School of Chemical and Petroleum Engineering

Acid-catalysed Reactions of Bio-oil in Liquid Phase

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This thesis is presented for the Degree of
Doctor of Philosophy
of
Curtin University

November 2016

Declaration

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

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

Signature: ……..……

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Abstract

Bio-oil, the pyrolysis product of renewable biomass, is a promising and prospective energy source. However, the undesirable properties of bio-oil restrained its application. Bio-oil need to be upgraded to be used as transport fuels. Acid treatment of bio-oil is an effective way to upgrade bio-oil. The fundamental understanding on the acid-catalysed reactions occurring during bio-oil esterification is essential to optimise the upgrading process.

To understand the reaction network during bio-oil esterification, the composition especially the amount of the heavy carboxylic acids and the phenolics were analysed first. A potentiometric titration method was successfully developed to quantify the content of strong and weak acidic components in bio-oil, which included heavy carboxylic acids and heavy phenolics. Heavy carboxylic acids represented 29-45% (mol basis) of total carboxylic acids and heavy phenolics dominated the total phenolic compounds in bio-oil.

During the thermal treatment of bio-oil in methanol, more aromatics were formed, while water favoured the conversion/polymerisation of aromatics in bio-oil. Both the formation of small phenolics in methanol and the consumption of small phenolics in water were confirmed by GC-MS results. In addition, the effect of weak acids such as acetic acids and formic acid on the conversion of aromatics in bio-oil was negligible, due to the low acidity, while a strong solid acid catalyst such as Amberlyst 70 was proved to be able to catalyse the conversion of aromatics in bio-oil.

Under acid-treatment condition, the behaviours of bio-oil in alcohol, water and phenol were distinctly different. Abundant coke was formed in the acid-treatment of bio-oil in water, which doubled that in alcohol rich medium. The difference was attributed to the stabilization effect of alcohols towards the reactive components in bio-oil. With phenol as a solvent, the coke formation of bio-oil via acid treatment was also higher than that in alcohols. Phenol is involved in the polymerisation reactions. The acid

catalysts are the key factors to affect the acid-catalysed reactions of bio-oil. The different catalytic behaviour of solid acid catalyst and mineral acid catalyst towards the acid-treatment of bio-oil was subsequently investigated. The hydrogen ions in the mineral acid catalyst such as sulfuric acid homogeneously dispersed in the reaction medium made the conversion of main components of bio-oil occur more efficiently and faster, while the steric hindrance of solid acid catalyst such as Amberlyst 70 negatively affected the conversion of the components in bio-oil.

Acknowledgements

I would like to give my sincere acknowledgements to my supervisors, Professor Chun-Zhu Li and Dr Xun Hu, for providing me the precious opportunity for my research. Without their valuable guidance, inspiration and support, this work would not have been done. I would also like to thank all the academic staff, postdoctoral researchers, postgraduate students, technical and administrative staff at Fuels and Energy Technology Institute, Curtin University.

I gratefully acknowledge the financial support for my study from the following sources:

- Australian Government funding through the Second Generation Biofuels Research and Development Grant Program
- Government of Western Australia via the Centre for Research into Energy for Sustainable Transport (CREST)
- Commonwealth of Australia under the Australia-China Science and Research Fund

I also express my gratitude to my scholarship providers, Curtin University and China Scholarship Council.

To my family, this thesis is dedicated to you. My husband Shuai Wang and my daughter Anni Wang gave me their love and encourage throughout my study. My parents and parents in law have given their grateful help in many mays.

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Chapter 1

Introduction

1.1 Importance of bio-energy

Fossil fuels including petroleum, coal and natural gas have dominated the energy supply for the last two centuries [1-2]. However, the fossil fuels are depleting and the use of fossil fuels leads to adverse impact on environment such as the emission of CO2, SOx and NOx. The renewable and environmentally benign energy gains significant attention in recent years. Among various types of renewable energy sources, biomass receives particular attention [3-8]. Biomass is renewable, abundantly available and intrinsically carbon-neutral, which is also the only source of renewable carbon. Moreover, the high similarities with fossil fuels make biomass an ideal alternative feedstock for existing fossil-fuel-based energy industries. Developing advanced technologies to effectively convert biomass to bio-energy is essential to alleviate the dependence on traditional fuels and can finally benefit our society and environment.

Two types of biomass, food-related biomass and non-food biomass, are applied to produce bio-energy [4, 5]. The biofuels from food-related biomass is called first generation biofuels. Its application is limited by the fact that the consumption of food-related biomass for energy threatens the food supply in the world. Therefore, more attention is focused on the non-food biomass, which largely refers to lignocellulosic biomass. The second generation biofuels from lignocellulosic materials can avoid the concerns of first generation biofuels and has the potential to replace traditional fuels.

With this prospective potential, some technologies have been developed to convert biomass into various kinds of bio-energy products [9]. They can be summarised to two main pathways: biochemical and thermochemical routes. Compared with biochemical processing, thermochemical conversion has much more potential, because almost all the components of biomass feedstock can be transformed in this thermochemical process. Pyrolysis, gasification and combustion are three main approaches for the conversion of biomass into bio-energy products [10, 11].

1.2 Upgrading of bio-oil via esterification

Pyrolysis is a process to transform biomass into a dark brown liquid named as bio-oil, which can be upgraded to bio-fuels or fuel additives [12-13]. Although the composition of bio-oil varies with the feedstock and the conditions of pyrolysis, some undesirable properties are common in most bio-oil. For example, numerous oxygen-containing compounds in bio-oil create low heating value, high corrosiveness and high instability [14-16].

The complex composition of bio-oil makes it unstable and has high tendency to polymerise even under ambient conditions. During the storage of bio-oil, the polymerisation of bio-oil increases the viscosity and average molecular weight of bio-oil, creating many difficulties for the further upgrading of bio-oil. More importantly, heating bio-oil, which is almost involved in all the upgrading processing, accelerates the polymerization of bio-oil. During esterification, catalytic cracking and hydrotreating processing of bio-oil, effective catalysts are essential to facilitate the upgrading. However, coke formation is one of the main challenges for esterification of bio-oil, which can deactivate catalyst and increase the process cost.

The undesirable properties of bio-oil are directly related to the presence of a wide range of organics in bio-oil [17-20]. Among all the oxygen-containing organics in bio-oil, carboxylic acids received particular attention, as they are the origin of high acidity of bio-oil [21-22]. More importantly, carboxylic acids are catalysts for the polymerization of bio-oil [23]. The esterification of bio-oil with alcohols is an effective way to convert carboxylic acids to neutral esters. Since the cracking reaction of bio-oil dominates at elevated reaction temperature, esterification is usually conducted below 250^{o}C [24-25]. During esterification, not only carboxylic acids can be converted, many other compounds with different types of functional groups are also converted, leading to the significant changes in the composition of bio-oil [26]. Esterification is thus an important step to improve the property of bio-oil, making it more suitable for downstream hydrotreatment [26-30].

1.2.1 Methods for the esterification of bio-oil

Although bio-oil contains small amount of alcohols, which are not enough to esterify the carboxylic acids in bio-oil, external alcohols are required to carry out the esterification. After reaction, remaining excessive alcohols need to be removed from the product, e.g. via distillation [31-33]. However, other important light components could also be removed together with alcohols during distillation, which are essential fractions to maintain the flow properties of bio-oil. Another issue is that distillation is an energy-intensive process, which would increase the process cost.

In addition to the excessive alcohols, water is another issue, which is present in bio-oil and is also the product of esterification. The presence of water in bio-oil could shift the reaction equilibrium to the side of carboxylic acids. In order to improve the conversion of carboxylic acids in bio-oil, an effective way is to remove water from the system. Some researchers applied on-line extraction and distillation during the esterification of bio-oil to remove water from the system to enhance the conversion of carboxylic acids. Mahfud et al adopted a high boiling-point alcohol like n-butanol to perform the esterification with a solid acid by reactive distillation to upgrade bio-oil [32]. In order to avoid the polymerisation of bio-oil at elevated temperatures, a low reaction temperature of 50-80°C and reduced pressure under 10 kPa were set for the esterification. With water being continuously removed, the equilibrium was successfully driven to the ester side, resulting in a water content of less than 5 wt% in the product. Sundqvist et al also used n-butanol as the alcohol to perform the esterification and a hydrocarbon (n-heptane or petroleum ether) as entrainer for the simultaneous azeotropic distillation [31]. The final product has low total acid numbers from 5 to 10 mg KOH/g and pH values from 4.0 to 5.6. However, although via the simultaneous removal of water, the high conversion of carboxylic acids can be achieved, the whole process is not cost effective as the distillation of water and other components of bio-oil requires the input of considerable amount of energy.

Instead of distilling water, Zhang et al added olefin into the system to consume water via hydration [34-35]. The hydration of olefin also produces alcohols, which can be

used for the esterification reactions. However, external alcohols were still needed, because olefin cannot be dissolved into bio-oil effectively, which can cause mass transfer limitation. With adding external alcohols, such problem could be resolved and the conversion of olefins increased dramatically. After the upgrading of bio-oil, the pH value of the product increased to 3.0 and water content dropped to 7.5%, while calorific value increased to 30.0 MJ kg^{-1}. The above esterification process has the advantages of reducing the water content in the products. However, the problem of using olefin as an esterification agent is the low solubility of olefin in bio-oil, which leads to low reaction efficiency and severe polymer formation.

Upgrading bio-oil with super-critical alcohols was also investigated. Peng et al compared the difference between sub-critical and super-critical esterification over HZSM-5 catalyst [36-37]. The super-critical esterification of bio-oil was more effective to convert acids in raw bio-oil into corresponding esters and to remove heavy components of bio-oil by cracking reactions. By comparing the GC-MS results of upgraded and raw bio-oil, it was found that the contents of acids, aldehydes, phenols and ketones decreased. However, elevated reaction temperatures applied as part of the supercritical condition favoured the formation of ether, which consumed alcohols, produced water and volatile ethers. Using catalyst with low acidity can suppress the etherification, however, weak acid catalysts were also not effective for the esterification.

Some researchers also tried to couple esterification and hydrogenation together to convert acids and the compounds with unsaturated functional groups at the same time [38]. Hydrogenation can not only suppress the coke formation in alcohols at high reaction temperatures, but also can saturate carbonyl and aliphatic carbon-carbon double bonds, which contributes greatly to coke formation, increasing the stability of bio-oil [39]. The use of bifunctional catalysts is essential to catalyse both esterification and hydrogenation, which, however, can increase the process cost. Furthermore, the reaction network involved in the esterification coupled with hydrogenation are very complex.

1.2.2 Reaction behaviour of carboxylic acids during bio-oil esterification

Compared with conventional fuels, bio-oil contains considerable amount of carboxylic acids that are the origin of the high corrosiveness and instability, leading to difficulties during piping, storage and refining of bio-oil [24-28]. The esterification of bio-oil with alcohols is regarded as an effective method to remove or consume these acids. Generally, the efficiency of esterification depends on the reaction conditions, the structure of the acids and the selection of effective acid-treatment catalysts. Hu et al found that carboxylic acids with long carbon chain or with aromatic rings have low reactivity during the esterification of bio-oil [40]. Steric hindrance was found to be the main reason for the different reactivity. Amberlyst 70 used in that study is a solid acidic resin catalyst with hydrogen ions dispersed on the local surface. Although this type of resin catalyst can swell in alcohols, making hydrogen ions in the inner pores accessible, the hydrogen ions were still not homogeneously dispersed. Thus, the acids with short carbon chain can easily diffuse to the catalytic sites, resulting in high conversion, while acids with long carbon chains, branched carbon chain and aromatic rings were too big to access the small pores, leading to low conversion. However, all the results were based on the light compounds detected by GC-MS, the reaction pathways of the heavy components are still unknown.

1.2.3 Reaction behaviour of aldehydes and ketones during bio-oil esterification

Under the acid-treatment conditions, in addition to carboxylic acids, the transformation of other kinds of reactive components could also take place. Aldehydes can be stabilised by acetalisation to form acetals. However, acetals are not as stable as esters at elevated temperatures. They may decompose or react with other reactive components, contributing to the polymerization of bio-oil [41]. Ketones are also an important portion of bio-oil, which are reactive towards polymerisation. Hu et al found that hydroxyl acetone in bio-oil can cross-polymerise with phenolics to form more reactive compounds [23]. One example is the formation of 1-(4-hydroxyl-3-methoxyphenyl)-2-propanone from hydroxyl acetone and guaiacol. Both aldehydes and ketones contain carbonyl groups which are an important contributor to the

polymerization of bio-oil. Since carbonyl groups of aldehydes and ketones cannot be effectively converted to stable components, some harsh treatment conditions should be adopted such as hydrodeoxygenation and catalytic cracking to alleviate their involvement in the polymerization of bio-oil.

1.2.4 Reaction behaviour of sugars and sugar-derived components during bio-oil esterification

Sugars, products from the degradation of cellulose and hemi-cellulose in biomass, are important components in bio-oil. The structure of some big and complex sugars existing in bio-oil is still unknown. Levoglucosan is a typical and simple carbohydrate in bio-oil and can be detected by GC-MS. Therefore, the reaction behaviours of levoglucosan under the condition of esterification have been investigated by some researchers [42-44]. In water-rich medium, glucose and 5-hydroxymethylfurfural, a degradation intermediate of levoglucosan, had high tendency to polymerise. While, in methanol, levoglucosan was mainly converted to methyl α-D-glucopyranoside and subsequently to 2-dimethoxymethyl-5-methoxymethylfuran and finally to methyl levulinate with a high selectivity of ca. 95% [43]. The protection of the reactive functional groups of levoglucosan and furans can effectively inhibit polymer formation. Hu et al found that other sugars including glucose, dianhydro-D-glucopyranose, 1,6-anhydro-D-talopyranose, 2,3-anhydro-D-mannosan, 3,4-anhydro-D-galactosan and 1,4:3,6-dianhydro-α-D-glucopyranose could also be converted into methyl levulinate in the methanol-rich medium, as shown in Figure 1-1 [44]. The different reaction routes of sugars in water-rich and in alcohol-rich media made the difference in the selectivity of methyl levulinate. The conversion of the reactive sugars in alcohol-rich medium into the relatively stable levulinates contributes to the improvement of the stability of bio-oil.

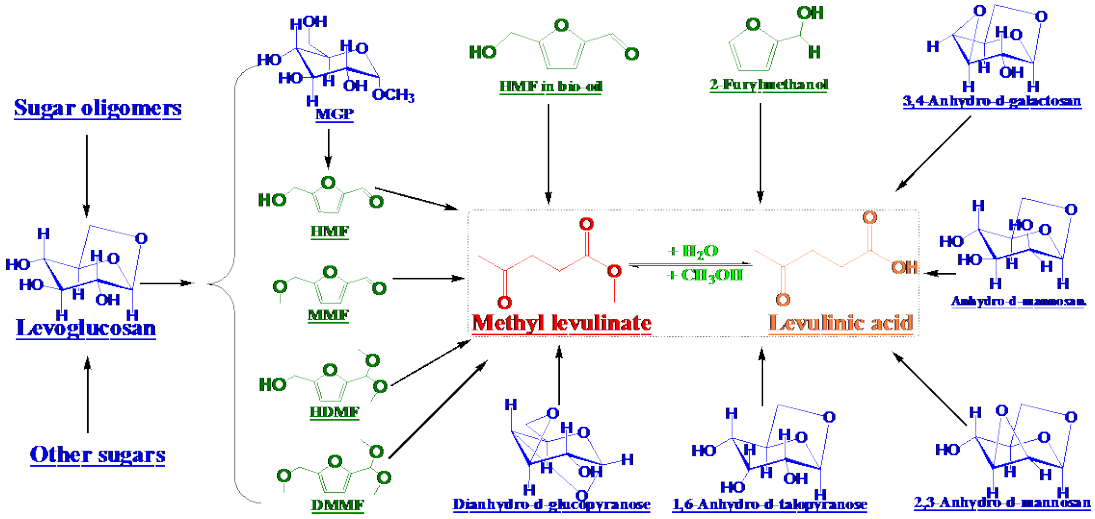

Figure 1-1. The reaction network for the formation of methyl levulinate in bio-oil esterification. Reprint from [44] with permission from the Royal Society of Chemistry.

Except from the simple sugars like glucose and levoglucosan, sugars with complex structure and high molecular masses also exist in bio-oil [45]. It is difficult to understand how these big sugars degrade under the conditions of esterification. Similar to heavy carboxylic acids, all the compounds with high molecular-mass encounter the steric hindrance during the acid-treatment of bio-oil over especially the solid acid catalyst.

1.2.5 Reaction behaviour of phenolics during bio-oil esterification

Phenolics are produced from the lignin in biomass, which is an abundant component in raw bio-oil. Light and simple phenolics can be detected by GC-MS, while heavy and complex phenolics with more than one aromatic rings and/or multiple functionalities cannot be identified by GC-MS. Hu et al found that the attached functional group on phenolics had a significant impact on the conversion of phenolics [46]. 4-vinylguaiacol and 3,4-dimethoxyacetophenone with carbon-carbon double bond and carbonyl functionalities were proved much more reactive than guaiacol with only hydroxyl group. However, the corresponding conversion products were not detected by GC-MS, therefore the detailed reaction pathways have not been fully

understood yet. One possible reaction route is polymerization, because the unsaturated functionalities made the aromatic rings more reactive towards polymerization [46].

1.2.6 Reaction behaviour of N-containing compounds during bio-oil esterification

N-containing compounds were identified in the bio-oil from mallee leaves, which can deactivate the catalysts during the upgrading of bio-oil [40]. Hu et al found that, compared with the high conversion of acetic acids in bio-oil produced from the pyrolysis of wood, almost no conversion of acetic acid in bio-oil produced from the pyrolysis of leaf were observed with low a loading level of Amberlyst 70 (3 wt.%). Under such low catalyst loading level, all acidic sites in the catalyst reacted with the N-containing compounds and deactivated. Therefore, with high catalyst loading, a part of the added catalysts was used to react with the N-containing compounds and were deactivated. The remaining can catalyse the reaction of bio-oil with methanol. The deactivated catalysts can be partially regenerated via ion exchange in sulphuric acids, while this method is not cost-effective

1.3 Purpose of this study

Bio-oil is a promising feedstock for the production of biofuels and fine chemicals. Bio-oil needs to be upgraded because of some undesirable properties such as high corrosiveness, low heating value and thermal instability. The acidity of bio-oil is because of the presence of abundant carboxylic acids and phenolics. However, the current analytical techniques cannot give accurate data about them, for example, GC-MS can only detect some light components of bio-oil. Titration can provide accurate information about acidities of petroleum products. However, directly applying the standard method ASTM D664 to analyse the acidic components in bio-oil cannot detect the weak acidities such as phenolics in bio-oil. The solvent used in ASTM D664 is comprised of 50% toluene, 49.5% isopropanol and 0.5% water. First of all, water should be avoided for the titration of weak acidities. Secondly, toluene cannot dissolve bio-oil well. Finally, isopropanol cannot guarantee for the slope point to be recognized. Therefore, a suitable solvent should be designed for the non-aqueous titration of bio-

oil. In addition, the titrant of ASTM D664 is potassium hydroxide, which is not suitable for the measuring glass electrodes [47]. Thus, a reliable non-aqueous titration method should be developed to analyse the acidities of bio-oil.

The large amount of oxygen-containing compounds caused the thermal instability of bio-oil. Bio-oil can be upgraded by esterification or hydrogenation. For these two upgrading technologies, the thermal treatment of bio-oil is involved. Understanding how some reactive components like aromatics behave during the thermal treatment of bio-oil is essential for developing advanced upgrading processes. During the esterification of bio-oil, it was found [43] that the solvent used during the heating up of bio-oil can drastically affect the behaviour of bio-oil. Figuring out the effects of different solvents on the reactive components of bio-oil can also provide vital information for optimising the reaction conditions for the upgrading of bio-oil. Therefore, this study also aims to investigate the reaction behaviour of different components in bio-oil in alcohol-rich or water-rich media under various experimental conditions.

Polymerisation reactions and coke formation reactions take place during the thermal treatment and acid-treatment of bio-oil, which could deactivate catalysts and block reactors, increasing the cost of bio-oil upgrading [48]. Under the acid-treatment conditions, the overall reaction network is rather complex. A full understanding of the reaction routes of the main components of bio-oil during esterification is essential to evaluate the effects of esterification on the composition of bio-oil. Two main kinds of acids, mineral acids and solid acid catalysts, have been used to catalyse the esterification of bio-oil [49-51]. Compared with the limited dispersion of hydrogen ions for solid acid catalysts such as Amberlyst 70, the mineral acids can spread the hydrogen ions homogeneously in bio-oil. Moreover, mineral acids are hard to get deactivated. However, the mineral acids are difficult to be separated from the products. The remarkable difference between the two kinds of acids can cause different effects on the esterification of bio-oil, which need to be investigated. In addition, the investigation of the formation of coke was also one central topic in this study as coke formation is one of the biggest challenges for the upgrading of bio-oil.

1.4 Scope of thesis

Chapter 2 describes the experimental procedures including the production of pyrolysis bio-oil, acid treatment reactions of bio-oil in an autoclave and techniques used to characterise the feedstock and the products.

Chapter 3 developes a potentiometric titration method to successfully quantify the strong organic acids such as carboxylic acids and weak acidities like phenolics in bio-oil. This provides a better understanding about the acidic functionalities in bio-oil.

Chapter 4 is mainly focused on coke formation during the acid-catalysed processing of bio-oil with different alcohols. Under acid-catalysed condition, water can promote coke formation, while alcohols can stabilise bio-oil.

Chapter 5 is devoted to the discussion on the effects of water and methanol as a solvent of bio-oil on the behaviour of aromatics in bio-oil during the thermal treatment processing.

Chapter 6 investigates different catalytic behaviours of a mineral acid and a solid acid catalyst during the esterification of bio-oil. The dispersion of hydrogen ions of catalysts can affect the behaviour of different components in bio-oil.

Chapter 7 summarises the main conclusions of this study and present the recommendations for future work.

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Chapter 2

Experimental Methods

2.1 Introduction

The reactor and operating procedures for carrying out this study are detailed in this chapter. The methods used to characterise bio-oil and products are also described.

2.2 Sample preparation

The bio-oils used in this study were prepared by a fluidised-bed reactor or a grinding pyrolysis reactor. The detailed procedures for producing bio-oils with the two reactors were described elsewhere [1-4]. The bio-oil sample produced from the pyrolysis of wood was prepared by Dr Manuel Garcia-Perez with the fluidised-bed reactor using the wood fraction of mallee eucalyptus loxophleba. The bio-oil produced from the pyrolysis of bark was prepared by Dr Daniel Mourant with the fluidised-bed reactor using the bark fraction of mallee eucalyptus loxophleba. The bio-oil sample produced from the pyrolysis of leaf was prepared by Dr Min He with the fluidised-bed reactor using the leaf fraction of mallee eucalyptus loxophleba.

Briefly, for fluidised-bed pyrolysis, nitrogen was needed for fluidising the silica sand bed at a velocity around twice the minimum fluidisation velocity. The feeding rate was controlled at around 1 kg/h and the reaction temperature varied from 350 to 600°C. About 1.0 kg of biomass was fed per run. Heating tapes were installed outside the walls of the reactor to supply heat to the reactor system. Two cyclones maintained at 420°C were used to separate the char particles from volatiles. The produced bio-oil vapours were condensed in a series of condensers. The first one was a jacketed tubular condenser with a cooling water coil, reducing the temperature from 420°C to nearly room temperature. The second condenser applied dry ice to cool aerosols to around -8°C. Most of the remaining aerosols were trapped by an aerosol filter. The produced bio-oil samples were stored in a freezer until being used in this study.

The grinding pyrolysis bio-oil sample was prepared by Dr MD Mahmudul Hasan with the grinding pyrolysis reactor with mallee woody biomass. The bio-oil sample in this study was prepared at 450°C with a rotation rate of 54 rpm. For grinding pyrolysis,

steel balls inside the reactor were used to crush biomass and also heat the biomass. The out layer of biomass was firstly converted into volatiles and biochar, and then steel balls within the rotating reactor ground and removed the produced char layer from the surface of biomass and the pyrolysis process continued. Two tandem cyclones were used to separate the solid char with vapours. After separation, the vapours were condensed in condensers cooled by water and dry ice in sequence. After condensation, some very fine particles mixed in the liquid bio-oil was filtered by filtration paper (average retention capacity of 1-2 μm). The final brown liquid named bio-oil was stored in a freezer before the use in the upgrading experiments. Compared with fluidised-bed pyrolysis, the grinding pyrolysis process does not need a high flow rate of carrier gas. Moreover, it does not have specific requirements for the supplied particle size of biomass and suits various biomass types.

2.3 Acid-catalysed reactions of bio-oil with alcohols

The acid-catalysed reactions of bio-oil were carried out in an EZE-seal stirred autoclave reactor system. It consisted of a 100 ml EZE-seal pressure reactor vessel, a high speed stirring device MAG075, a body lift mechanism, a ceramic band heater and a universal reactor controller. The reactor vessel was made of Hastelloy. On the reactor head, the fittings and valves were available for gas and liquid sample ports, cooling water inlet and outlet ports, a reactor gas inlet and a release system. A pressure gauge was installed on the reactor head to monitor the reactor pressure. Because of safety reasons, a rupture disc was used to limit the pressure in the reactor. The water cooling jacket was installed between the reactor head and the magnetic drive to cool down the reactor head. A thermowell was installed to measure the temperature inside the reactor. The reactor was designed to work at a maximum working pressure of 3300 psig/227 bar and a maximum reaction temperature of 850^{o}F/454 ^{o}C.

Generally, the experiments were conducted by the following procedure. Bio-oil and alcohol (or water) together with catalyst were charged into the 100 ml vessel at a chosen ratio The autoclave was then assembled and sealed. Nitrogen was used repetitively to evacuate air inside the autoclave. The autoclave was then heated to the

desired temperature at around 10ºC/min and at a stirring rate of 500 rpm. The selection of the stirring rate was based on our previous experience that, with the stirring rate of over 300 rpm, the mass transfer limitation could be minimised [5]. The initial pressure of the autoclave was set as 1 bar, while the final pressure depended on the vapour pressure of the reactants and reaction temperature. For some experiments, sampling was done to investigate the progress of the experiments. Reaction time of 0 minute meant the time when the reaction temperature just reached the required value, and a sample was taken immediately. After that, sampling was conducted at 20 min interval for 120 min. No sampling was taken during experiments for the quantification of coke.

The coke formed in experiments might be suspended in the liquid product, deposited on the surface of the solid catalyst or in the pores of the solid catalyst. It was difficult to separate the coke on/in the catalyst from the solid catalyst. Thus, the reacted catalysts were filtered and the mixed solution of methanol and chloroform at the volume ratio of 1 to 4 was used to wash the residue on the filtration paper until the filtrate was clear. The residue was then transferred into an aluminium foil and dried in an oven at 105ºC for four hours to obtain a constant weight. The fresh catalyst was also filtered and washed using the same procedure. In this case, the amount of coke in the experiment can be obtained by subtracting the fresh catalyst weight from the reacted catalyst weight.

2.4 Titration of bio-oil

A combination electrode with a high response rate was specially designed for non-aqueous potentiometric titration [6]. Automatic potentiometric titration instrument (Titroline Alpha 20 plus) with a resolution of 0.01 ml and a measuring electrode and reference Ag/AgCl electrode was used for non-aqueous titration [5]. Experiments were performed at room temperature. The titration method was programed for this study with the following parameters: measurement interval (2 s), delta mv/second (10), minimum time (3 s) and maximum time (12 s).

Each sample was titrated for at least 3 times to obtain results with good reproducibility. The titrant used was tetramethylammonium hydroxide (TMAH) dissolved in a mixture of methanol and isopropanol at a volume ratio of 1:10. The pure TMAH was unstable and was usually concentrated in water or methanol. Thus, 25 wt% TMAH in methanol was purchased from Sigma-Aldrich and was diluted with isopropanol to an accurate known concentration. The selection of isopropanol was based on the fact that isopropanol was less acidic than that of primary alcohols. The exact concentration of titrant applied in each titration was calibrated using potassium hydrogen phthalate with the known concentration. The solvent used to dissolve samples was acetone and tert-butanol at a volume ratio of 1:9. This solvent mixture can effectively avoid the levelling effect and obtain distinguishable endpoints. The detailed advantages of this solvent are discussed in Chapter 3.

The experimental number of hydrogen ion (n) produced during the neutralization reaction of model compounds was calculated using the following equation.

$$n = \frac{C_b V_b}{M_o} \quad (2\text{-}1)$$

C_b: the concentration of TMAH (mol/L).
V_b: the volume of titrant used at the corresponding stoichiometric point (ml).
M_0: the mass of model compounds (g).
The yields of acidic components in this study were defined as millimols of hydroxyl ion (y) consumed in the neutralisation reaction with acidic compounds per gram of biomass (on the dry basis of biomass), as is illustrated in the following equation:

$$y = \frac{C_b V_b}{M_1} Y \quad (2\text{-}2)$$

C_b: the concentration of TMAH (mol/L).
V_b: the volume of titrant used at the corresponding stoichiometric point (ml).
M_1: bio-oil mass (g).
Y: the yield of bio-oil on dry basis of biomass.

A typical titration curves is shown in Figure 2-1. Since it was not easy to get the accurate stoichiometric point on the titration curve, the derivative curve was applied. Each peak on the derivative curve related to a corresponding end point.

The amount of total carboxylic acids in a bio-oil sample can be quantified by this titration method. The amount of light carboxylic acids including acetic acid, propanoic acid, butanoic acid and levulinic acid can be quantified by GC-MS. Thus, the amount of heavy carboxylic acids in bio-oil was determined by subtracting the amount of light carboxylic acids from the amount of total carboxylic acids. The amount of heavy phenolics was determined in the same way.

