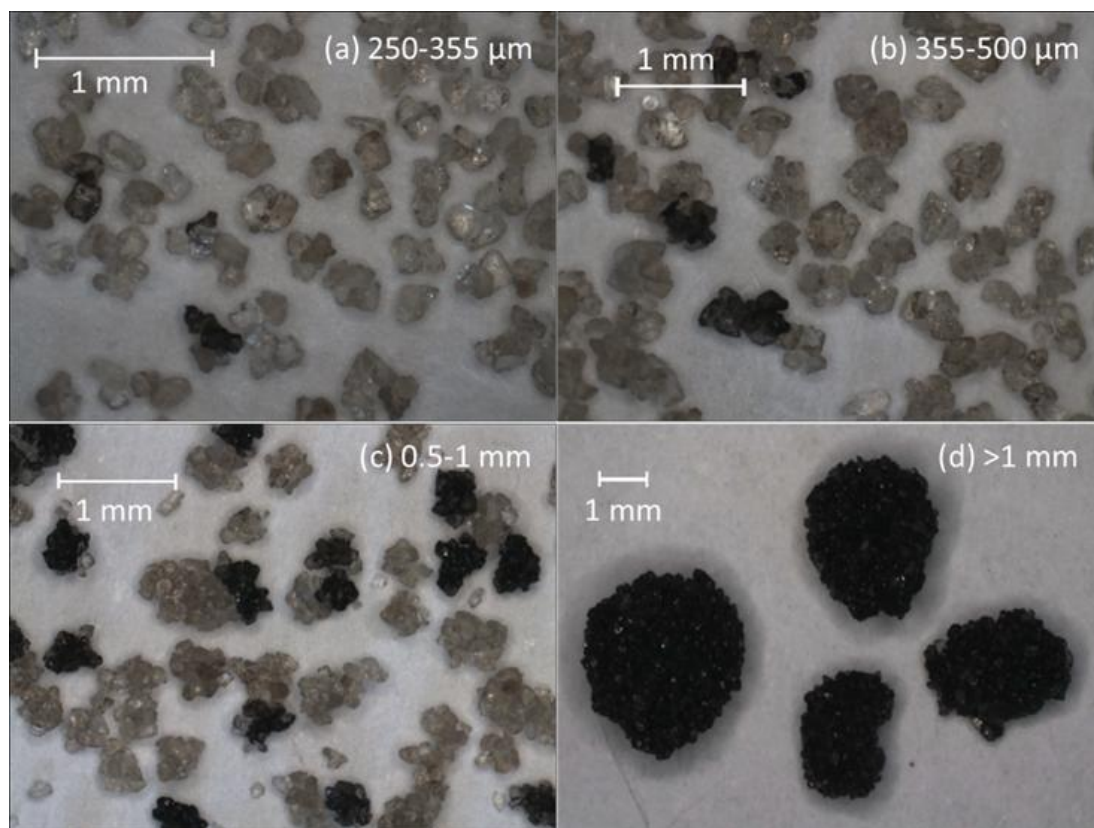
Figure 8-2 Optical images of bed agglomerates (collected from bio-oil fast pyrolysis at temperature of 500 °C) in size fraction of (a) 250–355 μm, (b) 355–500 μm, (c) 0.5–1 mm and (d) > 1 mm.

Figure 8-2 illustrates the typical optical microscope images of the bed samples collected in selected size fractions. The presence of bed agglomerates are clearly evident in these images, mainly in the form of agglomeration of multiple sand particles. These images also show that the silica sand particles appear to be coated with the bio-oil pyrolysis products (coke and/or tar) that adhere multiple sand particles into one bed agglomerate.
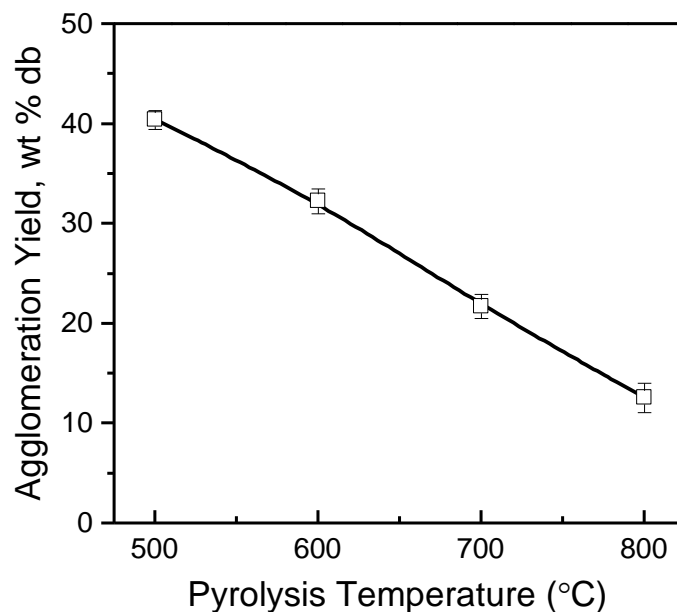
Figure 8-3 Agglomeration yields during fast pyrolysis of bio-oil at 500–800 °C.

