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

Bio-oil Upgrading via High-Pressure Reactive Distillation

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Declaration

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

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

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Abstract

Bio-oil is a promising and renewable energy source to substitute the depleting fossil fuels. The upgrading of bio-oil with the existing distillation technologies is mainly hindered by polymerisation due to the reactive nature of bio-oil when it is heated up during distillation. The distillation of bio-oil at high pressure can significantly reduce the extent of polymerisation. This study aims to upgrade the bio-oil produced from the pyrolysis of mallee woody biomass via high-pressure reactive distillation by investigating the roles of process parameters especially pressure and the major components of bio-oil.

The bio-oil distillation fraction yields and properties were evaluated to demonstrate the advantages of the distillation at elevated pressures over distillation at atmospheric pressure. The results indicate that high-pressure distillation can achieve high distillate yields with reduced polymerisation because high pressure can retain water and other light components in the liquid phase to reduce the extent of polymerisation. The distillate yield was around 90% when the distillation was carried out at 200 ^{o}C at a pressure higher than 20 barg.

The reaction and distribution behaviours of the major components of bio-oil including levoglucosan, carbonyl compounds and aromatic compounds were investigated. Levoglucosan would mainly undergo hydrolysis reaction during the high-pressure distillation whereas thermal polymerisation would dominate during the atmospheric pressure distillation. Most of levoglucosan during the high-pressure reactive distillation could be converted into small molecules and distilled out due to the presence of light components retained in the liquid phase by high pressure. However, during the atmospheric pressure distillation, most of levoglucosan would be mainly retained in the heavy residue to undergo polymerisation reactions.

In addition, high pressure could affect the distribution of carbonyl compounds in the bio-oil to accelerate the reaction of light carbonyl compounds and inhibit the reaction of heavy carbonyl compounds due to the higher reactivity of light carbonyl compounds. The acid-catalysed reactions would not lead to the significant consumption of carbonyl compounds. The base (e.g. NaOH) could remove the carbonyl compounds by acting as a catalyst to the aldol condensation reaction of aldehydes and ketones and neutralising the carboxylic acids during the high-pressure reactive distillation.

Moreover, the enrichment of aromatic compounds to the paste distillate fraction from the heavy residue and liquid distillate fractions was achieved by the high-pressure reactive distillation. The

increase of pressure would also contribute to the reduction of polymerisation and the production of aromatic monomers due to the hydrothermal environment.

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List of Publications

- ***H. Wang***, R. Gunawan, Z. Wang, L. Zhang, Y. Liu, S. Wang, M.D.M. Hasan, C.-Z. Li, High-pressure reactive distillation of bio-oil for reduced polymerisation, Fuel Processing Technology, 211 (2021) 106590.
- H. Wang, Y. Liu, R. Gunawan, L. Zhang, Z. Wang, C.-Z. Li, Reactions and distribution of levoglucosan during the high-pressure reactive distillation of bio-oil (submitted to Fuel)
- H. Wang, Y. Liu, L. Zhang, R. Gunawan, Z. Wang, C.-Z. Li, Conversion of carbonyl compounds in bio-oil via catalysed reactive distillation at high pressure (submitted to Fuel)

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Chapter 1

Introduction

1.1 Importance of renewable energy

With the increase of energy consumption and the environmental concern, it is essential to develop renewable energy for the sustainable development. The International Energy Agency reported that the total primary energy demand in the Stated Policies Scenario would increase from 14314 Mtoe (million tonnes of oil equivalent) in 2018 to 17723 Mtoe in 2040 [1]. The increased energy demand would cause serious environment challenges such as climate change and increased carbon footprint. However, the total primary energy demand will be 13279 Mtoe in the Sustainable Development Scenario which would require the increase of the "Direct use of renewables" from 482 Mtoe in 2018 to 1142 Mtoe in 2040. Therefore, it is necessary to develop and utilise the renewable energies.

Renewable energy is a promising source to substitute the depleting fossil fuels and to meet the increasing energy demand. Renewable energy could be generated in a sustainable way from the renewable and reliable sources and it mainly includes bioenergy, wind energy, solar energy and etc. Besides securing the energy supply, the utilisation of renewable energy could mitigate the environment issues caused by the extensive application of fossil fuels [2]. For example, the greenhouse gas emissions and the air pollution could be mitigated by utilising the renewable energy.

1.2 Biomass as a renewable energy source

Biomass mainly originates from the living or recently living organisms and it is the only carbon-containing renewable energy source. The abundant and inexpensive biomass is featured with the environment-friendly and carbon neutral advantages. To be specific, the CO_2 produced by the utilisation (e.g. combustion) of the plant biomass could be converted into the living plant by the photosynthesis and there would not be net addition to the total CO_2 in the atmosphere of the earth. Moreover, the sulphur and nitrogen contents in the biomass are lower than the traditional fossil fuels. In addition, it is promising to replace the petroleum as a sustainable source to produce fuels and chemicals [3]. Furthermore, it is also feasible to process the biomass using the existing refinery infrastructures [4].

Biomass could be collected from various sources, for example, the agricultural plant, forest wood and aquatic biomass [5]. Among various types of biomass, the lignocellulosic biomass, as a non-food and abundant feedstock, is a potential resource to produce bioenergy. It is mainly composed of cellulose, hemicellulose and lignin [6] and its utilisation would not affect the food supply of human. In this study, the mallee woody biomass was used to produce the bio-oil.

1.3 Conversion of biomass and bio-oil production

Biomass can be converted using thermochemical or biological routes [7], as is shown in Figure 1-1. The thermochemical conversion mainly includes combustion, gasification and pyrolysis. Combustion would provide heat for power generation by oxidation with excess oxygen. Gasification could convert the biomass into the syngas including H_2 and CO which could be further converted to hydrocarbon fuels through the Fischer-Tropsch synthesis [8]. Pyrolysis, as a thermal decomposition process, can convert biomass into gas, char and a liquid fuel called bio-oil in the absence of oxygen [9]. For the biological conversion, biomass would mainly be converted into ethanol by the fermentation [10].

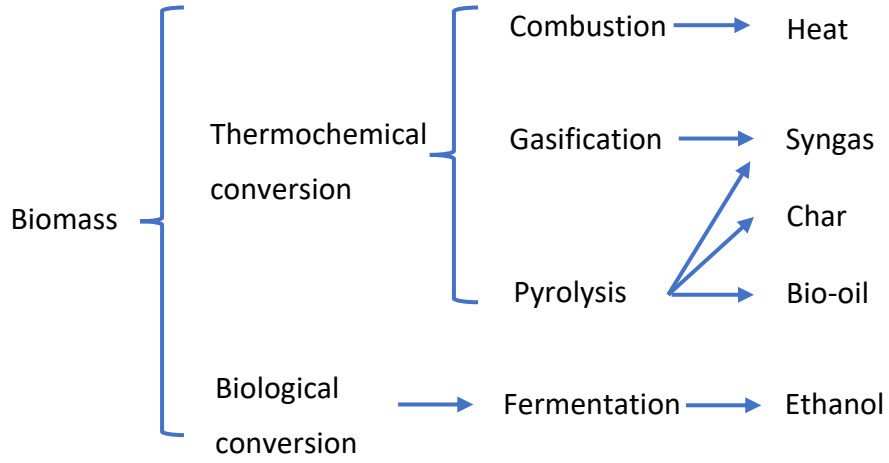

Figure 1-1. Conversion routes of biomass.

Among the conversion routes of biomass, the pyrolysis is vitally important because it could produce a wide range of useful products, especially the liquid bio-oil. According to the heating rate, pyrolysis could be divided into slow and fast pyrolysis. The heating rate of slow pyrolysis is less than 50 ^{o}C/min whereas that of fast pyrolysis is higher than 1000 ^{o}C/min. The slow pyrolysis could be used to produce the charcoal and it is featured with high char yield (e.g. 35%) and low bio-oil yield (e.g. 30%) [11]. In contrast, the fast pyrolysis of biomass could produce the bio-oil at high yield (e.g. 75 wt%) and it is generally featured with the following characteristics [9, 12].

- Very high heating rate (e.g. 1000 ^{o}C/min)
- Carefully controlled pyrolysis temperature (400 – 500 ^{o}C)
- Short residence time of the hot vapour (less than 2 s)
- Fast cooling of the pyrolysis vapour

During the fast pyrolysis, biomass would be rapidly heated and decomposed to produce vapour, non-condensable gases and char. Bio-oil, as the liquid product, could be acquired by the fast cooling and condensation of the pyrolysis vapour that is mainly composed of the dissociation products of biopolymers including the cellulose, hemicellulose and lignin. The composition, yield and properties of the produced bio-oil would be dependent on the feedstock biomass and the process parameters such as the pyrolysis temperature and the reactor configuration.

Generally, a fast pyrolysis process is composed of drying the feedstock biomass to minimise the H_2O content in the product bio-oil, grinding the feedstock biomass to small sizes to ensure the high heating rate, fast pyrolysis, separation and collection of pyrolysis products (e.g. char and bio-oil) [9, 11]. There are many types of reactors that could achieve the fast pyrolysis of biomass, such as the fluid bed reactor, transported bed reactor, ablative reactor and rotating cone reactor [13]. In this study, the fast pyrolysis was performed using a grinding pyrolysis reactor that could achieve the particle size reduction and pyrolysis simultaneously [14, 15]. The integration of grinding and pyrolysis could simplify the overall process and increase the process efficiency.

1.4 Bio-oil properties and upgrading

1.4.1 Properties of bio-oil

Bio-oil, as the major liquid product of biomass pyrolysis, is generally dark brown and has a smoky smell. Besides derived from the renewable biomass as is discussed above, the advantages of utilising the bio-oil are as outlined below:

- The bio-oil is featured with higher energy density than the original biomass. For example, the energy density of bio-oil on the volume basis could be 20 - 32 times than that of the raw biomass [16].
- The bio-oil is easy to be transported and processed due to its liquid form and flowability.
- The existing refinery infrastructure could be used to process bio-oil to accelerate the development of renewable bioenergy [17].
- The bio-oil would generally contain various kinds of organic compounds, some of which could be extracted and used directly as the high value-added chemical feedstock, such as the phenolic compounds.
- The bio-oil has lower sulphur and nitrogen content than the fossil fuels, which is environment -friendly.

Bio-oil is currently a standard commercial chemical with the specification described in ASTM D7544 [18]. As a valuable source, bio-oil could be utilised to produce fuels or value-added chemicals. However, it cannot be used directly as engine fuels because of the high oxygen and H_2O contents which would lead to the lower heating value than traditional hydrocarbon fuels. Generally, the H_2O content in a bio-oil could be about 30 wt% and is mainly derived from the original moisture in the raw biomass feedstock and pyrolysis reactions. The water in the bio-oil could cause immiscibility with the hydrocarbon fuels. On the other hand, the presence of water could decrease the viscosity and increase the flowability of bio-oil.

Generally, a bio-oil would contain various oxygenated compounds (~ 70 wt%), such as aldehydes, ketones, carboxylic acids and esters. The reactive components in bio-oil such as the aldehydes and ketones would cause undesired aging or phase separation during storage. Moreover, these highly reactive compounds in bio-oil may undergo polymerisation when it is heated up, which is one of the challenging bottleneck problems in the utilisation or upgrading of bio-oil [19]. Furthermore, the high concentration of carboxylic acids such as acetic acid would cause high acidity and corrosiveness.

1.4.2 Upgrading methods of bio-oil

It is essential to upgrade the bio-oil for further utilisation by improving its properties, such as enhancing the stability and decreasing the water content. The current upgrading routes could mainly be divided into two categories, including the physical and chemical methods. The physical methods mainly include distillation [20], emulsification [21] and solvent addition [22], whereas chemical methods include hydrotreatment [23], high-pressure thermal treatment [24], catalytic cracking [25], esterification [26] and aldol condensation [27].

Distillation would mainly separate the bio-oil into various fractions based on the volatility or boiling point of the bio-oil components. Generally, the distillate fractions of improved properties such as the increased heating value could be acquired via distillation [28]. Besides utilised as a physical separation unit, distillation could also be coupled with chemical reactions to further upgrade the bio-oil.

Emulsification of bio-oil is generally to mix the bio-oil with another immiscible fluid such as diesel to produce an emulsion with the help of a surfactant. A stable bio-oil in diesel emulsion might mitigate the acidity and viscosity problems to a certain degree due to the dilution of diesel [29]. However, the emulsification could not be universally applied to the bio-oil with different compositions

because acquiring an emulsion of bio-oil is very difficult and time-consuming and it is only a short-term upgrading method because the stability of the emulsion is not durable [21].

Solvent addition is referred to blending the bio-oil with extra polar solvent (e.g. methanol and ethanol) to improve the phase stability and decrease the viscosity and density of a bio-oil [30]. However, it may not be economically feasible to use the abundant solvent which is already a valuable fuel or chemical itself.

Hydrotreatment could deoxygenate the bio-oil using catalysts under high temperature and high pressure [31]. Typically, the conventional desulfurization catalysts (e.g. NiMo or CoMo on γ-Al_2O_3) and noble metal catalysts could be utilised for the hydrodeoxygenation of bio-oil [32]. Generally, after the catalytic hydrodeoxygenation, bio-oil could be converted into useful fuels with increased thermal stability, heating value and volatility [33]. However, the coke formation is still a major challenge and would usually lead to the reactor blockage and the deactivation of catalysts [34]. In addition, the light and heavy components in the bio-oil might behave differently during the hydrotreatment [35]. Therefore, it could be inferred that the separate hydrotreatment of the light and heavy components might be a feasible method to overcome the coke formation.

High-pressure thermal treatment (HPTT) could reduce the oxygen and water content by processing the bio-oil in the absence of catalysts or hydrogen at high temperature (200 – 350 ^{o}C) and high pressure (high enough to keep water in liquid state, e.g. 200 bar) [24]. A phase split would occur because of the polarity change of the bio-oil composition, forming an aqueous phase and an oil phase. Even though the oxygen content of the oil phase is decreased, the formation of components of high molecular weights due to polymerisation is also detected.

Catalytic cracking could also remove oxygen in the bio-oil using acidic zeolites and is generally conducted under more severe condition (e.g. higher temperature) than the hydrotreatment. Correspondingly, more coke might be formed due to the harsh reaction environment.

Esterification is mainly used to convert the carboxylic acids in bio-oil into esters using alcohols and the acid catalysts [36]. The esterification of bio-oil is generally conducted at temperature lower than 250 ^{o}C and could improve the bio-oil stability [26]. However, the coke formation would also occur during the bio-oil esterification [37] and the excess alcohols would be difficult to be recycled. In addition, there is a large number of heavy carboxylic acids that would have very weak acidities [38]. The large sizes of the heavy carboxylic acids might decrease the reactivity and thus the effectiveness of esterification.

Aldol condensation could convert the carbonyl compounds (e.g. the reactive aldehydes and ketones) into an aldol which could further undergo dehydration reaction to form the α,β-unsaturated

aldehyde or ketone. The aldol condensation could lead to the deoxygenation of bio-oil and help increase the liquid fuel yield and carbon efficiency by converting the low-molecular-weight carbonyl compounds into gasoline and diesel range compounds [27, 39].

1.5 Distillation of bio-oil

1.5.1 Advantages of bio-oil distillation

The exceedingly complicated composition and properties of bio-oil should be fully considered in the upgrading or direct utilisation of bio-oil. The species in the bio-oil would generally have a very wide range of molecule sizes and boiling points, for example, from the volatile methanol to the very large oligomers. In addition, the lighter species in bio-oil can have very different behaviour from the corresponding heavier species when the bio-oil is hydrotreated to produce liquid fuels and chemicals [40, 41]. Ideally, they should be hydrotreated under very different conditions. Therefore, it is necessary to separate the bio-oil into various fractions, e.g. based on their volatility or boiling points.

Distillation appears to be a suitable method to achieve such separation. It is a common operation unit in petroleum refinery and the existing infrastructure could be used to distil the bio-oil. Distillation could not only separate the bio-oil components into different fractions, but also improve the distillate composition and properties, such as the reduced water content and acidity [42], and improved stability [43].

Moreover, distillation could be combined with other upgrading methods [44]. It has been reported that distillation before the subsequent hydrotreatment could improve the product quality compared to the direct hydrotreatment of raw bio-oil [45]. Distillation could also be coupled with pyrolysis so that the bio-oil produced from the pyrolyser could be fractionated directly without condensing into liquid and heating up [46].

Furthermore, distillation could be utilised to enrich value-added chemicals from bio-oil [47-49]. For example, valuable chemicals such as benzene, toluene, and xylene can be separated from the partially deoxygenated bio-oil through distillation [50]. Besides the desired distillate acquired from the distillation, the heavy residue might be pyrolysed along with raw biomass [51, 52] or converted into the calcined coke that could be used for carbon anodes [53]. In addition, additives such as $CO(NH_2)_2$ could be utilised to improve the quality of distillate fractions during bio-oil distillation [54].

1.5.2 Vapour-liquid equilibria of bio-oil during distillation

The determination of the bio-oil phase equilibria, especially the vapour-liquid equilibria, is crucial to understand and optimise the bio-oil distillation [55-58]. The vapour-liquid equilibria of bio-

oil during the distillation would not only affect the distillate yield, but also influence the reactions while the bio-oil is heated up. Conversely, the reactions would also have an impact on the phase equilibria by changing the composition. Therefore, the reactions such as polymerisation would make it difficult to acquire the phase equilibrium data experimentally [59].

Generally, simulation is applied to investigate the phase behaviour of bio-oil by selecting compounds detected and quantified by GC-MS to represent the raw bio-oil [60]. For example, Zhang and Kong [61] conducted the simulation of bio-oil vaporisation at 800 K using 10 components quantified by GC-MS. In addition, it is generally assumed in the simulation that no reactions would take place during the distillation. Elkasabi and co-workers [62] simulated the distillation curve using the Pro-II software by assuming that the bio-oil components detected by GC-MS are not reactive and could be used to represent all the volatile components in bio-oil with negligible contribution from the bottom products and the lignin of high molecular weight.

1.5.3 Distillation techniques for bio-oil upgrading

Various distillation techniques have been utilised to upgrade the bio-oil, such as atmospheric distillation, vacuum (reduced pressure) distillation, flash distillation, stream distillation and molecular distillation [63-65]. Generally, the most important objective of bio-oil distillation is to recover the upgraded distillate at high yield. The typical distillation techniques with the operating conditions and distillate yield are summarised in Table 1-1. As it can be seen, all the factors including the bio-oil composition, distillation type, temperature and pressure would affect the distillate yield.

The high reactivity of the bio-oil would limit the distillate yield even though the bio-oil is produced from the condensation of pyrolysis vapour. When the bio-oil is heated at the atmospheric pressure to distil water and other light components, about 50 wt% of the bio-oil would be converted into solid residue [51, 66]. Bio-oil distillation is actually a reactive distillation process even though distillation is a physical separation process. The undesired side reactions would occur when the bio-oil is heated up because of the high reactivity of some bio-oil components. Polymerisation and cracking reactions would take place when the bio-oil is heated to as low as 140 ^{o}C at atmospheric pressure [67]. The polymerisation would become more significant at elevated temperature [68]. Even though vacuum distillation could achieve the evaporation at lower temperature, lower distillate recovery yield would be obtained due to the inevitable evacuation of vapour [42]. Moreover, besides the polymerisation, other reactions such as hydrolysis and decarbonylation would also affect the distillate yield. The sugar compounds, as one of the main components of bio-oil, might undergo hydrolysis reaction to form carbonyl compounds (e.g. aldehydes) which would promote the bio-oil polymerisation [69-71]. In addition, the reaction environment might affect the conversion route of

bio-oil components [72]. For example, levoglucosan would be hydrolysed into glucose in the water medium and be converted into methyl α-D-glucopyranoside in the methanol medium [73, 74]. Therefore, the low distillate yield and undesirable side reactions (e.g. polymerisation) are the bottleneck problems of the bio-oil distillation.

Table 1-1

Typical techniques of bio-oil distillation

Bio-oil feedstock	Distillation type	Temperature (°C)	Pressure	Distillate yield	Ref
Softwood bark	Atmospheric distillation	140	1 bar	11.7%	[67]
Rice husk	Atmospheric distillation	240	1 bar	51.86%	[51]
Algae	Vacuum distillation	160	40 mmHg	83.09%	[75]
Algae	Atmospheric distillation	200	101 kPa	75%	[76]
	Vacuum distillation	120	90 Pa	51%	
Corn stover	Atmospheric distillation	250	1 bar	84%	[42]
	Vacuum distillation	230	0.5 bar	73%	
Pine sawdust	Molecular distillation	130	60 Pa	83%	[77]
Pine sawdust	Molecular distillation	80	100 Pa	56.75%	[78]
Switchgrass	Flash distillation	380		77.5%	[79]
Birch wood	Steam distillation	105		14.9%	[80]
	Flash distillation	200	10 kPa	30.2%	

1.6 High-pressure reactive distillation of bio-oil

1.6.1 Reactive distillation of bio-oil

Reactive distillation would couple chemical reactions and distillation in a single reactor, which could achieve the upgrading and separation simultaneously. It could not only achieve high conversions by removing products to shift the reaction equilibrium, but also lower the cost because the reaction and distillation are integrated in one equipment [81-84]. Reactive distillation has been successfully used in the production of methyl tert-butyl ether (MTBE) and esters (e.g. methyl acetate) [85-87].