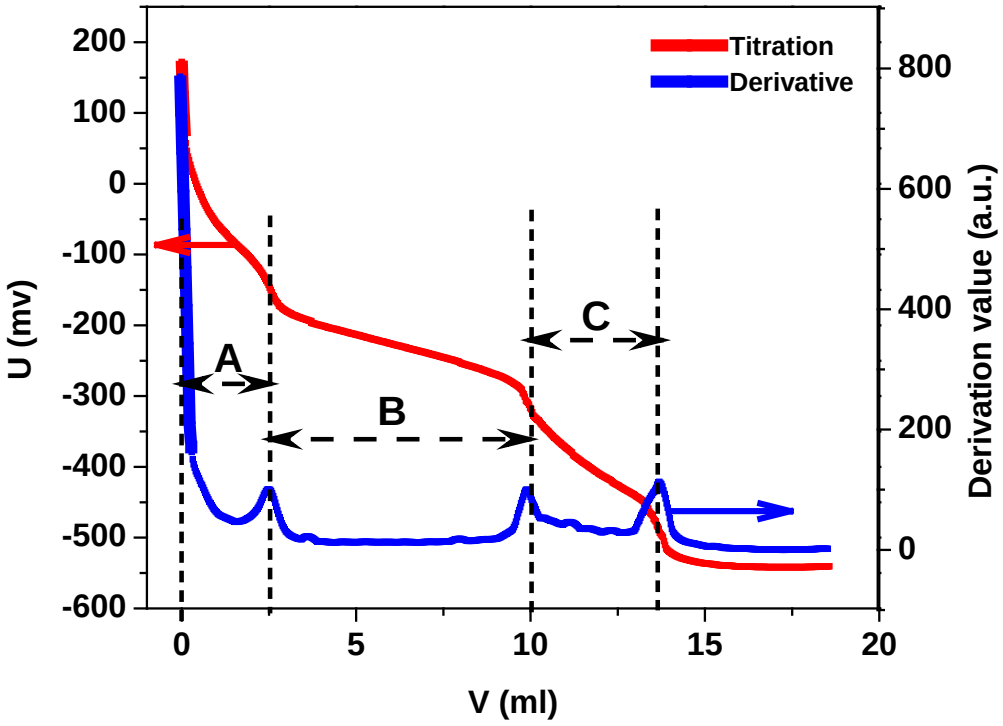

Figure 2-1. A typical titration curve of wood bio-oil produced at 500 °C. The titrant was TMAH and the solvent to dissolve bio-oil was acetone and tert-butanol at a volume ratio of 1:9. Reprint from [6] with permission from Elsevier.

2.5 Characterisation

2.5.1 GC-MS analysis

The bio-oil and esterification products were dissolved in tetrahydrofuran at a concentration of ca. 10 wt% (accurately known) for GC-MS analysis. This GC-MS (HP6890 GC and HP5973 MS) was equipped with an HP-INNOWAX capillary column having a length of 30 meters, a diameter of 0.25 millimeters and a film thickness of 0.25 micrometers [7]. The carrier gas was helium at a flow rate of 3.0 ml/min. For the analysis of a typical sample, a total of 1 µl of sample was injected into the injection port set at 250°C at a split ratio of 50:1. The temperature of the column was kept at 40°C for 1.6 minutes with helium as carrier gas. The temperature of the column increased from 40 to 260 °C at a heating rate of 10°C/min and was held for 7 minutes at 260°C

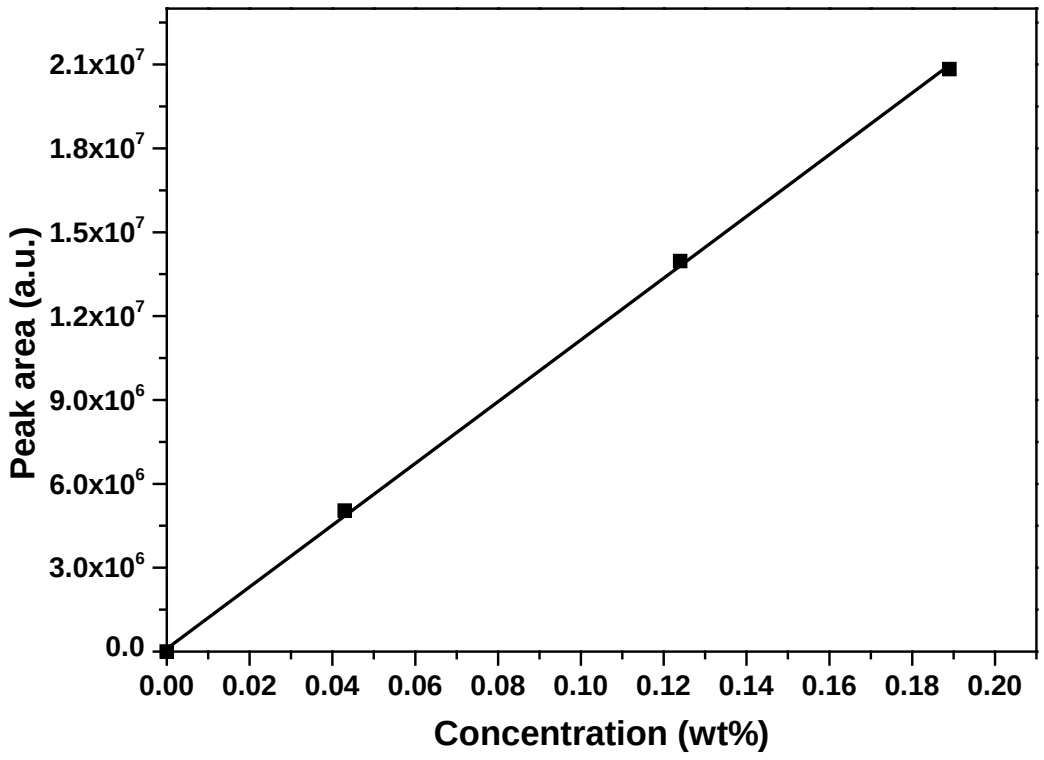

Figure 2-2. The calibration curve of guaiacol in tetrahydrofuran.

The identification of each compound was based on the comparison of its mass spectrum with data from the National Institute of Standards and Technology (NIST) [8, 9]. Standards were injected when available to confirm the identification of the compound and also the quantification. At the meantime, the calibration curve of the standards was also obtained by injecting standards with different concentrations. A typical calibration curve is shown in Figure 2-2. It was impossible to get standards for all the compounds. In this case, peak abundance was used to reflect the changes of the concentration of a compound.

The conversion of typical compound was as defined as follows (mol basis):

$$\text{Conversion } (\%) = \left(1 - \frac{M_1}{M_o}\right) \times 100\% \qquad (2\text{-}3)$$

M_1: amount of target compound in product
Mo: amount of target compound loaded in reactor

2.5.2 UV-fluorescence spectroscopy

UV-fluorescence spectroscopy can be used to characterise aromatic structure in the products [10-12]. Generally, a sample was firstly diluted with a mixture of methanol and chloroform at a volumetric ratio of 1 to 4. The solution was then diluted again with methanol. Different concentration was applied for different groups of sample. The principle of determining suitable concentration was to make sure the fluorescence intensity and the concentration were in linear relationship. One example is shown in Figure 2-3. The fluorescence intensity of the peak at 330 nm and the concentration of bio-oil are in linear relationship.

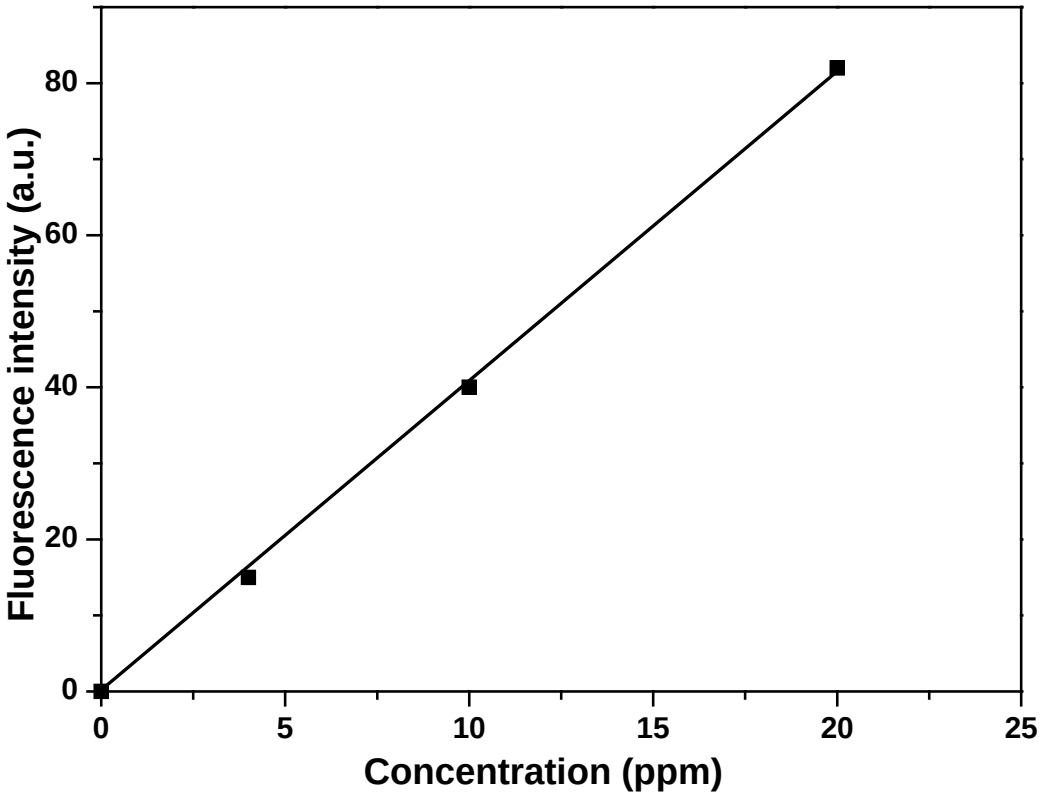

Figure 2-3. The relationship between fluorescence intensity of the peak at 330 nm and the concentration of grinding bio-oil.

In this study, a Perkin-Elmer LS50B spectrometer was used to analyse liquid samples. Briefly, a sample were loaded into a specific cell made of quartz, and then was placed into the chamber for analysis. The synchronous spectrum was recorded using a constant energy difference of 2800 cm^{-1} with a slit width of 2.5 nm and a scan speed of 200 nm/min. The spectra shown in this study represented the average of four scans. The wavelength can briefly reflect the aromatic ring size and abundance of the conjugated π bond in the sample. In general, compounds with big π-conjugated structures appeared at long wavelength.

2.5.3 FT-IR spectroscopy

A PerkinElmer spectrum GX FT-IR/Raman spectrometer was used to characterise both liquid samples and solid samples [13, 14]. The spectral resolution was 4 cm^{-1} and each sample was scanned for 10 times to get an average result. The liquid sample was

loaded into a sample cell, which consists of two pieces of CaF_2 windows, a 0.05 mm Teflon spacer and a 0.025 mm lead spacer in between the two windows. The solid sample was mixed with KBr at a concentration of 10 wt% and was grounded for 20 minutes. 0.1 gram sample was taken and made to be a flat pallet for analysis. Baseline correction was done manually by selecting several typical points. The spectra of C=C of aromatic ring and C=O functionalities in the range of 1800-1500 cm^{-1} can be deconvoluted by a curve fitting program (Galactic Grams 32) [13]. The nine Gaussian bands represented nine groups (Table 2-1) of compounds with C=C/C=O [13].

Table 2-1. A summary of peak/band assignments. Reprint from [13] with permission from Elsevier.

Band position (cm^{-1})	Width (cm^{-1})	Functional groups	Typical structures
1767	60	C=O stretching vibration	Lactones
1740	40	C=O stretching vibration	Unconjugated alkyl aldehydes and alkyl esters
1713	35	C=O stretching vibration	Carboxylic acids (and fatty acids)
1696	80	C=O stretching vibration	Unsaturated aldehydes, ketones
1654	70	C=O stretching vibration	Hydroxy unsaturated ketones, aldehydes
1606	95	Aromatic C=C ring breathing	Aromatics with various types of substitution
1565	75	Aromatic C=C ring breathing	Aromatics with various types of substitution
1517	20	Aromatic C=C ring breathing	Aromatics with various types of substitution
1501	20	Aromatic C=C ring breathing	Aromatics with various types of substitution

2.5.4 Thermogravimetric analysis

The potential coke yield refers to the residue after thermal treatment in the thermogravimetric analyser (PerkinElmer Pyris 1 TGA) under nitrogen atmosphere at 500°C. Generally, a sample of 10-20 mg was added into a crucible and weighed accurately in the instrument chamber. The temperature was then increased to 500°C at a heating rate of 10°C/min under nitrogen (100 ml/min). The temperature was held for 10 minutes at 500°C. The residue was defined as potential coke.

The potential coke was calculated as follows:

$$\text{Potential coke yield (\%)} = \frac{\text{mass of residue}}{\text{mass of sample}} \times 100\% \quad (2\text{-}4)$$

2.5.5 Elemental analysis

A ThermoScientific Flash 2000 CHNS/O analyser was used in this study to acquire elemental composition. The ash yield of raw bio-oil or thermal treatment products of bio-oil and solvents is zero. The C, H and N elements in the samples (wet basis) were determined directly while the oxygen (wet basis) content can be calculated by difference. The corresponding C, H, N and O on dry basis can be calculated as follows:

$$\mathrm{C_{dry\ basis}\ (wt\%)} = \frac{\mathrm{C_{wet\ basis}\ (wt\%)}}{100-\text{water content(wt\%)}} \times 100 \quad (2\text{-}5)$$

$$\mathrm{N_{dry\ basis}(wt\%)} = \frac{\mathrm{N_{wet\ basis}\ (wt\%)}}{100-\text{water content(wt\%)}} \times 100 \quad (2\text{-}6)$$

$$\mathrm{H_{dry\ basis}(wt\%)} = \frac{\mathrm{H_{wet\ basis}(wt\%)} - \frac{2}{18} * \text{Water content (wt\%)}}{100-\text{water content(wt\%)}} \times 100 \quad (2\text{-}7)$$

$$\mathrm{O_{dry\ basis}\ (wt\%)} = 100 - \mathrm{C_{dry\ basis}\ (wt\%)} - \mathrm{N_{dry\ basis}(wt\%)} - \mathrm{H_{dry\ basis}\ (wt\%)} \quad (2\text{-}8)$$

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Chapter 3

Quantification of Strong and Weak Acidities in Bio-oil via Non-aqueous Potentiometric Titration

3.1 Introduction

Bio-oil produced from renewable biomass has many potential applications such as the feedstock for production of value-added chemicals and bio-fuels [1-3]. However, bio-oil has many undesirable properties such as corrosiveness and high tendency to polymerisation, resulting from the abundance of organics in bio-oil including acids, aldehydes, ketones and oligomers [4-10]. Among these organics the acidic compounds such as carboxylic acid and phenolics deserve special attention as they are the origin of the corrosiveness of bio-oil and catalysts for polymerisation reactions [11-14].

Several analytical approaches have been applied to quantify acids and phenolic groups in bio-oil. For example, GC-MS can detect the volatile compounds, which accounts for 25-40 wt.% of the compounds in bio-oil [15-16], but not the large ones. Fourier transform infrared spectroscopy (FT-IR) can give the information about functional groups like carbonyls [17], while the details about the complex phenolics are not easy to obtain as a result of various substitutions. Thus, an analytic technique specially focusing on heavy acidic components in bio-oil has to be developed.

Titration is a reliable method for precisely quantifying acids with different strengths. Potentiometric titration has been applied to the acidity test of petroleum products using standard procedures such as American Society for Testing and Materials (ASTM D664). However, when directly applying ASTM D664 to analyse a bio-oil, some significant problems would be encountered.

The solvent used in ASTM D664 is a mixture of 50% toluene, 49.5% isopropanol and 0.5% water, which is not suitable for bio-oil titration for several reasons. The first one is that toluene is not a good solvent to dissolve bio-oil as there are many polar components such as water and acids in bio-oil.

The second one is that the acidity of isopropanol is not low enough to guarantee the weak acids such as phenol can be sensitively quantified. The reason is that the concentration of solvent is much higher than that of reactants, and the acidic solvent

will reverse the reaction near the stoichiometric point. As a consequence, the extremely weak acid cannot be titrated with a visible inflection point.

The third one is that water can compete effectively with very weak acidic compounds to donate proton. That is to say, water with pH scale of 0 to 14 can narrow the potential scale, resulting in the inflection in the titration curves for very weak acids small and endpoint detection relatively more difficult.

The fourth one is that the titrant of ASTM D664 (potassium hydroxide) is not good for the measuring glass electrodes. Most of potassium salts produced in the titration is usually insoluble in organic solvents, and the gelatinous precipitates would significantly reduce the sensitivity of the electrode. The sensitive part of the combined electrode is the ground porous membrane, so the precipitate of sodium salts will affect the precision of the glass electrode. Moreover, potassium ions can complete with hydrogen ions when the solvent pH is quite high. Thus, the presence of alkali metal ions is not favourable for detecting compounds having weak dissociation ability [18]. Therefore, a non-aqueous titration method which is special designed for analysis of the acidic components in bio-oil has to be developed. In this chapter, a titration method using quarternary ammonium hydroxide as titrant and a mixture of tert-butanol and acetone as solvent has been developed. The method overcomes the problems encountered in the ASTM D664 and can successfully quantify the concentrations of strong and weak acidities in the bio-oils from the pyrolysis of mallee biomasses.

3.2 Experimental

3.2.1 Preparation of bio-oil sample

In this study, three types of bio-oil were used. The wood bio-oil was produced by Dr Manuel Garcia-Perez with the fluidised-bed reactor from the mallee wood fraction. The bark bio-oil was produced by Dr Daniel Mourant with the fluidised-bed reactor from the mallee bark fraction. The leaf bio-oil was produced by Dr Min He with the

fluidised-bed reactor from mallee leaf fraction. The details of the fluidised-bed reactor and pyrolysis procedure can be found in Section 2.2, **Chapter 2**.

3.2.2 Titration of bio-oil

The non-aqueous potentiometric titration was applied in this study. The instrument (Titroline Alpha 20 plus) equipped with a combined electrode was used to quantify the acidic components in bio-oil. Tetramethylammonium hydroxide was chosen as titrant. The mixture of acetone and tert-butanol at a volume ratio of 1:9 was used as solvent to dissolve bio-oil, which can guarantee distinguishable endpoints to differentiate acidic components in bio-oil. A detailed description of the titration equipment and titration procedure can be found in Section 2.4, **Chapter 2.**

3.3 Results and discussion

3.3.1 Comparison of the titration method developed in this study with the ASTM D664 method

Considering the significant differences between bio-oils and petroleum oils, the standard method used in petroleum products cannot always be directly applied to bio-oil [23]. Compared with petroleum products, bio-oil contains more phenolic compounds with pKa around 10 (in water). However, as the ASTM D664 states, it was only applicable for the determination of the acids with a pKa lower than 9. So the ASTM D664 cannot be used to measure bio-oil having large amounts of phenolic compounds. The ASTM D664 method and our method were used to measure typical wood bio-oils. As shown in Figure 3-1a, only one inflection point of carboxylic acids was obtained when following ASTM D664, while Figure 3-1b indicated that three inflection points can be obtained with the method herein proposed. In this method, the mixture of tert-butanol and acetone was used to dissolve bio-oil, and the potassium hydroxide recommended by ASTM D664 was replaced with an organic base of tetramethylammonium hydroxide, which are the keys for the sensitivity of this method.

Choosing solvent in non-aqueous titration was vital to avoid levelling effect and obtain distinguishable endpoint. The use of the mixture of tert-butanol and acetone as solvent was based on several considerations. Firstly, the mixture of tert-butanol and acetone can dissolve bio-oils very well and provide a non-aqueous system for titration.

Secondly, tert-butanol has a fairly high dielectric constant (ξ=12) and good solvating ability for bio-oil. A high dielectric constant ensures the steady potential readings. Good solvating ability of tert-butanol prevents the occurrence of homoconjugation during the titration of acids. In solvents with good solvating properties, solutes interact with the solvent instead of undergoing self-condensation, and homoconjugation does not occur.

Finally, tert-butanol has a quite small autoprotolysis constant ($k_a=10^{-22}$) exhibiting a wide potential range and providing a good opportunity for differentiating titrations of mixtures of acids of different acidities. The potential of a glass electrode is given by the equation (25 °C), E = K + 0.059pH, where K is a constant including the asymmetry potential. One unit change of pH will cause a change in E of 59 mv. A wider pH scale will bring a corresponding wider millivolts range, while the pH scale is determined by the autoprotolysis constant. The autoprotolysis constant of water at 25 °C is 10^{-14}, so its pH scale is 14. While the autoprotolysis constant of tert-butanol is much smaller than water, the pH scale of tert-butanol is bigger than 14. Therefore, solvents with a small autoprotolysis constant will facilitate a good separation of mixtures of acids in the titration curve.

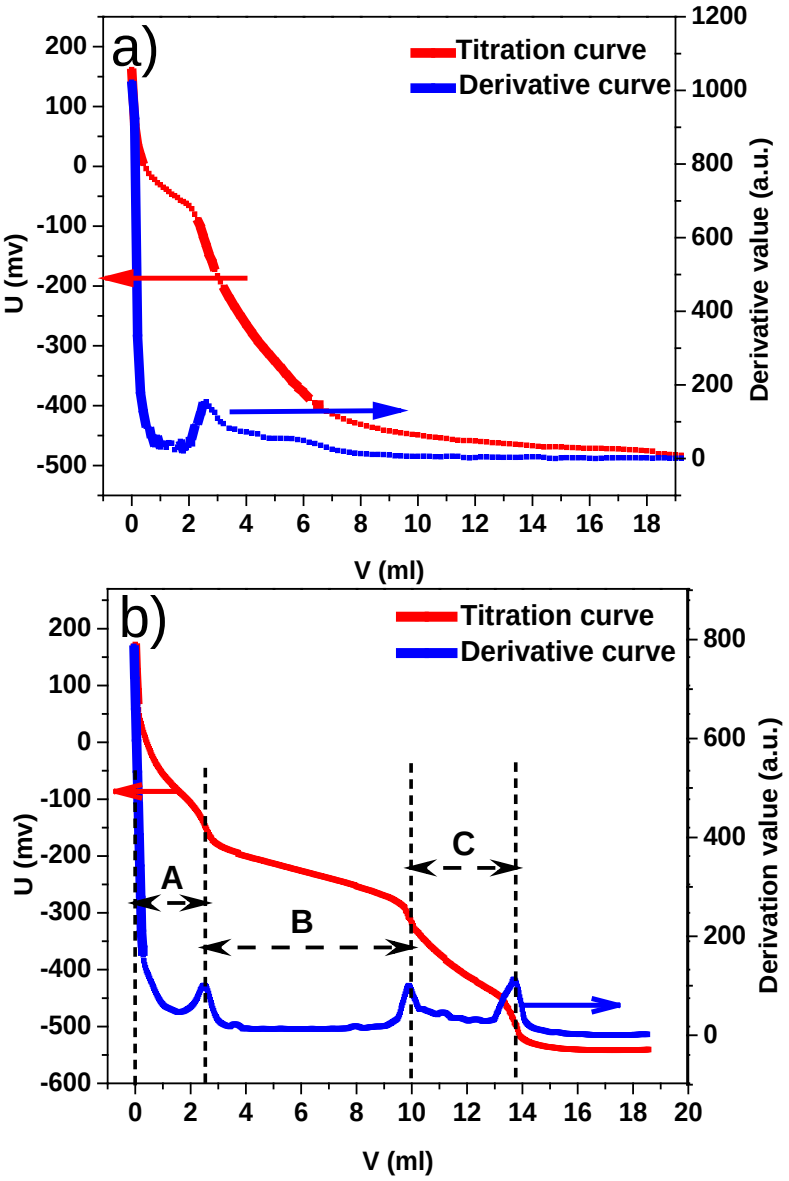

Figure 3-1. Typical titration curves of wood bio-oil produced at 500 °C. (a) The titrant is sodium hydroxide and the solvent is a mixture of 50% toluene, 49.5% isopropanol and 0.5% water. (b) The titrant is TMAH and the solvent is acetone and tert-butanol with a volume ratio of 1:9.

3.3.2 Quantification of the compounds in bio-oil

To demonstrate the validity of our non-aqueous titration technique, the titration of acetic acid and phenol, two main kinds of acidic compounds in the bio-oil, was conducted in the mixed non-aqueous medium which is the same as that used in the titration of bio-oils. Figure 3-2 showed the titration curve of the mixture of acetic acid and phenol. Two distinguishable inflection points were identified. With adding titrant, the acids with relative big dissociation constants were neutralised firstly, followed by the acidic compounds with relative small dissociation constants. Theoretically, every gram of acetic acid will produce 16.67 millimol of hydrogen ion during titration, calculated by equation (1), which is in a good agreement with experimental result, 16.44 millimol. The experimental acid number of phenol is also quite close to the theoretical one. The isolation effect of target compounds was remarkable with two different voltage ranges. Our titration method is sensitive and reliable to identify and distinguish acetic acid and phenol.

3.3.3 Assignment of peaks in the titration curves of typical wood bio-oil

A typical titration curve of wood bio-oil was presented in Figure 3-1b with three distinguishable inflection points obtained. The derivative curve was also presented to facilitate the identification of every inflection point. The volume of consumed base on X-axis from the start to first peak is defined as group A, while that from the first peak to the second peak was assigned as group B, and that from the second peak to the third peak was defined as group C.

In order to understand what kind of compounds are responsible for each peak, the standard substances were quantitatively added into bio-oil samples. In the titration experiment with a measured amount of acetic acids added (Figure 3-3a), the first peak shifted to the expected position (from 2.5 ml in Figure 3-1b to 3.2 ml in Figure 3-3a on X-axis), while the volume of consumed base on X-axis of group B and C did not change. Therefore, group A was confirmed as carboxylic acids, with pK_a of 3.5-5.0.

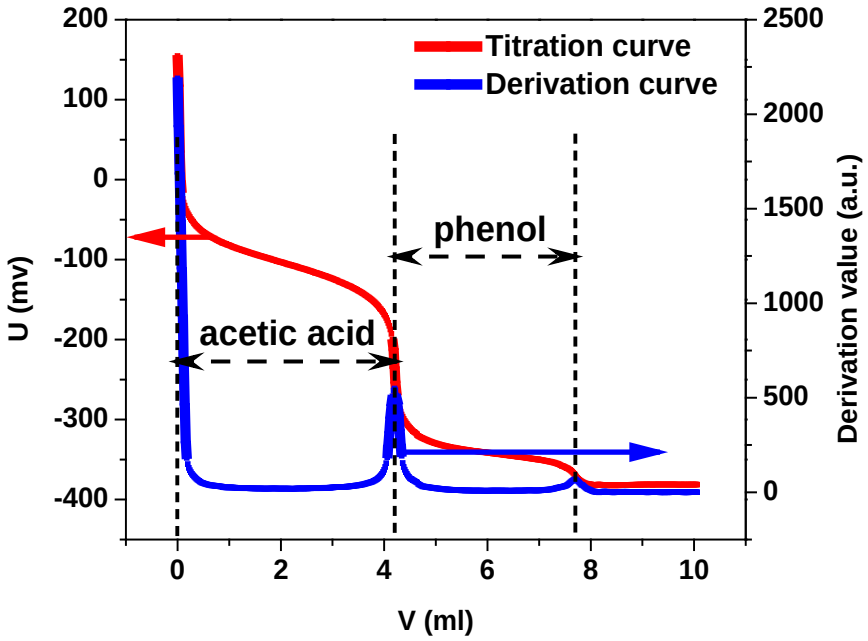

Figure 3-2. Titration curve of a mixture of acetic acid and phenol.

In another titration experiment, phenols ware quantitatively added into the bio-oil sample (Figure 3-3b), resulting in the volume of consumed base of group B being extended (from 10.0 ml in Figure 3-1b to 10.9 ml in Figure 3-3b on X-axis), while no variation of group A and C was observed. So group B was defined as phenolic compounds with pK_a of 8.0-10.0. Low voltage corresponds to high pK_a. Group C should be substances with even lower acidity than phenolic compounds. Further study will be carried out to identify group C.