The quantified agglomeration yields during the fast pyrolysis of bio-oil at various temperatures are plotted in Figure 8-3. It can be found that the agglomeration yield decreases gradually from ~40% to ~15% as the pyrolysis temperature increases from 500 °C to 800 °C. Similar trends between agglomeration yield and pyrolysis temperature was also observed in our previous study on fast pyrolysis of biomass (mallee leaf) in a fluidised-bed reactor but the reported agglomeration yield during biomass fast pyrolysis was considerably lower (only ~10%−2% at 500−700 °C).[71] Comparatively, the fast pyrolysis of bio-oil resulted in considerably more significant bed agglomeration. Therefore, it is of critical importance to understand the underlying mechanisms governing the severe bed agglomeration during bio-oil fast pyrolysis. Because the compositions of bio-oil is complex, subsequent investigations were then conducted to study bed agglomeration during the fast pyrolysis of bio-oil fractions and model compounds.
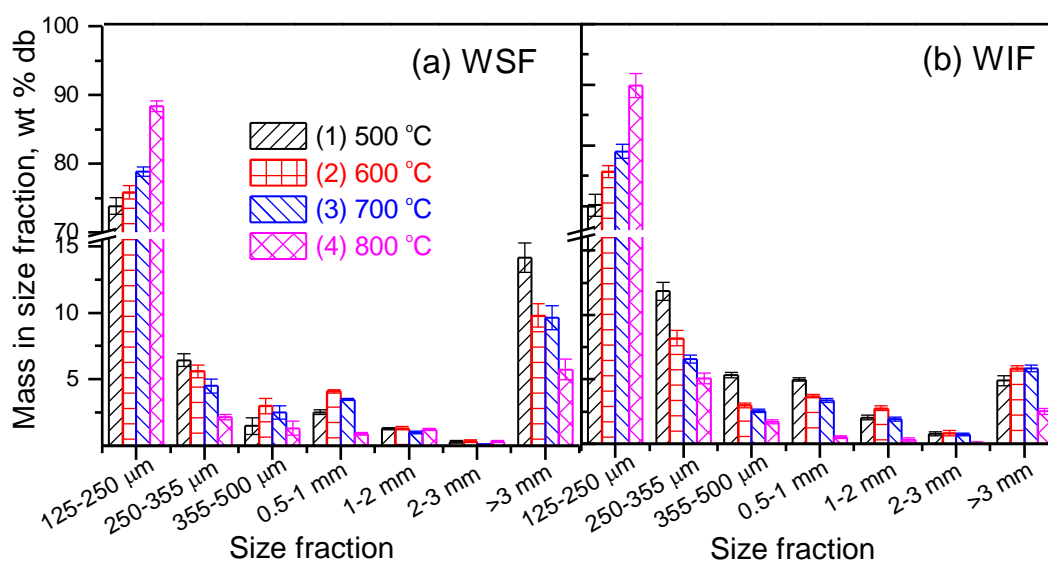
Figure 8-4 Particle size distribution of the bed samples collected from the fast pyrolysis of (a) WSF and (b) WIF which is dissolved in ethanol in a fluidised-bed pyrolysis reactor at 500–800 °C. WSF stands for water-soluble fraction; WIF stands for water-insoluble fraction.

8.3 Bed Agglomeration during the Fast Pyrolysis of Bio-oil Fractions and Model Compounds

Via cold-water precipitation, the bio-oil is separated into two fractions, WSF and WIF fractions. The WSF was used as-collected (without removal of added water) and WIF was redissolved in ethanol at the same concentration (27.3%) as it is in the bio-oil. Each fraction (WSF or WIF) was injected into the fluidised-bed for pyrolysis experiments. The results presented in Figure 8-4 clearly show the presence of bed agglomerates, i.e. those in the size fractions over 250 μm, indicating that bed agglomeration also takes place during the fast pyrolysis of WSF and WIF. The PSDs of bed samples after fast pyrolysis of WSF and WIF are similar to that of the bio-oil. However, WSF fast pyrolysis produces higher amount of the bed samples distributed