The bio-oil, as a complex mixture derived from biomass pyrolysis, could be upgraded by the reactive distillation. Almost all the publications about the reactive distillation of bio-oil focus on the

integration of esterification reaction with distillation to decrease the acidity, viscosity and water content of the distillate products [88, 89]. The major reaction is to convert the carboxylic acids (mainly acetic acid) in the bio-oil into esters using various alcohols (e.g. methanol) with the help of a catalyst. Because esterification is a reversible reaction limited by the equilibrium, the continuous removal of product esters could improve the conversion [90]. In addition, most of the integrated esterification and distillation of bio-oil were conducted at reduced or atmospheric pressure [91-93].

Moreover, the high reactivity of bio-oil would lead to some side reactions during the reactive distillation. For example, the polymerisation of reactive components such as furfural would cause the deactivation of catalyst during the reactive distillation, especially at high temperature [94]. To improve the distillate yield and properties, it is necessary to inhibit the polymerisation reaction and enhance the desired reactions.

1.6.2 High-pressure reactive distillation

Distillation can be classified into low-pressure (vacuum), atmospheric pressure and high-pressure distillation according to the operation pressure [95]. Currently, bio-oil distillation is mainly conducted at either atmospheric pressure or low pressure, as is shown in Table 1-1.

High-pressure distillation is referred to the distillation process carried out under elevated pressures higher than atmospheric pressure. It is generally utilised to separate the low-boiling-point components [96] or azeotropic mixtures [97], such as the separation of high-purity gas [98, 99], distillation of low-molecular-weight hydrocarbons (C_2-C_4) [100] and azeotropic distillation [95].

High-pressure distillation has many advantages as is outlined below.

- The increase of pressure would result in the increase of vapour density and viscosity and the decrease of liquid density and viscosity. In addition, the increasing pressure could also reduce the surface tension. These effects would make a significant change in the contact area between phases. For example, with increasing pressure, the decrease of the surface tension would let the bubbles become small and it would take more time for the bubbles to escape from the liquid [101].
- The presence of high pressure can improve the tray efficiency [102-105]. The tray efficiency during high-pressure distillation is around 100% whereas that during atmospheric pressure distillation is 60% - 75%.
- Increasing the pressure could lower the energy consumption of the process, enhance the mass transfer due to the increasing surface area of contact among phases, and improve the productivity because of the increasing throughput of the packing [106].

- Conducting the distillation at high pressure would influence the mass transfer kinetics and phase equilibrium. Pressure is a key parameter to determine the vapour-liquid equilibrium and could be used to control the coupling between the mass transfer and phase equilibrium.

To the best of my knowledge, no prior experimental research has been conducted about the high-pressure reactive distillation of raw bio-oil and only some simulation investigations using the mixture of model compounds have been reported. Khan and Adewuyi [107] simulated the high pressure reactive distillation of bio-oil at 10 bar using Aspen Plus software to optimise the conversion of bio-oil esterification and the recovery of product ester. In their study, high pressure was applied during the reactive distillation because it could lead to high column temperature even though the pressure itself has the least impact on the esterification conversion. Thus, the bio-oil could enter the reactive distillation reactor from the pyrolyser without heating or cooling [108]. Sandra and co-workers [109] analysed the energy consumption of biodiesel production at high temperature and pressure by using Aspen Plus simulation and concluded that increasing the conversion degree of triglycerides could reduce the energy consumption. The simulation of biodiesel production at high temperature and pressure conducted by Fernando and co-workers [110] showed that the utilisation of reactive distillation could lower the total heat input and reduce the emissions of pollutants such as CO and nitrogen oxides.

The bottleneck problems of bio-oil distillation discussed in Section 1.5 might be solved by high-pressure distillation which would change both phase equilibria and reactions of the bio-oil. To be specific, most of the reactions would take place when the bio-oil is being heated up. Besides the temperature and the bio-oil composition, pressure could change the phase equilibria which would influence the compositions and reactions in vapour and liquid phases.

1.7 Purpose of this study

Based on the above analysis, the bio-oil is clearly a promising fuel or chemical source. However, there are some bottleneck problems during the upgrading and utilisation of bio-oil, especially the polymerisation. To overcome these bottleneck problems, high-pressure reactive distillation could be utilised to upgrade the bio-oil. This would require a deep and thorough understanding about the high-pressure distillation of bio-oil.

This study aims to upgrade the pyrolysis bio-oil into useful distillate fractions with reduced polymerisation and improved properties via high-pressure reactive distillation. So far, there is little literature about the high-pressure reactive distillation of bio-oil, especially the experimental research about the raw bio-oil. This thesis would provide a detailed investigation about the bio-oil reactive

distillation at elevated pressure and advance the fundamental understanding about reaction mechanisms in the high-pressure reactive distillation of bio-oil. First, the effects of process parameters including pressure, temperature and holding time on the distillate yield and properties would be investigated. In addition, the distribution and reaction behaviours of the bio-oil major components, including sugar compounds, carbonyl compounds and aromatic compounds, would also be studied.

1.8 Contents of the thesis

This thesis is mainly composed of the following chapters:

Chapter 2 would describe the experimental and analytical methods including the experimental set-up and characterisation techniques of the distillation products. The simulation details using Aspen Plus would also be depicted.

Chapter 3-6 would present the experimental and simulation results and discussion. Each chapter would also contain introduction for the specific topic.

Chapter 3 would present the effects of process parameters including pressure, temperature and holding time on the yield of different fractions during the high-pressure reactive distillation of bio-oil.

Chapter 4 would present the distribution and reaction behaviours of levoglucosan during the high-pressure reactive distillation of bio-oil, especially the intensification of levoglucosan hydrolysis.

Chapter 5 would present the conversion of carbonyl compounds by base-catalysed aldol condensation reaction and neutralisation reaction based on the different reaction behaviours of the light and heavy carbonyl compounds.

Chapter 6 would present the enrichment of aromatic compounds to the paste distillate fraction by the application of pressure and base. The reactions of the aromatic compounds in the hydrothermal environment would also be discussed.

Chapter 7 would summarise the important conclusions of the thesis and recommendations of the future work.

The scope of this thesis is illustrated in Figure 1-2.

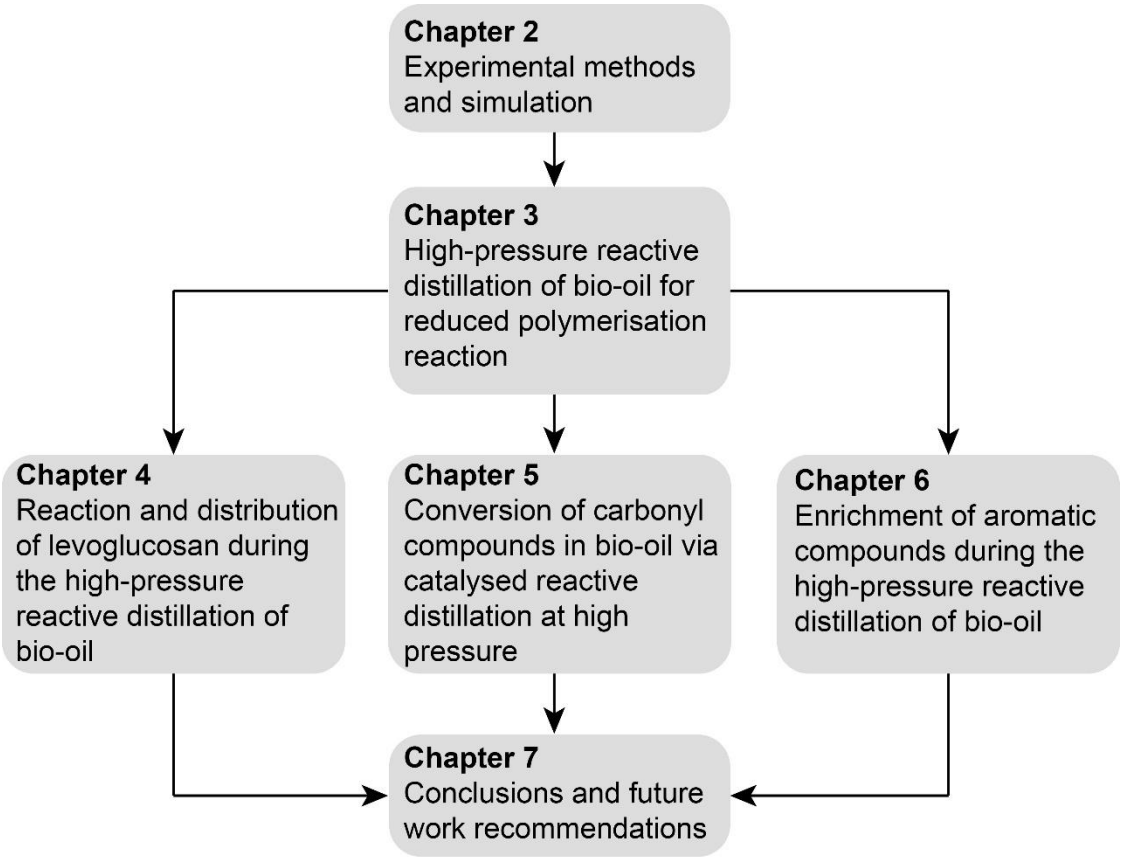

Figure 1-2. A flow chart showing the scope of this thesis.

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Chapter 2

Experimental methods and simulation

2.1 Introduction

This chapter mainly describes the experimental methods including the bio-oil production, high-pressure reactive distillation experiments and the characterisation methods of products. In addition, the simulation details using the Aspen Plus would also be described.

2.2 Bio-oil production

The bio-oil used in this thesis was produced by grinding pyrolysing mallee wood at 400 ^{o}C in a 100 kg/hour demonstration plant with the rotation speed being 45 rpm [1-3]. The grinding pyrolysis could achieve the pyrolysis and reduction of particle size simultaneously, which could entitle the pyrolyser to process biomass feedstock of different particle sizes. The produced bio-oil was first filtered and then stored at -10 ^{o}C in a freezer to prevent the possible aging. The typical physical properties of the bio-oil in this study are indicated in Table 2-1, with values from literature for comparison. GC-MS was utilised to quantify the chemical composition of the bio-oil with the result shown in Table 3-1 (See in Chapter 3 for more detail).

Table 2-1

Typical physical properties of the bio-oil in this study

Properties	Values of bio-oil in this study	Values in Ref. [4]
Phase	One phase	
Density (g/cm^3)	1.13	1.1 - 1.3
Viscosity (cP)	22.6 (at 26 ^{o}C)	35 - 1000 (at 40 ^{o}C)
pH	2.5	2 - 3

2.3 High-pressure reactive distillation experiments

The high-pressure reactive distillation experiments were performed in a high-pressure distillation system which mainly included a 100 mL autoclave and collective condensers. The autoclave (Autoclave Engineers) mainly included a vessel, a controller, a stirrer and an electric heater. Two sequential 150 mL sample cylinders of stainless steel (Swagelok) were immersed in the mixture of ice and water to condense the distillate fractions.

Typically, 50 mL bio-oil and other reactant were put into the reactor and N_2 was used to flush the assembled reactor three times to expel the air. Then the reactor was heated to the pre-set temperature and adjusted to the target pressure. If the target pressure is lower than the vapour

pressure of bio-oil, the extra pressure would be released slowly to keep the reactor at the target pressure. If the target pressure is higher than the vapour pressure of bio-oil, the high-pressure nitrogen would be used to pressurise the reactor to the target value. The stirring speed was 500 rpm. After holding at the target temperature and pressure for a pre-set period, the heater was turned off and the valve between the reactor and the first condenser was quickly opened to discharge the vapour phase in the reactor to the condensers. Then the heater was removed and the cooling water was started to cool down the reactor quickly. During the high-pressure distillation, the distillate fraction in the condensers could be further separated into a liquid phase on the top and a paste phase at the bottom by decanting. All the experiments were performed at least twice.

2.4 Characterisation of products

2.4.1 Gas chromatography-mass spectroscopy (GC-MS)

The samples were dissolved in tetrahydrofuran (THF) to approximately 2 wt% and characterised using an Agilent GC-MS (a 6890 GC and a 5973 Mass Selective Detector) with a HP-INNOWax column (length: 30 m, diameter: 0.25 mm, film thickness: 0.25 μm). 1 μL sample was injected with the front inlet temperature being 250 ^{o}C and the split ratio being 50:1. After holding at 40 ^{o}C for 3 min, the oven temperature was ramped to 260 ^{o}C at 10 ^{o}C/min and kept for 7 min [5]. The standard chemicals and/or the NIST mass spectral library were used to identify the individual compounds. The concentrations were quantified by using standards.

2.4.2 Thermogravimetric analysis (TGA)

A TGA Q5000 (TA Instruments) was utilised to perform the thermogravimetric analysis. The samples were heated up from 25 ^{o}C to 500 ^{o}C at 10 ^{o}C/min in a N_2 flow of 25 mL/min. The potential coke yield (PCY) is defined as the residue weight percentage after evaporation at 500 ^{o}C [6]. As the bio-oil was separated into two or three fractions after the distillation, the total change of all the fractions would be used to indicate the change of bio-oil by adding up the products of the fraction yield and the corresponding weight percentage at different temperature. The TGA and DTG data were extracted every 5 ^{o}C. TGA could be used to quantify the formation of large molecules (Chapter 5) and determine the extent of polymerisation (Chapter 6).

2.4.3 Fourier Transform infrared spectroscopy (FT-IR)

The bio-oil distillation fractions were diluted in THF to 2 wt% and characterised using a Perkin-Elmer Spectrum GX FT-IR/Raman spectrometer. The liquid sample cell was composed of CaF_2 windows

and a 0.05 mm Teflon spacer. Each sample was repeated twice with each spectrum scanned for 10 times. 6 Gaussian bands (1767 , 1740, 1713, 1696, 1654 and 1606 cm^{-1}) were used to deconvolute the spectra in the range of 1850 - 1540 cm^{-1} and the functional groups represented by each band are shown in Table 2-2 [7]. The H_2O in the bio-oil would mainly contribute to the 1654 cm^{-1} band [8]. The obtained peak areas were expressed on basis of per gram bio-oil by multiplying the area by the corresponding fraction yield.

Table 2-2

Band assignment for different functional groups [7].

Band position (cm^{-1})	Functional groups	Typical compounds
1767	C=O stretching vibration	Lactones
1740	C=O stretching vibration	Unconjugated alkyl aldehydes and alkyl esters
1713	C=O stretching vibration	Carboxylic acids
1696	C=O stretching vibration	Unsaturated aldehydes, ketones
1654	C=O stretching vibration	Hydroxy unsaturated ketones, aldehydes, H_2O
1606	Aromatic C=C ring breathing	Aromatics with various types of substitution

2.4.4 UV-fluorescence spectroscopy

The UV-fluorescence spectroscopy could be utilised to analyse the change of aromatic compounds. After dissolving the samples in the mixture solution of chloroform and methanol (volume ratio being 4:1) and then diluting them in methanol to 4 ppm (wt), the synchronous fluorescence spectra were measured using a Perkin-Elmer LS50B spectrometer [9]. The fluorescence intensity was expressed based on per gram bio-oil by multiplying the intensity and the yield of the corresponding distillation fraction.

2.5 Aspen Plus simulation

To determine the distribution of bio-oil components and the vapour-liquid equilibrium, the distillation was simulated using Aspen Plus V11 with the property method being NRTL and the components quantified by GC-MS (See Table 3-1 in Chapter 3 for more detail). Maltose was selected to represent the heavy components that could not be detected by GC-MS. The PT Envelope was used to calculate the pressure-temperature diagram. The Flash 2 model was used to analyse the vapour-liquid equilibrium.

To determine the component distribution in different phases during the distillation, the BatchSep model was utilised to simulate the whole distillation process with the property method being NRTL. The general specifications of the reactor such as the dimensions were based on the manual from Autoclave Engineers. The specifications for BatchSep block are shown in Table 2-3. The overall heat transfer coefficient was estimated by calculating the contribution from the thick Hastelloy reactor wall with its thickness of 6.5 mm and the thermal conductivity of 12.9 W/(m·^{o}C). The initial condition was set as "Initial charge" with the "Total initial charge" being 56 g bio-oil at 25 ^{o}C and 1 bar. Nitrogen at 25 ^{o}C and 100 bar was used to pressurise the reactor. The operating steps in the batch simulation were based on the experimental procedures in Section 2.3.

Table 2-3

Parameters of BatchSep model in Aspen Plus used for simulating the high-pressure reactive distillation of bio-oil

		Item	Parameter	Value
Reactor Setup	Configuration	Configuration	Batch distillation column	
			Number of stages	2
			Valid phases	Vapor-Liquid
		Overhead	Condenser	Partial
		Distillate receivers	Number of receivers	1
		Pressure & Holdups	Calculate from tray or packing hydraulics	
		Pot heat transfer	Rigorous	
		Initial condition	Initial charge	
	Streams	Pot charge	Bio-oil (BO-FEED)	
		Additional feeds	N2	Charge stage is 2
		Distillate receiver	Number of receivers	1
			Product stream	Distillate (LIGHT)
	Pressure & Holdups	Calculation Option	Calculated from tray or packing hydraulics	
		Overhead	Condenser pressure	1 bar
			Condenser inlet diameter	5 mm
	Condenser	Condenser type	Partial	
		Condenser specification	Temperature	0 °C
		Flash specification	Flash basis	Equation
	Pot	Geometry Specification	Pot orientation	Vertical
			Pot head type	Top: Flat Bottom: Hemispherical
			Diameter & Volume	Volume: 135 mL Diameter: 46 mm
	Reflux	Reflux Ratio	Liquid 1	0
Heat transfer	Configuration	Heat transfer model	Rigorous	
		Jacket	Heating, Jacket covers bottom	
			Jacket top height	55 mm
	Jacket Heating	Heat option	Specified medium temperature	
		Medium temperature	450 °C	
		Heat transfer coefficient	1984.6 Watt/sqm-K	
Initial Conditions	Main	Initial charge	Initial temperature	25 °C
			Initial pressure	1 bar
			Pad gas	Nitrogen
		Charge (Specify total charge)	Total initial charge	56 gm
	Distillate Receivers	Receiver: 1	Total initial charge	0 gm

2.6 References

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Chapter 3

High-pressure reactive distillation of bio-oil for reduced polymerisation: effects of process parameters

3.1 Introduction

The continuous depletion of the limited fossil fuels and the increasing environmental concerns necessitate the development of new renewable energy technologies. Bio-oil, as one of the most promising fuels to substitute the conventional fossil fuels, is derived from the pyrolysis of renewable and abundant biomass. Bio-oil is in a liquid form and has higher volumetric energy density than the bulky solid biomass substrate. However, the undesirable properties of bio-oil such as high oxygen contents, high water contents and thermal instability usually impede its direct utilisation [1, 2]. To overcome these challenges, it is essential to further upgrade the bio-oil.

Bio-oil may be upgraded via physical and/or chemical methods. The examples of physical methods include solvent addition [3], filtration, emulsification [4] and distillation [5, 6], whereas the examples of chemical methods include hydrotreatment [7-9], hydrocracking [10], high pressure thermal treatment (HPTT) [11] and esterification [12]. Since bio-oil is composed of hundreds of compounds with different boiling points and chemical properties, these compounds should ideally be processed under different conditions that are optimal for the corresponding compounds. Distillation, as a common unit operation in the petroleum refinery industry, may also be used to upgrade bio-oil or separate bio-oil before further upgrading. Nam and co-workers [13] conducted fractional distillation prior to the hydrotreatment of middle fraction (120 – 200 ^{o}C) and concluded that distillation followed by hydrotreatment can improve the biofuel quality in terms of elemental composition compared to the direct hydrotreatment of the whole bio-oil.

The bio-oil distillation techniques reported in the literature [5, 14-16] so far include atmospheric pressure distillation and vacuum distillation. The reactive components in bio-oil would generally undergo polymerisation that can lead to increases in molecular weight and decreases in distillate yield when the bio-oil is heated up. Boucher and co-workers [17] reported that bio-oil started to crack and polymerise when it was heated to 140 ^{o}C. Zhang and co-workers [16] carried out an atmospheric pressure distillation of bio-oil at 240 ^{o}C with the distillate yield being 52% and the formation of black solid as the residue. Even though the vacuum distillation can be conducted at lower temperature, the polymerisation is still quite severe [14, 18]. Therefore, due to the high reactivity of bio-oil, the excessive polymerisation of the reactive components in bio-oil is a major bottleneck problem when bio-oil is distilled at atmospheric or reduced pressures using the existing technologies. New technologies for separating bio-oil into different fractions with minimised polymerisation are essential.

High-pressure distillation, as a separation process carried out at elevated pressures, is generally used to separate the components with low boiling points, such as the distillation of high-

purity gas and the separation of low-molecular-weight hydrocarbons. It is found that the use of high pressure can enhance the mass transfer rates and influence the phase equilibria [19]. It is hypothesised for the first time that the change of phase equilibria can lead to different distributions of reactive components while the bio-oil is heated up, which in turn could further change the reaction network and thus the product properties. In this way, we regard the high-pressure distillation as a reactive distillation for bio-oil upgrading controlled by the pressure and could possibly be an effective technology to separate bio-oil [20].