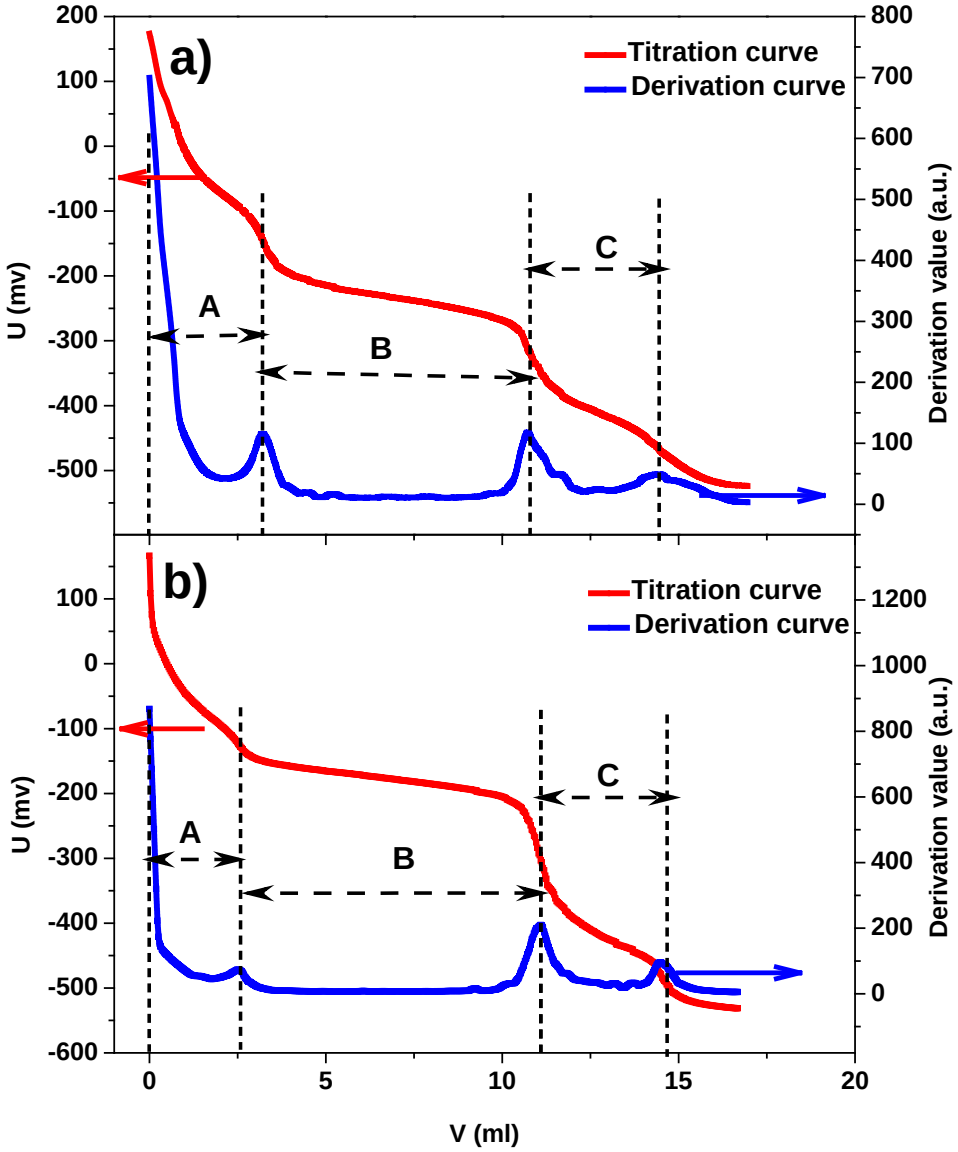

Figure 3-3. a) Titration curve of wood bio-oil produced at 500 °C and added acetic acid. b) Titration curve of wood bio-oil produced at 500 °C and added phenol.

3.3.4 Application of the titration method to determine the acidic components in bio-oil

3.3.4.1 Effects of pyrolysis temperature on the yield of acidic compounds

The yields of carboxylic acids and phenolic groups were calculated by equation (2). Figure 3-4 shows the yields of carboxylic acids and phenolic group produced from the mallee wood at the pyrolysis temperatures from 350 to 580 °C. In general, the changes in the yield of carboxylic acids as a function of pyrolysis temperature were much smaller than that of phenolic compounds. The amounts of carboxylic acids remained relatively unchanged at low temperatures of 350 and 375 °C. As the pyrolysis temperature was increased from 375 to 580 °C, the yield of carboxylic acids slightly declined. Three main components (hemicellulose, cellulose and lignin) of biomass had quite different pyrolysis characteristics. Hemicellulose and cellulose were the main origin of carboxylic acids. The pyrolysis of hemicellulose primarily happened at a lower temperature range of 220–315 °C [24], which was the main origin of carboxylic acids in bio-oil. The decomposition of cellulose occurred mainly at 315–400 °C, which contributes to the formation of a small portion of carboxylic acids in bio-oil. When the pyrolysis temperate was around 350 °C, the pyrolysis of hemicellulose almost finished. With pyrolysis temperature increasing further, some carboxylic acids with big molecular structures probably further decomposed. Therefore, the content of carboxylic acids reached the maximum at about 350 °C.

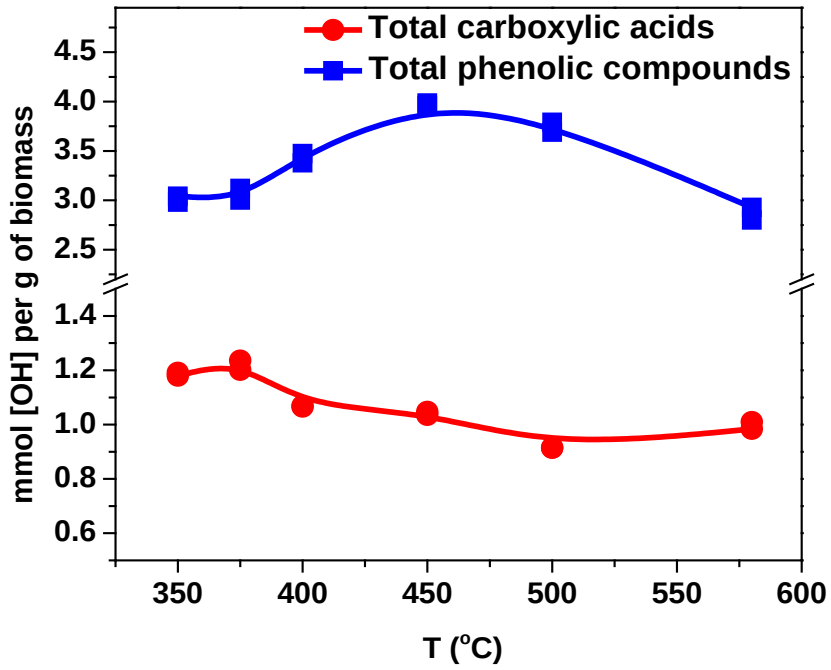

Figure 3-4. The contents of total carboxylic acids and phenolic compounds in wood bio-oil as a functional of pyrolysis temperature. Please note the change in the scale of Y-axis.

The yields of phenolic groups produced from mallee wood biomass were much more than that of carboxylic acids. It can be observed that the yield of phenolic groups reached a maximum at around 450 °C then decreased at higher pyrolysis temperatures. Lignin was the primary origin of phenolic groups. Its decomposition temperature range can spread from 160 to 900 °C [24]. The increase of pyrolysis temperatures promoted the decomposition of lignin. At high reaction temperature the secondary decomposition of newly formed phenolic compounds would occur.

3.3.4.2 Comparison of yields of carboxylic acids and phenolics obtained from titration and GC-MS

Figure 3-5 shows that the amount of total carboxylic acids detected by GC-MS roughly accounts for 55–70% (mol basis) of all carboxylic acids identified by the titration

method. The heavy carboxylic acids/ large phenolic groups were the ones which cannot be detected by GC-MS but were detectable via our method. These results indicated that around 29-45% (mol basis) heavy carboxylic acids exist in bio-oil, which have not been measured before [25-27]. In addition, as shown in Figure 3-5a the abundance of the heavy acids decreased with increasing pyrolysis temperature, the reason may be the decomposition of these big carboxylic acids at high pyrolysis temperatures. These acid groups were a major source for CO_2 formation during pyrolysis.

Figure 3-5c indicated that GC-MS only can detect approximately 3% (mol basis) of all phenolic groups in bio-oil. The phenolic compounds detected by GC-MS were mainly comprised of the light compounds such as guaiacol, 2-methoxy-4-methyl-phenol, phenol; p-cresol, m-cresol, 2-methoxy-4-propylphenol, eugenol, cis-isoeugenol, trans-isoeugenol, 2.6-dimethoxyphenol, vanillin, 4-allyl-2,6-dimethoxyphenol, and syringaldehyede. However, the majority of phenolic compounds in bio-oil are big aromatics, and these heavy aromatics may behave quite differently from that of light aromatics during bio-oil upgrading. The yield of large phenolic components reached a maximum at around 450-550 °C, which agreed well with the result reported by Garcia-Perez et al [20]. They found the peak centered at 340-360 nm on the UV fluorescence spectrum which represented the oligomeric compounds showed a maximum at around 450-550 °C. In fact, the catalytic behaviours of the heavy phenolics have not been fully understood yet due to the lack of effective methods to identify them. The titration developed in this study can be a simple but sensitive method to measure the abundance of the heavy phenolics, which would significantly contribute to the research on heavy phenolics (undetectable by GC-MS) during the catalytic reactions such as hydrogenation.

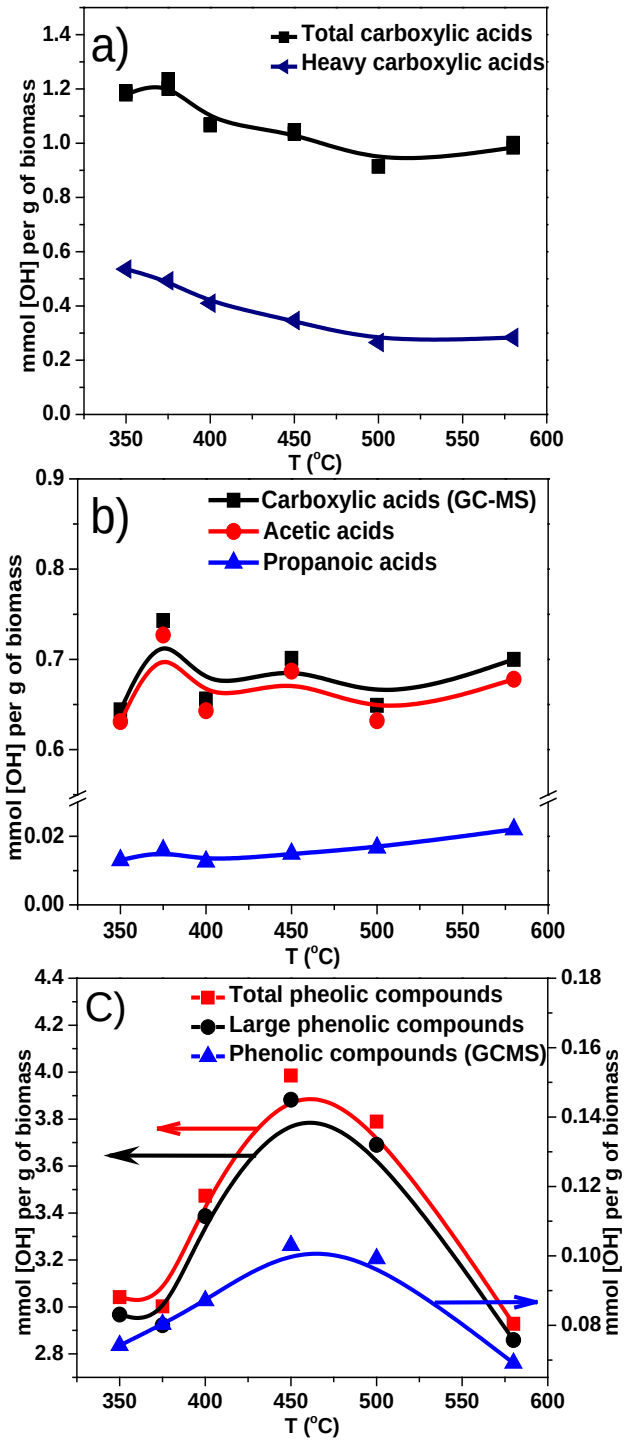

Figure 3-5. (a) The contents of total carboxylic acids and heavy carboxylic acids in wood bio-oil obtained by titration as a function of pyrolysis temperature. (b) The contents of several acids obtained by GC-MS as a function of pyrolysis temperature. (c) The comparison of the contents of phenolic compounds in wood bio-oil obtained by titration and GC-MS.

3.3.5 Comparison of the acidic components in the bio-oil from mallee woods, barks and leaves

The two phases of bark oils and leaf oils were all analysed by GC-MS and titrator. The results were presented in Figure 3-6 and Figure 3-7, respectively. The three types of biomass showed similar trends in the yields of both carboxylic acids and phenolic groups with the pyrolysis temperature. The carboxylic acids were produced in higher abundance from wood biomass than the other two types of biomass. This was due to the higher content of hemicellulose in wood biomass (40.7 wt.% in wood, 19.5 wt.% in bark, and 14.8 wt.% in leaf [22]), which is the main precursor for carboxylic acid. In addition, although wood and leaves contain similar amount of lignin (24.9 wt.% in wood, 14.4 wt.% in bark, and 25.9 wt.% in leaf [22]), the concentration of phenolic groups varied a lot. This might be because the manner for the connection of lignin with cellulose or hemicellulose in wood is different from that in leaves. This different connection exerts influence on the transformation of lignin to phenolics during pyrolysis of biomass, leading to the different production of phenolics in bio-oils from two kinds of biomass, wood and leaves.

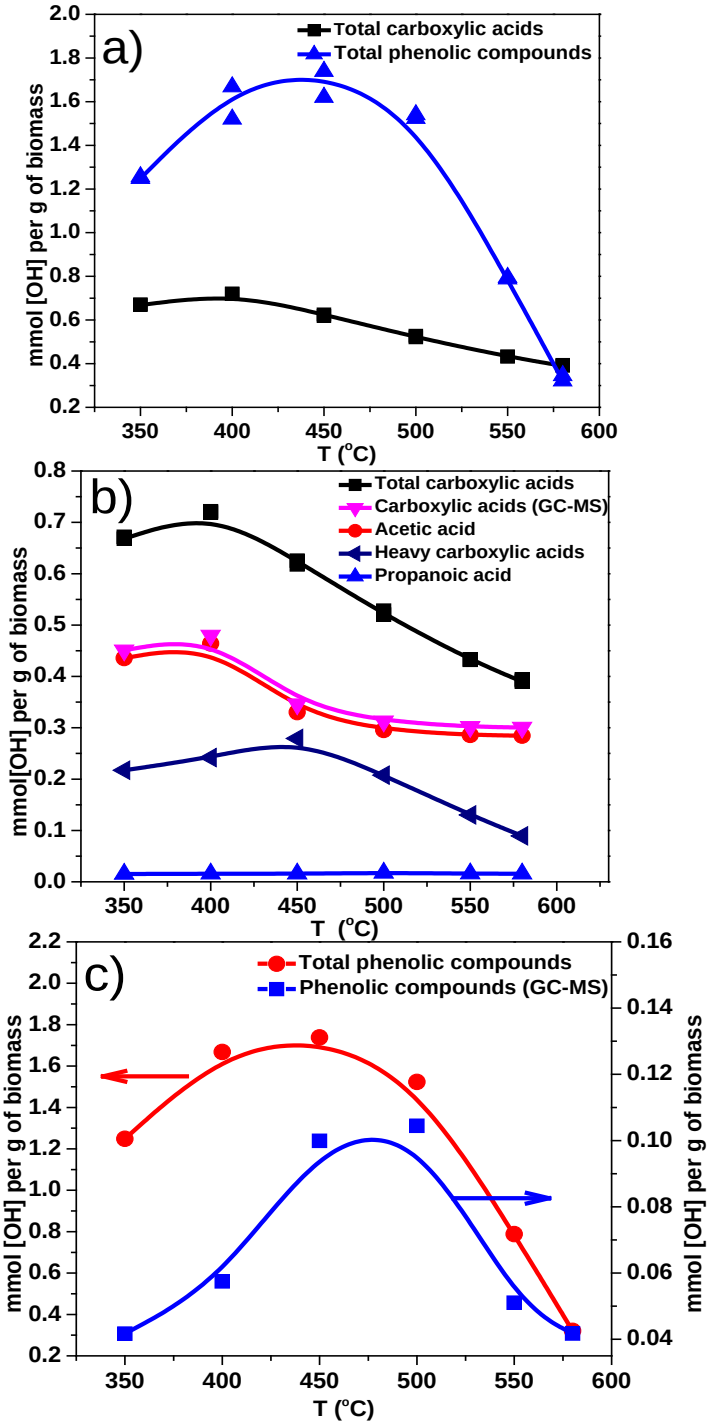

Figure 3-6. (a) The contents of carboxylic acids and phenolic compounds in bark bio-oil as a function of pyrolysis temperature. (b) The comparison of the contents of carboxylic acids in bark bio-oil obtained by titration and GC-MS as a function of pyrolysis temperature. (c) The comparison of the content of phenolic compounds in bark bio-oil obtained by titration and GC-MS as a function of pyrolysis temperature.

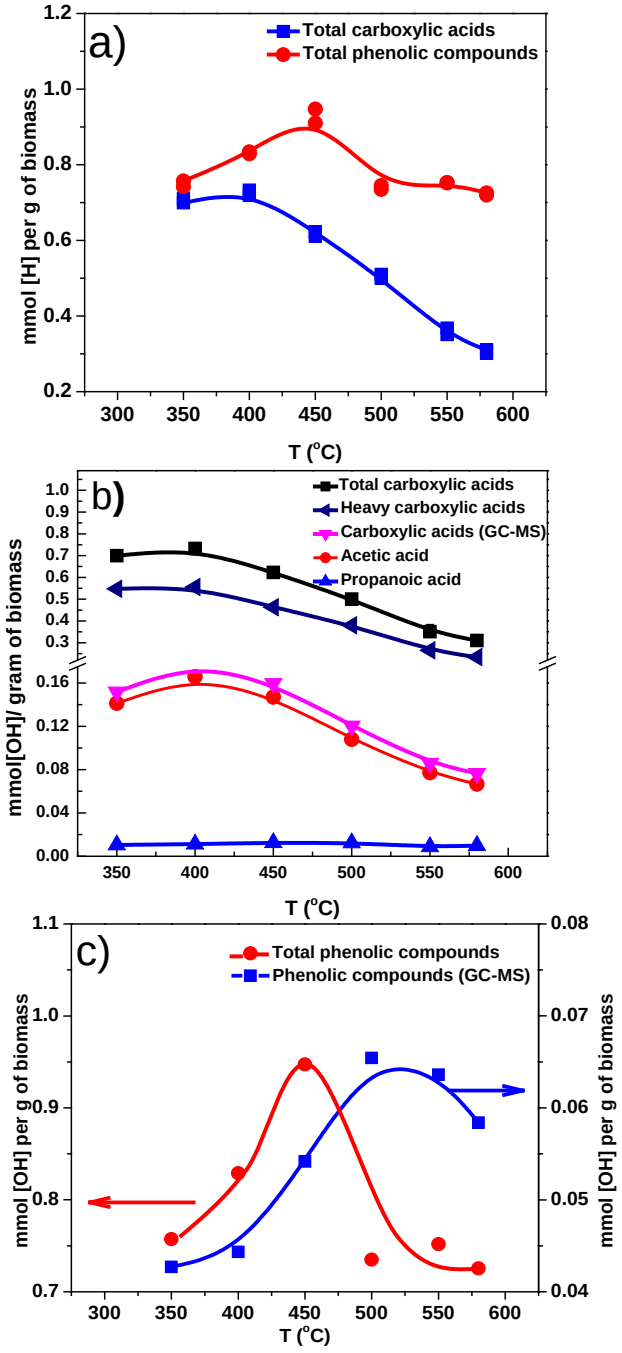

Figure 3-7. (a) The contents of carboxylic acids and phenolic compounds in leaf bio-oil as a function of pyrolysis temperature. (b) The comparison of the contents of carboxylic acids in leaf bio-oil obtained by titration and GC-MS as a function of pyrolysis temperature. (c) The comparison of the content of phenolic compounds in leaf bio-oil obtained by titration and GC-MS as a function of pyrolysis temperature.

The yields of heavy carboxylic acids and heavy phenolic components varied with different feed stock. As shown in Table 3-1, the proportion of heavy carboxylic acids of all carboxylic acids from leaf biomass (76% mol basis) was much higher than that from other two types of biomass. It may be because the leaves have more resinic acids. The similar portion of heavy carboxylic acids (25-45% mol basis) were obtained from wood and bark biomass. That is to say, the carboxylic acids produced from leaves mainly existed in the form of heavy carboxylic acids. When pyrolysis temperature is in the range of 350 to 580°C, the proportion of heavy carboxylic acids of total carboxylic acids in the bio-oil produced from leaves only varied from 75% to 78% (mol basis). However, the proportion of heavy carboxylic acids of all carboxylic acids in the bio-oils produced from the other two types of biomass varied significantly with increasing pyrolysis temperature. For the bio-oils produced from wood biomass, with increasing pyrolysis temperature in the range of 350 to 580°C, the proportion of heavy carboxylic acids of all carboxylic acids decreased from 45% to 29% (mol basis). For the bio-oils produced from bark biomass, with increasing pyrolysis temperature, the proportion of heavy carboxylic acids of all carboxylic acids firstly increased from 33% to 45% (mol basis) and then decreased to 23% (mol basis). Table 3-2 showed that the percentage contents of heavy phenolic compounds in the three kinds of bio-oils are all higher than 90% (mol basis). Therefore, the heavy phenolic components dominated the phenolic groups in all the three kinds of bio-oils.

Table 3-1 The proportions of heavy carboxylic acids of total carboxylic acids in the bio-oils from the pyrolysis of wood, bark and leaf at various temperatures.

Pyrolysis temperature (°C)	Heavy carboxylic acids (% mol basis)		
	Wood oil	Bark oil	Leaf oil
350	45	33	78
375	40	–	–
400	38	34	76
450	33	45	74
500	29	40	76
550	–	30	76
580	29	23	75

Table 3-2 The proportions of heavy phenolic components of total phenolic groups the bio-oils from the pyrolysis of wood, bark and leaf at various temperatures.

Pyrolysis temperature (°C)	Heavy phenolic components (wt.% mol basis)		
	Wood oil	Bark oil	Leaf oil
350	98	97	94
375	97	–	–
400	97	97	95
450	97	94	94
500	97	93	91
550	–	94	92
580	98	87	92

3.4 Conclusions

This study investigated the determination of strong and weak acidic components in bio-oil via a non-aqueous potentiometric titration. The aim of differentiating the carboxylic acids and phenolic groups were successfully completed via our developed method. The heavy carboxylic acids in bio-oil from wood represented about 29-45% (mol basis) of all carboxylic acids. The phenolic groups existed in bio-oil from the mallee wood were primarily in big aromatics, accounting approximately 97% (mol basis) of all phenolics. It was noteworthy that the portion of heavy carboxylic acids in bio-oil from leaves was much higher than that of bio-oils from wood and bark. The large phenolics accounted for more than 90% (mol basis) of all phenolics in all the three kinds of bio-oils. The titration method developed in this study provides a good means to measure the abundances of both light and heavy carboxylic acids and phenolics in bio-oil.

3.5 References

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Chapter 4

Reaction Behaviour of Light and Heavy Components of Bio-oil in Methanol and in Water

4.1 Introduction

Bio-oil is a liquid product produced from the pyrolysis of biomass, which is a renewable source of biofuels and chemicals [1-5]. However, bio-oil contains many oxygen-containing compounds, which lead to the thermal instability and high acidity of bio-oil, restricting the direct use of bio-oil as a transportation fuel [6-8]. Esterification and hydrotreatment are important routes for the upgrading of bio-oil to biofuels [9-12]. Both technology routes involve the thermal treatment of bio-oil [13-16]. During the thermal treatment of bio-oil, many oxygen-containing components become very reactive, leading to the polymerisation of bio-oil [17-23]. Understanding how the thermal treatment affects the polymerisation of the main components of bio-oil is essential to optimise the reaction conditions for the upgrading of bio-oil via esterification or hydrotreatment.

This study focuses on the reaction behaviour of aromatics in bio-oil during its thermal treatment in methanol and in water. The selection of methanol as a solvent was mainly because the esterification of bio-oil was generally performed in alcohols. The previous results from our group [24] indicated that carboxylic acids could be esterified with methanol. Reactive carbonyl functional groups in aldehydes could also be converted via acetalisation. Sugars and sugar oligomers, which were derived from the degradation of lignocellulosic biomass and played an important role in the stability/instability of bio-oil, can also be stabilised via the acid treatment in methanol [24, 25]. However, the reaction behaviour of aromatics in bio-oil under the condition of esterification is largely unknown.

In addition to the externally added alcohol, the most intrinsically abundant component in bio-oil is water. Water in bio-oil was mainly produced from the pyrolysis of biomass, amounting to 20-40 wt% of bio-oil [26-28]. In our previous studies [29, 30], we found that water imposed remarkable effect on the conversion of levoglucosan, the major anhydrate sugar in bio-oil. Understanding the reaction behaviour of the aromatics in bio-oil in alcohols and in water can provide very important information for developing advanced upgrading processes for the selective conversion of the aromatics in bio-oil.

4.2 Experimental

4.2.1 Preparation of bio-oil

The bio-oil sample was prepared by Dr MD Mahmudul Hasan using a grinding pyrolysis reactor at 450°C with 54 rpm rotating rate. A detailed description of the reactor system and experimental procedure can be found in Section 2.2, **Chapter 2**.

The light bio-oil and heavy bio-oil were obtained by vacuum distillation at 70°C. The mass ratio of the light part to the heavy part was ca. 1 : 2. The bio-oil feedstock in this study was one phase, although the water content was 30.0 wt.%. This amount of water was miscible with oligomeric lignin-derived compounds in bio-oil due to the solubilising effects of other polar hydrophilic compounds.

4.2.2 Thermal treatment of bio-oil

The thermal treatment of bio-oil was performed under nitrogen in an autoclave reactor. Typically, bio-oil or bio-oil with methanol or water at a mass ration of 1:1 were loaded into the reactor. After the reactor was assembled, nitrogen was used to purge the air inside for three times. The reactor was then heated to pre-set temperature and the residence time for each experiment was 120 minutes. Once the experiment was finished, the reactor was cooled down by a cooling coil with running water. The detailed description of the reactor can be found in Section 2.3, **Chapter 2**. One of the GC-MS spectra was was shown in Figure 4-1 and the identification of typical compounds was shown in Table 4-1 as well.

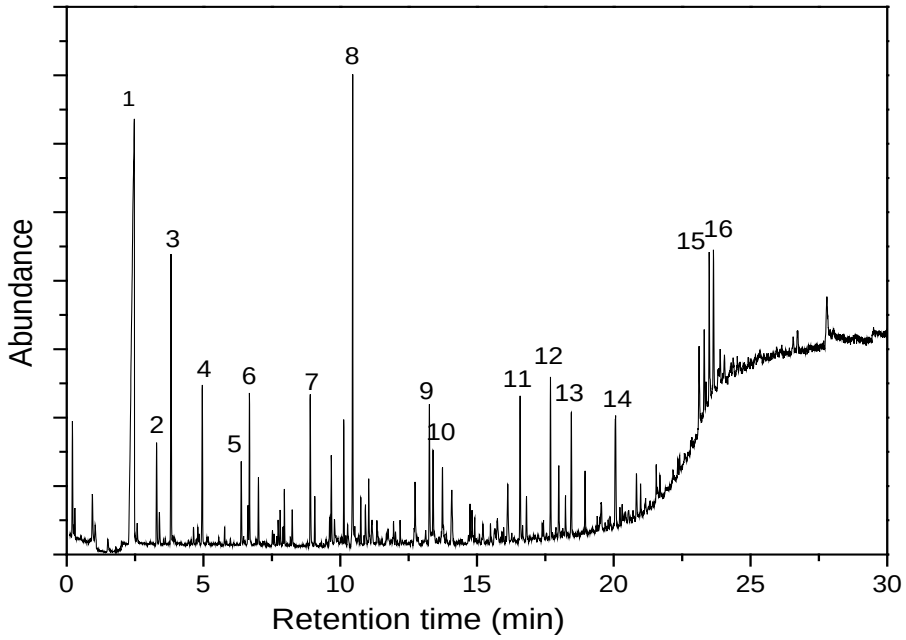

Figure 4-1. GC-MS spectrum of the bio-oil after esterification with methanol for 120 minutes at 170^{o}C. See Table 4-1 for the identification of the compounds.

Table 4-1. Identification of main peaks in bio-oil after the esterification with methanol for 120 minutes at 170 ^{o}C

No.	compounds	No.	compounds
1	water	9	1,2-cyclopentanedione, 3-methyl
2	2-propanone,1-methoxy	10	2-cylopenten-1-one, 2-hydroxy-3-methyl
3	Ethane,1,1,2-trimethoxy	11	Butanoic acid, dimethyl ester
4	2-propanone,1,1-	12	Phenol, 2,6-dimethoxy-
5	Acetic acid, dimethoxy-	13	1,2,4-trimethoxybenzene
6	2-propanone,1-hydroxy-	14	Phenol, 2,6-dimethoxy-4-(2-propenyl)-
7	Acetic acid	15	Ethanone, 1-(4-hydroxy-3,5-
8	Methyl levulinate	16	desaspidinol

4.2.3 Analytical methods

Bio-oil feedstock and thermal treatment products were analysed with GC-MS equipped with a HP-INNOWAX capillary column. The details of the instrument and procedure can be found in Section 2.5.1, **Chapter 2**. The conversion of typical compounds in bio-oil was defined in Equation 2-3, **Chapter 2**. The negative conversion is used to express the formation of given species.

A Perkin-Elmer LS50B spectrometer was used to analyse liquid samples to get the UV-fluorescence spectra of bio-oil feedstock and products. A detailed procedure can be found in Section 2.5.2, **Chapter 2**.

The potential coke yields of bio-oil feedstock and products were quantified by TGA. A detailed procedure was available in Section 2.5.4, **Chapter 2**.

A ThermoScientific Flash 2000 CHNS/O analyser was used to determine elemental composition of bio-oil feedstock and products. A detailed method can be found in Section 2.5.5, **Chapter 2.**

4.3 Results and discussion

4.3.1 Effects of carboxylic acids on the conversion of aromatics in bio-oil during thermal treatment

Table 4-1 summarises the reaction conditions and distribution of product from the thermal treatment of bio-oil. The reaction behaviour of bio-oil in methanol and water was quite different. With bio-oil or heavy bio-oil and external added water as reactants, the products obtained were a watery phase and a paste. In addition, with increasing reaction temperature, the portion of the paste increased, indicating the increase in the production of heavy compounds. This was probably due to the dominance of the condensation reactions at the high reaction temperatures. In the experiments of thermal treatment of bio-oil itself, the product produced at 130°C remained in one phase while

those produced at 180 and 230°C separated into a aqueous phase and a solid phase, indicating the occurrence of condensation and polymerisation reactions and the formation of the heavy components.