in size fraction >3.0 mm than bio-oil or WIF, especially at high temperatures (700 °C and 800 °C). Therefore, WSF fast pyrolysis tends to generate large agglomerates under the experimental conditions.
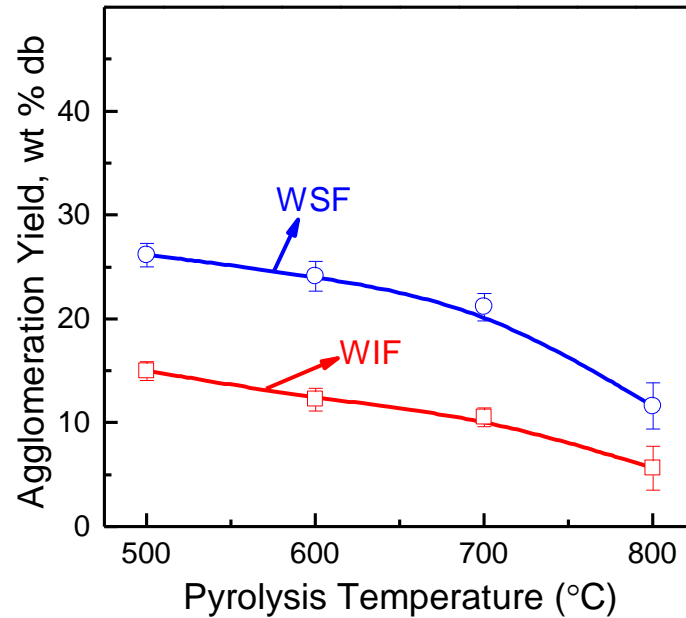
Figure 8-5 Agglomeration yields during fast pyrolysis of bio-oil fractions (WSF and WIF) at 500–800 °C. WSF stands for water-soluble fraction; WIF stands for water-insoluble fraction.

The agglomeration yields during fast pyrolysis of WSF and WIF at 500−800 °C are also plotted in Figure 8-5, benchmarking against that of the bio-oil in Figure 8-3. The agglomeration yields of both WSF and WIF fast pyrolysis are lower than that of bio-oil and decreases from 26.2% to 11.6% and 15.0% to 5.2%, respectively, as temperature increases from 500 °C to 800 °C. Pyrolysis of WIF has much lower agglomeration yields at all temperatures in comparison with that of bio-oil or WSF, while the agglomeration yield of WSF is only lower than that of the bio-oil at temperature below 700 °C. The results suggest that there are interactions between WSF and WIF within bio-oil during the fast pyrolysis of bio-oil. It is also surprising

to see that bed agglomeration of WSF fast pyrolysis surpasses that of WIF, indicating WSF is more likely the main responsible fraction for bed agglomeration during bio-oil fast pyrolysis. The extra water presented in the WSF as a result of water addition during cold-water precipitation may play a possible role in the bed agglomeration process. Therefore, model compounds were selected to simulate the WSF and bio-oil for subsequent experiments for understanding the potential interactions among various fractions and the effect of extra water.
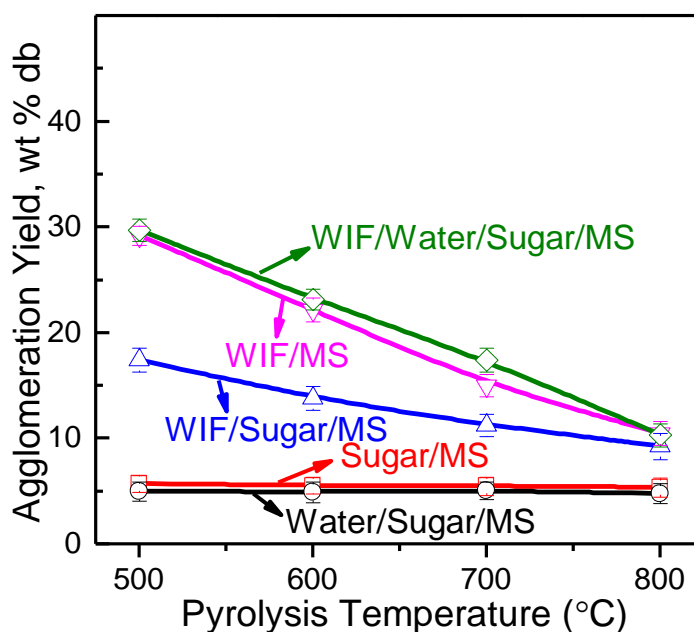
Figure 8-6 Agglomeration yields during fast pyrolysis of bio-oil model compounds at 500–800 °C. WSF stands for water-soluble fraction; WIF stands for water-insoluble fraction; MS stands for mixed solvent.