This paper aims to investigate the reactive distillation behaviour of pyrolysis bio-oil under elevated pressures with a particular focus on the effects of process parameters on the distillation fraction yields and properties. To demonstrate the advantages of high-pressure reactive distillation for bio-oil, the same bio-oil was also distilled at atmospheric pressure. The distillation products at different pressures were analysed with gas chromatography-mass spectroscopy (GC-MS), Fourier Transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA) to investigate the inhibition of polymerisation and the roles of H_2O during distillation.

3.2 Experimental

3.2.1 Materials

The bio-oil was produced from the grinding pyrolysis of mallee woody biomass in a 100 kg/hr demonstration plant of Renergi Pty Ltd, Australia [21] and stored in a freezer at -10 ^oC to prevent aging. The bio-oil was a single-phase brown liquid. The light components of bio-oil were determined by GC-MS with the results shown in Table 3-1. Tetrahydrofuran (≥99.9%) and levoglucosan (99%) were bought from Sigma-Aldrich and used without further purification.

3.2.2 Distillation experiment

The high-pressure distillation was performed in a 100 mL autoclave (Autoclave Engineers). It was mainly composed of a Hastalloy vessel, a MagneDrive II stirrer, an electric heater and a controller. The autoclave was connected to two sequential 150 mL stainless steel sample cylinders made of Swagelok components, which were immersed in an ice-water mixture to condense the distillates, as is shown in Figure 3-1.

Table 3-1

Light components of bio-oil

Composition	wt%
Water	29.5%
Acetic acid	9.2%
Formic acid	1.0%
Propanoic acid	0.3%
Phenol	0.1%
Guaiacol	0.2%
Syringol	1.0%
Levoglucosan	3.9%
Furfural	0.8%
Hydroxyacetaldehyde	2.9%
Hydroxyacetone	4.0%
Methanol	1.0%
Levulinic acid	0.1%
Hydroxymethylfurfural	0.3%
Syringaldehyde	0.2%

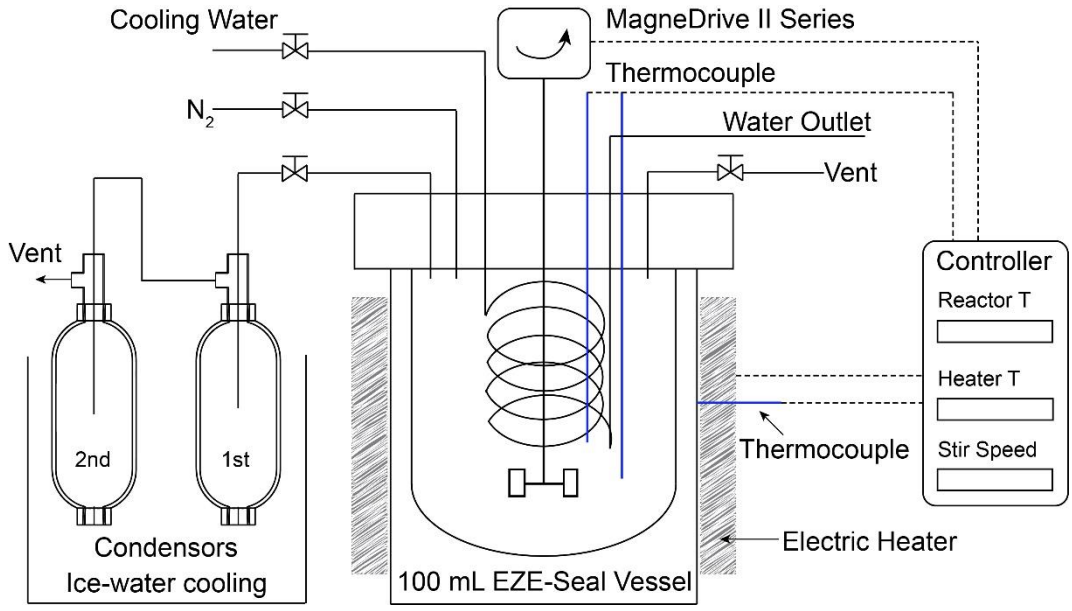

Figure 3-1. A schematic diagram showing the high-pressure distillation system.

50 mL bio-oil was loaded into the reactor and the stirring speed was set to 500 rpm. After the reactor was heated up to the target temperature and held for a pre-set period, the heater was

switched off and the vapour phase in the reactor was quickly released to the low-temperature condensers by opening the valve between the reactor and the condensers. When the pressure was suddenly released, to simulate the flash distillation, light species including water and other unreacted or newly produced species would be evaporated quickly and then condensed in the low-temperature condensers. The reactor was then cooled down quickly by removing the heater and starting cooling water that went through the cooling coil inside the reactor. The distillate and residue were collected from the condensers and reactor, respectively, and quantified by the mass differences of the condensers and reactor before and after distillation. Little was normally collected in the second condenser, indicating that the condensing system worked efficiently. If some distillate product was distributed into the second condenser, the light distillates in both condensers would be first mixed before sampling for analysis. All the experiments were performed in triplicates.

3.2.3 Product analysis

3.2.3.1 Gas chromatography-mass spectroscopy

All the samples were dissolved in tetrahydrofuran to 2 wt% and analysed by an Agilent GC-MS (a 6890 GC with a 5973 Mass Selective Detector) equipped with a HP-INNOWax column (length: 30 m, diameter: 0.25 mm, film thickness: 0.25 μm). The injection volume was 1 μL and the front inlet temperature was 250 ^{o}C with a split ratio of 50:1. After holding at 40 ^{o}C for 3 min, the oven temperature was ramped to 260 ^{o}C at 10 ^{o}C/min and then held for 7 min [22]. The individual compounds were identified by injecting standard chemicals and/or by comparison with the NIST mass spectral library.

3.2.3.2 Thermogravimetric analysis

To quantify the polymerisation extent, TGA was conducted with a TGA Q5000 (TA Instruments) by heating up samples from 25 ^{o}C to 500 ^{o}C at 10 ^{o}C/min in a nitrogen flow of 25 mL/min. The residue after evaporation at 500 ^{o}C is defined as the potential coke yield (PCY) [23]. The changes in the potential coke yield serves as a good indication of the polymerisation during distillation.

3.2.3.3 Fourier Transform infrared spectroscopy (FT-IR)

The distillation products including distillates and residue were diluted in tetrahydrofuran to 2 wt% and analysed with a Perkin Elmer Spectrum GX FT-IR/Raman spectrometer. A liquid sample cell with CaF_2 windows and a 0.05 mm Teflon spacer was used. Each spectrum was scanned for 10 times and each sample was repeated for 2 times. A typical FT-IR spectrum of the investigated bio-oil is shown in Figure 3-2 and the carbonyl functional group (C=O) would contribute to the high reactivity and

thermal instability of bio-oil. The spectra in the range of 1850 - 1540 cm^{-1} were deconvoluted using 6 Gaussian bands as in [24], including 1767 cm^{-1} (lactones), 1740 cm^{-1} (unconjugated alkyl aldehydes and alkyl esters), 1713 cm^{-1} (carboxylic acids), 1696 cm^{-1} (unsaturated aldehydes and ketones), 1654 cm^{-1} (hydroxy unsaturated ketones and aldehydes, H_2O) and 1606 cm^{-1} (aromatics with various types of substitution).The acquired peak areas were expressed based on per gram bio-oil by multiplying the area with the yield of the corresponding fraction [24]. The areas of bands 1767, 1740, 1713 and 1696 cm^{-1} were summed up as the total carbonyl content because water mainly contributed to the band 1654 cm^{-1} [25].

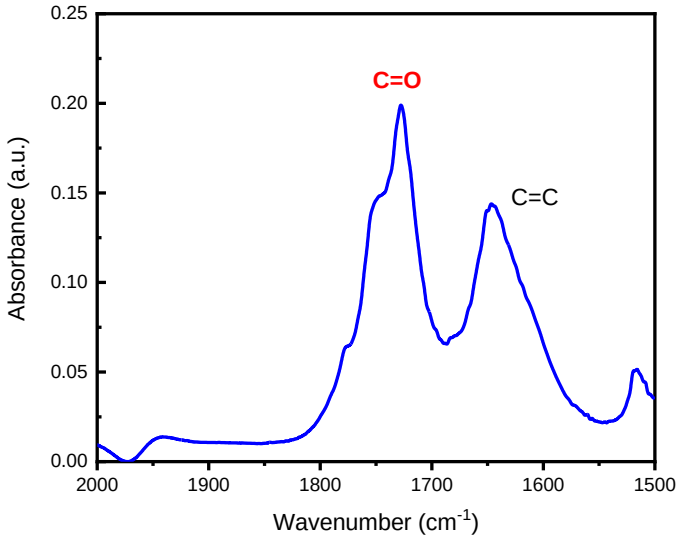

Figure 3-2. A typical FT-IR spectrum of the bio-oil used in this study.

3.2.3.4 Definitions of terms used

The terms of distillate, residue, liquid distillate and paste distillate are defined according to our experimental procedure in Figure 3-3. Bio-oil would be separated into a distillate in the condensers and a residue in the reactor after flash distillation. The distillate could also be separated into liquid distillate and paste distillate by decanting. To be specific, the paste distillate refers to the fraction that has left the reactor and the residue is the material that stays in the reactor regardless of its state. Concentration (wt%) is referred to the absolute weight concentration of a species in a sample. The yield of a species in a sample based on the bio-oil (wt% of bio-oil) is acquired by multiplying the concentration of the species by its corresponding yield of the sample.

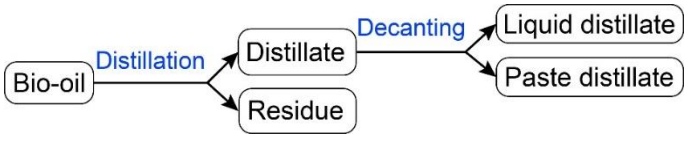

Figure 3-3. A flow chart showing the terms for fractions collected after distillation.

3.2.4 Aspen simulation

To approximate the pressure-temperature diagram and vapor-liquid equilibrium of bio-oil, simulation was conducted using Aspen Plus V10 with the components derived from the GC-MS result (Table 3-1) and the property method being NRTL. The pressure-temperature diagram was acquired using the PT Envelope. The vapor-liquid equilibrium of bio-oil during distillation was simulated using Flash 2 model. It is assumed that no chemical reactions take place when the reactor is being heated. The composition quantified by GC-MS accounts for 53.7 wt% of bio-oil. Maltose was used to represent the other heavy components in the bio-oil. Heavy components contribute little to the total vapour pressure.

3.3 Results and discussion

3.3.1 Improved yields of distillates at high pressure

3.3.1.1 Comparison between high-pressure distillation and atmospheric pressure distillation

To understand the role of pressure in reactive distillation, the pressure was controlled manually. The autogenous pressure by heating up 50 mL bio-oil in the closed 100 mL autoclave to 200 ^{o}C was 16 barg (see in Section 3.3.2.1 for more details). If the target pressure was lower than 16 barg, the extra pressure would be slowly released when the reactor pressure exceeded the target pressure. If the target pressure was higher than 16 barg, the reactor would be pressurised to the desired value by introducing additional high-pressure nitrogen when the reactor temperature reached 200 ^{o}C.

As is shown in Figure 3-4, the distillate yields at pressures higher than 20 barg and 200 ^{o}C were around 90%. However, the distillate yield was only 54% from atmospheric pressure distillation at 0 barg and 200 ^{o}C. Moreover, the residues of atmospheric pressure distillation and high-pressure distillation were in the form of hard solid and sticky paste, respectively, indicating that overall polymerisation was reduced during high-pressure distillation compared with that during the distillation at atmospheric pressure.

In the distillates, one liquid phase and one flowable paste phase were formed after the high-pressure distillation (Figure 3-3), rather than one liquid phase during the atmospheric pressure distillation. Both the liquid and paste distillates of high-pressure distillation were black whereas the distillate of atmospheric pressure distillation was yellow. Generally, the paste distillate in the bottom phase was much stickier than the liquid distillate in the top phase, but it was still flowable at room temperature. This observation infers that only light species can be distilled out at atmospheric pressure while somewhat heavier species can still be distilled out at higher pressures.

To understand the differences between the distillation at high pressure and that at atmospheric pressure, the complicated network of physical processes and chemical reactions when bio-oil is heated up must be considered. Bio-oil has abundant O-containing functional groups [24], some of which (e.g. carbonyl groups) are exceedingly reactive. Complicated reactions in parallel or in series can take place at the temperatures of distillation. Within the context of the present discussion, some reactions would increase the molecular sizes, i.e. polymerisation while other reactions (e.g. hydrolysis) would decrease the molecular sizes. The net outcome of distillation is determined by the competition between these two types of reactions.

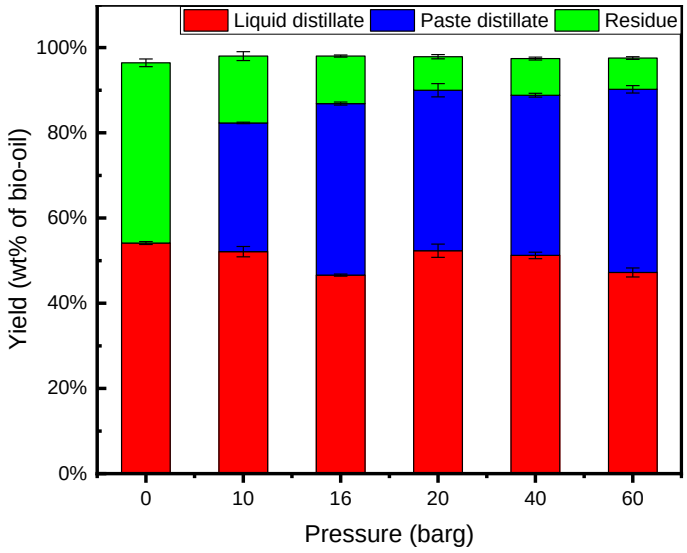

Figure 3-4. Effects of pressure on the overall yields (wt% of bio-oil) of liquid distillate, paste distillate and residue at 200 °C.

Bio-oil has a wide range of molecular mass distribution, ranging from water to heavy polymeric molecules resulting from the partial fragmentation of natural polymers such as cellulose, hemicellulose and lignin that existed in the raw biomass. On heating, some light molecules in bio-oil such as water would evaporate to turn a bio-oil liquid into a multi-phase system. At elevated temperatures during distillation, reactions can occur in each phase and among phases. In other words, the distillation of bio-oil is always a reactive distillation.

The effects of pressure on the distillation yields shown in Figure 3-4 are largely due to the changes in this multi-phase behaviour with increasing pressure, which in turn alters the reactions taking place in each phase and among phases during distillation. In another word, pressure would affect both the phase behaviour and reactions of the bio-oil components. As the overall vapour pressure of bio-oil is mainly determined by the light species (see Table 3-1), the effects of pressure on

distillation yields (Figure 3-4) would have mainly originated from the changes in the phase behaviour of light species with increasing pressure.

With increasing pressure, increasingly more light species such as water, formic and acetic acids in bio-oil (Table 3-1), which would have been in the vapour phase during atmospheric pressure distillation, would now be retained in the condensed liquid phase during high-pressure distillation. Detailed distribution of components is required to understand how the pressure would change the reaction environment and reduce the polymerisation. Based on the composition of bio-oil in Table 3-1 and using maltose to represent the heavy species, the distribution of light species in the vapour and liquid phases was simulated using the Aspen software (also see below). The simulation results for formic acid, acetic acid and water, as typical examples of light species, are shown in Figure 3-5. It is clear that these light species would tend to shift to the liquid phase with increasing pressure: almost all of these species would be in the liquid phase at pressures higher than 15 bar. The changes in the distribution of light species in different phases with increasing pressure would influence the outcomes of reactions in and among different phases, as will be broadly outlined below:

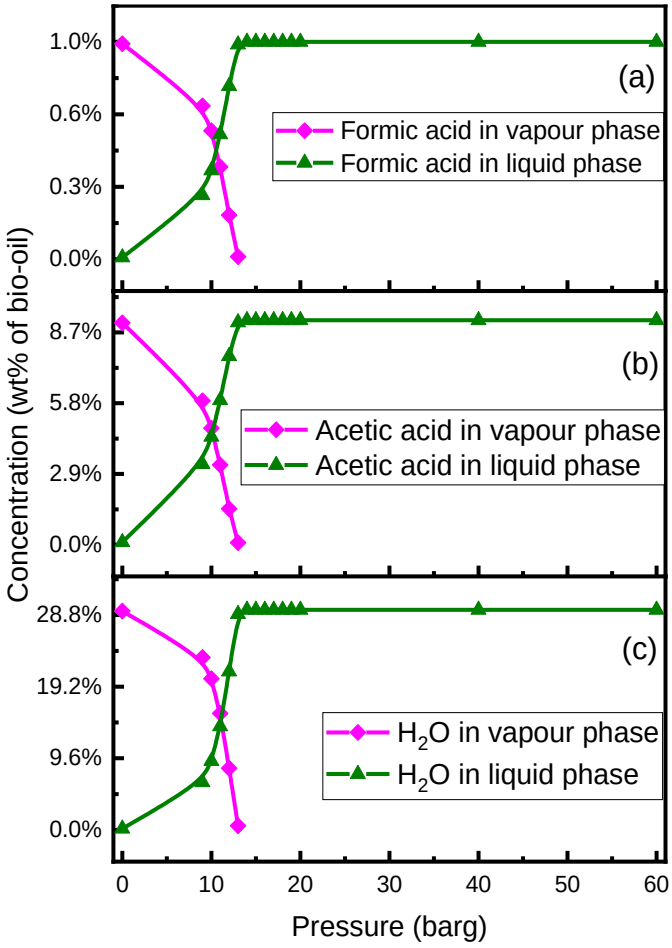

Figure 3-5. Effects of pressure on the concentrations of formic acid (a), acetic acid (b) and H_2O (c) during bio-oil vapor-liquid equilibrium at 200 °C based on calculation using the Aspen software.

- Altering reaction environments and the distribution of catalyst and reactants/products. The acidic nature of bio-oil is a key factor influencing the reactions in bio-oil. For example, acid is an important catalyst for many reactions in bio-oil; formic acid and, to a lesser extent, acetic acid are the most important organic acids in bio-oil due to their acidity (especially formic acid) and concentration in bio-oil (Table 3-1). As is shown in Figure 3-5a and 3-5b, both formic and acetic acids would mainly exist in the vapour phase during the atmospheric pressure distillation, drastically reducing the concentration of acids in the liquid phase. On the other hand, during the distillation at pressures above 14 barg, they would mainly exist in the liquid phase, available for catalysing many reactions.

  Water itself is not necessarily inert in a heated bio-oil. For example, water is a key reactant in hydrolysis reactions and also a key product from dehydration or other reactions in bio-oil. Evaporating water from bio-oil during the distillation at atmospheric pressure would greatly limit the hydrolysis reactions. Similarly, evaporating water would also shift the equilibria of water-forming reactions (e.g. dehydration), encouraging these reactions.
- Changing the concentration of reactants. For some reactions, water and other light species are not a reactant or product. The changes in the distribution of light species in different phases would change the concentration of reactants or products in these phases. According to Figure 3-5c, the evaporation of water and other light species during the distillation at atmospheric pressure would significantly concentrate and enhance the reactions of other heavy species in the condensed/liquid phase. Conversely, during the distillation at high pressures, water and other light species would tend to stay in the liquid phase, diluting the other reactants.
- Changing reactions among vapour and liquid phases. Some light species in the vapour phase may polymerise into heavier species that would then transfer to liquid phase. Conversely, heavy species in the liquid phase may also be decomposed (e.g. through hydrolysis) into light species and transferred to the vapour phase. As is indicated in Figure 3-4, more light species, especially those transferred to paste distillation, would be formed with increasing pressure. The transferred product may continue reactions depending on the remaining functional groups and reaction environment. In addition, pressure could intensify the mass transfer through the vapour-liquid phase interface.

While it is difficult to pinpoint the exact reactions responsible for the observed effects of pressure on the distillation yields in Figure 3-4, the effects of pressure can be broadly explained as follows. With increasing pressure, increasingly more water and light acids would be retained in the liquid phase, which would favour such reactions as hydrolysis that would tend to reduce the molecular sizes. The hydrolysis of sugar oligomers is a typical example. As a typical example of sugar compounds

that is within the capability of GC-MS, Figure 3-6 shows the levoglucosan yield as a function of pressure during the reactive distillation of bio-oil, which clearly indicates the consumption of levoglucosan through hydrolysis, even though there was some consumption during the heating up of bio-oil. It is believed that some higher sugar oligomers would have also been hydrolysed at high pressure.

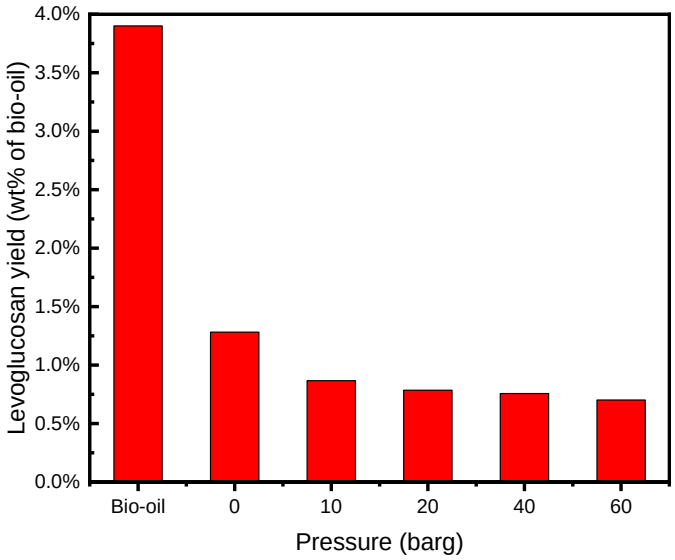

Figure 3-6. Effects of pressure on levoglucosan yield, wt% of bio-oil.