Figure 4-2 shows the fluorescence spectra of bio-oil feedstock and products after the thermal treatment. It can be seen that, with increasing reaction temperature, the intensity at wavelength 280-350 nm decreased, while that at wavelength 350-400 nm appeared to have increased. The observed decreases in fluorescence intensity at the short wavelength and increases at the longer wavelength indicated that aromatics with relatively small (one benzene ring) to medium ring (two fused benzene rings) sizes were consumed while large aromatic ring systems (three and more fused benzene rings) were formed. The phenomenon was more evident at 230°C (Figure 4-2). Therefore, higher temperature facilitated this transformation. This result was in good agreement with the shift of components from the water phase to the solid phase with the increasing reaction temperature (Table 4-1).

The thermal treatment of the light bio-oil and heavy bio-oil, separated via vacuum distillation at 70°C, were also performed. Figure 4-2b showed that almost no aromatics were observed in light bio-oil feed or the product after the thermal treatment. Most aromatics in bio-oil retained in the heavy fraction. Although majority of acetic acid, a main carboxylic acid in bio-oil, was removed and the acidity of heavy bio-oil decreased to pH of 3.7, compared with raw bio-oil with pH of 2.8, a similar trend of UV-fluorescence spectra was observed in Figure 4-2c. The thermal treatment led to the decrease of the fluorescence intensity of the small aromatics. It seems that the presence or absence of acetic acid did not affect the conversion of aromatics. In other words, acetic acid was not the effective catalyst for the conversion/polymerisation of the aromatics. In order to confirm this hypothesis, the thermal treatment of the heavy bio-oil with 4 wt.% of external added acetic acid was conducted. As is shown in Figure 4-2c, the effect of added acetic acid on the reaction behaviour of aromatics was negligible.

Table 4-2. Product distribution under different reaction conditions

Reaction medium	Mass ratio	Bio-oil type	Bio-oil (g)	Holding temperature (°C)	Product distribution	Aqueous phase (g)	Solid phase (g)
Methanol	1:1	Bio-oil	40	130	One phase	N/A	N/A
Methanol	1:1	Bio-oil	40	180	One phase	N/A	N/A
Methanol	1:1	Bio-oil	40	230	One phase	N/A	N/A
Methanol	1:1	L-bio-oil[a]	40	230	One phase	N/A	N/A
Methanol	1:1	H-bio-oil[b]	40	230	One phase	N/A	N/A
Water	1:1	Bio-oil	40	130	Two phase	66	13
Water	1:1	Bio-oil	40	180	Two phase	63	15
Water	1:1	Bio-oil	40	230	Two phase	59	17
Water	1:1	L-bio-oil	40	230	One phase	N/A	N/A
Water	1:1	H-bio-oil	40	230	Two phase	45	33
Water	1:1	H-bio-oil	40	230	Two phase	47	32
No	N/A	Bio-oil	80	130	One phase	N/A	N/A
No	N/A	Bio-oil	80	180	Two phase	40	39
No	N/A	Bio-oil	80	230	Two phase	37	42
No	N/A	L-bio-oil	80	230	One phase	N/A	N/A
No	N/A	H-bio-oil	80	230	One phase	N/A	N/A
No	N/A	H-bio-oil-AA[c]	80	230	One phase	N/A	N/A
No	N/A	H-bio-oil-FA[d]	80	230	One phase	N/A	N/A

[a]L-bio-oil refers to the light fraction of bio-oil obtained by the vacuum distillation at 70°C.

[b]H-bio-oil refers to the heavy fraction of bio-oil obtained by the vacuum distillation at 70°C.

[c]H-bio-oil-AA means 4 wt.% acetic acid was added into heavy bio-oil.

[d]H-bio-oil-FA means 3 wt.% formic acid was added into heavy bio-oil.

The reaction time of all the experiments is 120 minutes.

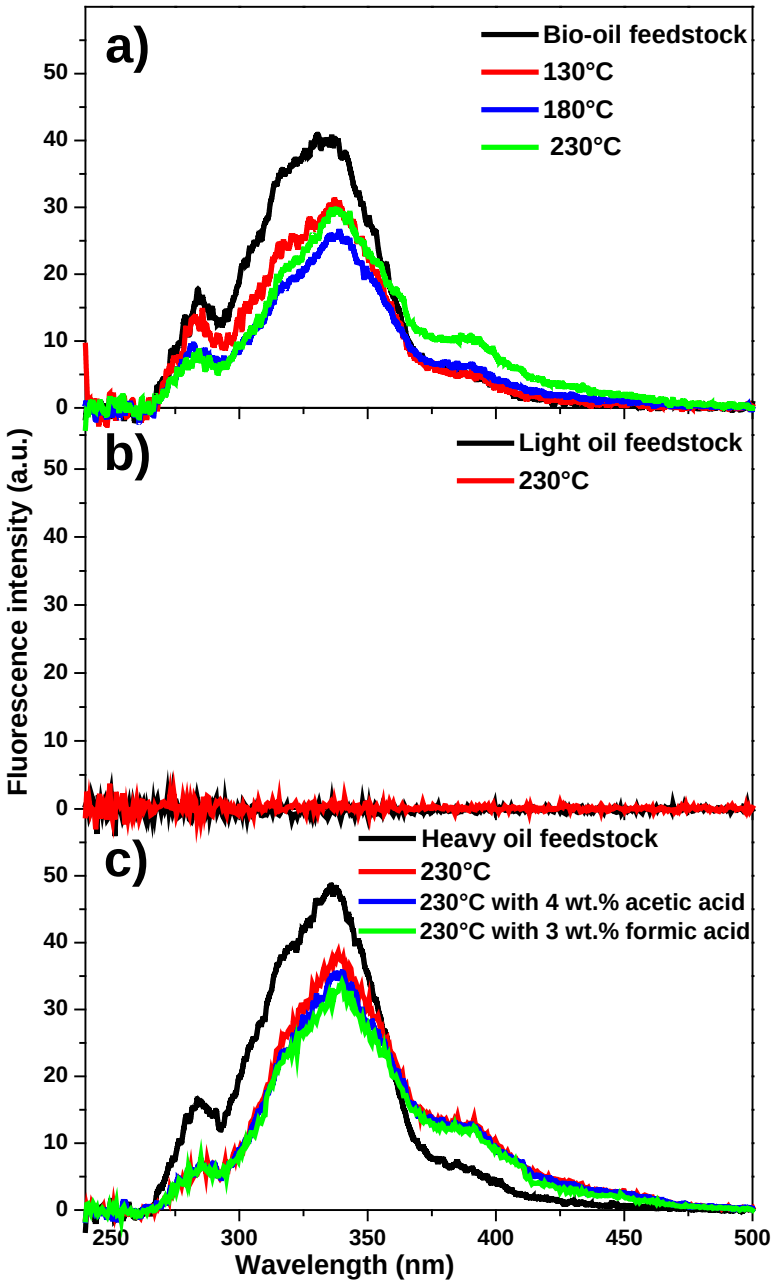

Figure 4-2. Constant energy (-2800 cm^{-1}) synchronous spectra of feedstock and the products from the thermal treatment of feedstock a) The whole bio-oil b) The light bio-oil. c) The heavy bio-oil. For the products with two phases, the fluorescence of the products in the two phases was combined based on the mass distribution of the products. The concentration of samples for the UV-fluorescence analysis was 10 ppm. The reaction time for thermal treatment of bio-oil is 120 minutes.

$$\text{Combined fluorescence intensity} = \text{Intensity (Liquid phase)} \times \frac{\text{the mass of liquid phase}}{\text{the mass of whole product}} + Intensity(Solid\ phase) \times \frac{\text{the mass of solid phase}}{\text{the mass of whole product}}$$

It was possible that the acidity of acetic acid was too weak to induce the polymerisation/conversion of the aromatics. Formic acid is another carboxylic acid in bio-oil with a stronger acidity and lower pKa (3.75), which might catalyse the polymerisation of the heavy aromatics. However, the result was similar to that with adding acetic acid. The adding of formic acid has little effect on the conversion/polymerisation of the heavy aromatics. The heavy aromatics were not sensitive to the presence of the carboxylic acids. In our previous study, we found that acetic acid and other carboxylic acids, which were detectable with GC-MS, only accounted for ca. 55-70% of the total carboxylic acids in bio-oil, the rest are heavy acids that could not be detected [31]. These heavy acids probably are the ones with the carboxylic group attached on aromatic rings and distributed in the heavy fractions of bio-oil, which might have stronger acidity than acetic acid and formic acid. The pKa of acetic acid is 4.76. The pKa of benzoic acid is 4.19 and the pKa of 2,5-dihydroxybenzoic acid is 2.97. The hydroxyl group on the benzene ring made the acidity of this compound increased significantly. This is the evidence to show the stronger acidity of aromatic acids. As a consequence, the effects of adding acetic acid and formic acid became negligible.

When a solid acid with strong acidity was applied, the reaction behaviours of the aromatics changed drastically. In methanol, the thermal treatment of bio-oil in the absence of a solid acid catalyst, i.e. Amberlyst 70, led to an overall increase of the fluorescence intensity of the aromatics, which will be discussed later. The aromatics were stable in methanol. However, with adding of Amberlyst 70 to the reaction medium, the fluorescence intensity of the aromatics decreased significantly (Figure 4-3). The presence of strong acidic sites in Amberlyst 70 in the reaction medium could effectively promote the polymerisation/conversion of the aromatics. Amberlyst 70 has a much stronger acidity with -SO_3H groupthan the heavy acids in bio-oil, which was able to catalyse the conversion of the heavy aromatics in bio-oil. In addition, the porous solid acid created steric difficulties for the products to “desorb” from the pores of Amberlyst 70, which would increase the conversion of aromatics. The weight of the catalyst after the reaction increased significantly from 4.88 g to 8.8g (dry basis), indicating that some components of bio-oil polymerized in the pores of the catalyst.

Amberlyst 70 is a solid acidic catalyst with limited pore sizes. Heavy molecules with big molecule size would have more difficulty than the light molecules with small molecule size to access the small pores. This is the origin for the steric hindrance.

4.3.2 Stability of the aromatics of bio-oil in water during thermal treatment

Water is the most abundant fraction in bio-oil, with a percentage ranging from 20 to 40 wt.% in raw bio-oil [27-29]. In order to understand the stability of the aromatics of bio-oil in water, thermal treatment of bio-oil with externally added water at 130, 180 and 230°C were carried out. Two phases, aqueous phase and solid phase, were obtained as the products (Table 4-2). The increasing reaction temperature promoted the polymerisation reactions and consequently the formation of the paste. The UV-fluorescence spectra are shown in Figure 4-4. Similar to the case of thermal treatment of bio-oil itself, the fluorescence at 280-350 nm, representing mono-aromatics and aromatics with two fused benzene rings, decreased while the abundance of the three-ring aromatics (350-400 nm) increased. The addition of water to bio-oil diluted the bio-oil, which would be expected to alleviate the polymerisation reactions. However, the dilution effects of water on polymerisation of the aromatics were negligible. The heavy bio-oil behaved similarly with the whole bio-oil during the thermal treatment in water (Figure 4-4c).

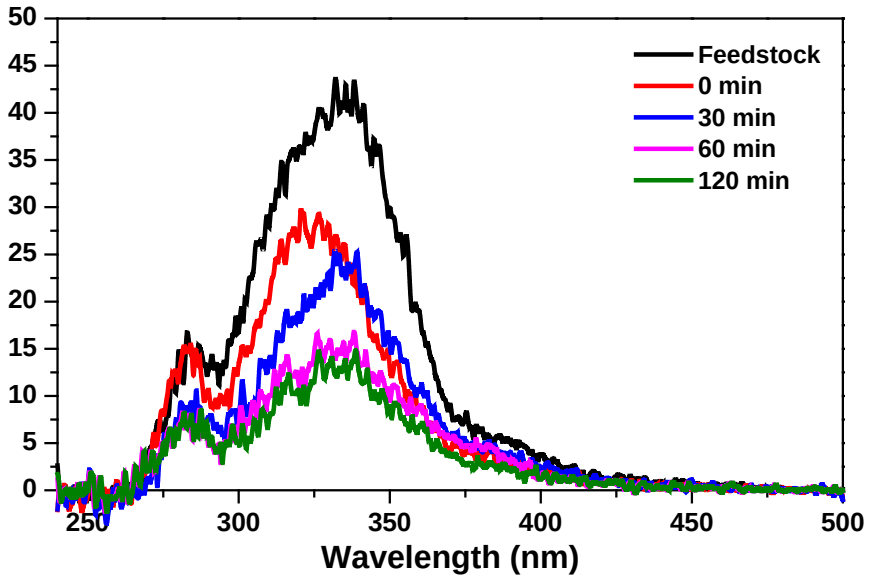

Figure 4-3. The fluorescence spectra of the feedstock (bio-oil/methanol) and products during the thermal treatment of bio-oil/methanol with Amberlyst 70 (15 wt.%) as the catalyst. Stirring rate: 500 rpm; reaction temperature: 170°C. The concentration of the samples for the UV-fluorescence analysis was 10 ppm.

4.3.3 Stability of the aromatics in methanol during thermal treatment of bio-oil

In the previous studies on the upgrading of bio-oil, methanol has been widely used to esterify carboxylic acids in bio-oil, and also been extensively applied in alcoholysis of sugars and sugar oligomers to produce fine chemicals such as 4-hydroxymethylfurfural (HMF) and alkyl levulinate [17, 18]. Compared with thermal treatment of bio-oil alone or bio-oil in water, bio-oil behaved quite differently in methanol (Figure 4-5a). During the thermal treatment of bio-oil itself or in water, the increase of intensity at the higher wavelength was accompanied with the decrease of intensity at the lower wavelength. In contrast, in the thermal treatment of bio-oil in methanol, the overall fluorescence intensity increased. The reason for the increase in intensity is possibly that additional aromatic ring systems, which showed intensity in the measurable wavelength range, were produced during the thermal treatment. In addition, with the increases in reaction temperature, the increases in the spectral intensity at the wavelengths of 360–400 nm were more predominant. This indicated that high reaction temperature favoured the formation of heavy aromatics.

The thermal treatment of heavy bio-oil in methanol was also performed, as shown in Figure 4-5c. The results confirmed the formation of additional aromatics during the thermal treatment in methanol. Bio-oil was produced from the pyrolysis of biomass with a short to medium residence time (seconds to minutes). The "pyrolysis" or degradation of the organics have not been completed yet. During the thermal treatment experiments in this study, although the reaction temperature was much lower than that for the pyrolysis experiment, the residence time was as long as 2 hours. During the thermal treatment, it was believed that the "pyrolysis" of some heavy organic components continued. Some reactive intermediates including radicals might be produced. They could polymerise at the elevated reaction temperature if they could not be stabilised. In the thermal treatment of bio-oil itself and in water, the fluorescence intensity of the aromatics decreased remarkably. They might react with these reactive intermediates and polymerised. To the contrary, in methanol, the fluorescence intensity was even increased to some extent. It was probably because methanol could stabilise the reactive intermediates produced during the thermal treatment, preventing their cross-polymerisation with the aromatics. In other words, the polymerisation in bio-oil was retarded in methanol to the extent that additional aromatics were formed and can be seen in UV-fluorescence spectra. On the contrary, the un-retarded polymerisation in water would lead to the formation of polymer. Alternatively, there is another possible explanation for the overall intensity increase in methanol and intensity decrease at short wavelength but increase at long wavelength in water. The raw bio-oil contained big aromatics in heavy molecules. They cannot be well detected by UV-fluorescence, due to energy-transfer process. During the thermal treatment of bio-oil in methanol, they were released, stabilised and appeared in the UV-fluorescence spectra.

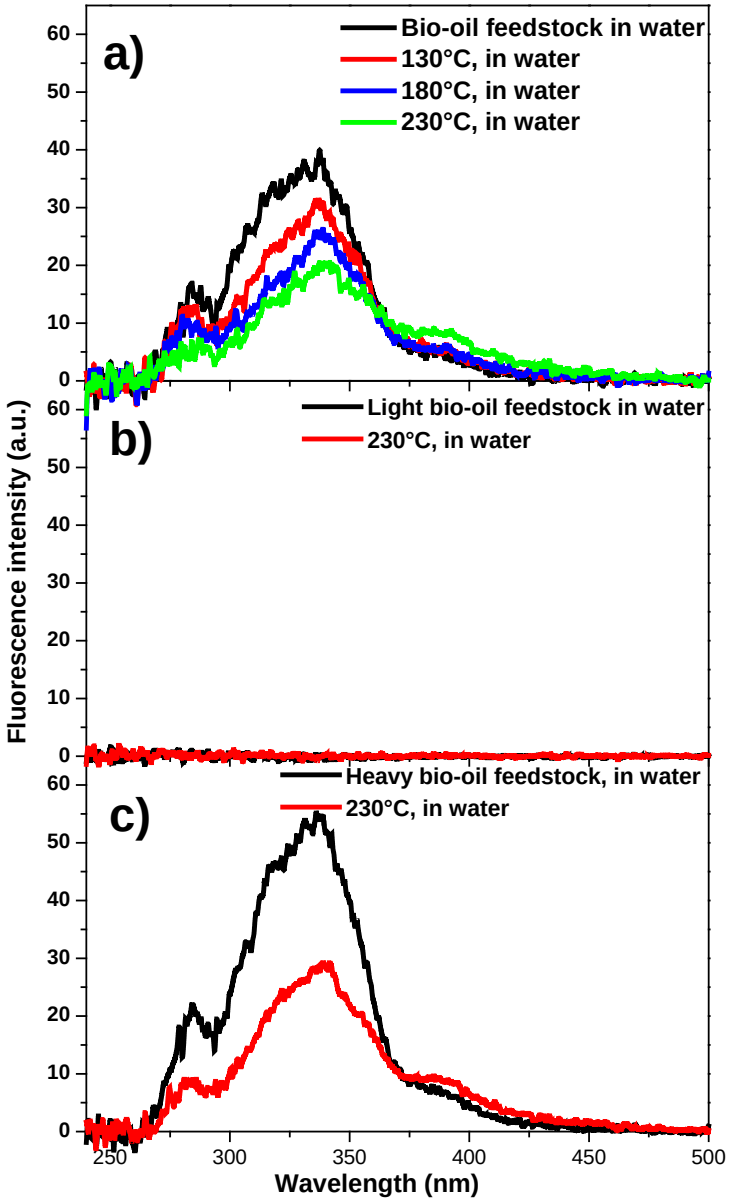

Figure 4-4. Constant energy (-2800 cm^{-1}) synchronous spectra of feedstock in water and the products from the thermal treatment of feedstock in water. a) The whole bio-oil. b) The light bio-oil. c) The heavy bio-oil. For the products with two phases, the fluorescence of the products in the two phases was combined based on the mass distribution of the products. The feedstock in water refers to the mixture before heating up. The concentration of samples for UV-fluorescence analysis was 10 ppm. The reaction time for thermal treatment of bio-oil with water is 120 minutes at the mas ratio of 1:1.

Combined fluorescence intensity =

$$\text{Intensity (Liquid phase)} \times \frac{\text{the mass of liquid phase}}{\text{the mass of whole product}} + Intensity(Solid\ phase) \times \frac{\text{the mass of solid phase}}{\text{the mass of whole product}}$$

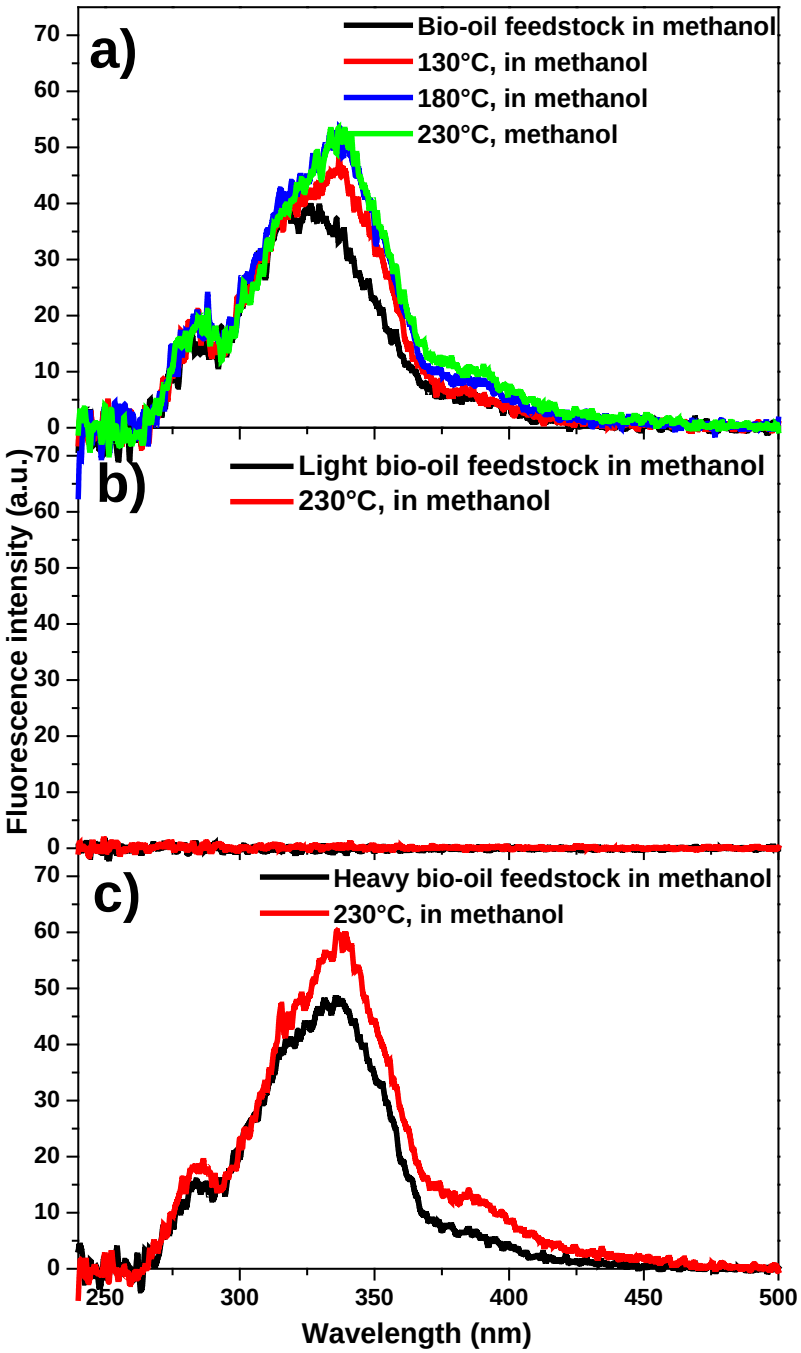

Figure 4-5. Constant energy (-2800 cm^{-1}) synchronous spectra of bio-oil feedstock and thermal treatment products of bio-oil in methanol. a) The whole bio-oil. b) The light bio-oil. c) The heavy bio-oil. The concentration of samples for the UV-fluorescence analysis was 10 ppm. The reaction time for thermal treatment of bio-oil with methanol is 120 minutes at the mass ratio of 1:1.

4.3.4 Comparison of the conversion of typical compounds in bio-oil in different solvents

4.3.4.1 Conversion of carboxylic acids

As is shown in Table 4-3, organic acids (acetic acid, propionic acid, butanoic acid, and pentanoic acid) were not converted but produced (shown as negative conversion) during the thermal treatemtn of bio-oil in the water-rich medium. In the experiments of thermal treatment of bio-oil itself, small conversion of these organic acids can be observed at a low reaction temperature of 130°C. However, the formation of these typical organic acids was observed with increasing reaction temperature. In comparison, in methanol, the conversion of these organic acids (based on carboxylic acids themselves) at 230°C reached 72 to 78%. The main products of these carboxylic acids would be esters. However it is impossible to detect all the products by GC-MS. There was still 20 to 30% organic acids not converted in the mixture of bio-oil/methanol. However, they could not effectively catalyse the polymerisation reactions, although acids are the catalysts for polymerisation of bio-oil [22]. Clearly, alcohols can stablise bio-oil. Carboxylic acids can be converted into esters [24]. Aldehydes can be stabilised by acetalisation to form acetals [24]. Sugars, like levoglucosan, in methanol were mainly converted to methyl α-D-glucopyranoside and subsequently to 2-dimethoxymethyl-5-methoxymethylfuran and finally to methyl levulinate with a high selectivity [29-30]. The protection of the reactive functional groups of levoglucosan and furans can effectively inhibit polymer formation. Thus, the chance for their involvement in polymerisation was minimised, even in the presence of carboxylic acids.

4.3.4.2 Conversion of phenolics

At 130°C, in methanol, almost all the phenolics in bio-oil shown in Tables 4-4 and 4-5, which were detectable by GC-MS, were not consumed, but were produced. These phenolics have mono-rings, showing the fluorescence intensity at wavelength of 275-300 nm. During the characterisation of the products after thermal treatment of bio-oil

in methanol at 130°C (Figure 4-5), it was found that fluorescence intensity at wavelength between 275 and 300 nm increased to some extent. The result was in line with that in Table 4-4, where additional mono-ring phenolics were produced after the thermal treatment of bio-oil in methanol.

In comparison, in the thermal treatment of bio-oil itself or in water, the conversion of the mono-ring phenolics was remarkable. For example, the conversion of cis-isoeugenol, cis-phenol, 2,6-dimethoxy-4(1-propenyl) and benzaldehyde, 4-hydroxy-3,5-dimethoxy can reach 94.7, 96.9 and 79.6%, respectively. Correspondingly, the fluorescence intensity at wavelength of 275–300 nm also decreased accordingly (Figure 4-2 and Figure 4-4). Clearly, the mono-ring phenolics were very reactive during the thermal treatment of bio-oil itself or in water. Possibly, they reacted with other reactive components in bio-oil or polymerised. In methanol, these mono-ring phenolics were stabilised. Moreover, the abundance of the phenolics even increased, which further proved that the mono-ring phenolics could be stabilised in methanol. Although the heavy phenolics could not be detected with GC-MS, the tendency for the change in their abundance could be similar to that of the mono-ring phenolics (Figure 4-4), indicating that the heavy phenolics also could be stabilised in methanol, but not in water.

Table 4-3. Conversion of water and typical carboxylic acids in bio-oil

Compounds	Reactant mixture	Conversion (%)		
		130 °C	180 °C	230 °C
Water	Bio-oil	2.5	-1.6	-11.4
	Bio-oil/water	1.8	-1.8	-2.6
	Bio-oil/methanol	-8.0	-13.6	-23.0
Acetic acid	Bio-oil	3.2	0.2	-1.0
	Bio-oil/water	-7.7	-12.4	-17.3
	Bio-oil/methanol	38.4	64.6	77.9
Propanoic acid	Bio-oil	-3.6	-15.6	-26.7
	Bio-oil/water	-18.0	-25.7	-43.8
	Bio-oil/methanol	39.9	59.9	73.1
Butanoic acid	Bio-oil	5.8	4.0	1.3
	Bio-oil/water	-0.6	-3.7	-13.0
	Bio-oil/methanol	31.3	52.1	72.3
Pentanoic acid	Bio-oil	4.9	-2.7	-6.6
	Bio-oil/water	0.9	-13.1	-22.9
	Bio-oil/methanol	33.1	51.4	78.6

Table 4-4. Conversion of typical phenolics without unsaturated substituents in bio-oil

Compounds	Reaction medium	Conversion (%)		
		130 ºC	180 ºC	230 ºC
Phenol	Bio-oil	4.3	4.9	11
	Bio-oil/water	9.1	5.6	4.2
	Bio-oil/methanol	-0.4	2.0	-0.3
o-Cresol	Bio-oil	8.2	13.2	16.9
	Bio-oil/water	11.9	18.3	12.6
	Bio-oil/methanol	-3.4	-0.2	-4.9
p-Cresol	Bio-oil	4.5	3.9	19.3
	Bio-oil/water	6.0	6.8	18.3
	Bio-oil/methanol	-4.8	-1.4	2.9
m-Cresol	Bio-oil	20.0	35.6	42.2
	Bio-oil/water	31.6	44.1	42.1
	Bio-oil/methanol	-10.5	-3.6	3.2
Guaiacol	Bio-oil	3.1	3.0	-1.5
	Bio-oil/water	6.1	7.1	-4.3
	Bio-oil/methanol	-2.2	1.5	-7.2
2-Methoxy-4-methylphenol	Bio-oil	6.9	7.0	19.2
	Bio-oil/water	10.6	14.8	16.0
	Bio-oil/methanol	2.0	2.2	1.6
4-Ethyl-2-methoxyphenol	Bio-oil	4.9	0.1	9.0
	Bio-oil/water	4.6	8.6	10.8
	Bio-oil/methanol	-77.0	-22.1	-20.5
2,6-Dimethoxyphenol	Bio-oil	7.8	8.5	5.0
	Bio-oil/water	52.1	10.5	0.6
	Bio-oil/methanol	-5.0	-2.2	-8.3
1,2,4-Trimethoxybenzene	Bio-oil	10.4	9.9	10.8
	Bio-oil/water	22.5	17.4	7.2
	Bio-oil/methanol	-9.9	-9.4	-14.4

Table 4-5. Conversion of typical phenolics with unsaturated substituents in bio-oil

Compound	Reaction medium	Conversion (%) 130 °C	180 °C	230 °C
Eugenol	Bio-oil	7.1	5.1	43.0
	Bio-oil/water	3.9	21.9	51.4
	Bio-oil/methanol	-103.6	-18.9	3.2
Isoeugenol (Z)	Bio-oil	37.9	94.9	94.7
	Bio-oil/water	48.9	100	77.9
	Bio-oil/methanol	-5.9	6.9	54.4
Isoeugenol (E)	Bio-oil	58.6	52.1	75
	Bio-oil/water	52.1	60.0	62.6
	Bio-oil/methanol	-88.5	-62.1	-59.5
2,6-Dimethoxy-4(2-propenyl)phenol	Bio-oil	11.0	9.8	39.9
	Bio-oil/water	0.8	10.1	41.7
	Bio-oil/methanol	0.4	5.3	9.2
2,6-Dimethoxy-4(1-propenyl)phenol (Z)	Bio-oil	35	89.1	96.9
	Bio-oil/water	41.1	93.5	97.3
	Bio-oil/methanol	-0.3	19.9	54.5
2,6-Dimethoxy-4(1-propenyl)phenol (E)	Bio-oil	55.9	50.7	78.3
	Bio-oil/water	51.1	62.0	68.6
	Bio-oil/methanol	-43.8	-38.4	-42.9
1-(4-Hydroxy-3.5-dimethoxy phenyl), ethanone	Bio-oil	-2.5	-2.4	13.8
	Bio-oil/water	-7.0	-7.7	-3.3
	Bio-oil/methanol	-295.2	-89.7	-53.4
Vanillin	Bio-oil	8.8	28.6	77.5
	Bio-oil/water	7.6	24.6	57.7
	Bio-oil/methanol	4.7	9.4	27.9
4-Hydroxy-3,5-dimethoxybenzaldehyde	Bio-oil	8.7	29.8	79.6
	Bio-oil/water	11.4	26.9	58.9
	Bio-oil/methanol	-71.0	-10.7	17

With the increases in reaction temperature, the formation of these mono-rings in bio-oil was not increased in the thermal treatment of bio-oil in methanol. In comparison, production of the aromatics with two fused benzene rings or three fused benzene rings was promoted at higher reaction temperatures in methanol, as is shown in Figure 4-5. The results indicate that there was a shift from the production of mono-ring phenolics to the production of relatively heavier ones. In thermal treatment of bio-oil itself or in water, the conversion of the mono-ring phenolics was drastical and the formation of the heavy phenolics was also significant. The consumption of the mono-ring phenolics along with the formation of the heavy phenolics clearly indicated the polymerisation of the mono-ring phenolics to form the heavy phenolics.