Figure 8-6 presents the results on agglomeration yields during the pyrolysis of bio-oil model compounds at 500−800 °C. The mixed solvent (MS) was prepared to represent the light organic fraction in bio-oil excluding water and pyrolysis lignin in bio-oil, taking into consideration of major chemical families in bio-oil.[240]

Levoglucsan was used as a model compound to represent sugars in WSF (that has a total sugar content of ~7%[124, 240]). The Water/Sugar/MS and Sugar/MS mixtures were then prepared to simulate the WSF with and without water. The WIF/Water/Sugar/MS and WIF/Sugar/MS mixtures were prepared to simulate bio-oil with and without water. WIF/MS mixture with same WIF concentration was also prepared for comparison. Figure 8-6 shows that the agglomeration yields during the fast pyrolysis of formulated WSF with and without water (i.e. Water/Sugar/MS and Sugar/MS) at 500−800 °C are both about 5.0% at all temperatures. This indicates the presence of extra water in the formulated WSFs has insignificant effect on the agglomeration yields during pyrolysis. The agglomeration yield during MS fast pyrolysis is only 2.0% at 500 ℃ which is lower than that of the formulated WSFs. The results indicate that sugar or the light organic fraction in bio-oil alone only plays a minor role in bed agglomeration during bio-oil fast pyrolysis.

Compared to that of WSF (26.2%−11.6% at 500−800 °C), the agglomeration yield of the formulated WSF is considerably lower. It has been reported that WSF obtained at water to bio-oil ratio of 0.5:1 still has fused aromatic compounds,[58] which is absent in the formulated WSF. Interactions between light organic compounds/sugar and those fused aromatics could have contributed to the high agglomeration yield of WSF fast pyrolysis.

Considering the agglomeration yields of bio-oil are higher than those of WSF or WIF, interactions between WSF and WIF must have taken place during bio-oil pyrolysis and such interactions lead to synergy in bed agglomeration. Therefore, it is essential to design experiments for investigation into this important aspect. Experiments were then conducted for the fast pyrolysis of WIF/MS mixture. As shown in Figure 3c, the agglomeration yields of the WIF/MS mixture are 9.3−17.4%, which are similar with those of WIF redissolved in ethanol, indicating that the contribution of the

interactions between WIF and light organic compounds in bio-oil to bed agglomeration is insignificant.

Furthermore, Figure 8-6 shows that after pyrolysis, the agglomeration yields of WIF/Water/Sugar/MS and WIF/Sugar/MS mixtures (i.e. the formulated bio-oil with and without water) are almost same, decreasing from ~29.5% at 500 °C to 10.5% at 800 °C. The results indicate the insignificant effect of water on the agglomeration yields during pyrolysis which is consistent with former finding that the extra water in WSF has insignificant effect on bed agglomeration during WSF pyrolysis. It is noteworthy that the agglomeration yields of formulated bio-oils (i.e. WIF/Water/Sugar/MS and WIF/Sugar/MS) are considerably higher than the sum of formulated WSFs and WIF/MS mixture especially at temperature below 700 °C. This indicates that the interactions between WIF and sugar is responsible for bed agglomeration during bio-oil fast pyrolysis, and the contribution of such interactions to bed agglomeration decreases with increasing temperature and becomes insignificant at 700 °C or higher. As the WIF is mainly composed by lignin-derived oligomers,[217, 218] it is plausible to reason that such interactions are mainly between the lignin-derived oligomers and sugars. Such a mechanism also explains the surprisingly high agglomeration yield during the pyrolysis of WSF because the incompletely separation of bio-oil leads to the produced WSF still containing some lignin-derived aromatic compounds,[58] which can interact with sugars within the WSF.

Figure 8-7 Correlation between (a) the reduction in the agglomeration yield due to solvent washing and pyrolysis temperature, (b) the yield of tar and pyrolysis temperature. WSF stands for water-soluble fraction; WIF stands for water-insoluble fraction.

8.4 Correlations between Bed Agglomeration and the Formation of Tar and Coke in Bed Samples

The bed agglomerates were further washed by solvent to quantify the yields of solvent-soluble organic matter (i.e. tar) and solvent-insoluble organic matter (i.e. coke) in bed agglomerates. The bed samples after solvent washing were also re-sieved to determine the reduction in bed agglomeration yields as a result of solvent washing. Figure 8-7a clearly shows that after solvent washing, the reductions in agglomeration yield decreases with increasing pyrolysis temperature, from 22.1% at 500 °C to 6.2% at 800 °C for bio-oil and from 16.0% at 500 °C to 5.9% at 800 °C for the WSF, respectively. Moreover, the tar yields of bed samples collected from the fast pyrolysis of bio-oil and the WSF decrease with increasing pyrolysis temperature (see Figure 8-7b). The tar yields due to solvent washing of bed samples are 35.5% at 500 °C and 15.3% at 800 °C for bio-oil, which are higher than 29.2% at 500 °C and