As it can be seen from Figure 3-4, pressure could also contribute to the distribution between the liquid and paste distillates. On the one hand, pressure can reduce the polymerisation of reactive organics that are usually in the paste distillates after distillation, which may lead to the increase of paste distillate yield. TGA curves in Figure 3-7 support that the pressure increase could decrease the potential coke yield of the paste distillates and residues. Moreover, the weight loss rates for the sample produced at 10 barg in Figure 3-7a are higher than that at 20 – 60 barg when the TGA temperature is lower than 125 ^{o}C, which is due to the higher content of light organic compounds in the paste distillate at 10 barg. In addition, the redistribution in the phase separation may be caused by the polarity change of components [12,26]. When bio-oil is heated up, the components would be changed due to chemical reactions. For example, decarbonylation and decarboxylation reactions can remove some oxygen from the O-containing compounds to decrease the polarity and the solubility of components in water, and thus leading to the yield increase of paste distillate which is featured with higher organic content and lower water concentration (~15 wt%).

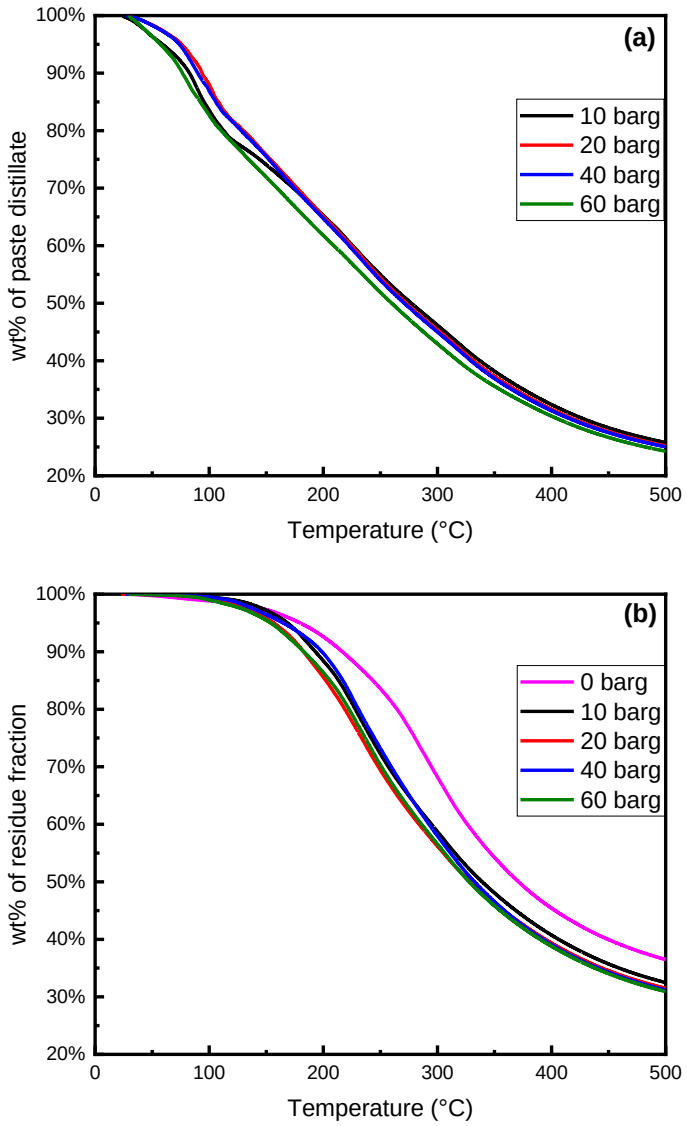

Figure 3-7. TGA curves of paste distillates (a) and residues (b) from different pressure.

3.3.1.2 Inhibited polymerisation by high pressure

As high pressure can reduce the polymerisation more effectively than atmospheric pressure during bio-oil distillation, the potential coke yield from high-pressure distillation is lower than that from atmospheric pressure distillation as is shown in Figure 3-8. Lower potential coke yield means smaller molecular sizes and less polymerisation of the reactive species (e.g. carbonyl compounds) because of the changed phase behaviour of light components (e.g. H_2O) by pressure. To prove that the increased water concentration in the liquid phase could reduce polymerisation, additional 15 wt% water (based on bio-oil) was added to autoclave to conduct high-pressure reactive distillation at 40 barg and 200 °C and the potential coke yield was further decreased by the added water as is shown in Figure 3-8. This clearly indicates that the retained light components in the liquid phase during high-pressure distillation would reduce polymerisation.

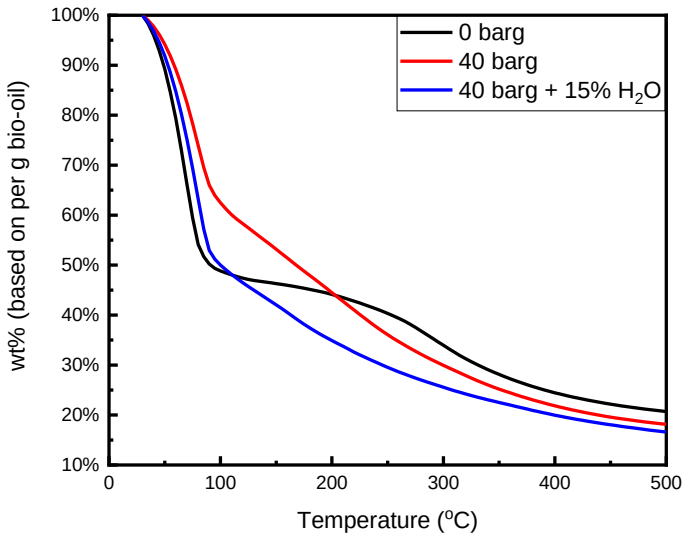

Figure 3-8. TGA curves at different distillation pressure and H_2O concentration to prove that polymerisation is decreased in the presence of pressure and increased H_2O concentration. Distillation was conducted at 200 °C.

As discussed in Section 3.3.1.1, the reactive carbonyl compounds may cause polymerisation in bio-oil, for example, through the aldol condensation reactions. The distribution of light species affected by pressure would change the reaction pathways and kinetics of carbonyl compounds in bio-oil. For example, the concentration increase of water in liquid phase with increasing pressure would dilute the carbonyls to decrease the polymerisation rate. As is shown in Figure 3-9, more carbonyl functional group is consumed during the atmospheric pressure distillation than during the high-pressure distillation. This further supports that high pressure could reduce polymerisation during bio-oil distillation.

3.3.1.3 H_2O distribution in the products

Water, the most abundant individual component in bio-oil, would not only contribute to the reduced polymerisation, but also affect the phase separation of the distillates after distillation and thus the product properties. High water concentration would decrease the heating value and viscosity of the product. The water concentration in each fraction is shown in Figure 3-10a. The liquid distillate is featured with the highest water concentration (48% - 55%) and the residue is featured with the lowest water concentration (1% - 3%). The water concentrations of paste distillates are around 15% and the relatively low water content could render the paste distillate as a promising product for further upgrading to high-value added fuels or chemicals.

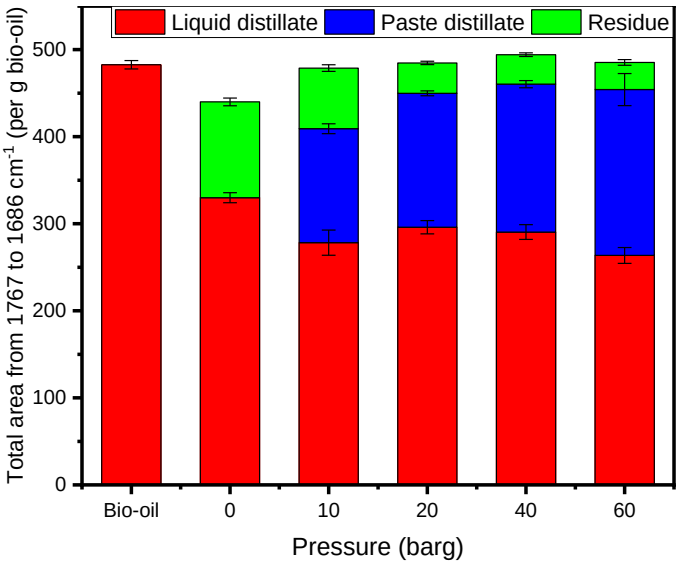

Figure 3-9. Effects of pressure on the total carbonyl area from 1767 to 1686 cm^{-1} (per g bio-oil) quantified by FT-IR. The error bar represents one standard error.

The water distribution in each fraction shown in Figure 3-10b indicates that most of the water is transferred to the distillate, especially the liquid distillate. The yields of water in the residue decreased slightly with increasing pressure. Moreover, the higher total water yield than the water in the bio-oil indicates that additional water was produced during the reactive distillation, probably by dehydration reaction. For example, the dehydration in the aldol condensation of carbonyls may produce water [27].

3.3.2 High-pressure reactive distillation at autogenous pressure

3.3.2.1 Effects of temperature on the high-pressure distillation

Temperature is obviously an important factor influencing the high-pressure distillation. To determine the vapour pressure of bio-oil experimentally, distillation experiments were conducted at autogenous pressure that was generated by the vapour itself when the bio-oil was heated up in the closed vessel from 140 to 280 °C with an interval of 20 °C. The experimentally measured and simulated pressure-temperature profiles as a function of temperature are compared in Figure 3-11. It can be seen that the experimental pressure is higher than the calculated pressure especially when temperature is higher than 180 °C. This is believed to have resulted from chemical reactions taking place with increasing temperature that formed light species, while the simulation assumed that no reactions took place among bio-oil species. The hydrolysis reactions discussed in Section 3.3.1.1 may contribute to the increase of light species. In addition, the formation of extra water by dehydration

reactions would also contribute to the increase of the vapour pressure. Moreover, decarbonylation and decarboxylation reactions that could happen at >180 °C would contribute to the gas formation, which is in good agreement with the decrease of the overall yield after 180 °C [28].

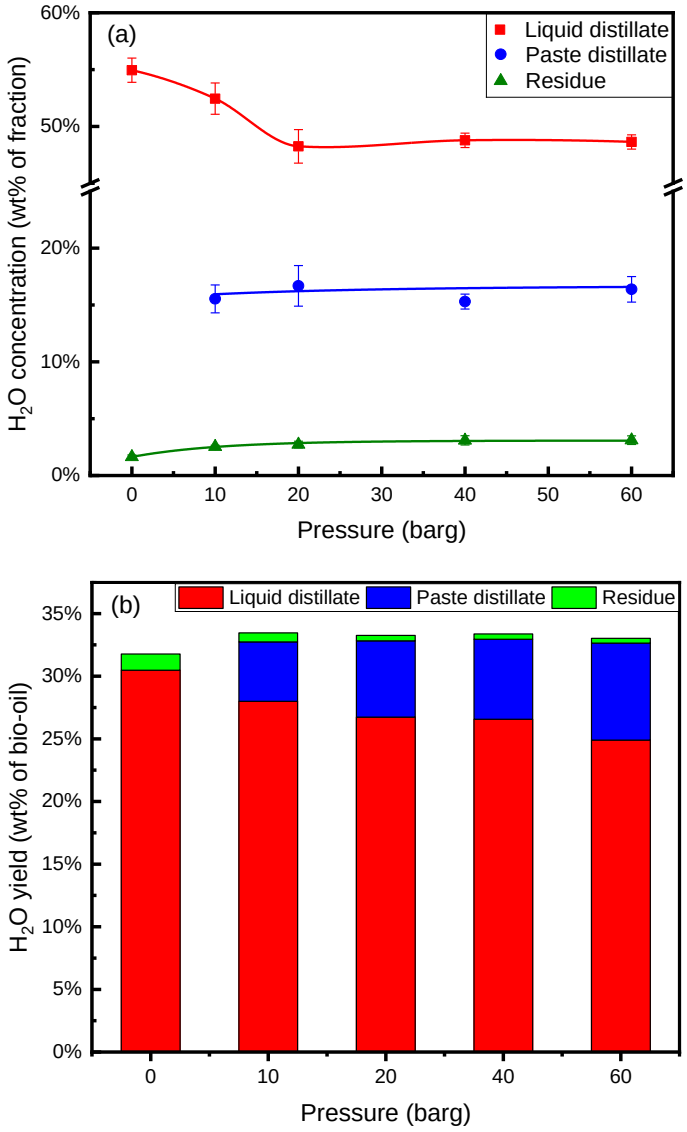

Figure 3-10. Effects of pressure on the H_2O concentration (a) and yield, wt% of bio-oil (b). Distillation was performed at 200 °C and held for 2 min.

To determine the formation of non-condensable gases such as CO_2 and CO from decarbonylation and decarboxylation reactions, an experiment without distillation was performed. 50 mL bio-oil was heated up to 200 °C and held for 2 min. Then the heater was switched off and cooling water was started immediately. After the reactor was cooled to room temperature, the reactor

pressure was 2.7 barg, which was close to the pressure difference of 3 bar between the experimental and simulated pressures at 200 °C in Figure 3-11. Therefore, this experiment confirmed the formation of light species (gases) that are not condensed at room temperature.

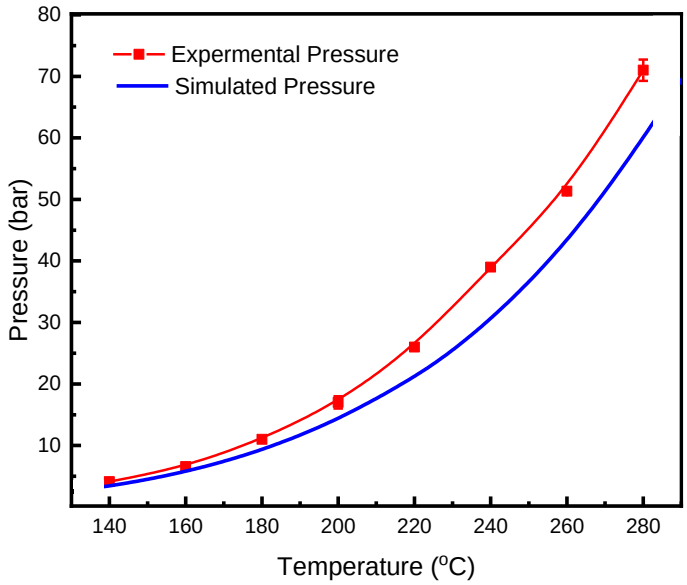

Figure 3-11. Comparison of the measured and simulated pressure-temperature diagram.

Besides the reactions that could reduce molecular sizes, polymerisation could become quite severe when temperature is higher than 220 °C, which can be evidenced by the decrease of liquid and paste distillates yields in Figure 3-12. The increased molecular sizes due to polymerisation would decrease the volatility and thus the distillate yield. Furthermore, the appearance change of residues also indicates that high temperature can lead to the increasing severity of polymerisation. The appearance of residues in the reactor also changed with temperature, from flowable liquid (140 - 180 °C) to sticky paste (200 - 240 °C) that did not have flowability, and finally to hard solid (260 - 280 °C).

3.3.2.2 Effects of holding time on the distillation yield

Experiments were carried out to understand the progress of chemical reactions during distillation. On reaching the target temperature, the reaction mixture was held at the target temperature for a pre-set period of holding time before it was cooled down. The increasing reaction extent of decarbonylation and decarboxylation with time may have caused the slight decreases in the overall yield in Figure 3-13a, which can be evidenced by the intensified separation between liquid and paste distillates in Figure 3-13b. This can also be confirmed by the pressure increase from 16 to 20 barg when the holding time was increased from 2 to 30 min. Moreover, reactions such as hydrolysis may also contribute to the increase of vapor pressure by producing more light species, which would

also be supported by the increase of distillate yield in Figure 3-13a. In addition, polymerisation may also lead to more coke formation on the reactor wall, which would also decrease the observed overall yield in Figure 3-13a.

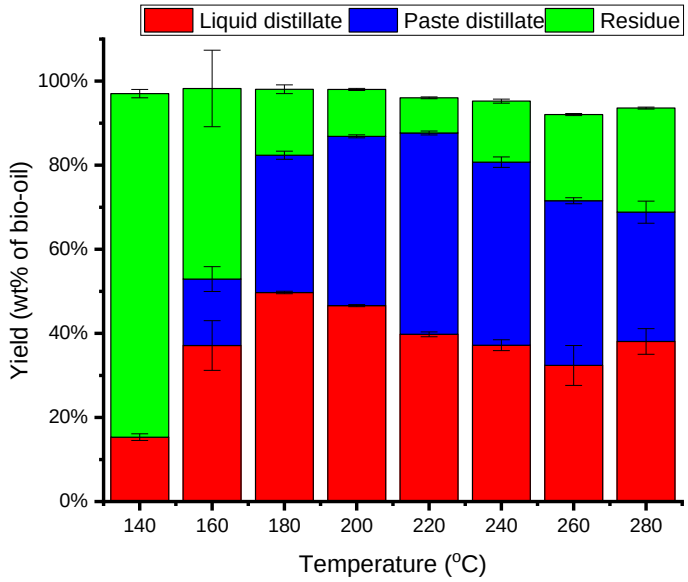

Figure 3-12. Effects of temperature on the yields of liquid distillation, paste distillate and residue at autogenous pressure. Distillates could be separated into a liquid distillate and a paste distillate when temperature was higher than 140 °C.

In addition, the water content in the liquid distillate increases with increasing holding time as is shown in Figure 3-14a, which could be caused by the intensified separation of the liquid distillate and paste distillate (Figure 3-13b) and the increase of total water yield (Figure 3-14b) due to the dehydration reaction.

Based on the above analysis, it can be seen that the high-pressure reactive distillation could achieve high distillate yield with reduced polymerisation. It could be used as an independent process to upgrade the bio-oil or integrated with other processes such as hydrotreatment, as is detailed elsewhere [20].

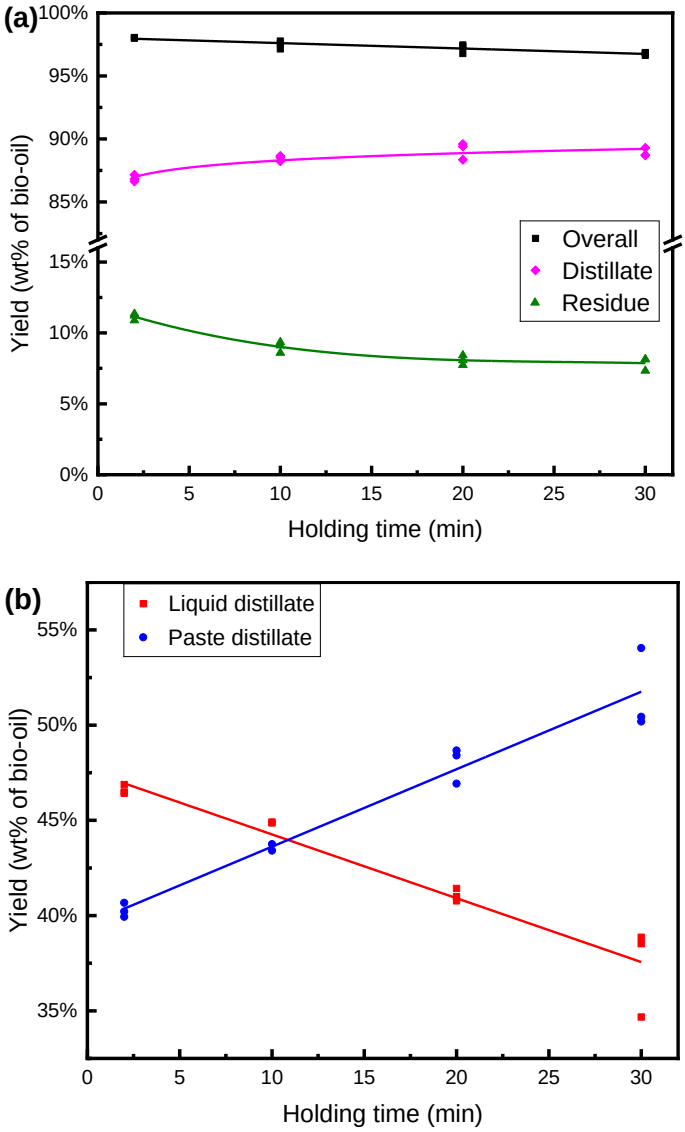

Figure 3-13. Effects of holding time on (a) distillate, residue and overall yields and (b) liquid and paste distillate fraction yields. To examine the roles of reactions in high-pressure reactive distillation, distillation experiments were conducted by holding for 2, 10, 20 and 30 min at 200 °C and autogenous pressure.