In addition, as is shown in Tables 4-4 and 4-5, it was found that the functionalities significantly affected the reactivity of the phenolics. The phenolics having saturated functionalities such as methyl and methoxy group were not reactive, showing low conversions (Table 4-3). The compounds like isoeugenol (Z), isophenol (E), 2,6-dimethoxy-4(1-propenyl)phenol (Z), 2,6-dimethoxy-4-(1-propenyl)phenol (E), vanillin, 4-hydroxy-3,5-dimethoxybenzaldehyde contain big conjugated π bond and the unsaturated functionalities attached to the benzene ring, which made these compounds more reactive than the ones without unsaturated functionalities during thermal treatment of bio-oil itself or in water

4.3.5 Characterisation of the products

The product obtained from thermal treatment of bio-oil at 130°C for two hours remained one phase. The elemental analysis results were shown in Table 4-6, where it can be seen that the carbon content increased compared with that of bio-oil due to the formation of more water after reaction. After thermal treatment of bio-oil at 180 and 230°C, a solid phase was formed. Compared with the bio-oil feedstock, the solid phase has much lower oxygen content and relatively higher carbon content. The formation of the solid phase was associated with the loss of oxygen. The loss of oxygen is via production of water in dehydration reactions, followed by condensation reaction to produce polymeric chains. These insoluble polymers caused phase separation. The separation of solid phase from the aqueous phase also indicated that the components in the solid phase became more hydrophobic, indicating the loss of the oxygen-functionalities. Polymerisation is a process in which reactive compounds combine to form bigger compounds generally with the loss of some simple molecules such as water, which would decrease the content of oxygen in thermal treatment products

Table 4-6. Water content and elemental content (dry basis) of bio-oil feedstock and products

Sample name	Water content (%)	N (%)	C (%)	H (%)	O (%)
Bio-oil feedstock	30.0	0.2	52.9	4.7	42.2
130°C, product	34.0	0.2	56.1	4.4	39.3
180°C, solid phase	10.2	0.2	66.4	5.0	28.5
230°C, solid phase	14.2	0.1	66.0	4.8	29.0
130°C in water, solid phase	9.1	0.2	66.8	6.2	26.8
180°C in water, solid phase	5.0	0.2	68.0	5.5	26.3
230°C in water, solid phase	9.0	0.2	71.0	5.9	22.9

4.3.6 Potential coke quantified via TGA

The potential coke yields of bio-oil feedstock and products were presented in Table 4-7. After the thermal treatment of bio-oil itself at 130°C, the potential coke yield was almost the same to that of the bio-oil feedstock, which indicated that the composition of bio-oil did not change much. With the further increasing the reaction temperature to 180 and 230°C, potential coke yield increased to 18.5 and 21.9 wt.%, respectively. Thus, higher reaction temperature favoured the formation of heavy components, which contributed to the formation of potential coke. When external water was added to bio-oil, the potential coke yield of the corresponding products was similar to that of thermal treatment of bio-oil itself. In contrast, the potential coke yield in the product with methanol almost remained unchanged or even lower after thermal treatment at 130, 180 and 230°C. It was clear that bio-oil was stabilised in methanol during thermal treatment.

Table 4-7. Potential coke yield of liquid products quantified by TGA

Reactant mixture	Holding temperature (°C)	Potential coke yield (wt.%)
Bio-oil feedstock	N/A	11.3
Bio-oil	130	11.8
Bio-oil	180	18.5
Bio-oil	230	21.9
Bio-oil/water	130	13.5
Bio-oil/water	180	17.5
Bio-oil/water	230	21.7
Bio-oil/methanol	130	11.0
Bio-oil/methanol	180	11.4
Bio-oil/methanol	230	12.8

4.4 Conclusions

The reaction behaviour of the components in bio-oil during thermal treatment in water or in methanol was distinctly different. In water, aromatics with one to two fused benzene rings were consumed, while heavy aromatics with three and more fused benzene rings were produced. The light phenolics possibly polymerised to form the heavy ones in water, especially the ones with the unsaturated funcationalities. In comparison, the products from thermal treatment of bio-oil in methanol had a higher overall fluorescence intensity, indicating the formation of more aromatics from mono-rings to three or more fused benzene rings. These heavy aromatics were stabilised in the thermal treatment of bio-oil in methanol. GC-MS results confirmed this different reaction behaviour of the mono-phenolics in the thermal treatment of bio-oil in water and in methanol. In addition, it was found that weak acids like acetic acid and formic acid had negligible effects on the reaction behaviour of aromatics in bio-oil, due to their low acidity. Bio-oil contains some heavy carboxylic acids, which probably have similar or stronger acidity than aliphatic acid. However, the aromatics were sensitive to the acids such as Amberlyst 70 catalyst with much stronger acidity. The understanding of the reaction behaviours of the aromatics of bio-oil during thermal treatment is of importance for the process optimization in upgrading of bio-oil.

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Chapter 5

Formation of Coke during the Esterification of Pyrolysis bio-oil

5.1 Introduction

Bio-oil is a liquid product from the pyrolysis of biomass, which can be upgraded to the biofuel [1-5]. During the upgrading of bio-oil, for example via hydrotreating, coke formation is found to be one of the biggest bottle-neck challenges as it can block reactor and lead to fast catalyst deactivation [6-11]. Bio-oil thus needs to be stabilised before the further treatment under harsh conditions [12-14]. Esterification in alcohols is one method to stabilise bio-oil through the removal of the reactive compounds such as sugars and furans via various acid-catalysed reactions [15].

Various acid catalysts has been applied in the esterification of bio-oil, including mineral acids, solid acidic resin, supported acid catalysts and sulfated metal oxides. The inorganic liquid acid catalysts can disperse homogeneously in bio-oil. However, the difficulty to separate them from products, high corrosiveness and low recyclability restrain their application. In comparison, solid acid catalysts can easily recover from product mixture and could be reused, which had been widely employed as catalysts via esterification of bio-oil [16-20]. The studies about bio-oil esterification were mainly focused on the transformation of bio-oil into the required products and the development of catalysts [21-25], while the coke formation during esterification has hardly been noticed. Coke formed during esterification cannot be neglected as it can deactivate solid acid catalysts, lower the efficiency of the process and increase the cost [26].

Various reaction parameters affect the coke formation during the esterification of bio-oil. For example, various alcohols can be used to esterify bio-oil, but they have different structures and possibly have different effects on coke formation. In addition, alcohols can suppress the polymerisation of sugars under the esterification conditions [15]. However, it has not been cleared whether these alcohols can also suppress the polymerisation reactions in bio-oil or not. Further to this, it has also not been cleared about the contribution of water towards the polymerisation of bio-oil as water is the most abundant compound in bio-oil.

Understanding the effects of different alcohols and water on coke formation during esterification could help to understand the mechanism for coke formation. This will further help to develop the countermeasures to suppress the coke formation. Thus, in this study the characteristics of coke formation from bio-oil in various alcohols (methanol, ethanol,1-propanol,1-butanol, ethylene glycol), phenol (another form of "alcohol") and water under a wide range of reaction conditions were investigated. The functional groups and structures of the coke were analysed with FT-IR and UV-fluorescence spectroscopy.

5.2 Experimental

5.2.1 Preparation of bio-oil

The wood bio-oil used in this study was prepared by Dr Daniel Mourant with the fluidised-bed reactor at 500°C from mallee wood biomass. A detailed description of reactor system and experimental procedure can be found in Section 2.2, **Chapter 2**. Bio-oil sample was kept in fridge until being used and after being used.

5.2.2 Acid-catalysed reaction of bio-oil in methanol or water

A Hostelloy autoclave was used to conduct the acid-catalysed reaction of bio-oil in solvents. The mass ratio of bio-oil and alcohols/phenol/water was 1:2. The reaction temperature was ranging from 90 to 170 ^{o}C and reaction time was set in the range of 30 to 360 minutes. The specific parameters of typical experiments were shown in Table 5-1. The flowchart of the reaction system was illustrated in Figure 5-1.

Table 5-1. The yield of coke with different upgrading parameters.

Reaction medium	Mass ratio[a]	Bio-oil (g)	Reaction time (min)	Reaction temperature (°C)	Catalyst[b] loading (wt.%)	Coke yield[c] (wt.%)
Water	1:2	25	120	170	15	27.6
Methanol	1:2	25	120	RT[d]	15	2.9
Methanol	1:2	25	120	170	15	15.4
Ethanol	1:2	25	120	170	15	15.4
1-Propanol	1:2	25	120	170	15	15.5
1-Butanol	1:2	25	120	170	15	15.6
Ethylene glycol	1:2	25	120	170	15	18.0
Methanol	1:2	25	120	90	15	3.2
Methanol	1:2	25	120	130	15	7.9
Methanol	1:2	25	120	170	5	10.4
Methanol	1:2	25	120	170	10	14.8
Methanol	1:2	25	30	170	15	11.5
Methanol	1:2	25	360	170	15	16.2
Methanol	1:1	40	120	170	15	15.4
Methanol	1:1	40	120	170	15	20.0[e]
Phenol	1:2	20	120	170	15	19.6

[a] The mass ratio refers to the ratio of bio-oil to reaction medium.

[b] The catalyst loading was based on the mass of bio-oil and solvent.

[c] $coke\ yieid = \frac{the\ mass\ of\ obtained\ \ insoluble\ material}{the\ mass\ of\ added\ bio-oil} \times 100\%$

[d] Reaction occurred at room temperature.

[e] total $coke\ yieid = \frac{the\ mass\ of\ obtained\ soluble\ and\ insoluble\ material}{the\ mass\ of\ added\ bio-oil} \times 100\%$

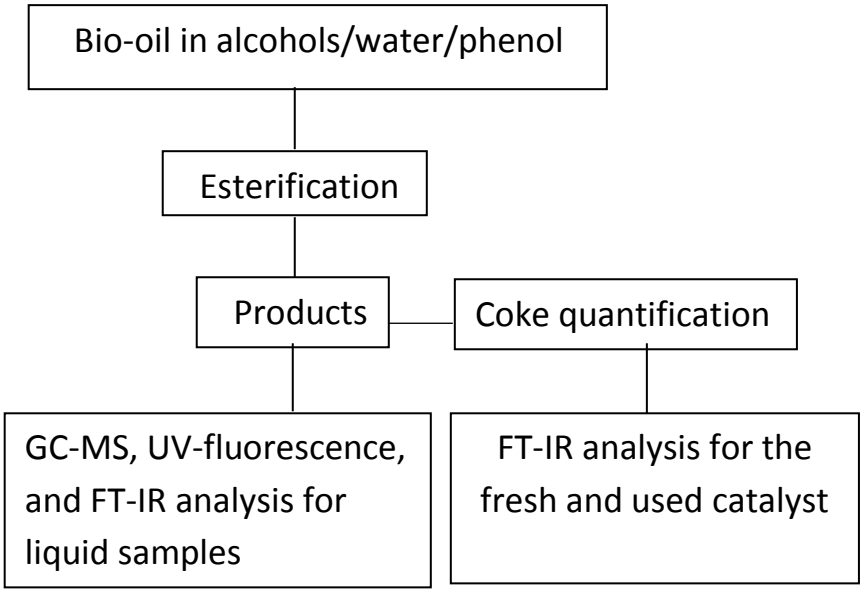

Figure 5-1. The flowchart of the reaction system.

Typically, the bio-oil and alcohols with the mass ratio of 1:2 were loaded into an autoclave vessel at room temperature. The autoclave was flushed with nitrogen for three times to exclude air and then sealed in nitrogen atmosphere. The reactor was then heated up to the target temperature at a stirring rate of 500 rpm in 20 min. Once reaction temperature reached the set value, a sample was taken immediately and the rest were taken at 20 min intervals until the end of the experiment. In some other experiments no sampling was taken with the purpose of determining the amount of coke formed during the esterification of bio-oil. The polymeric material formed was collected together with catalyst, washed with acetone, and dried in an oven at 105°C for four hours to constant weight to measure the coke formed.

5.2.3 Analytical methods

The products were analysed using an Agilent GC-MS (6890 series GC with 5973 series MS detector) equipped with a capillary column (HP-INNOWax). The bio-oil samples were diluted with acetone first to ca. 10 wt.% and was then injected into the injection port with a split ratio of 50:1. More details of the instrument and experimental procedure can be found in Section 2.5.1, **Chapter 2.**

UV-fluorescence spectra of samples were recorded using a Perkin-Elmer LS50B spectrometer, indicating the information about the relative size and concentration of aromatic rings. The UV-fluorescence spectra of samples were recorded with a constant energy difference of -2800 cm-1 and a scan speed of 200 nm/min. Samples were diluted with methanol to minimise the effect of self-absorption. The intensity of UV-fluorescence is in a linear relationship with the concentration of sample. The excitation wavelength indicates the size of aromatic rings. A detailed description of the instrument and procedure can be found in Section 2.5.2, **Chapter 2**.

FT-IR spectra were recorded using a Perkin-Elmer Spectrum GX FT-IR/Raman spectrometer in the 4000–500 cm^{-1} range with a spectral resolution of 4 cm^{-1} at room temperature. The solid catalyst was dried at 105°C for two hours, ground to powder, mixed with KBr (ca. 2 wt.%) and pressed into a pellet for the acquisition of the spectra. Liquid samples were diluted by isopropanol and then was injected into a liquid sample cell formed by CaF2 windows with a spacer size of 0.025 mm in between. A detailed procedure can be found in Section 2.5.3, **Chapter 2**.

5.3 Results and discussion

5.3.1 Coke formation in different alcohols and water

Table 5-1 shows the coke formation during the acid-treatment of bio-oil with various alcohols and water. Alcohols can stabilise bio-oil. Carboxylic acids can be converted into esters [27]. Aldehydes can be stabilised by acetalisation to form acetals [28]. Sugars, like levoglucosan, in methanol were mainly converted to methyl α-D-glucopyranoside and subsequently to 2-dimethoxymethyl-5-methoxymethylfuran and finally to methyl levulinate with a high selectivity. The protection of the reactive functional groups of levoglucosan and furans can effectively inhibit polymer formation [29-30]. The effects of methanol and 1-butanol on the coke formation were quite similar (coke yield: 15.4 wt% versus 15.6 wt%), although 1-butanol has a long carbon chain and methanol has a short one. The longer aliphatic carbon chain in 1-

butanol does not have remarkable impact on the amount of coke formed. The steric effect of different sizes of the alcohols with the different carbon chain during esterification of bio-oil was relatively small.

However, more coke was formed in the esterification of bio-oil with ethylene glycol. The multiple hydroxyl groups in ethylene glycol made the alcohol very reactive. For example, the conversions of phenol and 2, 6-dimethoxy phenol in bio-oil (Figure 5-2) were similar in methanol and 1-butanol but relatively higher in ethylene glycol. The conversion of 2,6-dimethoxy phenol increased rapidly in alcohols within the first 30 minutes, reaching a plateau after 40 minutes in methanol and butanol. However, in ethylene glycol, the conversion kept increasing with the prolonged reaction time. Similar phenomenon was observed in the conversion of phenol. However it is very difficult to identify the exact products from the conversion of 2,6-dimethoxy phenol due to the complexity of bio-oil, but UV-fluorescence characterization (Figure 5-3) can give us a clue about the reactivity of aromatics in different alcohols.

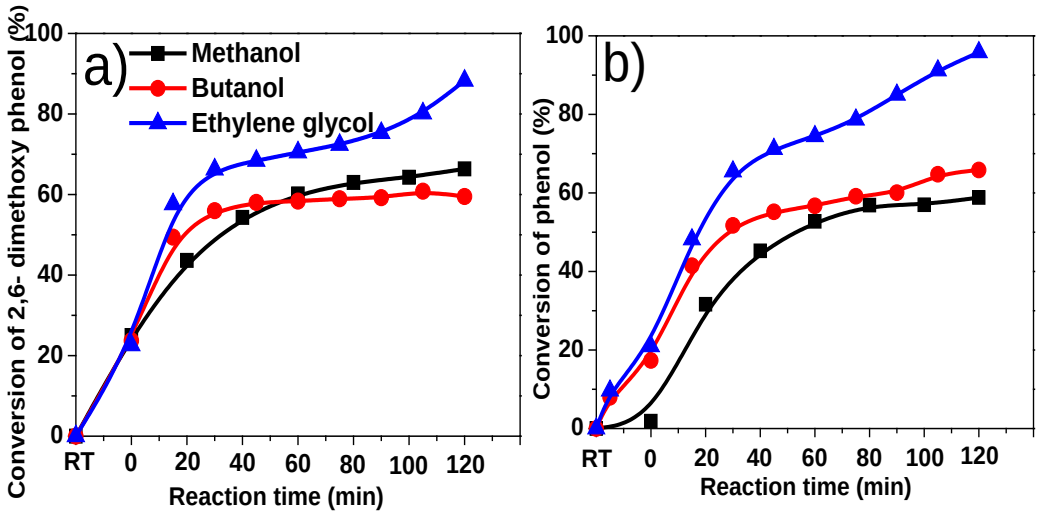

Figure 5-2. Effects of different alcohols on the conversion of some phenolic compounds in bio-oil. a) 2,6-dimethoxy phenol. b) phenol. Temperature: 170°C; Catalyst loading: 15wt.%; Stirring rate: 500 rpm; Residence time: 120 min; RT: reaction mixture at room temperature.

Figure 5-3 shows the fluorescence intensity of the aromatics in the esterified bio-oil versus reaction time. The decreases in the intensity with reaction time indicate that some aromatics were transformed from liquid phase into solid phase (form coke). Increasing the holding time from 0 to 60 min, the fluorescence intensity of the aromatics in all alcohols declined significantly, indicating the polymerisation of these aromatics. This agrees well with the conversion trend of phenol and 2, 6-dimethoxyphenol shown in Figure 5-2 at the same time frame.

After 60 min of residence time, in methanol and 1-butanol the fluorescence intensity reached a steady state and the reactions also reached an equilibrium, but in ethylene glycol the intensity continued to decrease, which is also well related with the continuous conversion of phenol and 2,6-dimethoxyphenol in ethylene glycol with progress of the reaction. These results clearly indicate that ethylene glycol is more reactive towards the aromatics in bio-oil than methanol and 1-butanol. Ethylene glycol with two hydroxyl groups tend to form big molecules by cross-coupling reaction.

Water is an important product from the fast pyrolysis of biomass. It plays a key role in the coke formation from bio-oil. Compared with the coke yield in methanol, the coke yield in water almost doubled. Although water also has a hydroxyl group, it did not show the same effect of coke formation as methanol and 1-butanol. Water and alcohols behaves differently during acid-treatment of bio-oil, leading to very different amount of coke formation. Carboxylic acids in bio-oil are the catalysts for the polymerisation of bio-oil [8]. In alcohol-rich medium, the carboxylic acids are converted to neutral esters [21]. In comparison, water cannot remove the carboxylic acids in bio-oil, but in converse promotes their formation [21]. In addition to carboxylic acids, some other reactive compounds in bio-oil such as aldehydes can also be stabilised. C6 sugars and furans like HMF and furfuryl alcohol in bio-oil can be stabilised and finally converted to alkyl levulinate in alcohols rich medium [31]. However, in water, sugars such as levoglucosan tended to polymerise to coke [31, 32]. The difference created the distinct tendency of coke formation during the acid-treatment of bio-oil in methanol and in water.

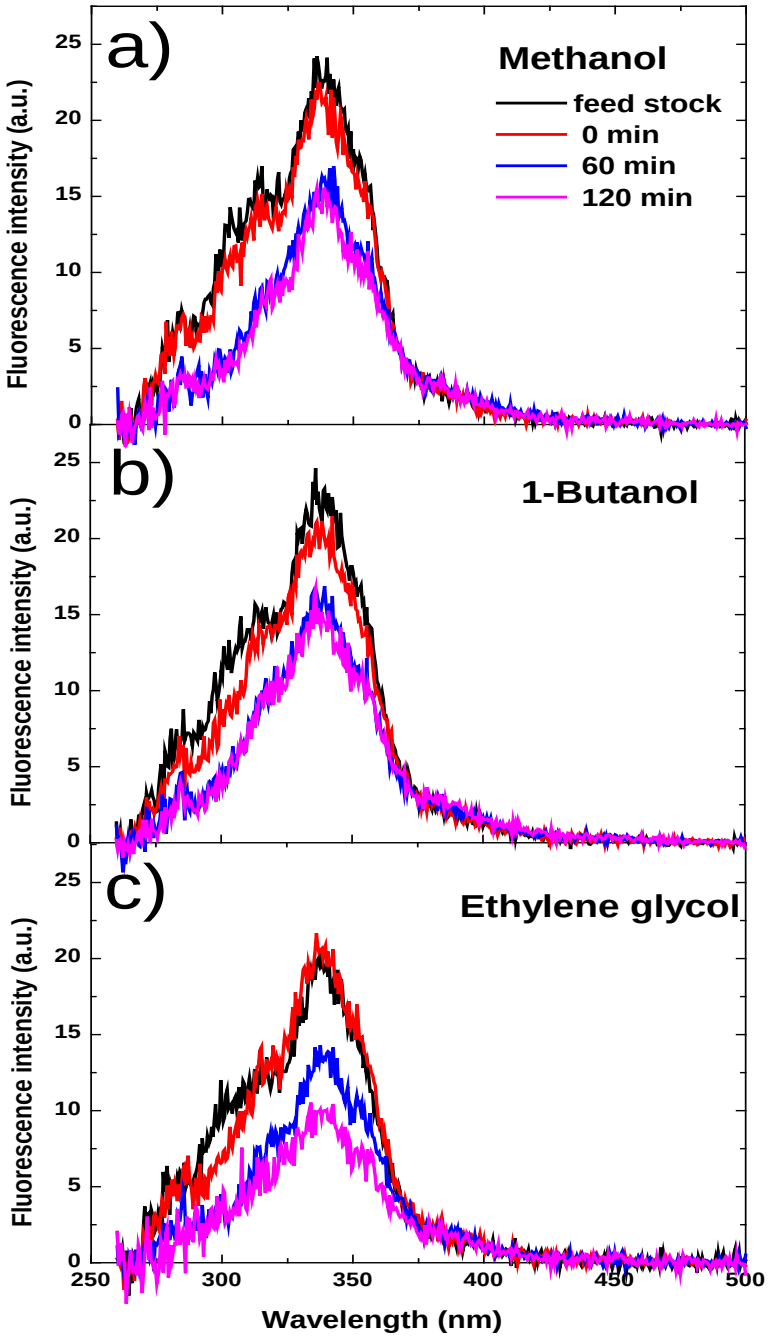

Figure 5-3. The fluorescence intensity of the mixture of bi-oil and methanol as a function of reaction time. a) The mixture of bi-oil and methanol. b) The mixture of bi-oil and 1-butanol. c) The mixture of bi-oil and ethylene glycol. Catalyst loading:

15 wt.%; Stirring rate: 500 rpm; Reaction temperature: 170°C; Residence time; 120 min.

5.3.2 Coke formation in phenol

Similar to alcohols and water, phenol also contains a hydroxyl group. Phenol is more acidic than alcohols and water, and the polymerisation of bio-oil may be different in phenol. As shown in Table 5-1 the coke amount formed in phenol is 19.6%, which is relatively higher than that in methanol. This is because in phenol with Amberlyst 70 some of the aromatics with bigger aromatic rings were converted to coke by condensation reactions. As is shown in Figure 5-4, the peak centred at 275 nm representing mono-benzene ring increased after the reaction, while the peak centred at 330 nm representing the aromatic ring systems having two or more fused benzene rings decreased [33]. Phenol as one of the reactants contributed to the intensified peak centred at 280 nm. After the acid-treatment, although phenol was consumed, the intensity of the peak representing mono-rings increased, indicating some hydrolysis reactions happened, producing more products with single rings. The decrease of the intensity of peak ranging from 300 to 375 nm elucidate the condensation and polymerisation reactions occurred. In addition, according to GC-MS analysis, some new aromatics are detected in the product, while the abundance of others increased significantly after the acid-treatment of bio-oil in phenol, as is shown in Figure 5-5. It is believed that phenol reacted with the components in bio-oil, forming these bigger aromatics and more coke.

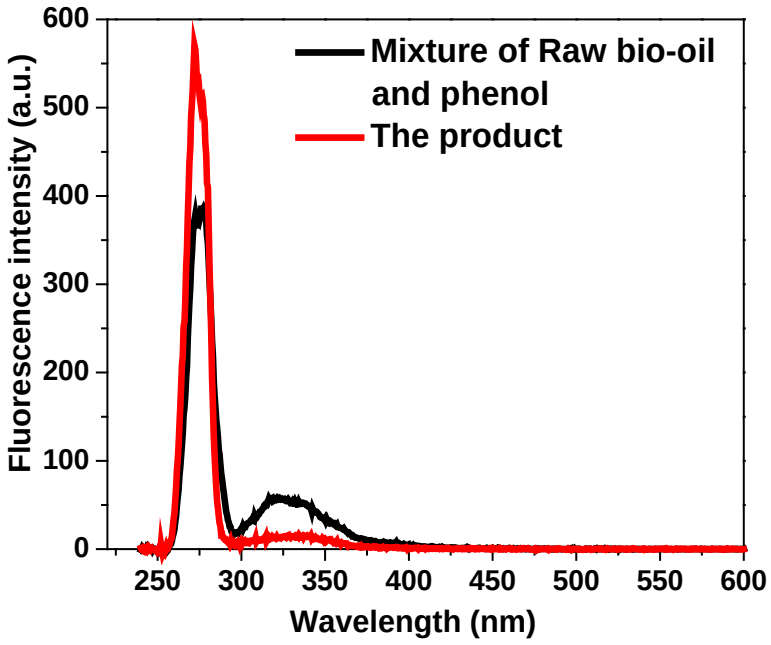

Figure 5-4. Constant energy (-2800 cm^{-1}) synchronous spectra of the mixture of raw bio-oil/phenol and product from acid treatment of bio-oil/phenol. Catalyst loading: 15 wt.%; Stirring rate: 500 rpm. Reaction temperature: 170°C; Residence time: 120 min.