3.7 at 800 °C for the WSF, respectively. However, for WIF, both the tar yields (3.87–2.6%) and the reductions (6.7–3.0%) in agglomeration yields as results of solvent washing are very low and only the latter one decreases with increasing pyrolysis temperature while the former one remain similar. This is attributed to the thermal cracking of bio-oil and WSF.[218] It was observed previously that the yield of "washed tar" from lignin-derived oligomers (or WIF) was very low when pyrolysis temperature is higher than 500 °C, due the decomposition of large molecules and its enhanced evaporation.[218]
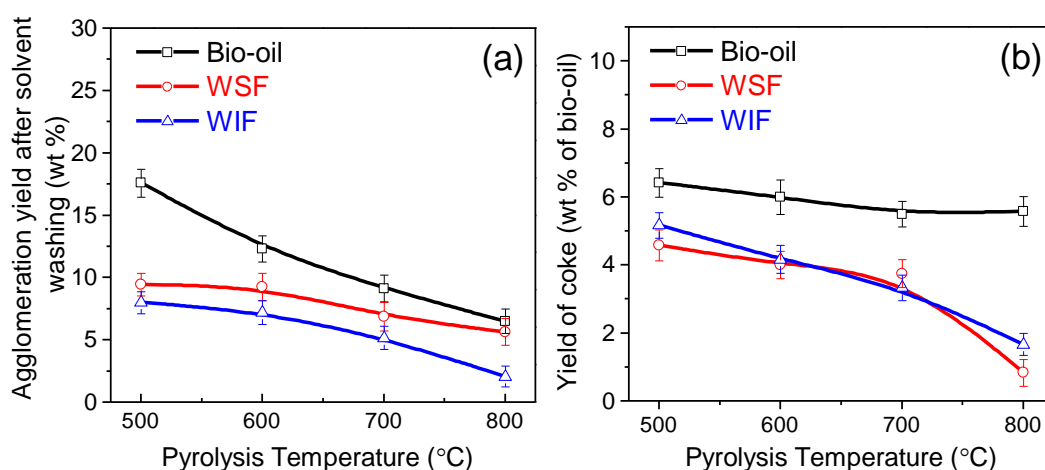
Figure 8-8 Correlation between (a) the agglomeration yield after solvent washing and pyrolysis temperature, (b) the yield of coke and pyrolysis temperature. WSF stands for water-soluble fraction; WIF stands for water-insoluble fraction.

Figure 8-8b shows that the coke yields of bed samples collected from the fast pyrolysis of bio-oil, WSF and WIF all decrease with increasing pyrolysis temperature (from 6.4 to 5.5%, 4.6 to 0.83% and 5.2 to 1.7% as pyrolysis temperature increases from 500 °C to 800 °C, respectively). Less coke is formed at higher temperatures, attributed to the intensified decomposition reactions.[217] The coke yield of bio-oil is the highest while that of WSF is the lowest but only slightly