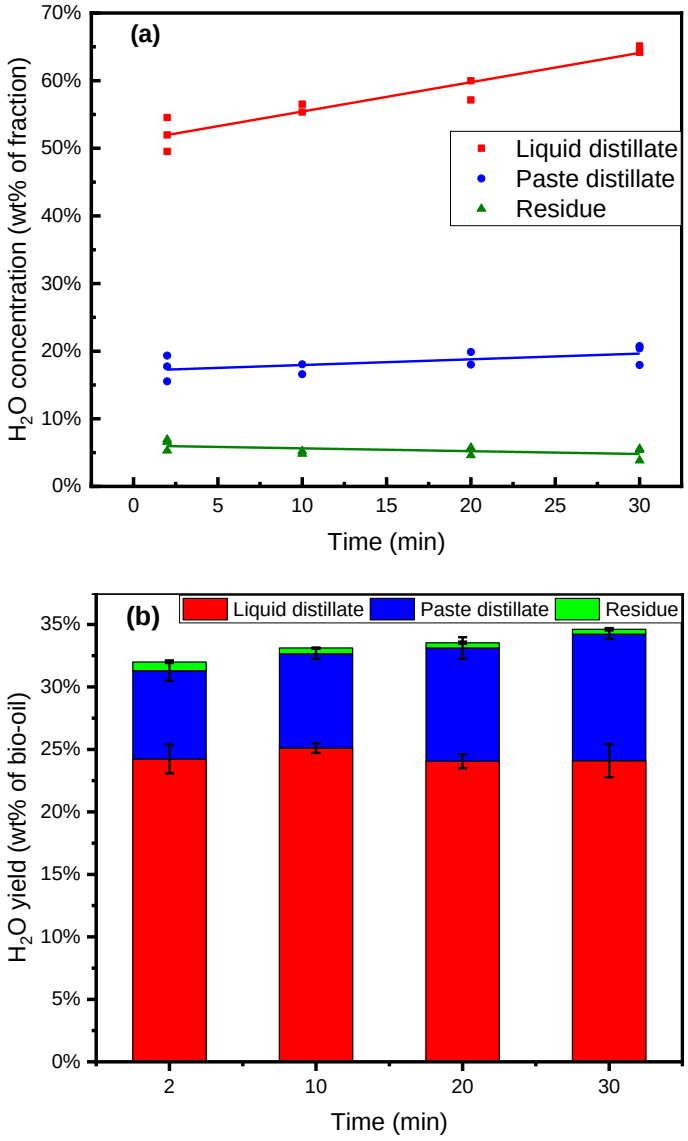

Figure 3-14. Effects of holding time on the (a) H_2O concentration (wt% of fraction) and (b) H_2O yield (wt% of bio-oil). Distillation experiments were conducted at 200 °C and autogenous pressure.

3.4 Conclusion

High-pressure reactive distillation of bio-oil from the pyrolysis of mallee woody biomass was carried out in this study. The bio-oil could be separated into fractions of liquid distillate, paste distillate and residue after distillation. High-pressure distillation is more advantageous than atmospheric pressure distillation in terms of the high distillate yield and product properties. The distillate yield is 90% at 200 °C when the distillation pressure is not lower than 20 barg. The reason for the high distillate yield of the high-pressure distillation is that high pressure would change the phase behaviour of light species in the bio-oil, which would influence the reactions in and among different phases. The

presence of water and other light species in the liquid phase retained by the high pressure can reduce the polymerisation and favour such reactions as hydrolysis that would tend to decrease the molecular sizes. More water is formed under the current experimental condition by dehydration reactions and most of the water is transferred into the liquid distillate.

3.5 Acknowledgements

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Chapter 4

Reaction and distribution of levoglucosan during the high-pressure reactive distillation of bio-oil

4.1 Introduction

The pyrolysis of renewable biomass can produce a bio-oil that is a promising alternative to the petroleum resource. It is necessary to upgrade the bio-oil for many practical applications by improving its properties. The separation of components and subsequent upgrading of fractions is an effective method to achieve the bio-oil upgrading. Distillation could be used to fractionate bio-oil according to the boiling point of components. However, because of the high reactivity of bio-oil, its severe polymerisation would usually decrease the distillate yield and lead to coke formation. High-pressure reactive distillation is a new technology being developed as an effective method of bio-oil upgrading and it could achieve high-yield distillates with reduced polymerisation by conducting distillation at high pressure [1, 2]. The application of pressure would change the vapour-liquid equilibria and the reactions in bio-oil during distillation.

Various species in bio-oil might behave differently during the high-pressure reactive distillation depending on their physical and chemical properties. Sugars derived from the thermal decomposition of cellulose and hemicellulose in biomass would play a key role during the high-pressure reactive distillation of bio-oil. For example, the sugars may polymerise to form large compounds that could decrease the distillate yield. Alternatively, sugar compounds could also undergo reactions to reduce their molecular sizes. Thus, the investigation of distribution and reaction behaviour of sugar compounds is crucial for the understanding of the high-pressure reactive distillation of bio-oil.

As a typical anhydrous sugar, levoglucosan is a major component of the bio-oil and it is mainly produced by the thermal decomposition of cellulose [3]. Levoglucosan could undergo entirely different reactions depending on the exact reaction environment. For example, levoglucosan in an aqueous solution could be hydrolysed into glucose in the presence of an acid catalyst [4, 5]. The hydrolysis products, especially the carbonyl compounds, may undergo further reactions, such as aldol condensation and esterification. On the other hand, the thermal polymerisation of levoglucosan might also occur, forming large oligomers [6]. The oligomers would then decrease the distillate yield due to the large molecular weight and high boiling points. Therefore, the levoglucosan behaviour influenced by the reaction environment would affect both the reaction and distillation of bio-oil during the reactive distillation.

The reaction environment is determined by many factors such as pressure, temperature and solvent. The previous literature has reported the influence of levoglucosan and acid concentrations in the aqueous solution on the kinetics of levoglucosan hydrolysis [4, 7]. Our previous work has investigated the acid-catalysed treatment of levoglucosan using different solvents and concluded that

the solvent would influence the conversion efficiency and product distribution [8]. In addition, pressure would affect the vapour-liquid phase equilibria which need to be considered simultaneously with reactions during the reactive distillation. However, little is known about the effects of pressure on the levoglucosan behaviour during distillation, especially in raw bio-oil in the presence of intrinsic carboxylic acids as the catalyst and water as a reactant and a solvent.

The objective of this chapter is to investigate the reactions and distribution of levoglucosan during the high-pressure reactive distillation of bio-oil. First, the reaction behaviour of levoglucosan during the high-pressure reactive distillation of bio-oil was investigated, including the effects of pressure and temperature on the reaction environment. Then, the effects of the recirculation of the liquid distillate on the behaviour of levoglucosan during reactive distillation were investigated.

4.2 Experimental

4.2.1 Materials

The bio-oil derived from mallee woody biomass was provided by Renergi Pty Ltd, Australia and it was produced by the grinding pyrolysis at 100 kg/hr [9, 10]. It was stored at -10 ^{o}C to prevent the possible degradation. The bio-oil density is 1.13 g/mL. The levoglucosan concentration in the investigated bio-oil is 3.9 wt%. Tetrahydrofuran (⩾99.9%), acetic acid (⩾99.7%), levoglucosan (⩾ 98%), hydroxymethylfurfural (HMF, 99%) and levulinic acid (99%) were bought from Sigma-Aldrich. The chemicals were used without further purification.

4.2.2 Distillation experiment

A 100 mL autoclave reactor (Autoclave Engineers) connected with two 150 mL condensers (made with Swagelok sample cylinders) was utilised to carry out the high-pressure reactive distillation, as was depicted previously [2]. 50 mL bio-oil mixed with other chemicals such as water and acetic acid was loaded into the reactor. After flushing with nitrogen, the reactor temperature was increased to the target value and kept for a desired period of time (e.g. 2 min) at the target pressure. If the target pressure was below the autogenous vapour pressure of bio-oil (e.g. 16 barg at 200 ^{o}C), the additional pressure would be released slowly to maintain the reactor pressure at the target value. If the target pressure is above the vapour pressure, high-pressure nitrogen would be used to pressurise the reactor when the reactor temperature reached the target value. Then the heater for the reactor was shut down and the pressure was immediately released (i.e. flash distillation) through opening the valve between the autoclave and the condensers, which could achieve the separation of distillate into the condensers while retaining the residue in the autoclave. After cooling down, the distillate could be

further separated into a liquid distillate and a paste distillate via decanting. The paste distillate has a lower water content than the liquid distillate.

4.2.3 Gas chromatography–mass spectroscopy (GC-MS)

The products were analysed using an Agilent GC-MS (a 6890 GC and a 5973 Mass Selective Detector) with a HP-INNOWax column (length: 30 m, diameter: 0.25 mm, film thickness: 0.25 μm). The samples were first dissolved in tetrahydrofuran to 2 wt% of diluted solution (±0.1%, the specific dilution ratio of each sample was used to correct the measured GC-MS peak area) and then 1 μL sample was injected with a front inlet temperature of 250 ^{o}C and a split ratio of 50:1. The oven temperature was ramped from the initial temperature of 40 ^{o}C (holding for 3 min) to 260 ^{o}C (holding for 7 min) at a rate of 10 ^{o}C/min [11]. Standard chemicals and the NIST mass spectral library were used to identify the components.

4.3 Results and discussion

4.3.1 Reaction behaviour of levoglucosan at different pressures

Bio-oil, as a multicomponent system, would undergo multiphase reactions during the high-pressure reactive distillation. When the bio-oil is heated up in the reactor, it would exist in vapor and liquid phases that are governed by the phase equilibria. Generally, levoglucosan in the bio-oil would react before reaching its normal boiling point (385 °C at 1 bar) during distillation. Bio-oil is a complicated mixture including many species that may react with levoglucosan, such as water and acetic acid that are two major light components of bio-oil. The component distribution and process parameters may affect the reaction environment for levoglucosan. Our previous work [12] has revealed that levoglucosan may undergo hydrolysis reaction in the presence of H_2O and an acid catalyst. Moreover, levoglucosan may also undergo thermal polymerisation in the absence of water and acid [13]. Therefore, the reaction environment can drive the reactions of levoglucosan in opposite reaction pathways.

The distribution of components in different phases is a function of composition, pressure and temperature. Pressure is a key parameter to determine the vapour-liquid equilibria when a bio-oil of a certain composition is heated up to the target temperature, which would change the composition in different phases. As is shown in Figure 4-1a, most of the levoglucosan (LG) is kept in the liquid phase and negligible amount of levoglucosan is in the vapour phase when the bio-oil is heated to 200 ^{o}C at different pressures. However, high pressure would increase the concentrations of H_2O and acetic acid (AcOH) in the liquid phase in the reactor (Figure 4-1b). The change of the molar ratio of H_2O/LG and

AcOH/LG as a function of pressure would influence the reaction environment of levoglucosan and thus the product distribution.

The bio-oil distillation was conducted at 200 °C with the pressure being 0, 5, 10, 20, 40 and 60 barg and the holding time of 2 min [2]. The bio-oil was separated into one liquid distillate in the condensers and one solid residue in the autoclave during the atmospheric pressure distillation (P = 0 barg). However, during the high-pressure reactive distillation, bio-oil would first be divided into distillate in the condensers and residue collected from the autoclave. The distillate could further undergo phase separation to form liquid and paste distillates that are flowable at room temperature. The amount of paste distillate formed at 5 barg was too small to be collected. The levoglucosan concentration in different fractions acquired after the reactive distillation is shown in Figure 4-2a. The distribution of levoglucosan during the flash distillation and decanting is mainly determined by its boiling point and solubility, respectively. The residue has the highest levoglucosan concentration (in agreement with the data in Figure 4-1a) and the paste distillate has the lowest concentration of levoglucosan, which could be due to the relatively high boiling point of levoglucosan (around 385 °C at 1 bar) [14] and the low solubility in the paste distillate, respectively. During the high-pressure reactive distillation, most of levoglucosan was converted into small molecules (e.g. HMF and levulinic acid) in the distillate, which could be proved by the high distillate yield (around 90 wt%). During the atmospheric pressure distillation, most of levoglucosan was retained as the levoglucosan-derived products in the residue in the form of solid.

The altered distribution of reactants by pressure (Figure 4-1b) would further affect the conversion of levoglucosan and thus the products, especially in the liquid phase. According to Figure 4-2b, the increasing pressure would accelerate the conversion of levoglucosan although the effects of pressure may plateau at high pressures, which qualitatively corresponds to the changes in the H_2O/LG and AcOH/LG ratios in Figure 4-1b. Apparently, the ratio increases of H_2O/LG and AcOH/LG due to the elevated pressure would enhance the levoglucosan conversion by changing the reaction environment.

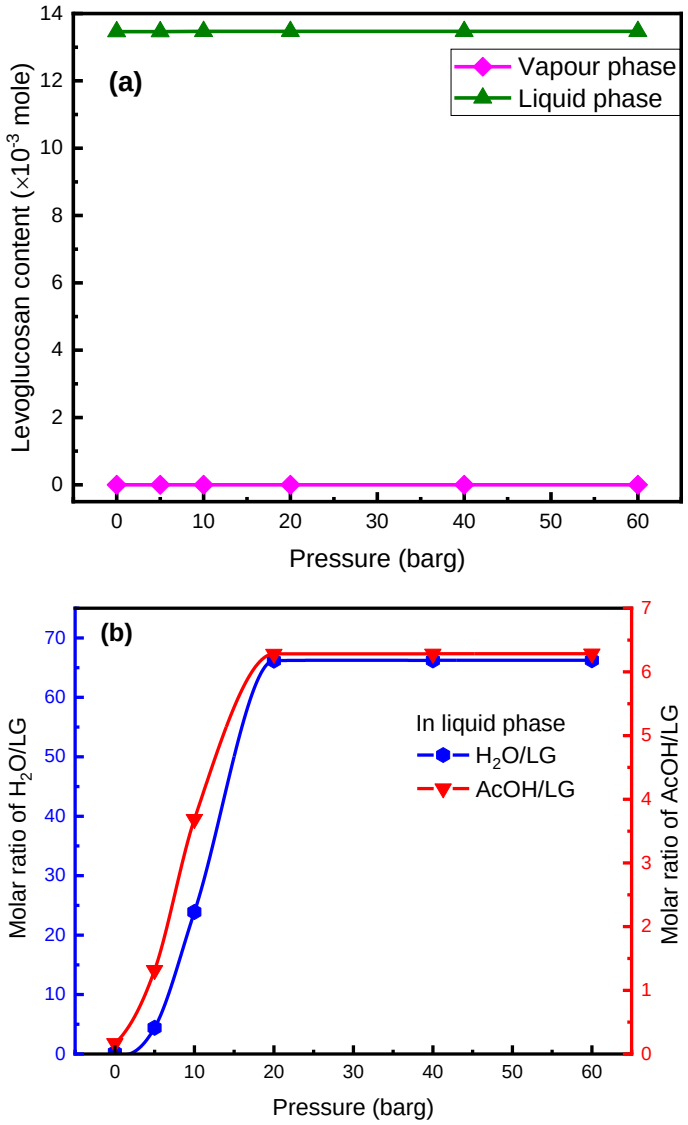

Figure 4-1. Distribution of levoglucosan and key reactants (H_2O and acetic acid) in the vapour and liquid phases in the reactor when bio-oil is heated to 200 °C. There is 2.2 g (~0.014 mol) levoglucosan in 56 g bio-oil. The distribution was simulated using Aspen Plus without chemical reactions. LG and AcOH denote levoglucosan and acetic acid, respectively.

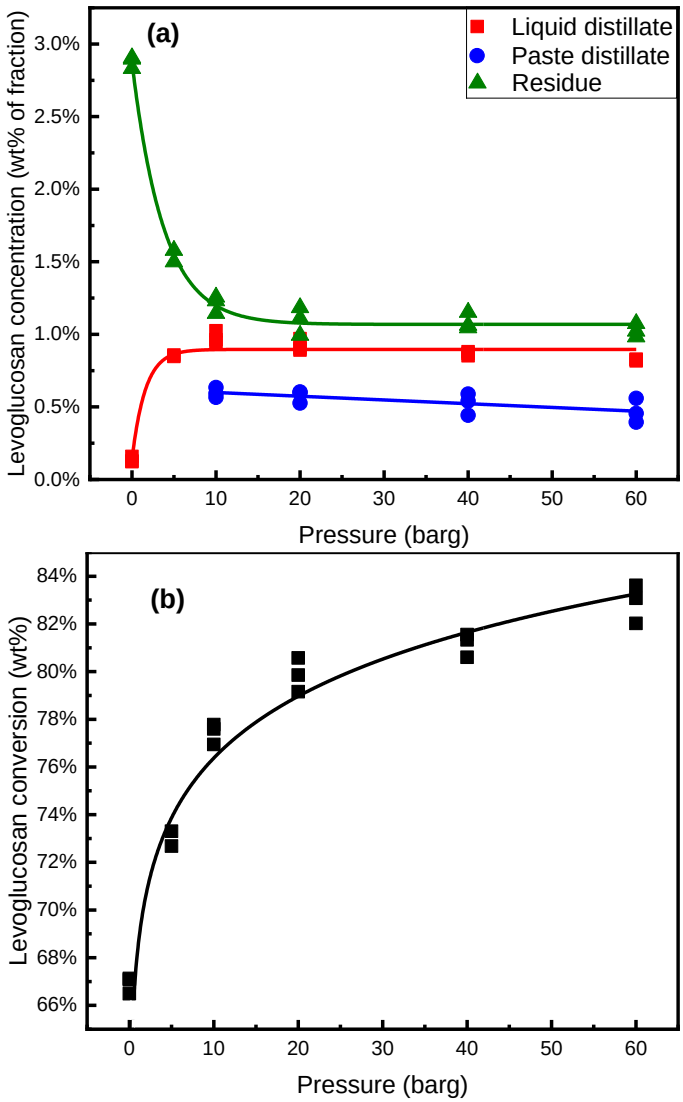

Figure 4-2. Effects of distillation pressure on (a) levoglucosan concentration (wt% of fraction) in the products and (b) levoglucosan conversion during reactive distillation of bio-oil. Distillation experiment was conducted at 200 °C and the holding time of 2 min. Concentration (wt%) refers to the absolute concentration of levoglucosan in a sample on the weight basis. Conversion is defined as the wt% of levoglucosan in the bio-oil that was consumed during the reactive distillation. Some data in this figure were published previously [2].

The changed reaction environment in the liquid phase by the pressure would alter the dominant reaction pathways of levoglucosan. Levoglucosan could undergo hydrolysis and polymerisation, as is shown in Figure 4-3. The dominant reaction would depend on the specific reaction environment, such as reactant composition and catalyst. The hydrolysis and polymerisation would compete in the levoglucosan conversion and the favourable environment for each reaction is different. The hydrolysis reaction necessitates the presence of H_2O and acid catalyst, whereas the

absence of H_2O would favour the thermal polymerisation of levoglucosan. As most of the levoglucosan is in the liquid phase (Figure 4-1a), the reactions in the liquid phase are crucial for the levoglucosan and the reactions in vapour phase are negligible due to the low concentration of levoglucosan. H_2O and acetic acid, as two most abundant components in the investigated bio-oil, could take part in the hydrolysis reaction of levoglucosan in the liquid phase. Levoglucosan could first be hydrolysed into glucose that is more reactive and would continue to react in the water medium [15]. The molar ratios of H_2O and acetic acid to levoglucosan in the liquid phase would change the reaction outcome as the conversion of levoglucosan is determined by the overall outcome of the parallel hydrolysis and polymerisation. For instance, the increase of H_2O and acetic acid in the liquid with increasing pressure (Figure 4-1b) could intensify the hydrolysis reaction, which could be proved by the increase of the derivatives of levoglucosan hydrolysis products such as HMF and levulinic acid with increasing pressure, as is shown in Figure 4-4. The enhanced hydrolysis as the dominant reaction pathway would explain the increasing conversion of levoglucosan in Figure 4-2b.

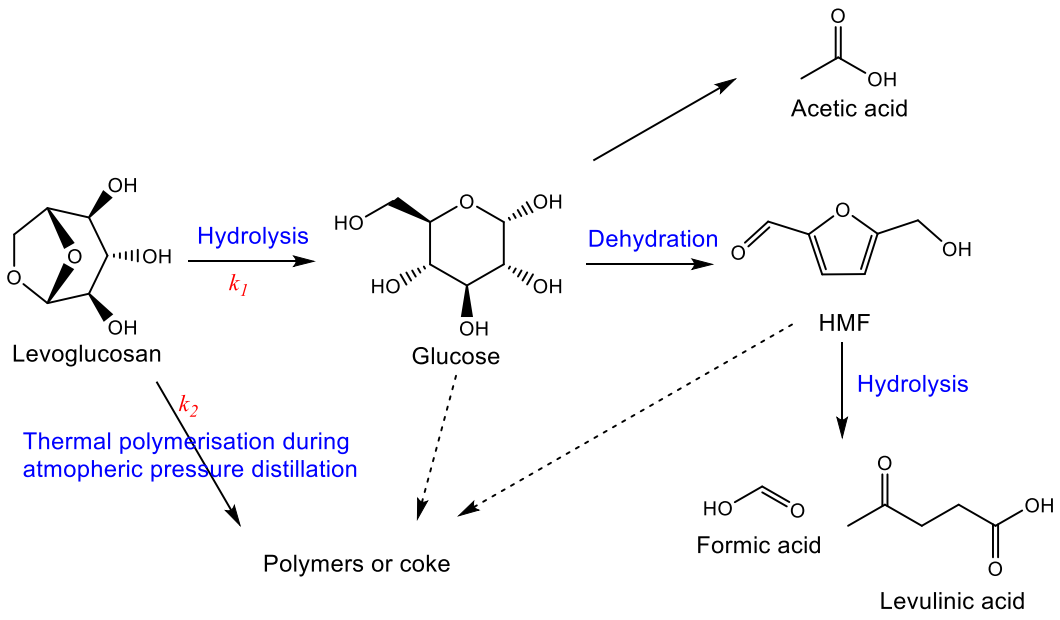

Figure 4-3. Reaction pathways of levoglucosan during bio-oil distillation.