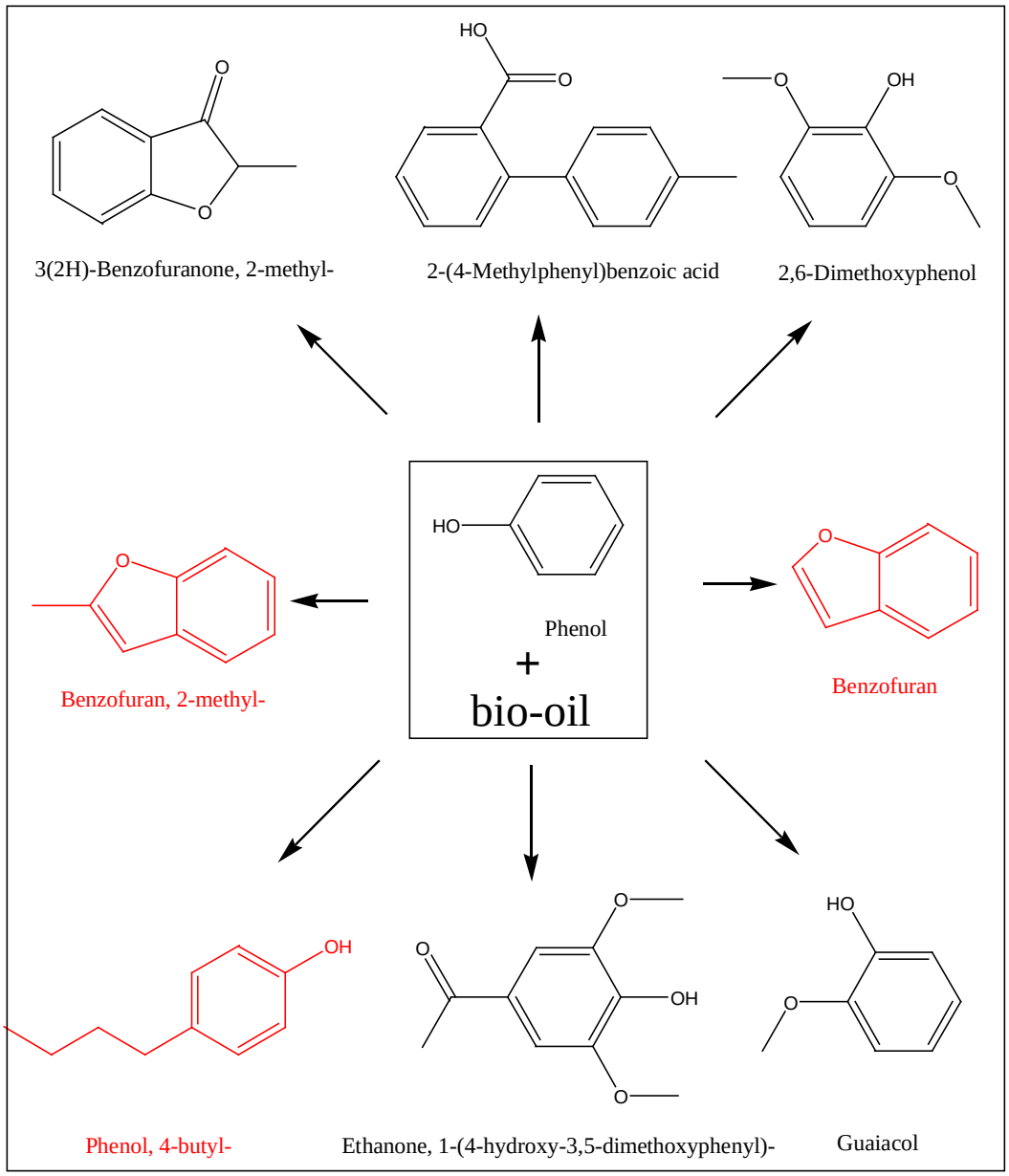

Figure 5-5. Typical compounds produced during the reaction of bio-oil and phenol at 170°C for 120 minutes with the presence of Amberlyst 70.

5.3.3 Effects of reaction temperature on coke formation

Reaction temperature significantly affects the formation of coke during esterification. As expected, coke yield increased with the increase of reaction temperature. It is noteworthy to mention that even at room temperature, a small amount of coke was formed, mechanism of which has not been cleared but there are two possible reasons. Firstly, small particles such as char produced from the pyrolysis of biomass might deposit on the catalyst. Secondly, bio-oil from the fast pyrolysis of biomass was not a very stable mixture of organics. Some components in bio-oil may be already reactive enough in the presence of acid catalyst at room temperature to condense.

The coke yield at 90°C only increased by 0.3% when compared with the coke yield at room temperature, which means the coke formation at 90°C may followed similar mechanism with that at room temperature. The majority of components in bio-oil such as levoglucosan have not yet started their reactions at such a low temperature. When the reaction temperature was increased to 130 and 170°C, much more coke was formed. Clearly, the components in bio-oil became reactive and participated in the condensation reactions at elevated temperatures. These are also in a good agreement with characterisation of the products with UV fluorescence.

As is shown in Figure 5-6, at 90°C, the fluorescence intensity of the bio-oil/methanol mixture did not show any clear decreases with reaction time, while at elevated reaction temperature of 130 and 170°C they decreased significantly, indicating serious coke formation. However, due to the complexity of bio-oil, it is difficult to identify the source or precursors for coke formation. Thus, special attention was paid to some typical compounds to gain some better understanding about the formation of coke.

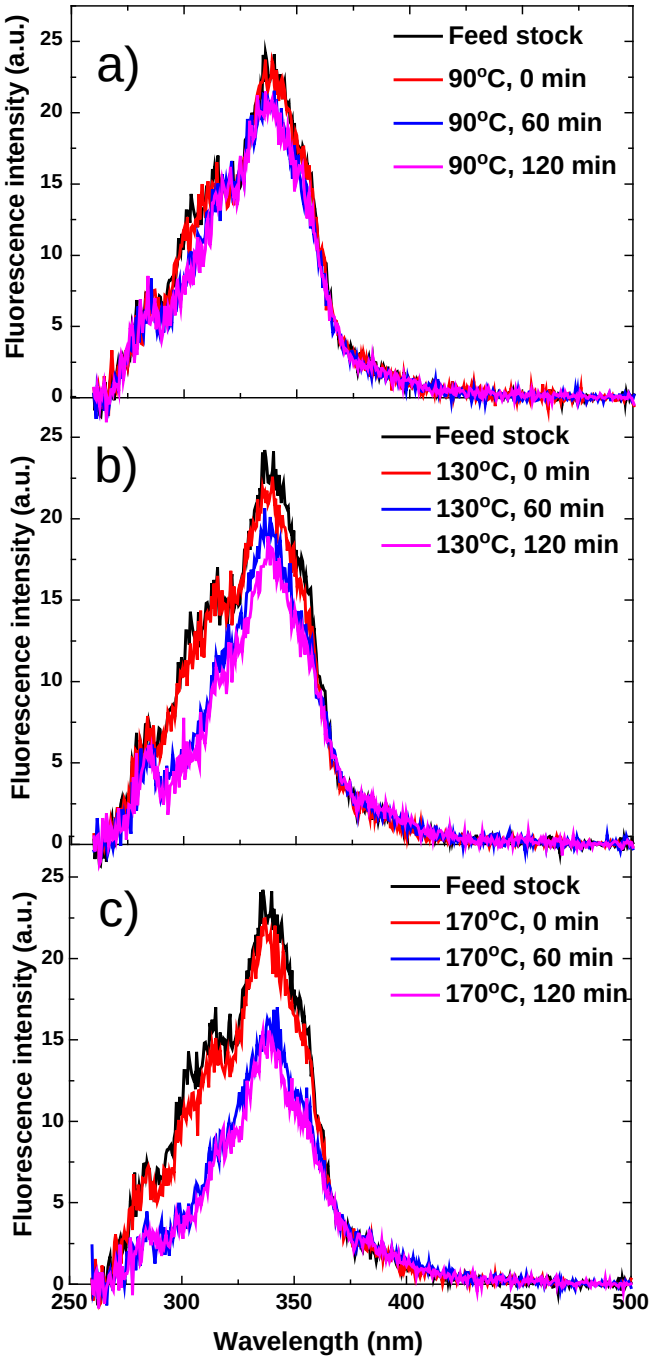

Figure 5-6. Constant energy (-2800 cm^{-1}) synchronous spectra of the mixture of bi-oil and methanol as a function of reaction time at different reaction temperatures a) Reaction temperature: 90°C. b) Reaction temperature: 130°C. c) Reaction temperature: 170°C. Catalyst loading: 15 wt.%; Stirring rate: 500 rpm; Residence time: 120 min.

As is shown in Figure 5-7, aromatics can be very reactive at elevated temperatures (i.e. 170°C) but they have different reactivity due to their different molecular structures. Trans-4-propenyl-2, 6-dimethoxyphenol and cis-4-propenyl-2, 6-dimethoxypheno with big conjugated π bonds were more reactive than 4-allyl-2, 6-dimethoxy phenol, resulting in almost 95% of conversion at 130 and 170°C. Apparently, the functional groups could significantly affect reactivity. However, it is difficult to identify all their corresponding products. Possibly, the products were heavy polymers which cannot be detected with GC-MS.

In order to understand the reactivities of aromatics in bio-oil with different structures during esterification with methanol, three typical aromatics in bio-oil, isoeugenol, 2,6-dimethoxyphenol and 1,2,4-trimethoxyphenol, were chosen for model compound experiments. The UV-fluorescence results of isoeugenol showed that some soluble polymer was formed, as is shown in Figure 5-8. Two broad peaks were obtained, centred at 280 and 375 nm, respectively. The peak centred at 280 nm represented compounds with mono-benzene ring, which was the reactant here. The peak centred at 375 nm represented compounds with around three fused benzene rings [34-36], which were the products. The fluorescence intensity of reactant decreased and meanwhile fluorescence intensity of products increased with prolonged reaction time, indicating the polymerization of isoeugenol. However, the soluble polymer cannot be identified with UV-fluorescence in the model compounds experiments of 2,6-dimethoxyphenol and 1,2,4-trimethoxyphenol. This indicates that these two compounds without C=C bonds in their side chain are more stable.

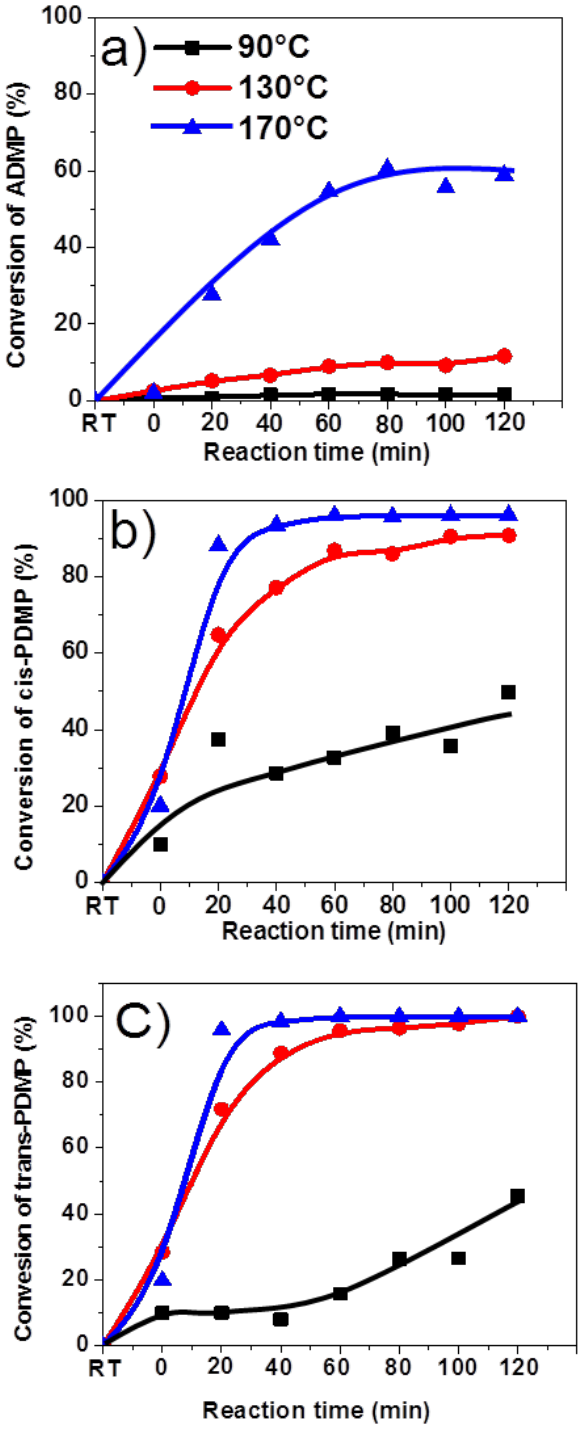

Figure 5-7. Effects of reaction temperatures on the conversion of some typical compounds in bio-oil. a) 4-Allyl-2, 6-dimethoxyphenol (ADMP). b) cis-4-Propenyl-2, 6-dimethoxyphenol (cis-PDMP). c) trans-propenyl-2, 6-dimethoxyphenol (trans-PDMP). Solvent: Methanol; Catalyst loading: 15 wt.%; Stirring rate: 500 rpm; Residence time: 120 min; RT: reaction mixture at room temperature.

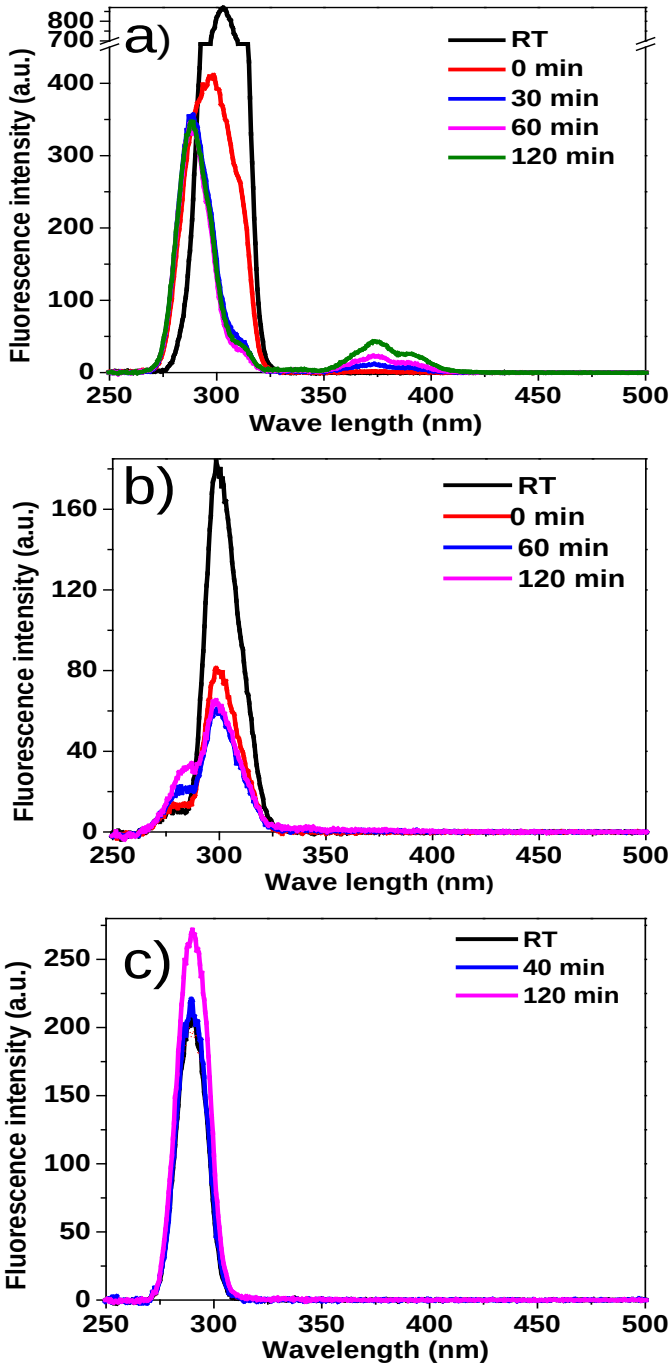

Figure 5-8. Constant energy (-2800 cm^{-1}) synchronous spectra of reactants versus reaction time over acid-treatments of model compound in methanol. a) Isoeugenol samples were diluted in methanol to 30 ppm. b) 2,6-dimethoxyphenol samples were diluted to 300 ppm. c) 1,2,4-trimethoxyphenol samples were diluted in methanol to 30 ppm.

5.3.4 Effects of catalyst loading and reaction time on coke formation

Catalyst loading can also affect the coke formation but not much. With the increase of catalyst loading from 10 to 15%, coke yield almost unchanged (14.8%). However, with low catalyst loading of 5%, coke yield is only 10.4%. Obviously, the amount of coke formed is related to the amount of acidic sites available to the reactants. Amberlyst 70 is a solid acid resin catalyst, and most of active sites (hydrogen ions) are located deep in the polymeric structure of catalyst [37]. Easy access to the hydrogen ions promoted the acid-catalysed reactions including polymerization reactions. The higher the loading of catalyst, the higher chance they polymerised.

Residence time also significantly affect coke formation. The coke yield in the experiment with only 30 min of residence time was 11.5%, which is close to that in the experiment with 120 min residence time (15.4%). This indicates that the majority of coke formation has already occurred in the first 30 min. The polymerization of the reactive compounds proceeds very quick, which can deactivate the solid acid catalysts and affect the conversion of other components. In addition, it was noteworthy to mention that the prolonged reaction from 120 to 360 min only increased the yield of coke by 0.8%. From 120 to 360 min, the components of bio-oil remain almost unchanged and bio-oil was stabilised under these conditions.

5.3.5 Characterisation of coke by FT-IR spectroscopy

In order to understand property of the coke formed, the fresh catalyst and used catalyst were characterised with FT-IR. The results are shown in Figure 5-9a. Figure 5-9b was the corresponding deconvolution results of Figure 5-9a. Each band was obtained by following the method developed in the previous study from our group [38]. The detailed method can be found in Chapter 2. The peak centred at 1606 cm^{-1} refers to C=C bond in aromatic ring, and the peak centred at 1696 cm^{-1} refers to C=O bond of unsaturated aldehydes and ketones. Compared with that of the fresh catalyst, the intensity of peaks at 1606 and 1696 cm^{-1} increased significantly for the used catalyst. This indicates that the coke on catalyst was primarily comprised of big aromatics and unsaturated aldehydes and ketones.

The abundance of the big aromatics, unsaturated aldehydes and ketones in the unwashed catalyst is higher than that of washed one, indicating that the main components of the soluble polymeric material in bio-oil were also big aromatics and unsaturated aldehydes and ketones. The big aromatics and unsaturated aldehydes and ketones are likely the precursors for coke formation.

The polymerization was accompanied by the dehydration of the reactive components in bio-oil to form carbon double bonds, which was proved by FT-IR results of bio-oil. As are shown in Figure 5-10, the two peaks between 3000 and 2800 cm^{-1}, which represent the stretching vibrations of C-H bond in alkanes, decreased with reaction time. Meanwhile, the peaks centred at 1720 and 1650 cm^{-1}, which represent stretching vibration of C=O double bond and C=C bond respectively, increased with reaction time. These two phenomena prove that more unsaturated compounds with these functional groups were formed during the esterification of bio-oil with methanol.

5.3.6 Characterisation of soluble polymer by UV-fluorescence spectroscopy

Soluble polymeric material is considered to be largely the precursor of insoluble polymeric material. Methanol/chloroform at the volume ratio of 1:4 was used to wash the used catalyst. The fluorescence spectra of the washed solution from catalyst, raw feed stock solution and liquid product were shown in Figure 5-11. The ratio of aromatics with two fused benzene rings to mono aromatic ring for liquid product is higher than that in feed stock solution. The ratio of the aromatics with three more fused benzene rings to the aromatics with two fused benzene rings for wash solution from catalyst is higher than those for liquid product and feed stock solution. These clearly indicate that there are more big aromatic rings in the wash solution from catalyst than that in feed stock solution and liquid product solution. This is the direct evidence about the important contribution of the aromatics to coke formation during esterification

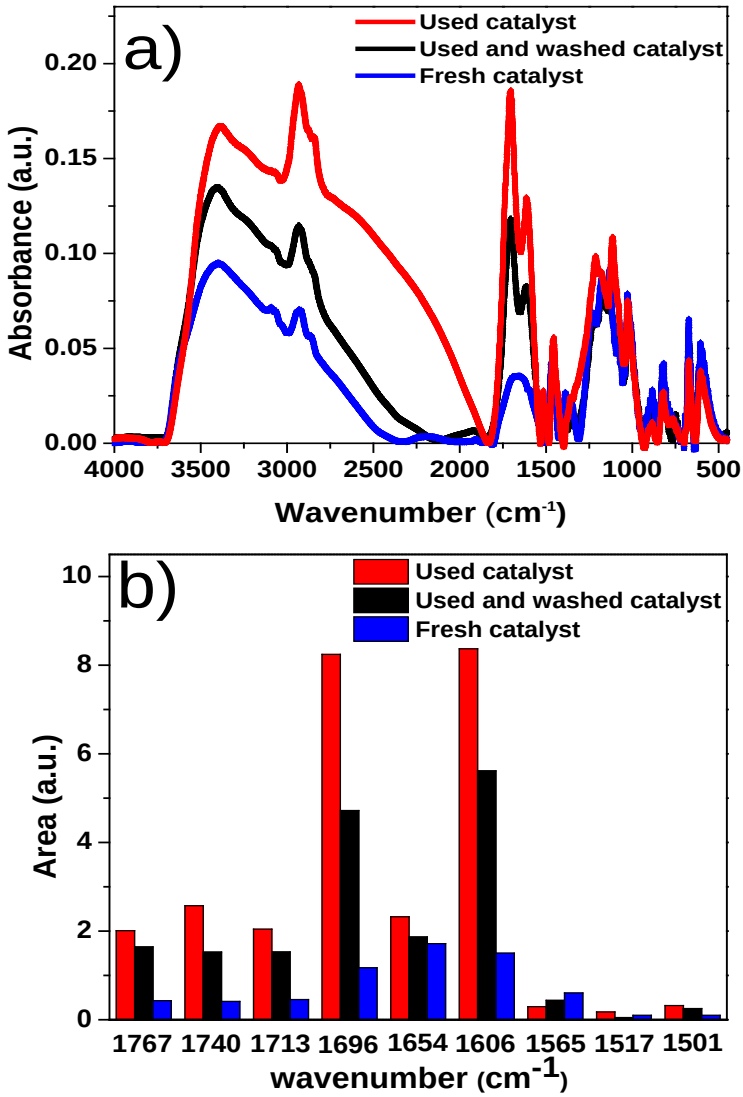

Figure 5-9. a) FT-IR spectra of fresh catalyst, used catalyst, and used and washed catalyst. b) Band areas of the deconvolution. The used catalyst is from the experiment of methanol and bio-oil with mass ratio of 2:1, catalyst loading of 15 wt.%, and stirring rate of 500 rpm reacted in the autoclave for 120 minutes.

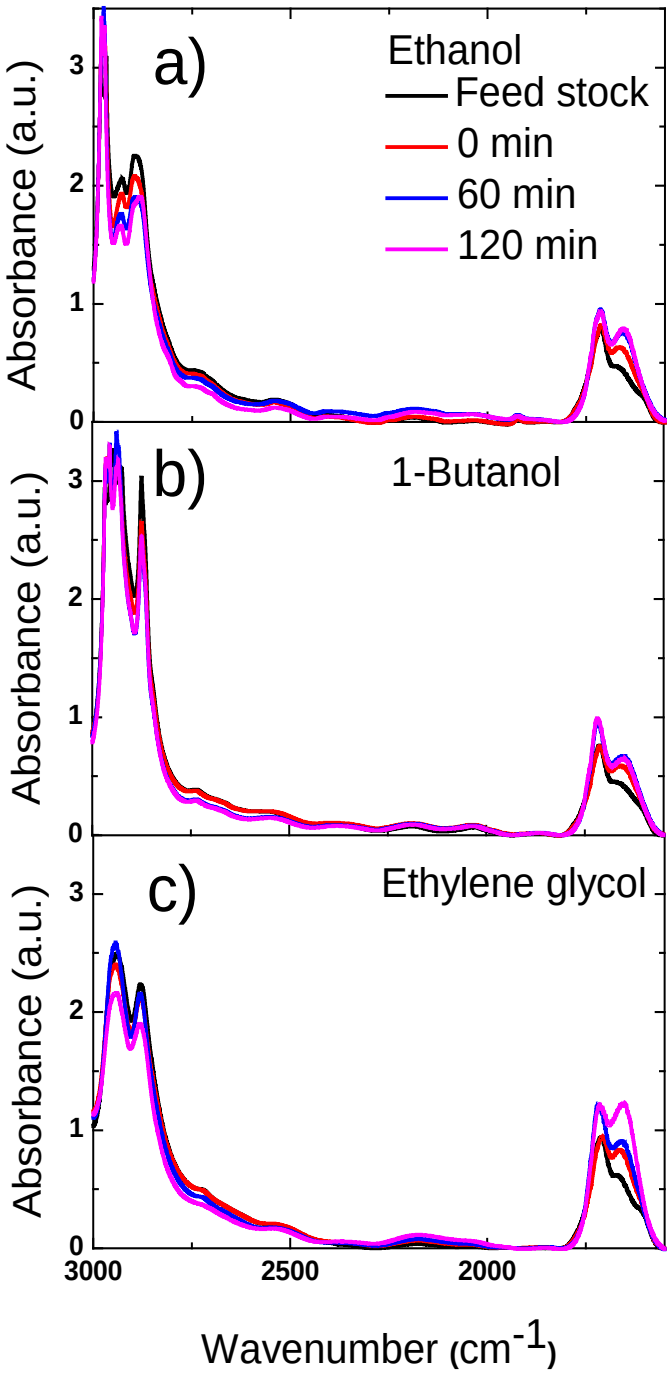

Figure 5-10. FT-IR spectra of the mixture of bio-oil and alcohols as a function of reaction time. a) The mixture of bio-oil and ethanol. b) The mixture of bio-oil and 1-butanol. c) The mixture of bio-oil and ethylene glycol.

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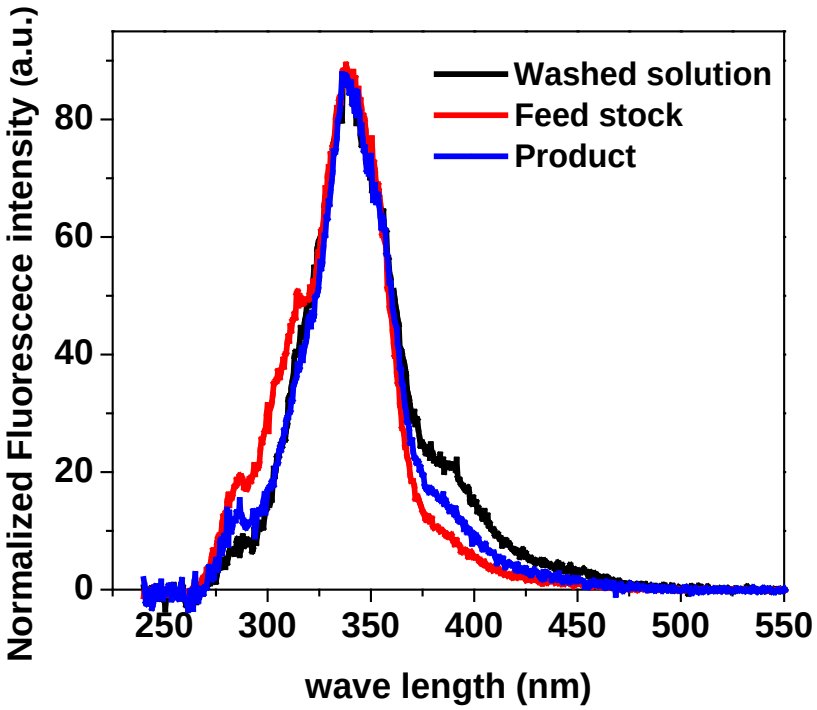

Figure 5-11. Constant energy (-2800 cm^{-1}) synchronous spectra of wash solution, feed stock solution and liquid product solution. Samples were diluted in methanol to different concentrations. The used catalyst is from the experiment of methanol and bio-oil with mass ratio of 2:1, catalyst loading of 15 wt.%, and stirring rate of 500 rpm reacted in the autoclave for 120 minutes.

5.4 Conclusions

This study reported the effects of alcohol, water, reaction temperature and catalyst loading on coke formation during the esterification of bio-oil. Coke yields during esterification in the mono-alcohols (methanol ethanol, 1-propanol and 1-butanol) were similar, which were independent of the size of alcohols. A higher coke yield was obtained in ethylene glycol due to its multiple hydroxyl groups. The coke yield in water is much higher than those in alcohols. Alcohols can stabilise the reactive components of bio-oil such as carboxylic acids, aldehydes and sugar oligomers, while water promotes the polymerisation of bio-oil. Phenol as a typical phenolic compound also boosted the coke formation of bio-oil. Small mono-rings were produced and

meanwhile, the aromatics with fused benzene rings were consumed. Higher reaction temperatures, longer residence time and higher catalyst loading also favour the polymerisation of bio-oil. FT-IR characterizations of soluble polymeric material and insoluble polymeric material showed that aromatics were the dominant components in these two kinds of polymeric materials. The UV-fluorescence results indicated that small aromatics in bio-oil underwent polymerisation to form big fused aromatics.

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5.5 References

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Chapter 6

Acid-treatment of Bio-oil in Methanol: The Distinct Catalytic Behaviours of a Mineral Acid Catalyst and a Solid Acid Catalyst

6.1 Introduction

Bio-oil, the liquid product from the pyrolysis of biomass, is a complex mixture of various organics [1-4]. The complexity of bio-oil leads to the instability of bio-oil, creating many difficulties for its applications [5-9]. Bio-oil has to be upgraded to improve its stability for the further upgrading via such technologies as hydrotreatment [10-12]. Esterification is a simple method to transform the carboxylic acids in bio-oil into neutral esters [13-15]. In our previous study, we found that esterification could not only transform the acids in bio-oil, but also other components such as sugars, aldehydes and many other reactive components [16-18]. Esterification is thus an important way of upgrading of bio-oil. Although a considerable amount of acids intrinsically exists in bio-oil, they are not able to efficiently catalyse the esterification of bio-oil, due to their relatively weak acidity [19]. External catalyst is thus required and is also one of the key factors affecting the efficiency of esterification of bio-oil.

Mineral acids and solid acid catalysts are two main kinds of acid catalysts used in the esterification of bio-oil [20-29]. The difference of the two types of catalysts can be remarkable. Mineral acids such as sulfuric acid and hydrochloric acid have strong acidity and the hydrogen ions can disperse homogeneously in bio-oil. The steric barrier for accessing the hydrogen ions is negligible. Moreover, it is difficult to deactivate the mineral acid catalyst via polymerisation reactions as the hydrogen ions are dispersed in liquid medium, but not confined on the surface of a support. In comparison, solid acid catalysts like solid acidic resin (e.g. Amberlyst 70) show quite different physicochemical properties. The hydrogen ions are confined in the local vicinity of the catalyst, but not dispersed homogenously in the reaction medium. Filling of the pores of the catalyst via polymerisation could easily deactivate the catalyst [23].