lower than that of WIF. The WSF has much less possibility to form coke than WIF during pyrolysis at temperatures above 450 °C because the WIF has considerably higher concentration of aromatic species, which act as precursors for coke formation.[217, 218] In despite of the low yields (less than 6.4%) of coke in comparison to the tar yields, coke does play a significant role in the formation of bed agglomeration. As shown in Figure 8-8a, after solvent washing, the agglomeration yields for bio-oil, WSF and WIF are still high and also decreases with increasing temperature, following the same sequence of bio-oil>WSF>WIF as those before solvent washing.
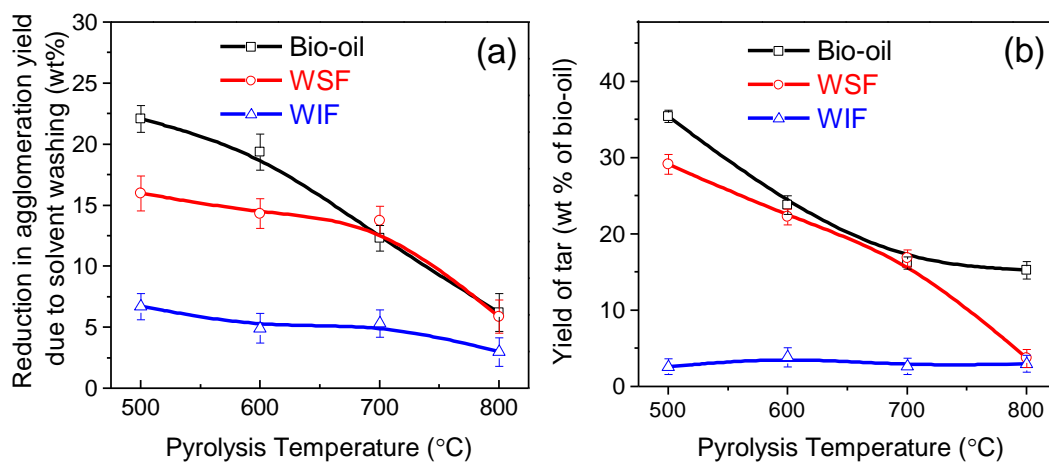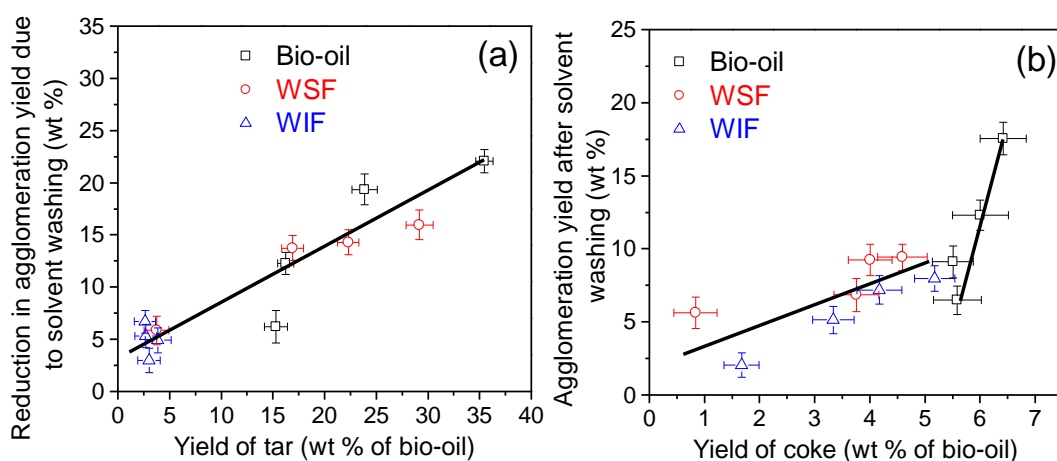

Figure 8-9 Correlation between (a) the reduction in the agglomeration yield due to solvent washing and the yield of tar and (b) the agglomeration yield after solvent washing and the yield of coke. WSF stands for water-soluble fraction; WIF stands for water-insoluble fraction.

The correlations between the reduction in agglomeration yields and tar yield and between the agglomeration yield after solvent washing and the coke yield are plotted in the panel e and f of Figure 8-9. It can be seen that the all experimental data for the reduction in agglomeration yields and tar yields obtained from all feedstock (bio-oil,

WSF and WIF) fits into one single broadly linear correlation. This indicates the role of such tars generated from various feedstock play a similar role in the formation of bed agglomeration. For the correlation between the agglomeration yields after solvent washing and the coke yield, it is interesting to see that the experimental data obtained from both WSF and WIF broadly fit into one single broadly linear correlation when WSF or WIF is pyrolyzed individually. While the experimental data from bio-oil also fits into a broadly linear correlation, the gradient of the trend line is considerably steeper than that of the correlated line for the data from WSF and WIF. This clearly indicates that synergy between the WSF and WIF during fast pyrolysis in enhancing bed agglomeration.

8.5 Conclusions

This study investigates the bed agglomeration of bio-oil during fast pyrolysis in a fluidised-bed reactor at different temperatures. The results show that the agglomeration yield of bio-oil at 500 °C is as high as 40% and then decrease to 15% with temperature increase to 800 °C. Based on the studies of bed agglomeration of bio-oil fractions and model compounds, the interactions between lignin-derived oligomers and sugar is found to be responsible for bed agglomeration during bio-oil fast pyrolysis and the higher agglomeration yield of WSF (26.2–11.6%, 500–800 °C) compared to that of WIF (15.0–5.2%, 500–800 °C). Such interactions decrease with increasing temperature and become insignificant at 700 °C or higher. The studies of bed agglomeration of bio-oil fractions and model compounds also indicates the insignificant effect of water on bed agglomeration during pyrolysis of bio-oil or WSF. Bed agglomeration of bio-oil during fast pyrolysis also has broadly liner correlation with the formation of tar and coke in bed samples. The gradient of the trend line for the data from bio-oil is considerably steeper than that of the correlated line for WSF

and WIF which indicates that synergy between the WSF and WIF during fast pyrolysis in enhancing bed agglomeration.