Conversely, the direct polymerisation of levoglucosan, as the competing reaction of hydrolysis, would be reduced when the hydrolysis reaction is intensified by the application of pressure. During the atmospheric pressure distillation, levoglucosan would be converted mainly through thermal polymerisation. The dominant polymerisation would also contribute to the solid formation of the residue during the atmospheric pressure distillation. In addition, hydrolysis would be inhibited to a certain degree due to the lack of reactants, which is evidenced by the low yields of HMF and levulinic

acid during the atmospheric pressure distillation in Figure 4-4. This is because most H_2O and acetic acid would be evaporated from the liquid phase and transferred to either the vapour phase in the reactor or collected in the condensers during the atmospheric (P=0 barg) or low pressure distillation. However, pressure would increase the H_2O and acetic acid concentrations in the liquid phase and decrease the polymerisation of levoglucosan. Due to the high boiling point, levoglucosan would mainly be in the liquid phase (Figure 4-1a) and its hydrolysis products (e.g. HMF and levulinic acid) would contribute to the high distillate yield during the high-pressure reactive distillation.

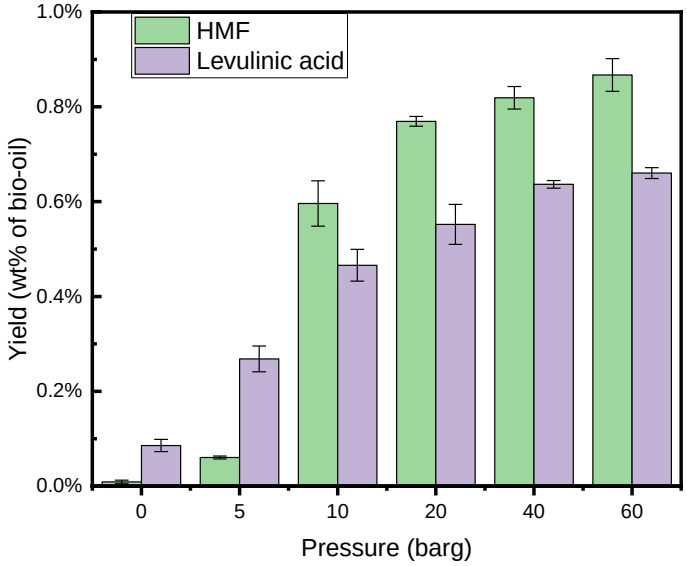

Figure 4-4. Yield (wt% of bio-oil) of the typical hydrolysis products HMF and levulinic acid as a function of pressure. Distillation was conducted at 200 ^oC and the holding time of 2 min. Yield of a species (wt% of bio-oil) was referred to the sum of all the fraction yields that were calculated by multiplying the species concentration and the corresponding yield of the fraction.

According to the above analysis, the increasing pressure would accelerate the hydrolysis and depress the polymerisation by increasing the H_2O and acetic acid content in the liquid phase. In addition, the levoglucosan concentration in the liquid phase could be decreased due to the dilution by H_2O and acetic acid, which would further control the product distribution. The competition between the hydrolysis and polymerisation is determined by the relative reaction rate. The hydrolysis and polymerisation may have different kinetics parameters, such as the reaction order and activation energy. As is shown in Figure 4-3, the hydrolysis and polymerisation (recombination of at least two molecules) reaction rates are assumed to be apparently first [7] and second order [6] with respect to the levoglucosan concentration, respectively. The reaction rates are defined as follows:

Hydrolysis rate:

$r_1 = k_1[\mathrm{LG}]$ Eq.(4-1)

Polymerisation rate:

$r_2 = k_2[\mathrm{LG}]^2$ Eq.(4-2)

Overall levoglucosan conversion rate:

$-\frac{d[LG]}{dt} = r_1 + r_2 = k_1[\mathrm{LG}] + k_2[\mathrm{LG}]^2$ Eq.(4-3)

, where $[\mathrm{LG}]$ denotes the molar concentration (mol/L) of levoglucosan, k_1 (min^{-1}) and k_2 ($L \cdot mol^{-1} \cdot min^{-1}$) are the rate constants, r_1 and r_2 are the rate ($mol \cdot L^{-1} \cdot min^{-1}$) of hydrolysis and polymerisation, *t* (min) is the reaction time.

To compare the relative rate of the parallel reactions, the ratio of the two reaction rates is as follows:

$\frac{r_1}{r_2} = \frac{k_1}{k_2[\mathrm{LG}]}$ Eq.(4-4)

It can be inferred that a lower levoglucosan concentration would cause a higher ratio. This would explain that the decreased levoglucosan concentration by the pressure, i.e. dilution of levoglucosan by the water and other light species transferred into the liquid phase by increased pressure, is relatively favourable for the hydrolysis.

To verify the importance of pressure on the distribution of reactants, extra H_2O (5 wt%, 10 wt% and 15 wt% based on bio-oil) was added to bio-oil to perform reactive distillation at 200 °C and 40 barg. H_2O is a reactant and the essential reaction medium, which could achieve the dissolution of levoglucosan and the dissociation of carboxylic acid. The increase of H_2O would lead to the increase of the molar ratios of H_2O/LG in the liquid phase and accelerate the hydrolysis reaction (Figure 4-5a). The added water could still further improve the hydrolysis of levoglucosan, even though the original molar ratio of water to levoglucosan in bio-oil is about 66:1, which is much higher than the reaction stoichiometric ratio of 1 for the levoglucosan hydrolysis. This could further support the above-mentioned conclusion that the diluted levoglucosan would favour the hydrolysis rather than the parallel polymerisation, which could be evidenced by the yield increase of hydrolysis products in Figure 4-5b. Besides diluting the levoglucosan, H_2O is also a key reactant for the hydrolysis.

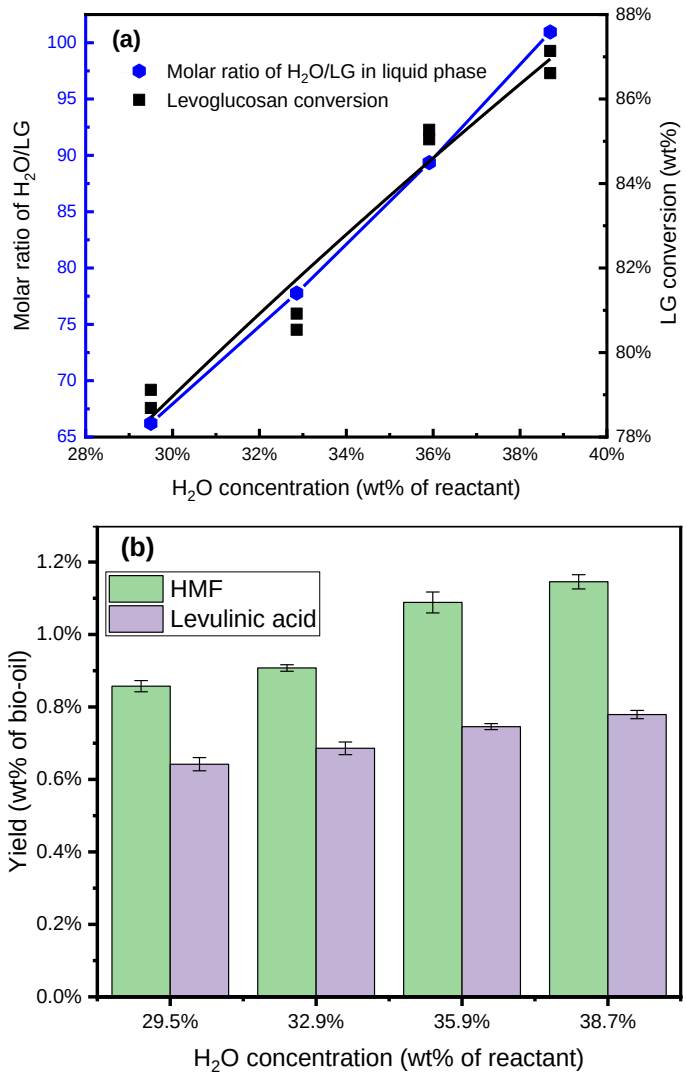

Figure 4-5. Effects of H_2O concentration on (a) the molar ratio of H_2O/LG in the liquid phase and levoglucosan conversion at 200 °C and 40 barg, and (b) hydrolysis product yield (wt% of bio-oil). The molar ratio was acquired by Aspen Plus simulation. The experiments were performed at 200 °C and 40 barg to determine the levoglucosan conversion and product yield.

In addition, pressure could also alter the reaction environment by affecting the catalyst, especially acetic acid. Acetic acid is a catalyst and a product for the reaction of levoglucosan in bio-oil and its concentration is 9.2 wt% in the investigated bio-oil. Extra acetic acid (2 wt%, 4 wt% and 8 wt% based on bio-oil) was added to bio-oil to perform reactive distillation at 200 °C and 40 barg. As is indicated in Figure 4-6, the increasing acetic acid concentration would lead to the increase of levoglucosan conversion. Higher concentration of acetic acid would generate more H^+ in the system to catalyse the hydrolysis of levoglucosan. Conversely, the decreased concentration of H^+ would slow

down the levoglucosan reaction. This would explain the inhibited hydrolysis during the atmospheric pressure distillation.

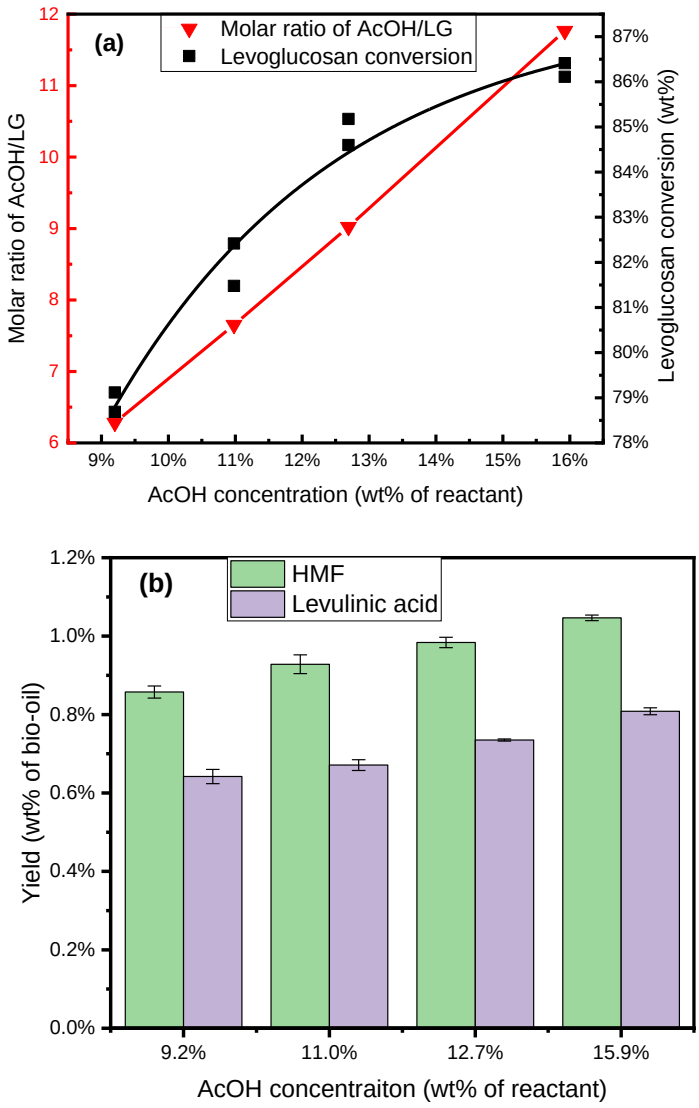

Figure 4-6. Effects of acetic acid concentration on the (a) molar ratio of AcOH/LG in the liquid phase and levoglucosan conversion (wt%) and (b) yield of HMF and levulinic acid (wt% of bio-oil). The molar ratio was acquired by Aspen Plus simulation. The experiments were conducted at 200 °C and 40 barg to determine the levoglucosan conversion and product yield.

4.3.2 Levoglucosan reaction as a function of temperature

To determine the effects of temperature, high-pressure reactive distillation was conducted from 140 to 280 °C with the increment of 20 °C and the pressure was generated by the system itself. According to Figure 4-7a, the conversion of levoglucosan would be accelerated significantly by the increase of temperature because both hydrolysis and polymerisation are intensified by the elevated

temperature. The intensified hydrolysis can be supported by the yield increase of levulinic acid in Figure 4-7b.

In addition, temperature could also affect the reactant distribution. The molar ratio decreases of H_2O/LG and AcOH/LG with increasing temperature (Figure 4-8) would also decrease the reaction rate ratio of hydrolysis to polymerisation. The distribution in Figure 4-8 was acquired by simulation without chemical reactions. However, the reactions of levoglucosan would indeed occur and affect the distribution in return, even though the reactions were not included in the simulation.

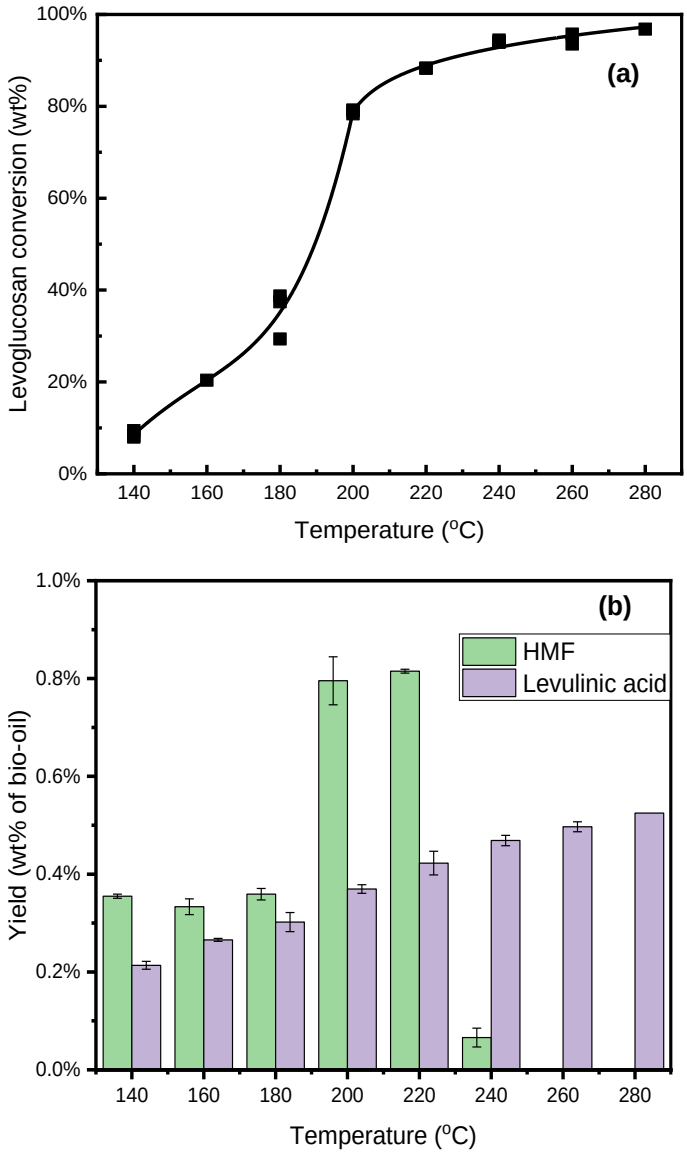

Figure 4-7. Effects of temperature on (a) the levoglucosan conversion (wt%) and (b) the hydrolysis products. The bio-oil distillation was performed at autogenous pressure that is produced by the vapour itself and the holding time of 2 min.

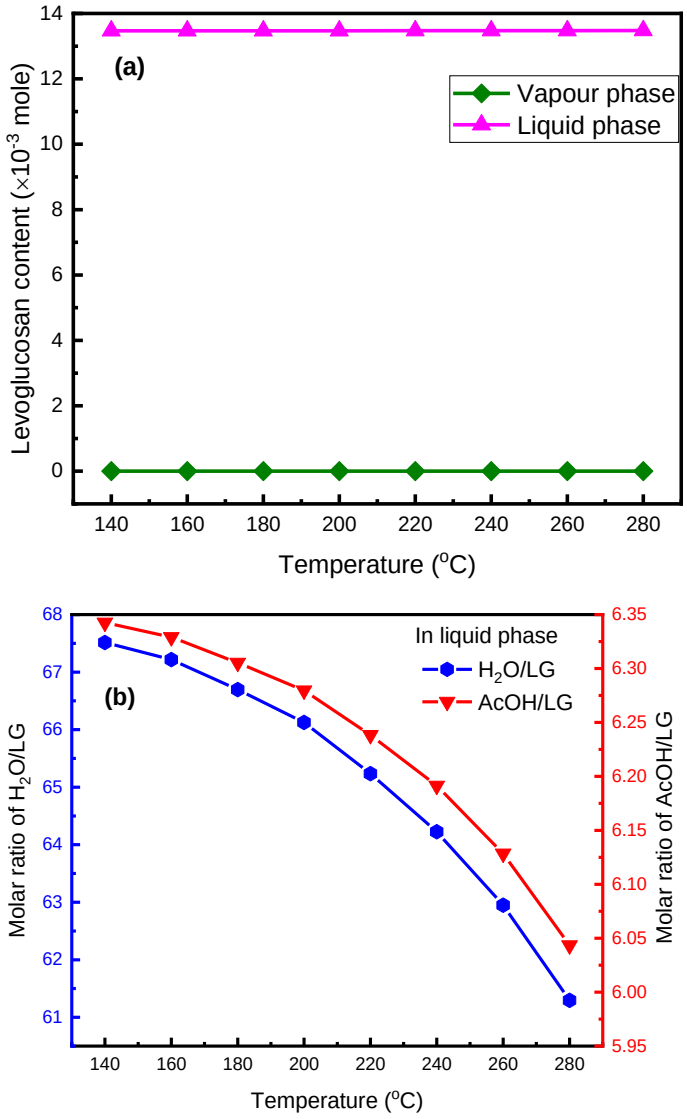

Figure 4-8. Effects of temperature on the (a) distribution of levoglucosan, and (b) molar ratio of H_2O and AcOH to levoglucosan in liquid phase. The distribution was simulated using Aspen Plus without chemical reactions.

4.3.3 Effects of recirculating liquid distillate

Based on Sections 4.3.1 and 4.3.2, the reaction environment would affect the reaction of levoglucosan and the distribution of light components plays an important role in altering the reaction environment. The liquid distillate derived from the high-pressure reactive distillation of bio-oil could be recirculated because the concentrations of water and acetic acid in the liquid distillate are as high as 53.9 wt% and 14.5 wt%, respectively. In addition, there is also unreacted levoglucosan in the recirculated liquid distillate (Figure 4-2a), which could be further converted in the recirculation. According to Figure 4-9a and 4-9b, the increase of the recirculated liquid distillate would intensify the levoglucosan hydrolysis because the recirculation of liquid distillate would decrease the levoglucosan

concentration in the reactant (Figure 4-9a) and the dilution by the recirculated liquid distillate would favour relatively the hydrolysis as is indicated by the increase of levoglucosan conversion in Figure 4-9a and the yield increase of the hydrolysis products in Figure 4-9b.

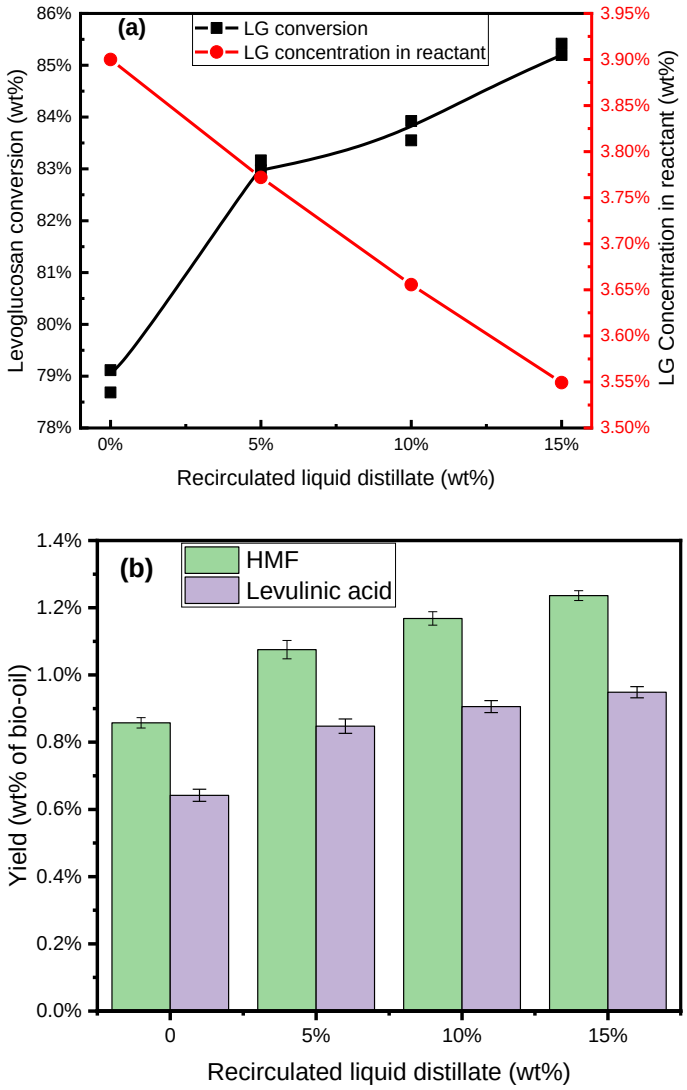

Figure 4-9. Effects of recirculated liquid distillate wt% (based on bio-oil) on (a) the levoglucosan conversion (wt% of levoglucosan in reactant) and concentration in reactant (wt%), and (b) HMF and levulinic acid yield (wt% of bio-oil). LG denotes levoglucosan. Experiments were performed at 200 °C and 40 barg with the holding time of 2 min.