Compared with mineral acids, the local concentration of the hydrogen ions on or near the external and internal surface of a solid acid catalyst is much higher than that in the reaction medium [20]. A solid acid catalyst is thus less corrosive than a mineral acid to the reactor. In addition, solid acid catalysts can be easily separated and recycled, while separation of mineral acids from the liquid products is very difficult and energy-

intensive. Solid acid catalysts thus have better potential for esterification of bio-oil, due to the recyclability and low corrosiveness. However, the hydrogen ions mainly disperse in the pore of the solid acid catalyst, which creates an issue for accessing the hydrogen ions on/in catalyst, especially for the heavy components in bio-oil. It is thus important to understand how the dispersion of hydrogen ions and steric effects affect the esterification of bio-oil, which provides essential information for the development of an effective solid acid catalyst for the esterification of bio-oil.

In this study, we focused on the effects of the dispersion of hydrogen ions on the conversion of the main components of bio-oil during esterification. Sulfuric acid and Amberlyst 70, which are two typical acid catalysts with distinct dispersion of hydrogen ions in bio-oil, were evaluated in the esterification of bio-oil and their reaction behaviours will be compared.

6.2 Experimental

6.2.1 Preparation of bio-oil

The bio-oil used in this study was produced by Dr MD Mahmudul Hasan. Mallee wood biomass was pyrolysed in a grinding pyrolysis reactor at 450°C with 54 rpm rotating rate. A detailed description of the reactor system and experimental procedure can be found in Section 2.2, **Chapter 2**.

6.2.2 Acid-catalysed experiments

An autoclave (Autoclave Engineers) assembled with a magnetic stirring device was used to conduct the acid-catalysed conversion of bio-oil. In a typical experiment, bio-oil and methanol at mass ratio of 1:1 with a chosen catalyst (Amberlyst 70 or sulfuric acid) loading was loaded to the autoclave at room temperature. The acid-catalysed reactions were performed in nitrogen. The stirring rate was 500 rpm. The reactor was heated up to the required temperature (70, 120 or 170°C). Once reaching the required temperature, one sample was taken for analysis and others were taken subsequently at

a time interval of 30 minutes. The residence time for each experiment was 120 minutes. Once an experiment was complete, the furnace was took off from the reactor and the valve of the cooling coil in the reactor was opened to use running water to cool down the reactor. All the products including used catalyst and liquid were collected and filtered. The residue on the filtration paper was washed with a mixed solution of methanol and chloroform at a volume ratio of 1 to 4 until the filtrate was colourless. The solid residue was then dried in oven at 105°C for 4 hours to constant weight. A more detailed description of the reactor and procedure can be found in Section 2.3, **Chapter 2**.

In order to compare the catalytic effects of Amberlyst 70 and sulphuric acid on the same basis, the amount of hydrogen ions in sulphuric acid catalyst loaded was equal to that in the Amberlyst 70 loaded.

6.2.3 Analytical methods

In this study, bio-oil and the products were analysed by GC-MS. A detailed procedure can be found in Section 2.5.1, **Chapter 2**.

The UV-fluorescence spectra of feedstock and products were recorded with a PerkinElmer LS50B spectrometer. A detailed procedure can be obtained in Section 2.5.2, **Chapter 2**.

The potential coke yields were obtained with a thermogravimetric analyser (PerkinElmer Pyris 1 TGA). The detailed procedure can be found in Section 2.5.4, **Chapter 2**.

6.3 Results and discussion

6.3.1 Transformation of aromatics during the esterification of bio-oil in the presence of Amberlyst 70

As shown in Figure 6-1, at 70°C for both the Amberlyst 70 at loadings of 3, 8 and 15wt.% and different loadings of sulfuric acid, the intensity of UV-fluorescence for the aromatics in the products kept almost similar. Polymerisation of the aromatics might not take place to an appreciable level under mild conditions.

At a higher reaction temperature of 120°C (Figure 6-2) and with increasing catalyst loading, the fluorescence intensity decreased with reaction time. Higher catalyst loading and higher reaction temperature clearly promoted the conversion of the aromatics via possible polymerisation reactions. This was also further evidenced by the acid treatment of bio-oil at 170°C with the different loadings of catalyst (Figure 6-3). In addition, in Figure 6-2c and Figure 6-3c, the fluorescence spectra at 60 min and 120 min were almost the same. Obviously, the aromatics that can be converted have already been converted under the employed conditions, and the rest were stable under the experimental conditions.

In addition, the decrease of the fluorescence intensity at the different wavelengths was not uniform, which was clearer in Figure 6-3a, where the fluorescence at 325–375 nm decreased with reaction time, while the fluorescence at < 325 nm remained unchanged. The fluorescence at < 290 nm represents the mono-rings, while that at 290-330 nm represents the aromatics with 2 fused benzene rings. The fluorescence at > 330 nm represents the aromatic ring systems with 3 and more fused benzene rings [30-32]. Clearly, at 170°C with the low catalyst loading (3 wt.%), the large aromatic systems could be converted or polymerised first. At Amberlyst 70 loading of 8 and 15wt%, the difference became negligible as the acid catalyst promoted the conversion of both the small and large aromatics.

6.3.2 Transformation of aromatics during the esterification of bio-oil in the presence of sulfuric acid

In the presence of sulfuric acid, the aromatics in bio-oil had higher conversion. Sulfuric acid can be homogeneously dispersed in the mixture of bio-oil and methanol. The heavy components in bio-oil had much less difficulties for accessing hydrogen ions of sulfuric acid. This was because the hydrogen ions can approach the heavy components with little steric hindrance. In comparison, the hydrogen ions from Amberlyst 70 can only be accessed on the local surface (mostly internal surface) of the catalyst. This meant that the heavy components had to overcome the steric hindrance to diffuse into the pores of the catalyst to access the catalytic sites. This created distinctly different catalytic behaviours of the catalyst. As shown in Figure 6-1d, even at 70°C, aromatics may have already started to be converted in the presence of sulfuric acid, while with Amberlyst 70 as the catalyst under the similar reaction conditions, no conversion of the aromatics was observed (Figure 6-1a).

At the elevated reaction temperatures of 120 and 170°C, even under low sulfuric acid loading (Figures 6-2d and 6-3d), conversion of not only the large aromatics but also the small ones with mono-rings took place. At 170°C with the loading of sulphuric acid equal to 15 wt.% Amberlyst 70, the fluorescence intensity reached the minimum in the first 30 minutes (Figure 6-3f), which was much faster than that with Amberlyst 70 under similar conditions (Figure 6-3c). Clearly, in the acid treatment of bio-oil with sulfuric acid as a catalyst, the homogeneous dispersion of hydrogen ions has significant influence on the conversion of the aromatics.

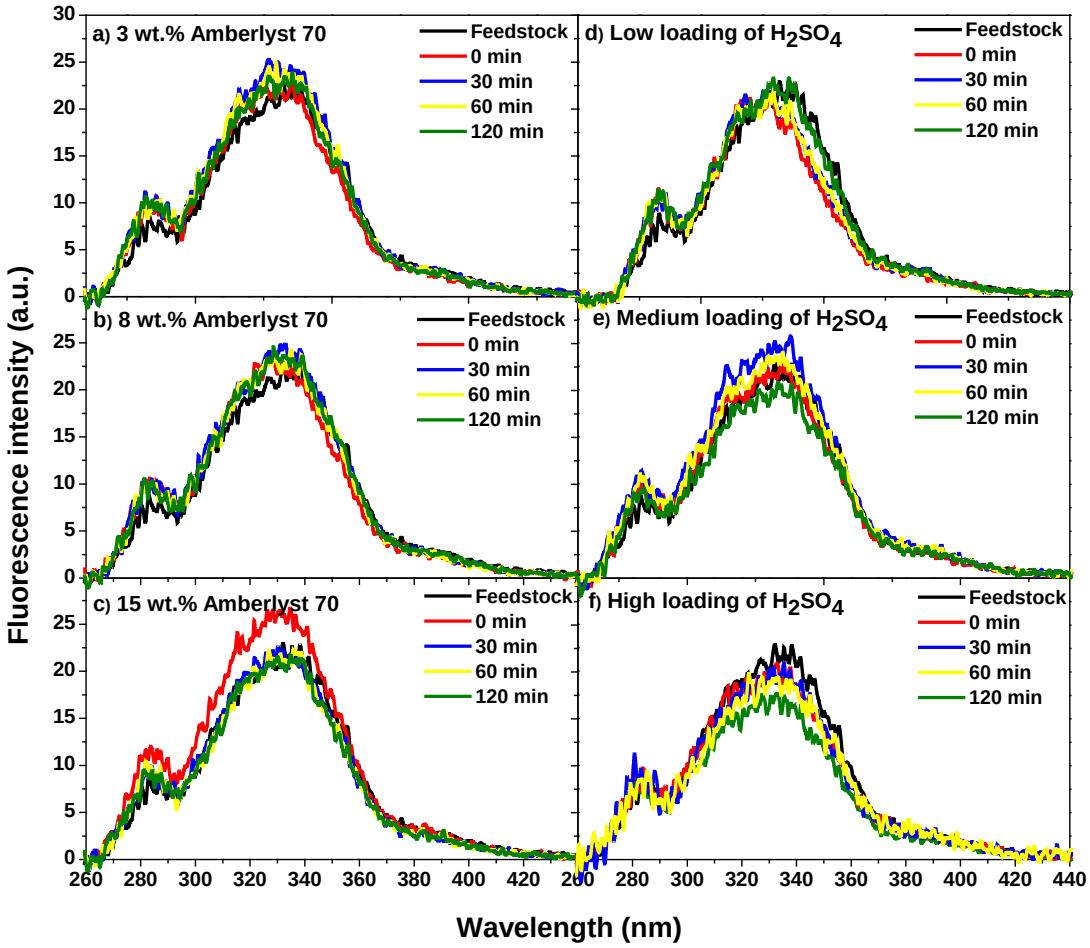

Figure 6-1. The fluorescence spectra of bio-oil feedstock and the products from acid treatment of bio-oil in methanol at 70°C with a stirring rate of 500 rpm as a function of reaction time with Amberlyst 70 (a, b, c) or sulfuric acid (d, e, f) as the catalysts. The fluorescence intensity is on bio-oil basis. Low, medium and high loadings of H_2SO_4 mean the hydrogen ions applied were equal to the amount of hydrogen ions in the cases of 3, 8 and 15 wt.% Amberlyst 70, respectively.

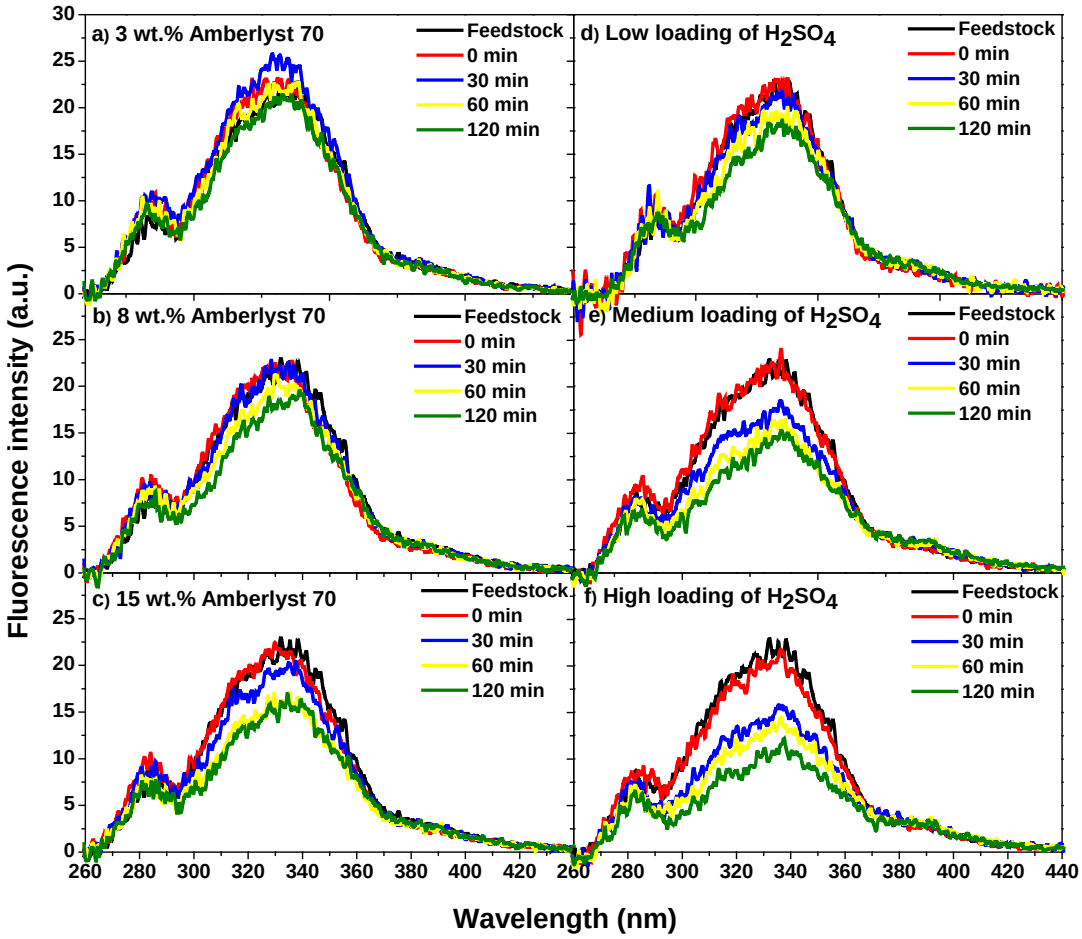

Figure 6-2. The fluorescence spectra of bio-oil feedstock and the products from acid treatment of bio-oil in methanol at 120°C with a stirring rate of 500 rpm as a function of reaction time with Amberlyst 70 (a, b, c) or sulfuric acid (d, e, f) as the catalysts. The fluorescence intensity is on bio-oil basis. Low, medium and high loadings of H_2SO_4 mean the hydrogen ions applied were equal to the amount of hydrogen ions in the cases of 3, 8 and 15 wt.% Amberlyst 70, respectively.

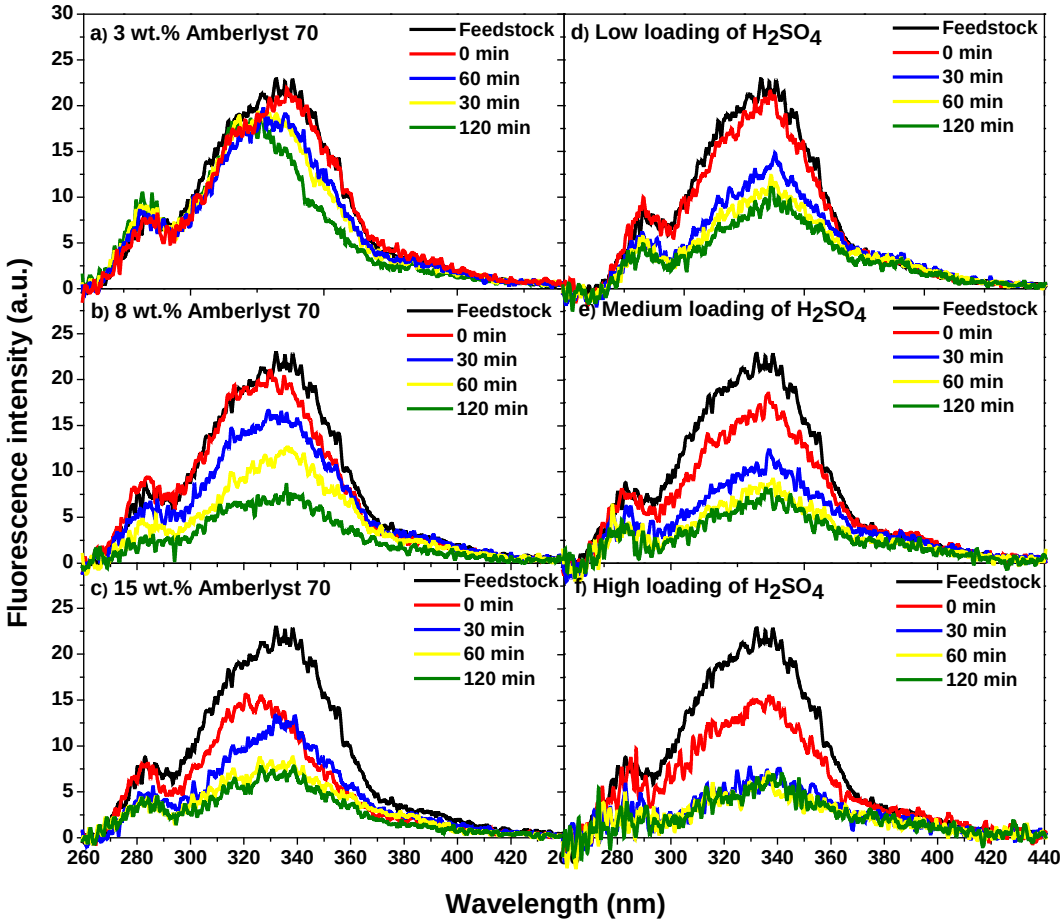

Figure 6-3. The fluorescence spectra of bio-oil feedstock and the products from acid treatment of bio-oil in methanol at 170°C with a stirring rate of 500 rpm as a function of reaction time with Amberlyst 70 (a, b, c) or sulfuric acid (d, e, f) as the catalysts. The fluorescence intensity is on bio-oil basis. Low, medium and high loadings of H_2SO_4 mean the hydrogen ions applied were equal to the amount of hydrogen ions in the cases of 3, 8 and 15 wt.% Amberlyst 70, respectively.

6.3.3 Conversion of typical compounds in bio-oil

6.3.3.1 *Carboxylic acids*

The transformation of carboxylic acids into neutral esters is one of the most important targets for the esterification of bio-oil. Using the mineral acid and solid acid catalyst, the conversions of the carboxylic acids like acetic acid were very different. With sulfuric acid as the catalyst, the conversion of acetic acid in bio-oil took place very quickly, reaching the plateau of ca. 82% during the ramping of temperature (Figure 6-4a) with either the low loading or high loading at 70°C. In contrast, over the Amberlyst 70 with the loading of 3 wt.%, the conversion of acetic acid could not reach the reaction equilibrium at the end of the test. Even at the reaction temperature of 120 and 170 °C with Amberlyst 70 as the catalyst, acetic acid conversion could not reach the equilibrium during the ramping of temperature, while with sulphuric acid as the catalyst, it did. From the results in Figure 6-4, it could conclude that sulphuric acid was very active for the conversion of acetic acid. The reaction conditions required to achieve the conversion of acetic acid in bio-oil were much milder than that using Amberlyst 70, which was related to the homogeneous dispersion of the hydrogen ions in the reaction medium when sulphuric acid was used as the catalyst.

For other carboxylic acids such as formic acid (Figure 6-4), propanoic acid (Figure 6-5) and butanoic acid (Figure 6-5), their conversions were also faster in the presence of sulphuric acid than in the presence of Amberlyst 70. Sulphuric acid was far more active for the conversions of the carboxylic acids than that of Amberlyst 70 at the same loading of hydrogen ions. In addition, it was found that different carboxylic acids in bio-oil had different reactivities towards esterification. In general, the heavier the carboxylic acid, the slower the conversion. This was in line with our previous studies [13, 15]. With the prolonged reaction time, the conversions of carboxylic acids could reach equilibria. However, it was found that the conversion of carboxylic acids started to decrease at end of the test, which is more evident at high reaction temperature and high catalyst loading. Carboxylic acids can be formed from other reactions e.g. formic acid formed from the dehydration of sugars and rehydration of HMF into levulinic acid

[18, 33], which also contributed to the decreased conversion of carboxylic acids at higher temperatures and catalyst loadings. In addition, the decreased conversion of the carboxylic acids was also related to the water formation during the acid-treatment of bio-oil, which will be discussed in the following section.

6.3.3.2 *Water*

Water was one of the main products from the acid treatment of bio-oil in methanol. Large amounts of water can be produced during this process. Not only esterification but also polymerisation and etherification between methanol can produce abundant water. As shown in Figure 6-6, in general, water formation was promoted by high reaction temperature and high catalyst loading. Compared with water formation in the experiments catalysed by sulfuric acid, much more water was produced in the experiments catalysed by Amberlyst 70. However, the conversions of carboxylic acids in bio-oil with Amberlyst 70 were lower than those with sulfuric acid, which meant less water was produced from the esterification of carboxylic acids. Thus, other reactions took place in the presence of Amberlyst 70, leading to the water formation. It was observed that the vapour pressure of the experiment with Amberlyst 70 loading of 15 wt% at 170 °C increased monotonously to 50 bar at the end of the test, while the vapour pressure with sulfuric acid as the catalyst under the "same" condition only increased to 25 bar. The reason for this high vapour pressure was the formation of dimethyl ether. The formation of the significant amount of dimethyl ether was confirmed by GC-MS, as shown in Figure 6-7. Dimethyl ether has a very low boiling point (-24°C) and it is gas at room temperature. GC-MS used in this study was not configured to analyse gases. However, via the GC spectrum we could observe the amount of dimethyl ether formed over sulphuric acid catalyst and over Amberlyst 70 catalyst were not in one magnitude. This was related to the density of the hydrogen ions in the reaction medium or in the local area of the reaction medium.

In the comparable experiments with sulphuric acid or Amberlyst 70 as the catalysts, the total amounts of hydrogen ions were equal, but the acid concentrations were quite different. For sulfuric acid, the hydrogen ions dispersed homogenously in bio-oil,

providing a roughly uniform density of hydrogen ions. In contrast, bio-oil/methanol and Amberlyst 70 were in heterogeneous phase. The hydrogen ion of the -SO_3H group of Amberlyst 70 can only be accessed on the local vicinity of the solid catalyst [19]. Although Amberlyst 70 can swell significantly in polar solvents like methanol, making more hydrogen ions in inner surface accessible by components in bio-oil, the dispersion of hydrogen ions was limited to the local vicinity of the catalyst. This created some steric hindrance for some big molecules such as big aromatics accessing the acidic sites.

The steric hindrance however, probably did not affect much the etherification of methanol. Methanol is a small molecule and has little difficulties of entering the pores of Amberlyst 70 to access the acidic sites. The formed dimethyl ether via etherification of methanol can also escape from the pores. In addition, the hydrogen ions in the local vicinity of the solid catalyst was much higher in Amberlyst 70 than in sulphuric acid catalyst with the same loading of hydrogen ions. It is believed that this could promote the etherification of methanol. The etherification of methanol was an undesirable reaction, which consumed methanol and produced significant amount of water. The presence of water in the reaction medium could not only lower the heating value of bio-oil, but also negatively affect the conversions of carboxylic acids via esterification. As shown in Figure 6-4, where with higher loading of Amberlyst 70 at higher reaction temperature, the conversion of acetic acid reached a maximum and then decreased with prolonged reaction time. This was because the produced water shifted the reaction medium back to the acid direction.

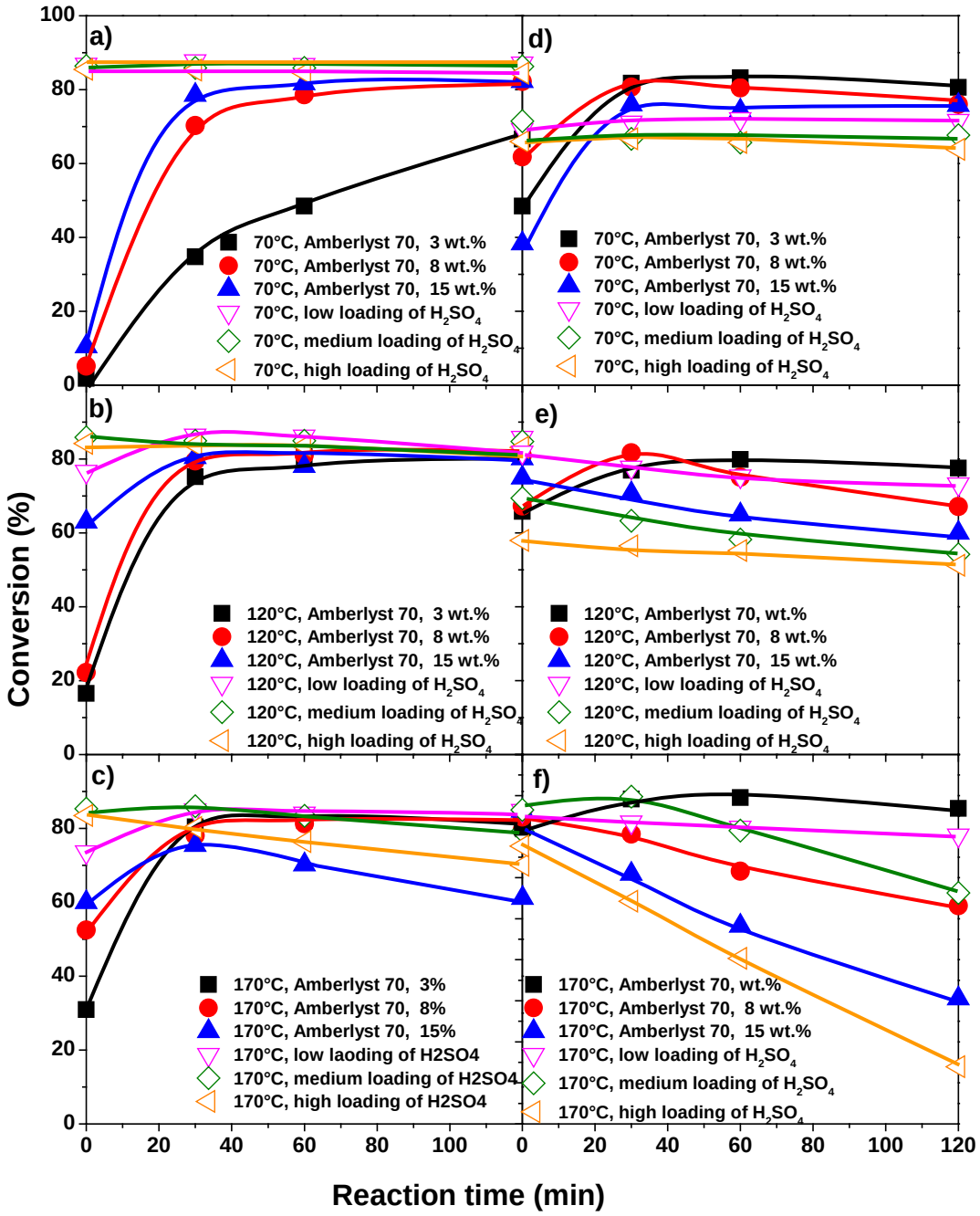

Figure 6-4. The conversions of acetic acid (a, b, c) and formic acid (d, e, f) in bio-oil at different reaction temperatures, catalyst loading amounts and catalyst types. Low, medium and high loadings of H_2SO_4 mean the hydrogen ions applied were equal to the amount of hydrogen ions in the cases of 3, 8 and 15 wt.% Amberlyst 70, respectively. Stirring rate: 500 rpm; residence time: 120 min.

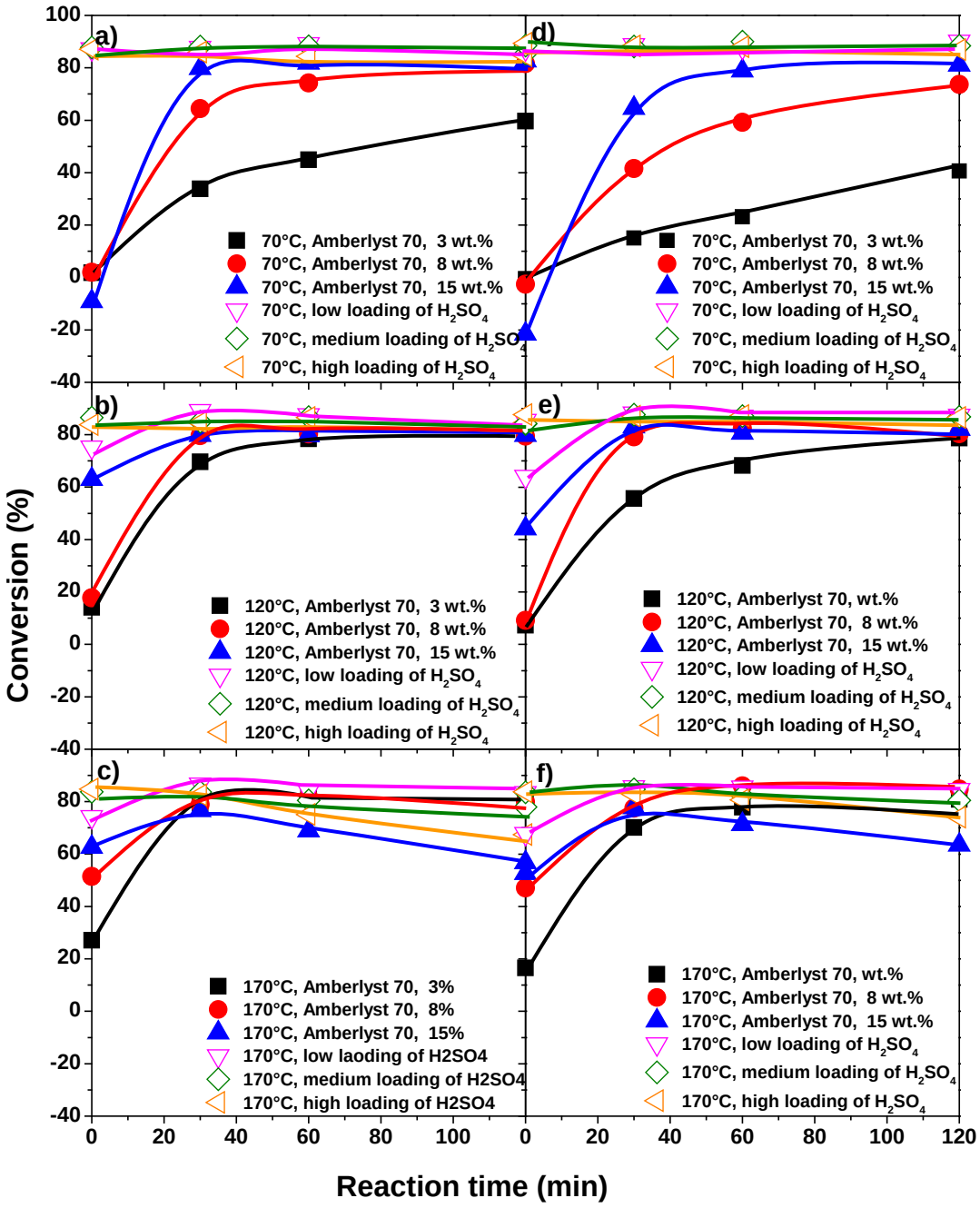

Figure 6-5. The conversions of propanoic acid (a, b, c) and butanoic acid (d, e, f) in bio-oil at different reaction temperatures, catalyst loading amounts and catalyst types. Low, medium and high loadings of H_2SO_4 mean the hydrogen ions applied were equal to the amount of hydrogen ions in the cases of 3, 8 and 15 wt.% Amberlyst 70, respectively. Stirring rate: 500 rpm; residence time: 120 min.