Chapter 9 Conclusions and Recommendations

9.1 Introduction

This chapter concluded the significant discoveries of the present investigation. Overall, this thesis has described a series of systematic study on fuel properties and fast pyrolysis of bio-oil and its derived fuel mixtures. The bio-oil derived fuel mixtures employed in this experimental program include water-soluble fraction (WSF), G/methanol/bio-oil (GMB, G stands for glycerol) and CG/methanol/bio-oil (CGMB, CG stands for crude glycerol) blends, G/WSF (GWSF) and CG/WSF (CGWSF) blend, GMB/biochar (GMBB) and CGMB/biochar (CGMBB) slurries, and GWSF/biochar (GWSFB) and CGWSF/biochar (CGWSFB) slurries. Firstly, this study has explored the fuel properties and ageing of GMBB and CGMBB slurry fuels. Secondly, ignition behaviour of bio-oil and bio-oil based fuel mixtures were investigated via two methods, i.e. thermogravimetric analysis (TGA) method and an ASTM-based method. Thirdly, this thesis also has reported about the cold flow properties of bio-oil and its derived fuel mixtures determined by differential scanning calorimetry. Finally, fundamental understanding about bed agglomeration phenomenon during fast pyrolysis of bio-oil in a fluidised-bed reactor under different temperatures was achieved. Detailed findings from this PhD study and some recommendations for future work are listed below.

9.2 Conclusions

Conclusions are outlined based on the four targets of this thesis study which detailed below.

9.2.1 Fuel properties and ageing of glycerol/methanol/bio-oil/biochar and crude glycerol/methanol/bio-oil/biochar slurry fuels

- Biochar loading level plays an important role in the fuel properties of both GMBB and BB slurry fuels. With the biochar loading level increases, the water content and total acid number (referred to as TAN) of slurry fuels decrease while the viscosity increases.

- Compared to BB bioslurry, GMBB bioslurry have lower water content, viscosity and TAN due to the presence of both methanol and glycerol. The addition of methanol and glycerol also reduce the leaching of AAEM species from biochar into liquid phase.

- FCGMBB slurry fuels have equivalent to or even better fuel properties in comparison with GMBB slurry or FCGMB blend. This also proves the major impurities contained in FCG have little effect on the fuel properties of fuel samples.

- After ageing, the TAN and viscosity of both GMBB and FCGMBB slurry fuels decreased while the water content increased which can be attributed to the esterification, acetalization and/or polycondensation reactions.

9.2.2 Ignition temperatures of various bio-oil based fuel blends and slurry fuels

- The bio-oil and WSF are difficult to ignite with ignition temperatures being 506 °C and 511 °C respectively. This may attributed to the carbonaceous solid produced by cracking reactions at high temperature. WSF has a slightly

higher ignition temperature compare with bio-oil indicates water has negative effect on ignition.

- Slurry fuels containing CG have lower ignition temperatures than other slurry fuels due to the catalytic effect of sodium salt in CG on ignition.

- The ignition temperatures of slurry fuels are higher compared to their corresponding fuel blends due to the addition of biochar although it has an ignition temperature of 375 °C which is lower than that of blend fuels. This may because some fuel components evaporated before ignited during TGA analysis which resulted in more carbonaceous solid and less volatile.

- The ASTM-based method is dominated by ignition of vapour phase while the TGA method is dominated by ignition of solid residue after evaporation.

9.2.3 Differential scanning calorimetry studies on the cold flow properties of fuel mixtures from bio-oil, crude glycerol, methanol and/or biochar

- Bio-oil has a T_{MP} of 21.9 °C which is considerably lower than that of WSF with T_{MP} being 8.7 °C for the reason that WSF has a very high water content (61.6%). This indicates that both bio-oil and WSF have problems on direct utilization when the weather is cold and thus limited their applications.

- All components except water in FCGs decrease the T_{MP} of fuel samples due to solvent effect and their ability in reducing the T_{MP} follows the order of NaCl > NaOH > methanol > glycerol > soap.
- FCGMB and FCGWSF have much better cold flow properties than bio-oil and WSF respectively, due to the addition of FCG. Compare to FCGs, glycerol has better ability on improving cold flow properties of bio-oil based

fuels because the presence of water because water has negative effect in cold flow properties.

- Biochar particles in slurry fuels have very little effect on the cold flow behaviour of bio-oil based fuels, only lead to a decrease of barely 4 °C in the T_{MP} when biochar loading rate is 20%.

9.2.4 Bed agglomeration during bio-oil fast pyrolysis in a fluidised-bed reactor

- With the pyrolysis temperature increase from 500 to 800 °C, the bed agglomeration yield of bio-oil, WSF and WIF decrease from 40.0% to 15.0%, 26.2% to 11.6%, and 15.0% to 5.2%.