4.4 Conclusion

The distribution and reactions of levoglucosan during the high-pressure reactive distillation of bio-oil were investigated in this study. It is found that pressure would play an important role in the levoglucosan conversion during the bio-oil distillation. During the atmospheric pressure distillation, light species such as water and acetic acids that are reactants and catalysts for the hydrolysis of

levoglucosan would separate from the heavy species including levoglucosan, some levoglucosan would be converted into solid via thermal polymerisation due to the lack of hydrolysis reactants and catalysts in the liquid phase and most of the unreacted levoglucosan would be retained in the residue. However, during the distillation at elevated pressure, hydrolysis is favoured over polymerisation because high pressure could keep water and carboxylic acids in the liquid phase to facilitate the hydrolysis of levoglucosan and the further reactions of the hydrolysis products. Most of the levoglucosan would be hydrolysed into small molecules and transferred into the distillate during the high-pressure reactive distillation. In addition, the reaction environment plays an important role for levoglucosan reaction and the dilution by water would relatively favour its hydrolysis and depress its polymerisation. Moreover, the recirculation of liquid distillate could be used to intensify the levoglucosan hydrolysis due to the high concentrations of water and acetic acid in the recirculated distillate.

4.5 References

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Chapter 5 Conversion of carbonyl compounds in bio-oil via catalysed reactive distillation at high pressure

5.1 Introduction

The pyrolysis of the renewable biomass can produce a liquid bio-oil with high yields. The thermal decomposition of cellulose, hemicellulose and lignin in biomass would produce various oxygenated compounds. For example, cellulose and hemicellulose would be converted into sugars and carbonyl compounds. The decomposition of lignin would produce some aromatic compounds. The carbonyl compounds in bio-oil mainly include aldehydes, ketones, carboxylic acids, esters and lactones [1].

The carbonyl compounds in bio-oil especially aldehydes and ketones are highly reactive. For example, the carbonyl compounds tend to polymerise due to their high reactivity when the bio-oil is heated up [2]. The reactions of carbonyl compounds during storage would usually decrease the phase stability of bio-oil [3]. Moreover, the high concentration of carboxylic acids (e.g. acetic acid) would cause the high acidity and corrosiveness of bio-oil. In addition, the polymerisation of the reactive components in bio-oil may also be catalysed by the carboxylic acids [2].

To overcome the bottleneck problems (e.g. polymerisation) caused by the abundant carbonyl compounds, various techniques have been developed to convert or stabilise the carbonyl compounds, such as esterification [4] and aldol condensation [5]. The acid-catalysed treatment of bio-oil in alcohol would convert the carboxylic acids and aldehydes into esters and acetals via the esterification and acetalization, respectively [6]. However, the formed acetal may also condense to undesirable polymers [7] and the excessive alcohol would be difficult to be separated from the aqueous products. The aldol condensation could also be used to convert the aldehydes and ketones, which would lead to the deoxygenation of bio-oil and the increase of carbon chain length of the reactant [8]. The liquid fuels yield and the carbon efficiency could be increased by the aldol condensation of the light carbonyl compounds with their content in the bio-oil being up to 25 wt% [9]. In addition, both the acid and base catalysts could be used to catalyse the aldol condensation [10].

High-pressure reactive distillation could be used for bio-oil upgrading to achieve high yield of distillate and reduce the polymerisation of the reactive species in bio-oil [11, 12]. Pressure is a key factor during the reactive distillation and it could affect the coupling between the reaction and vapour-liquid equilibrium. In addition, pressure might also play an important role in the separation of the light and heavy products. The aldol condensation could be coupled with the high-pressure reactive distillation to stabilise the reactive carbonyl compounds in the bio-oil and separate the products. However, little is known about the separation and reaction behaviours of light and heavy carbonyl compounds in the real bio-oil at high pressure, especially in the presence of an acid or base catalyst.

This study aims to investigate the reaction behaviour of carbonyl compounds during the high-pressure reactive distillation of bio-oil in the presence of acid and base catalysts. First the effects of pressure and acetol concentration will be investigated to understand the reactions of carbonyl compounds in an acidic environment. Then the NaOH as a base would be used as a catalyst and neutralising agent to remove the carbonyl compounds.

5.2 Experimental

5.2.1 Materials

The bio-oil was acquired from Renergi Pty Ltd, Australia [13]. It was produced from the grinding pyrolysis of mallee woody biomass and stored at –10 ^{o}C in a freezer to minimise the possible aging. Tetrahydrofuran (THF, ≥99.9%), formic acid (≥98%), acetic acid (≥99.7%), furfural (≥99%), acetol (90%), glycolaldehyde dimer, syringaldehyde (98%) and NaOH (≥98%) were all bought from Sigma-Aldrich. These chemicals were used without further treatment.

5.2.2 Distillation experiment

The distillation equipment was composed of a 100 mL autoclave (Autoclave Engineers) and two 150 mL condensers (made of Swagelok sample cylinders) in series [12]. To investigate the effects of pressure, the bio-oil was heated to 200 ^{o}C and the target pressure. 200 ^{o}C is selected because it is in the optimal temperature range of 180 - 220 ^{o}C [12]. If the target pressure is less than the vapour pressure of bio-oil (16 barg at 200 ^{o}C), the excessive pressure would be released slowly to maintain the desired pressure. If the desired pressure is greater than the vapour pressure, high-pressure nitrogen would be used to pressurise the reactor. To determine the effects of the reactant composition and catalyst, the reactive distillation condition was to heat up 50 mL bio-oil and the added chemicals (e.g. base) to 200 ^{o}C and pressurise the system to 40 barg with high-pressure nitrogen once the temperature reached 200 ^{o}C. 40 barg was used because it could maintain most of the components in the liquid phase while the bio-oil was under vapour-liquid equilibrium at 200 ^{o}C. Then the pressure was discharged to achieve the flash distillation after holding for 2 min via opening the valve in the middle of the reactor and condensers. The vapour would be transferred into the condensers and undergo phase separation to form a liquid distillate fraction and a paste distillate fraction. The liquid/solid phase would be retained in the reactor. Each experiment was repeated at least twice.

5.2.3 Fourier Transform infrared spectroscopy (FT-IR)

Bio-oil distillation products were diluted in THF to 2 wt% and characterised in a liquid sample cell made of CaF_2 windows and a 0.05 mm Teflon spacer. The FT-IR spectra were acquired using a Perkin-Elmer Spectrum GX FT-IR/Raman spectrometer by scanning each sample twice. 6 Gaussian bands ranging from 1850 - 1540 cm^{-1} were deconvoluted, including 1767 cm^{-1} (lactones), 1740 cm^{-1} (unconjugated alkyl aldehydes and alkyl esters), 1713 cm^{-1} (carboxylic acids), 1696 cm^{-1} (unsaturated aldehydes and ketones), 1654 cm^{-1} (hydroxy unsaturated ketones and aldehydes) and 1606 cm^{-1} (aromatics with various types of substitution) [14]. The area was expressed based on per g bio-oil by multiplying a Gaussian band area and the corresponding fraction yield. The error bar was represented by the standard deviation.

5.3 Results and Discussion

5.3.1 Reaction behaviour of carbonyl compounds in an acidic environment

Carbonyl compounds with various structure or molecule weight may behave differently during the high-pressure reactive distillation. For example, the molecule size of carbonyl compounds is a key factor to determine the boiling point and thus the phase behaviour when a bio-oil is heated up. Three typical carbonyl compounds including acetol, furfural and syringaldehyde were quantified by GC-MS to investigate their reaction behaviours. They have different physical properties, e.g. the boiling points are 145.5°C for acetol, 162°C for furfural and 322°C for syringaldehyde. They also differ in chemical structures, e.g. the carbonyl groups are connected to aliphatic structure (in acetol), furan ring (in furfural) or aromatic ring (in syringaldehyde) as they originate from hemicellulose/cellulose and lignin in biomass. Acetol and furfural are used to represent the light carbonyl compounds and syringaldehyde is used to represent the heavy carbonyl compound that is within the detection capacity of the GC-MS. As is shown in Figure 5-1a and Figure 5-1b, the high-pressure reactive distillation would intensify the consumption of furfural and acetol when compared to the atmospheric pressure distillation, especially between 0 and 10 barg. However, the consumption of syringaldehyde is inhibited in the presence of high pressure, as is illustrated in Figure 5-1c. Therefore, it can be inferred that the reaction of light carbonyl compounds rather than the heavy carbonyl molecules would be favourable under the high-pressure condition. Moreover, the carbonyl compounds would be produced in acidic environment. Acetol and furfural would be produced from cellulose/hemicellulose-derived sugars and syringaldehyde would be produced from lignin-derived species in bio-oil. The final yield is determined by the overall result of the simultaneous consumption and production.

The different reaction behaviour of the light and heavy carbonyl compounds as a function of pressure could be largely caused by the component distribution when the bio-oil was under vapour-liquid equilibrium at 200 °C. As is shown in Figure 5-2, during the atmospheric pressure distillation (pressure = 0 barg), most of the light carbonyl compounds are distilled to the condensers and the heavy carbonyl compounds are retained in the liquid phase and converted into solid in the reactor. The temperatures of the reactor and condensers are 200 °C and 0 °C, respectively. However, during the high-pressure distillation, both the light and heavy carbonyl compounds would be kept in the liquid phase, especially when pressure is higher than 20 barg, and the conversion of light carbonyl compounds would be favoured due to the less steric hindrance than the heavy carbonyl molecules. Besides the influence of steric hindrance, the reactivity of carbonyl compounds would also play a role during the consumption.

To verify the above conclusion about the reaction behaviour of the light and heavy carbonyl compounds, the effects of acetol concentration were investigated by adding extra acetol of 5 wt%, 10 wt% and 15 wt% (based on bio-oil) to conduct the reactive distillation at 200 °C and 40 barg. Among the carbonyl compounds in the bio-oil, glycolaldehyde and acetol are the abundant and reactive aldehyde and ketone in the investigated bio-oil, with the concentration being 2.9 wt% and 4.0 wt%, respectively. The glycolaldehyde would be all consumed under the current experiment condition (200 °C and 40 barg, See Figure 5-3) and thus acetol was used to illustrate the effects of pressure on the light carbonyl compounds.

Almost all the acetol is in liquid phase at 200 °C and 40 barg (see Figure 5-4), and it might react with itself or other carbonyl compounds in the liquid phase, for example, the furfural (Figure 5-2). The self-aldol condensation product of acetol could be detected by GC-MS with the mechanism shown in Scheme 5-1. As is shown in Figure 5-5, the furfural conversion (wt%) increases with increasing added acetol because acetol could undergo aldol condensation reaction with furfural [15]. This also indicates the carbonyl compounds would undergo cross aldol reaction with other carbonyl compounds in the bio-oil, especially the reactive light carbonyl compounds. The conversion of syringaldehyde only slightly increases with increasing acetol concentration, which is probably caused by its lower reactivity than furfural.

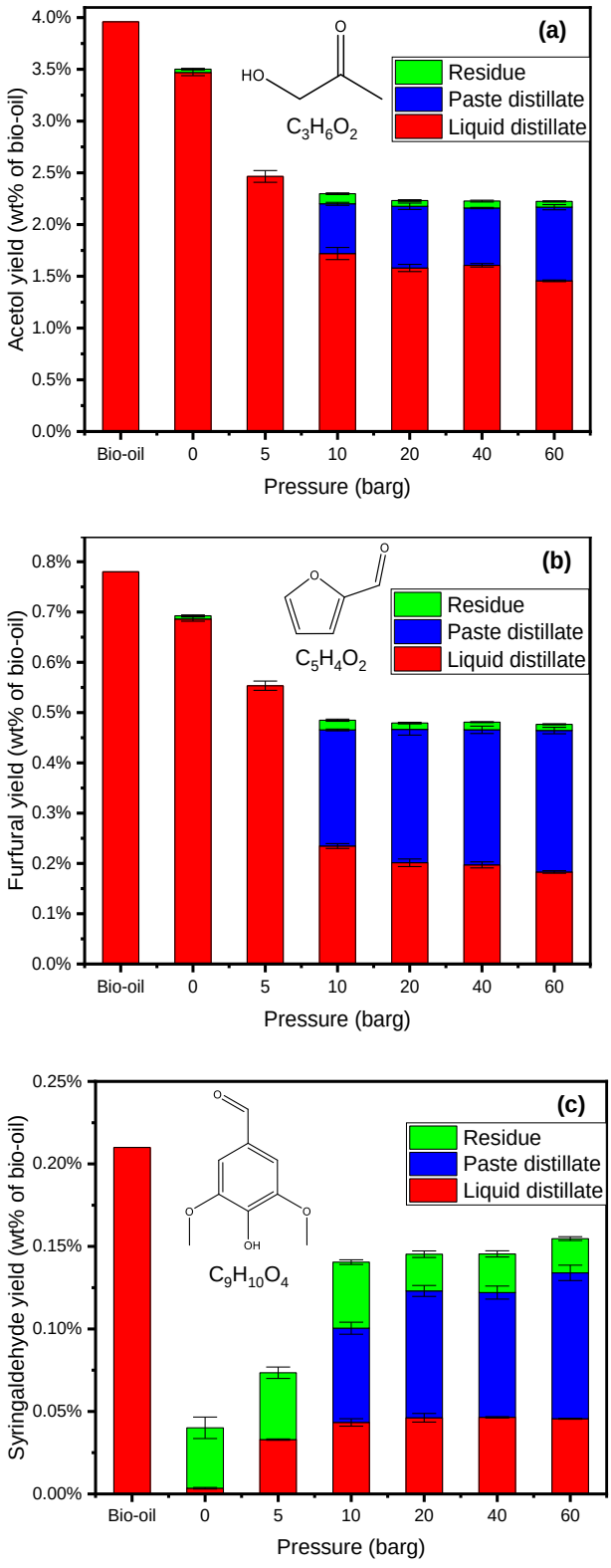


Figure 5-1. Effects of pressure on the yield (wt% of bio-oil) of (a) acetol, (b) furfural and (c) syringaldehyde during the reactive distillation of bio-oil. Distillation was performed at 200 °C and the holding time of 2 min. Yield, wt% of bio-oil, was obtained by multiplying the experimentally measured species concentration (wt%) and the yield of the corresponding fraction.

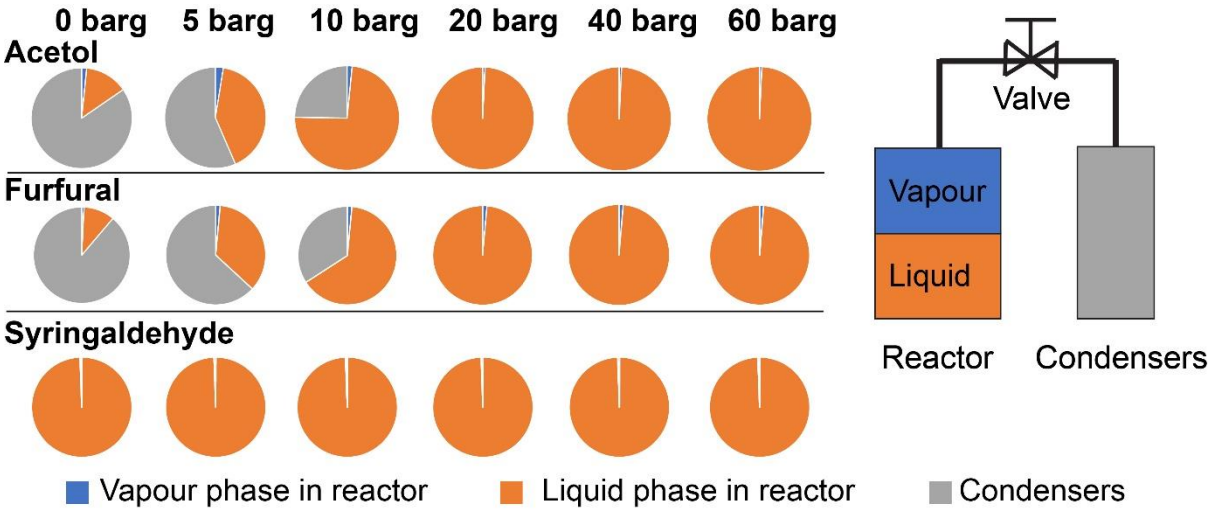


Figure 5-2. Effects of pressure on the distribution of acetol, furfural and syringaldehyde in different phases when bio-oil is heated to 200 °C. The distribution was acquired by Aspen Plus simulation without chemical reactions.

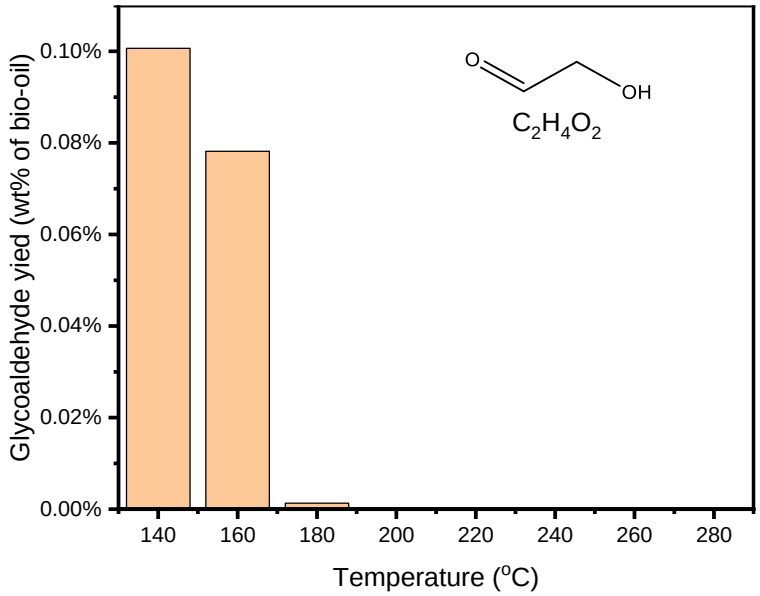


Figure 5-3. Effects of distillation temperature on the glycolaldehyde yield. The experiments were conducted from 140 °C to 280 °C at autogenous pressure with the holding time of 2 min.

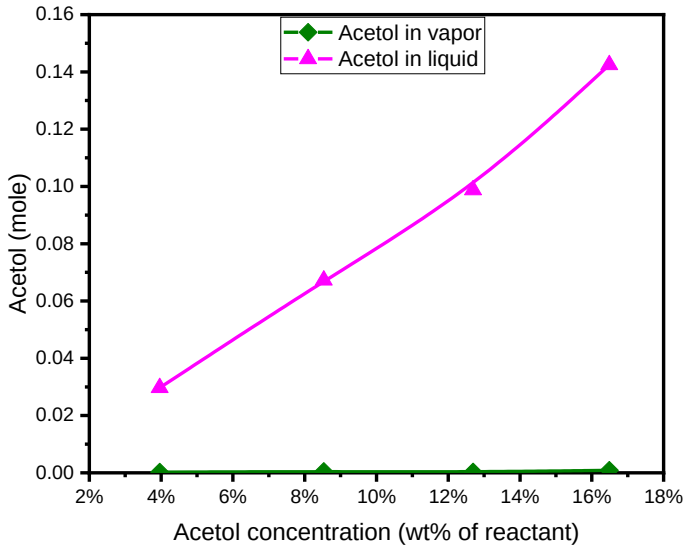
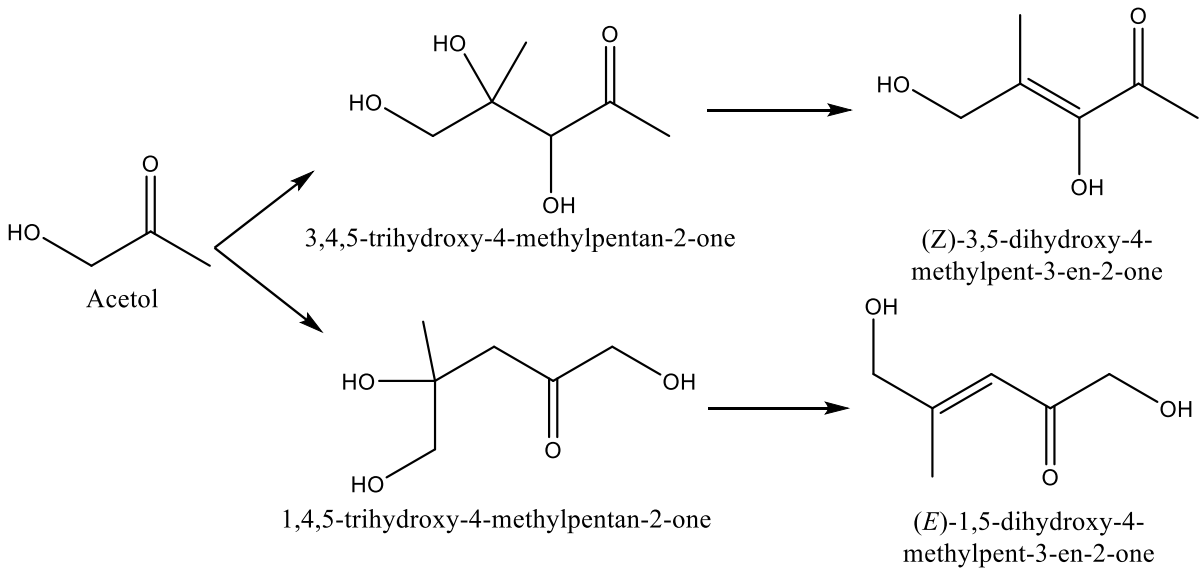


Figure 5-4. Distribution of acetol in the reactor at 200 °C and 40 barg. The distribution was simulated using Aspen Plus without chemical reactions.