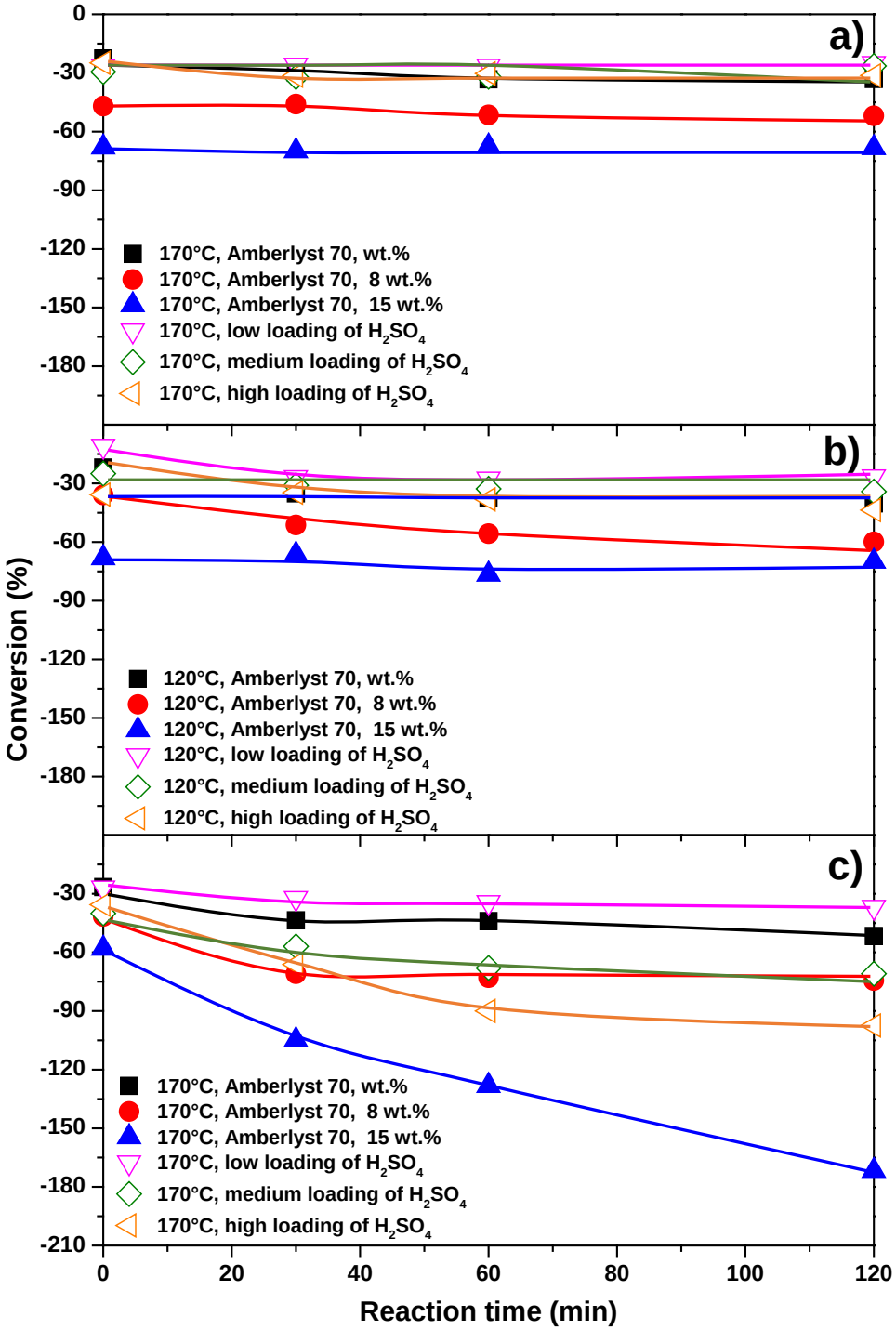

Figure 6-6. The conversion of water in bio-oil at different reaction temperatures, catalyst loading amounts and catalyst types. Low, medium and high loadings of H_2SO_4 mean the hydrogen ions applied were equal to the amount of hydrogen ions in the cases of 3, 8 and 15 wt.% Amberlyst 70, respectively. Stirring rate: 500 rpm; residence time: 120 min.

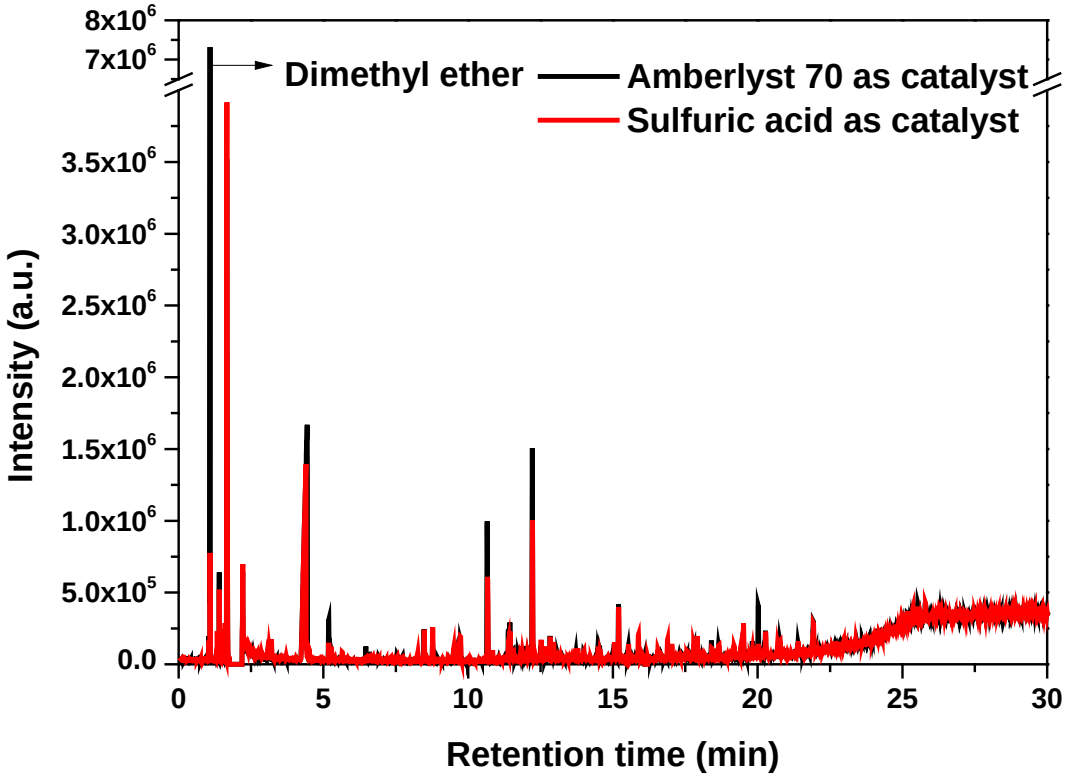

Figure 6-7. GC-MS chromatograms of the esterification products of bio-oil in methanol using Amberlyst 70 or sulfuric acid as the catalyst at 170°C. The catalyst loading of Amberlyst 70 was 15 wt.% and that of sulfuric acid was equal in terms of the loading amount of hydrogen ions.

6.3.3.3 *Levoglucosan*

Levoglucosan, an important sugar in bio-oil, can be transformed via acid-catalysed reactions [34]. At a low reaction temperature of 70°C, in experiments catalysed by Amberlyst 70, the conversions of levoglucosan were minus, which meant that some levoglucosan was produced and the conversion of levoglucosan had not happened yet under these experimental conditions (Figure 6-8). This result was in line with our previous ones that levoglucosan could be produced from the hydrolysis of some sugar oligomers [35]. Except simple sugars like levoglucosan, some sugar oligomers also existed in bio-oil [36]. These oligomers can undergo further reactions like hydrolysis to produce more levoglucosan under the acid-catalysed condition. With the increasing

catalyst loading of Amberlyst 70 and reaction temperature, the conversion of levoglucosan became appreciable. The hydrolysis of sugar oligomers and the transformation of levoglucosan occurred simultaneously under acidic conditions.

In contrast, when sulfuric acid was used as the catalyst, the conversion of levoglucosan was accelerated significantly. As shown in Figure 6-8a, the conversion has already reached the equilibrium during the ramping. The conversion of levoglucosan seemed to be independent of reaction temperature, reaching ca. 60-84% conversion with low sulfuric acid loading and 95-100% conversion with medium to high sulfuric acid loadings. In comparison, with Amberlyst 70 as the catalyst, the conversion of levoglucosan was strongly related to the loading of the catalyst and the reaction temperature. The sugars and heavy sugar oligomers made them hard to access the active sites of the solid catalyst, which resulted in slow and low conversions. Comparing the conversion of levoglucosan over sulphuric acid catalyst with that over Amberlyst 70 catalyst, it was clear that the dispersion of the hydrogen ions was critical for the conversion of levoglucosan. Steric hindrance was an important factor negatively affecting the conversion of levoglucosan over Amberlyst 70. This also applied to the esterification of the carboxylic acids, as discussed above. It needs to note that the steric hindrance not only affect the access to hydrogen ions, but also affect the escape or desorption of the products from the pores, especially the heavy ones formed. In our previous study, we found that substantial amount of polymer/coke was formed on/in Amberlyst 70 after the esterification of bio-oil. Meanwhile, the sizes of the catalyst beads clearly increased, indicating the filling of the pores of catalyst with the coke/polymer when the catalyst swelled in the reaction medium [23].

6.3.3.4 *Phenolics*

The conversions of typical phenolics are illustrated in Figure 6-9. In general, using sulphuric acid catalyst, the conversions of the phenolics in bio-oil were faster than using Amberlyst 70 catalyst. For example, when using sulfuric acid as the catalyst, the conversion of 2,6-dimethoxy-4(2-propenyl)- (Figure 6-9)in bio-oil was largely affected by the loading amount, but only varied slightly with the reaction temperature. The concentration of hydrogen ions in the reaction medium was clearly important. However, although the acid concentration over Amberlyst 70 was high, the conversion over Amberlyst 70 was low. The steric hindrance clearly imposed more effects on the conversions of the phenolics. Similar results were observed for the conversions of benzaldehyde, 4-hydroxy-3,5-dimethoxy- (Figure 6-9) and other phenolics like trans-2,6-dimethoxy-4(1-propenyl)-, cis-2,6-dimethoxy-4(1-propenyl)- (results are not shown here).

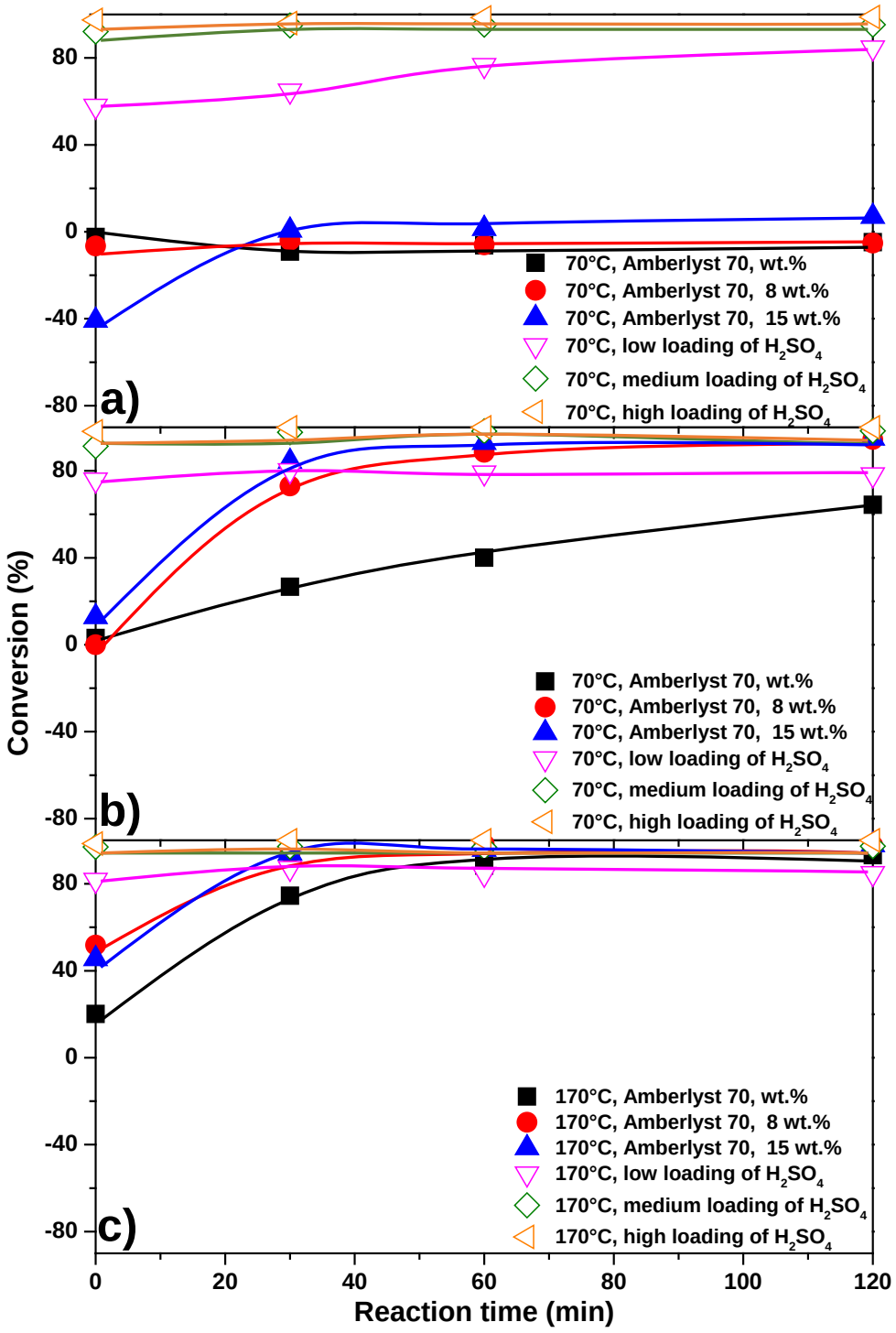

Figure 6-8. The conversion of levoglucosan in bio-oil at different reaction temperatures, catalyst loading amounts and catalyst types. Low, medium and high loadings of H_2SO_4 mean the hydrogen ions applied were equal to the amount of hydrogen ions in the cases of 3, 8 and 15 wt.% Amberlyst 70, respectively. Stirring rate: 500 rpm; residence time: 120 min.

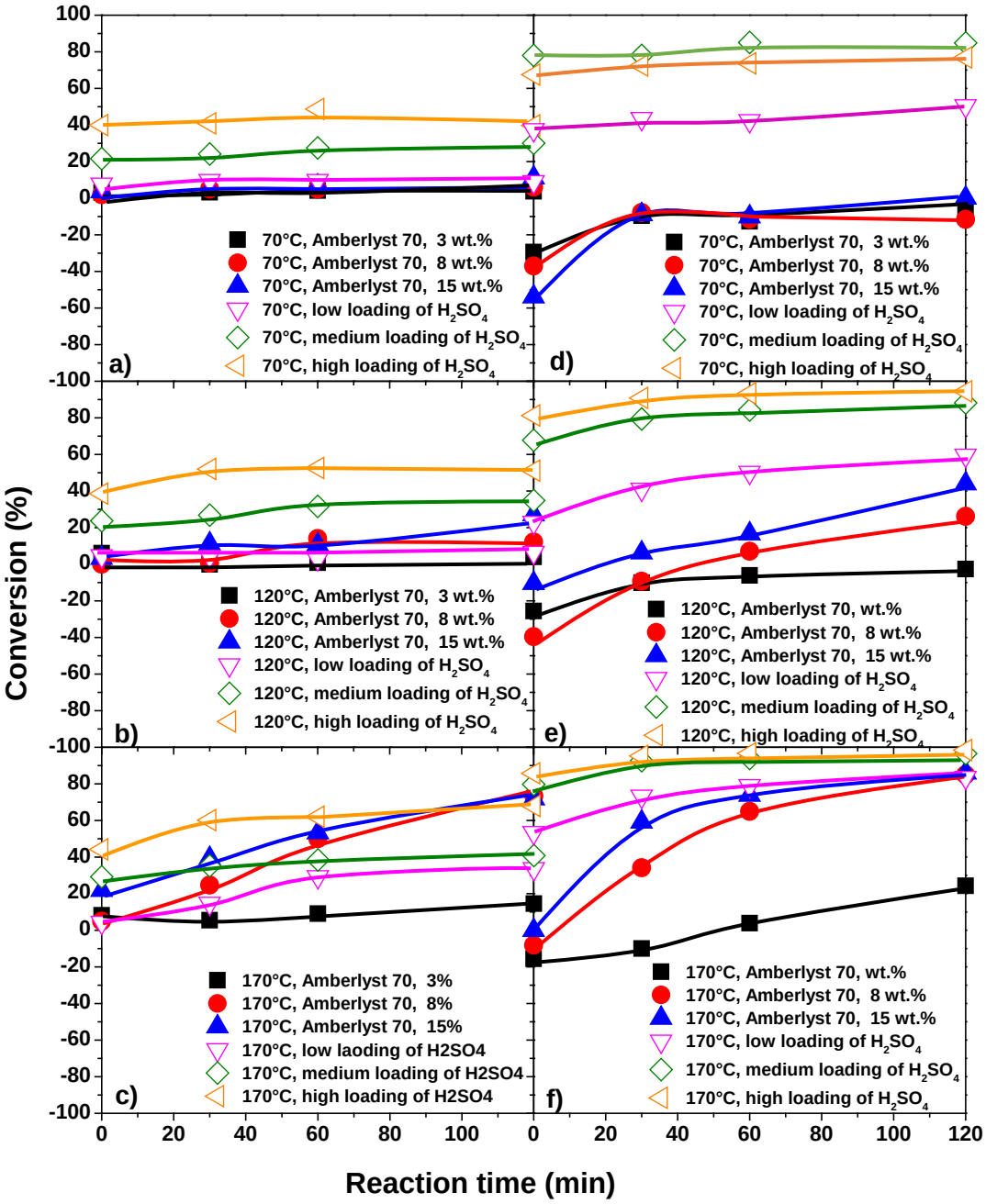

Figure 6-9. The conversions of 2,6-dimethoxy-4(2-propenyl)phenol (a, b, c) and 4-hydroxy-3,5-dimethoxybenzaldehyde (d, e, f) in bio-oil at different reaction temperatures, catalyst loading amounts and catalyst types. Low, medium and high loadings of H_2SO_4 mean the hydrogen ions applied were equal to the amount of hydrogen ions in the cases of 3, 8 and 15 wt.% Amberlyst 70, respectively.

6.3.4 Coke formation

For experiments catalysed by Amberlyst 70, the coke formation could be quantified, because almost all the coke deposited on/in the solid catalyst. While for the experiments catalysed by sulfuric acid, we tried to filter the solid products formed (if any) but it was not successful. The polymer formed was too fine to be filtered. Only at 170°C, with medium to high sulfuric acid loadings, solid phases were formed and separated from liquid phases via filtration. The yields of solid phase under medium sulfuric acid loading (0.816 g sulfuric acid of 98 wt.%) was 12.2 wt.% and that under high sulfuric acid loading (1.530 g sulfuric acid of 98 wt.%) was 21.3 wt.%.

The coke formed in the experiments catalysed by Amberlyst 70 was illustrated in Table 6-1. With increasing reaction temperature, the yields of coke increased. Higher reaction temperature clearly promoted the polymerisation reactions. In addition, the loading of Amberlyst 70 also significantly affected the coke formation. The higher the loading of Amberlyst 70, the higher the amount of coke. Clearly, the availability of acidic sites promoted the formation of coke during the acid-treatment of bio-oil.

The yields of the potential coke were also measured, as shown in Table 6-1. With Amberlyst 70 as the catalyst, the yields of potential coke from the liquid products were lower than that from bio-oil feedstock. This was because the polymerisation of the reactive components took place inside the pores of the catalyst. Consequently, the heavy components formed from polymerisation or the coke formed were incorporated into the pores of the catalyst. The components in the liquid products were relatively light. However, with sulphuric acid as the catalyst, the heavy products formed from the polymerisation were dispersed in the reaction medium at low sulphuric acid loading, leading to the high yield of potential coke. With the increase of sulphuric acid loading, the liquid products were separated into a liquid phase and solid phase. The solid phase was mainly the heavy products, while the liquid products became lighter than that of bio-oil. This is because the heavy components polymerised and formed solid products, and the rest in the liquid medium are mainly light components.

Table 6-1. Potential coke formation determined by TGA and coke formation determined by filtration

Sample conditions	Potential coke yield (wt.%)[a]	Coke yield (%)[b]
Bio-oil feedstock	11.2	N/A
70°C, 3wt% Amberlyst 70	8.4	2.64
70°C, 8wt% Amberlyst 70	8.8	3.30
70°C, 15wt% Amberlyst 70	9.2	4.72
120°C, 3wt% Amberlyst 70	10.2	3.89
120°C, 8wt% Amberlyst 70	10.6	5.80
120°C, 15wt% Amberlyst 70	12.6	6.22
170°C, 3wt% Amberlyst 70	11.4	6.39
170°C, 8wt% Amberlyst 70	10.6	12.05
170°C, 15wt% Amberlyst 70	9.4	15.97
70°C, low H_2SO_4 loading	21.8	N/A
70°C, medium H_2SO_4 loading	24.0	N/A
70°C, high H_2SO_4 loading	26.0	N/A
120°C, low H_2SO_4 loading	21.4	N/A
120°C, medium H_2SO_4 loading	23.8	N/A
120°C, high H_2SO_4 loading	26.0	N/A
170°C, low H_2SO_4 loading	21.2	N/A
170°C, medium H_2SO_4 loading	15.4	N/A
170°C, high H_2SO_4 loading	14.8	N/A

[a]Potential coke yield refers to that from the TGA characterisation of liquid products (on bio-oil basis).

[b]Coke yield refers to the solid coke formed (on bio-oil basis).

The residence time for all acid-treatment experiments is 120 minutes.

6.4 Conclusions

The catalytic behaviours of a mineral acid catalyst, sulfuric acid, and a typical solid acid catalyst, Amberlyst 70, were investigated in the acid treatment of bio-oil in methanol. It was found that the acid-catalysed reactions were closely related to the dispersion of the hydrogen ions in the reaction medium. The hydrogen ions of sulphuric acid were homogeneously dispersed in the reaction medium, which facilitated the esterification of the carboxylic acids, the hydrolysis of the sugars like levoglucosan and the conversion of the phenolics and the large aromatics. As for Amberlyst 70, the hydrogen ions were mainly concentrated in the local surface of the catalyst, the conversion of the above mentioned components were relatively slower over Amberlyst 70. Steric hindrance created some difficulties for accessing the hydrogen ions in the inners pores of the catalyst, which contributed to the lower conversion rate of the components in bio-oil. However, it was found that some reactions like the etherification of methanol could be promoted remarkably over Amberlyst 70. The high concentration of hydrogen ions over Amberlyst 70 was clearly essential for the etherification reactions. The etherification of methanol was undesirable for esterification as it consumed methanol, produced water and created high operating pressure. How to increase the accessibility of hydrogen ions in the solid acid catalyst is crucial to increase its efficiency for catalysing the esterification of bio-oil.

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Chapter 7

Conclusions and Recommendations

7.1 Introduction

The purpose of this study was to gain fundamental understanding of the acid-catalysed reactions in bio-oil during the low temperature thermal treatment in alcohols and water. The key findings from each chapter of this thesis are summarised in the following sections.

7.2 Conclusions

7.2.1 Quantification of strong and weak acidities in bio-oil via non-aqueous potentiometric titration

- A non-aqueous potentiometric titration method has been developed to quantify the carboxylic acids and phenolics in bio-oil.

- The heavy carboxylic acids, which cannot be identified with GC-MS, account for ca. 29–45% (mol basis) of all the carboxylic acids in the bio-oil from mallee wood.

- Both the heavy and light phenolic components could be identified with the titration method developed, while GC-MS can only identify some light phenolic compounds (3% mol basis). Heavy phenolics dominated the total phenolic compounds in bio-oils.

- The titration method was further applied to the determination of the concentrations of acidic components in the bio-oils from mallee wood, bark and leaves. The pyrolysis of mallee wood produced the highest yields of acidic components while that of leaves produced the lowest. The successful development of the titration method for the quantification of these heavy carboxylic acids and phenolics provides useful information for the further upgrading of bio-oil.

7.2.2 Reaction behaviour of light and heavy components of bio-oil in methanol and in water

- The behaviour of main components in bio-oil was distinctly different in water and methanol. Water promoted the formation of big aromatics, via possibly the polymerisation of the small aromatics and other reactive components in bio-oil. In contrast, after thermal treatment of bio-oil in methanol, more aromatics, which was evidenced by UV-fluorescence spectroscopy, were produced. It attributed to the stabilisation and the production of aromatics from the heavy molecules in bio-oil.
- GC-MS results confirmed the consumption of mono-rings during heating up bio-oil in water, and their formation of in methanol.

- Carboxylic acids like acetic acid and formic acid had negligible impact on the conversion of aromatics in bio-oil, while strong acid catalysts such as Amberlyst 70 can boosted the conversion of aromatics.

7.2.3 Formation of coke during the esterification of pyrolysis bio-oil

- The amounts of coke formed from the acid-treatment of bio-oil in various alcohols are half of that in water. Alcohols stabilise the reactive components in bio-oil such as sugars, furans, aldehydes, carboxylic acids and phenolics. On the other hand, water promotes the polymerisation of these components.

- Experimental parameters also affect the coke formation during the acid-treatment of bio-oil in alcohols. The elevated reaction temperature, long residence time, and high dosage of catalyst significantly promoted the coke formation.

- The soluble polymeric material and insoluble polymeric material was characterised with FT-IR and UV-florescence spectroscopies. The results show

that the coke formed is highly aromatic. The aromatics in bio-oil have a significant contribution to the formation of coke during the esterification of bio-oil.

7.2.4 Acid-treatment of bio-oil in methanol: The distinct catalytic behaviours of a mineral acid catalyst and a solid acid catalyst

- Acid-catalysed reactions of bio-oil can be effectively catalysed by sulfuric acid, due to the homogeneous dispersion of hydrogen ions. On the contrary, for Amberlyst 70, the hydrogen ions was constrained in vicinity of the solid catalyst, creating steric hindrance, which made the conversion of main components in bio-oil lower.

- The etherification of methanol, an undesirable reaction, was favoured in the presence of Amberlyst 70, which serves as an example of steric effects of Amberlyst. The formation of dimethyl ether consumed methanol and produced abundant water, negatively affect the conversion of carboxylic acids in bio-oil.

7.3 Recommendations

1. The effects of aliphatic alcohols including methanol, ethanol, propanol and butanol on the acid-catalysed reactions of bio-oil has been investigated in detail in this study. However, the detailed effects of benzyl alcohols on the acid-treatment of bio-oil has not been well understood. They may have a different reaction pathway in the acid-treatment of bio-oil. Benzyl alcohols with high boiling point allow the removal of water and esters to drive the esterification to complete.

2. The effect of sulphuric acid and Amberlyst 70 on the behaviour of bio-oil with methanol has been investigated in this study. Both of them were Bronsted acid. The Lewis acid can also be catalyst in the acid-catalysed reactions, which may change the behaviour of bio-oil and have different reaction pathway. Therefore,

the understanding of reaction mechanism of bio-oil over Lewis acid as catalyst is required.

3. The non-aqueous potentiometric titration method developed in this study can quantify the acidic components in raw bio-oil. However, the acid treatment products of bio-oil in methanol or water is difficult to be quantified, due to the presence of large amounts of water and methanol. In addition, the solvent used to dissolve bio-oil cannot dissolve the acid-treatment products well. Therefore, the modification of this method or pre-treatment of the bio-oil products after acid treatment is suggested to be done for future study.

Appendix I

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Title: Quantification of strong and weak acidities in bio-oil via non-aqueous potentiometric titration

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Publication: Fuel

Publisher: Elsevier

Date: January 2014

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