- Based on the investigations on bed agglomeration of both bio-oil fractions and model compounds, the high bed agglomeration yields of bio-oil and WSF are attributed to the interactions between sugar and lignin-derived oligomers. The results also show that such interactions weaken with pyrolysis temperature increase and water has insignificant effect on bed agglomeration during bio-oil or WSF fast pyrolysis.

- The bed agglomeration yield versus the tar (and/or coke) yield follows broad linear correlations. The gradients of the trend line for the data from WSF and WIF are gentler than that of the corresponding line for bio-oil which suggests the synergy effect between WSF and WIF on enhancing the bed agglomeration during fast pyrolysis.

9.3 Recommendations

Based on the outcome of this PhD project, recommendations for future work are listed below considering several research gaps:

1. This PhD thesis focuses on fuel properties of fuel blends and slurry fuels prepared from formulated CG and the effect of impurities in CG on fuel properties. However, industrial CG has more complex compositions than the formulated CG. Fuel properties of fuel mixture prepared from industrial CG need to be characterised. Cold flow behaviour and ignition behaviour of the prepared fuels also need to be investigated.

2. Limited by present experiment rigs, this study has characterised the cold flow properties by the DSC melting process with determination of melting point. Future works need to devise suitable experimental facilities for determining the pour point, cold filter plugging point or frozen point of the fuels.

3. Limited by time frame, this PhD research has not completed the study on bed agglomeration during bio-oil derived fuel mixtures in a fluidised-bed reactor. This can be an important research topic in future work, particularly considering the effect of impurities in CG and biochar on bed agglomeration.

4. Since fuel properties of bio-oil derived fuel mixtures meet the requirements for further combustion/gasification utilizations, future experimental research are also required for understanding the atomization and combustion/gasification behaviour of these fuel mixtures for practical applications.

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APPENDIX Ⅰ : ATTRIBUTION TABLES
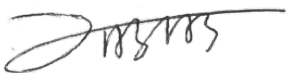
A. Fuel properties and ageing of bioslurry prepared from glycerol/methanol/bio-oil blend and biochar, <u>Wenran Gao; Mingming Zhang; Hongwei Wu*</u>, Fuel, 2016, 176, 72-77.

Authors and full affiliations:

	Conception and design	Experiments conduction & data acquisition	Data processing & analysis	Interpretation & discussion	Manuscript writing, revision and finalisation	Final Approval
Mingming Zhang	×			×	×	×
I acknowledge that these represent my contribution to the above research output. Sign:						
Hongwei Wu	×		×	×	×	×
I acknowledge that these represent my contribution to the above research output. Sign:						
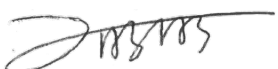
B. Ignition temperatures of various bio-oil based fuel blends and slurry fuels, Wenran Gao; Mingming Zhang; Hongwei Wu*, Fuel, 2017, 207, 240-243.

Authors and full affiliations:

	Conception and design	Experiments conduction & data acquisition	Data processing & analysis	Interpretation & discussion	Manuscript writing, revision and finalisation	Final Approval
Mingming Zhang	×			×	×	×
I acknowledge that these represent my contribution to the above research output. Sign:						
Hongwei Wu	×		×	×	×	×
I acknowledge that these represent my contribution to the above research output. Sign:						
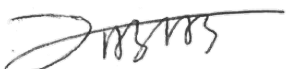
C. Differential scanning calorimetry studies on the cold flow properties of fuel mixtures from bio-oil, crude glycerol, methanol, and/or biochar, <u>Wenran Gao; Mingming Zhang; Hongwei Wu*</u>, Energy & Fuels, 2017, 31 (8), 8348-8355.

Authors and full affiliations:

	Conception and design	Experiments conduction & data acquisition	Data processing & analysis	Interpretation & discussion	Manuscript writing, revision and finalisation	Final Approval
Mingming Zhang	✕			✕	✕	✕
I acknowledge that these represent my contribution to the above research output. Sign:						
Hongwei Wu	✕		✕	✕	✕	✕
I acknowledge that these represent my contribution to the above research output. Sign:						

D. Bed Agglomeration during Bio-oil Fast Pyrolysis in a Fluidised-bed Reactor, Wenran Gao; Mingming Zhang; Hongwei Wu*, Energy & Fuels, 2018, 32 (3), 3608-3613.

Authors and full affiliations:

	Conception and design	Experiments conduction & data acquisition	Data processing & analysis	Interpretation & discussion	Manuscript writing, revision and finalisation	Final Approval
Mingming Zhang	×			×	×	×
I acknowledge that these represent my contribution to the above research output. Sign:						
Hongwei Wu	×		×	×	×	×
I acknowledge that these represent my contribution to the above research output. Sign:						

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