Scheme 5-1. Reaction mechanism of acetol self-aldol condensation.

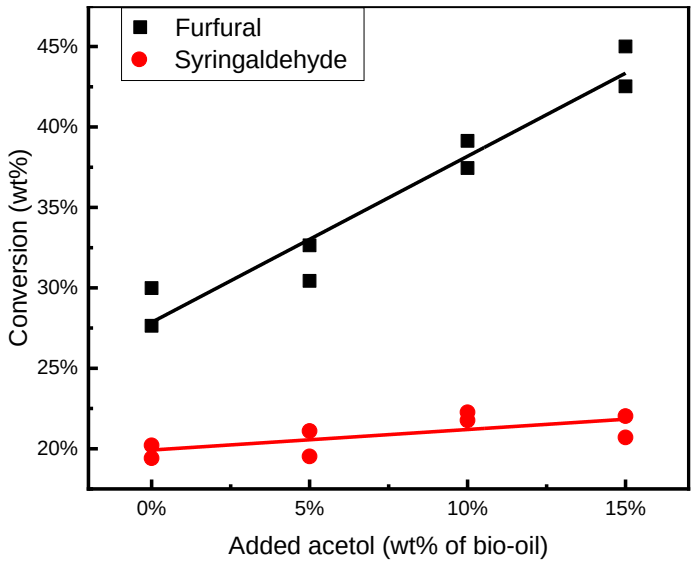


Figure 5-5. Effects of added acetol concentration (wt% of bio-oil) on conversion (wt%) of furfural and syringaldehyde. The reactive distillation was performed at 200 °C and 40 barg with the holding time of 2 min.

Compared to the reactive aldehydes and ketones, carboxylic acids are relatively stable during the bio-oil reactive distillation at elevated pressure. The effects of pressure on the yields of the typical carboxylic acids are shown in Figure 5-6. In addition, more carboxylic acids (e.g. acetic acid) are produced in the presence of high pressure, probably due to the enhanced hydrolysis of sugar components in the bio-oil. Furthermore, the carboxylic acids may act as catalysts for the other carbonyl compounds, for example, the acid-catalysed aldol condensation in Figure 5-5.

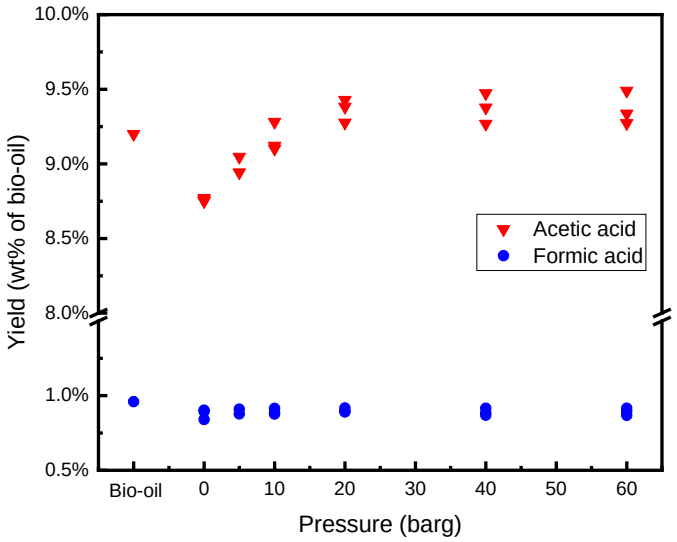


Figure 5-6. Formic and acetic acid yield (wt% of bio-oil) as a function of pressure. Distillation was conducted at 200 °C and the holding time of 2 min.

The FT-IR analysis can provide an overall quantification of all the carbonyl compounds in the distillation products. Three deconvoluted Gaussian bands of 1767 cm^{-1} (lactone), 1740 cm^{-1} (unconjugated alkyl aldehyde and alkyl ester) and 1713 cm^{-1} (carboxylic acid), were discussed previously [14]. As is shown in Figure 5-7, most of the carbonyl compounds are distributed into the distillate fractions during the reactive distillation, especially the liquid distillate. This is because the carbonyl functional groups would increase the polarity of the molecules. Moreover, due to the complex composition of bio-oil and the high reactivity of carbonyl compounds, many carbonyl compounds could be produced and consumed simultaneously during distillation, depending on the specific reaction condition and the structure of the carbonyl compound. For example, high pressure could accelerate the production of carbonyl compounds from the hydrolysis of sugar components [12]. According to Figure 5-7, the band areas of the three kinds of carbonyl compounds all increase slightly with increasing distillation pressure, which indicates that the high pressure can help produce more carbonyl compounds or inhibit the consumption of carbonyl compounds as an overall result.

The high carboxylic acid concentration of bio-oil would generally create an acidic environment for the bio-oil reactive distillation at high pressure. The presence of pressure would contribute to the formation of an acidic environment by retaining the light carboxylic acids in the liquid phase when the bio-oil is heated up [12]. As is shown in the Figure 5-8, most of the carbonyl compounds, including the aldehydes, ketones and carboxylic acids, are retained in the liquid phase when the bio-oil is heated to 200 ^{o}C and 40 barg. The aldehydes and ketones would undergo aldol condensation reaction catalysed by the intrinsic carboxylic acids, such as the formic and acetic acids. In addition, more carbonyl compounds including the carboxylic acids themselves would be produced by the acid-catalysed hydrolysis.

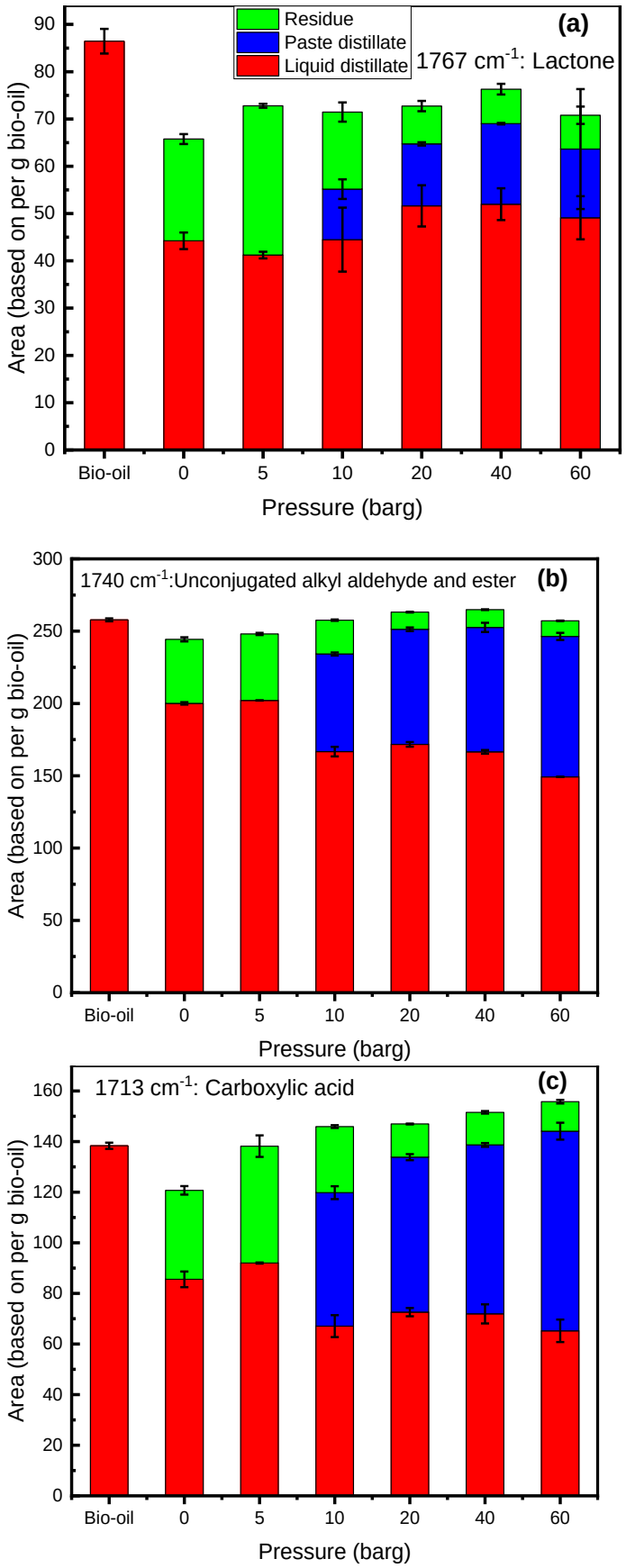


Figure 5-7. Band areas from the FT-IR spectral deconvolution of bio-oil and distillation products at different pressure. Distillation was conducted at 200 °C and the holding time of 2 min.

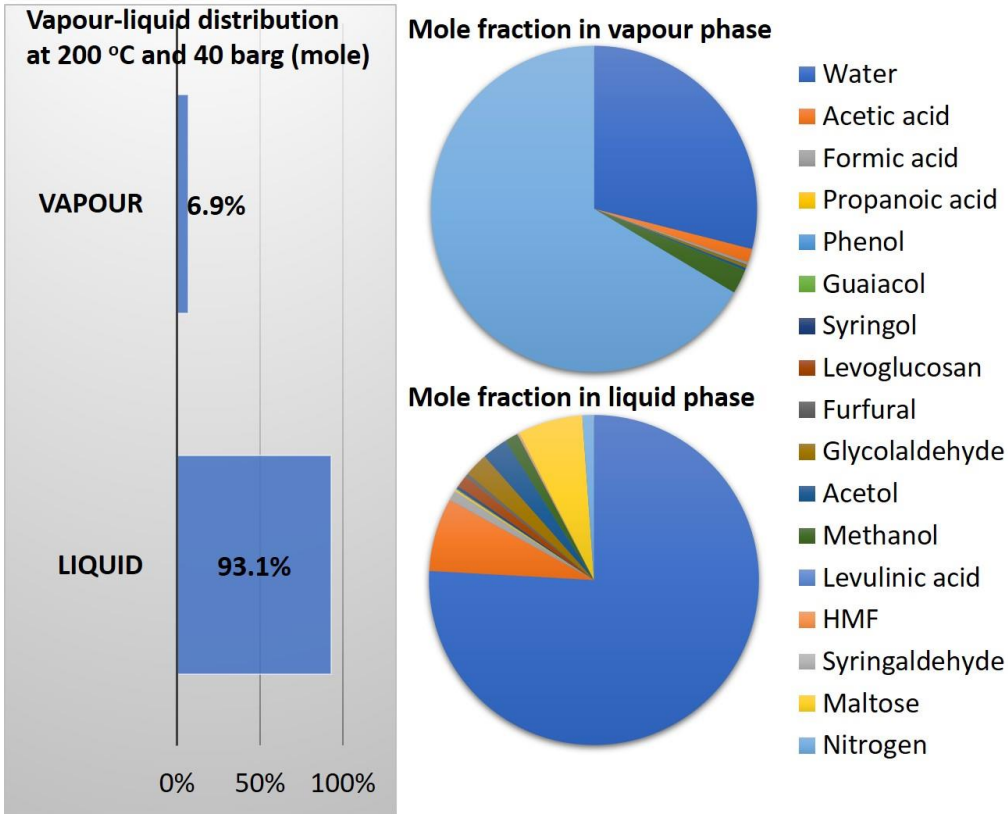


Figure 5-8. Component distribution in vapour and liquid phases when bio-oil is heated to 200 °C and 40 barg. Nitrogen is used to pressurise the reactor. The distribution was acquired by Aspen Plus simulation without chemical reactions.

5.3.2 Removal of carbonyl compounds via base

The high concentration of carbonyl compounds may cause the product instability due to their high reactivity. Based on Section 5.3.1, it can be concluded that the acid-catalysed reactions do not lead to the significant consumption of carbonyl compounds. Therefore, base was used here to neutralise the carboxylic acids and decrease the acidity. Moreover, base could also catalyse the aldol condensation reaction of carbonyl compounds.

5.3.2.1 Neutralisation of carboxylic acids by base

As is shown in Figure 5-9a, the FT-IR band area of carboxylic acids would decrease with increasing NaOH concentration, which indicates that the addition of base can lead to the consumption of carboxylic acids. The added base would react with the carboxylic acids through the acid-base neutralisation reaction. With the increase of base concentration, the yields of formic acid and acetic acid decrease significantly as expected (Figure 5-9b and 5-9c). In addition, as is shown in Figure 5-9d,

the pH values of the liquid distillate fractions also increase with increasing base concentration due to the neutralisation of carboxylic acids.

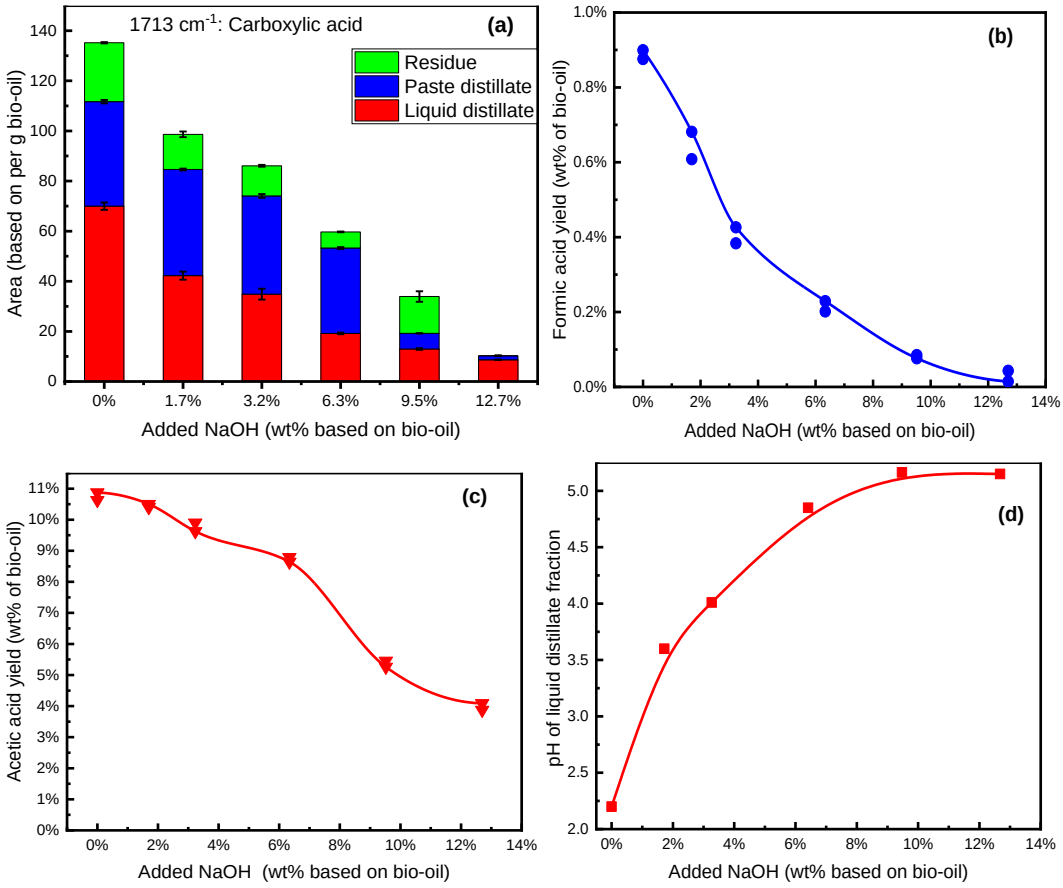


Figure 5-9. Effects of added NaOH concentration on: (a) FT-IR band area of carboxylic acid at 1713 cm^{-1}, (b) formic acid yield (wt% of bio-oil), (c) acetic acid yield (wt% of bio-oil) and (d) pH of liquid distillate fraction. Distillation was conducted at 200 ^{o}C and 40 barg with the holding time of 2 min.

In addition, the presence of base would also contribute to the consumption of ester. The ester may react with water to generate a carboxylic acid which could be neutralised by the base, as is indicated in Figure 5-10.

5.3.2.2 Base-catalysed aldol condensation

Besides neutralising the carboxylic acids, the added NaOH would also catalyse the aldol condensation of carbonyl compounds, such as the aldehydes and ketones. This could be confirmed by the FT-IR band area decrease of carbonyl functional groups in Figure 5-10b. The increased NaOH concentration at high temperature and high pressure would create a vigorous environment for the irreversible conversion of carbonyl compounds via the base-catalysed aldol condensation.

Even though the aldol condensation reaction of carbonyl compounds could be catalysed by both the acid and base, the carbonyl compounds would have different behaviour in the presence of an acid and a base during the high-pressure reactive distillation of bio-oil. Apparently, a base could achieve the removal of carbonyl compounds whereas an acid would not cause the significant consumption of carbonyl compounds. As is discussed in Section 5.3.1, the acid-catalysed hydrolysis of sugar would produce more carbonyl compounds. The presence of base would limit the hydrolysis of sugar compounds (e.g. levoglucosan). In addition, under an acidic condition, the product yield is low and side reactions other than aldol condensation may be favoured [16]. For example, acetol may react with guaiacol with the catalysis of an acid [2].

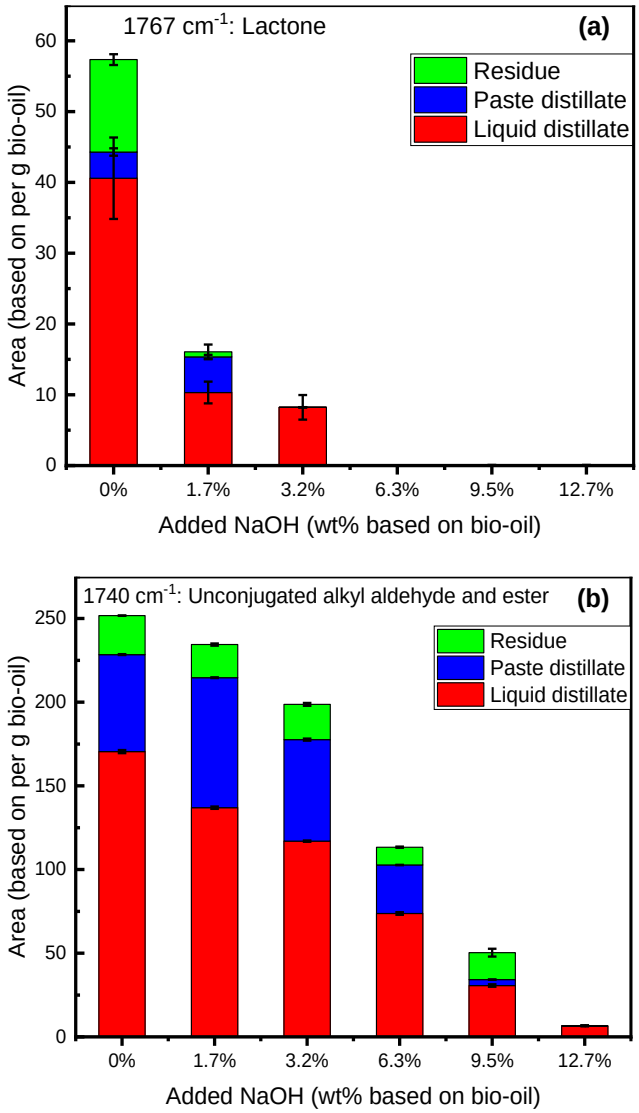


Figure 5-10. Typical carbonyl functional group change as a function of the added NaOH concentration (wt% based on bio-oil). Distillation was conducted at 200 °C and 40 barg with the holding time of 2 min.

The typical carbonyl compounds including aldehydes and ketones are also quantified with the result shown in Figure 5-11. The increase of NaOH concentration could lead to the decrease of the yields of acetol, furfural and syringaldehyde. Apparently, this would support that the base-catalysed aldol condensation reaction is more effective for the removal of carbonyl compounds in bio-oil than the acid-catalysed aldol condensation (Figure 5-1). Acetol could undergo self- and mixed aldol condensation, whereas furfural and syringaldehyde would mainly undergo Claisen-Schmidt condensation due to the absence of α-hydrogen. In addition, the conversion of the light carbonyl compounds would still be favoured compared to the heavy carbonyl compounds in the presence of base catalysts, which could be evidenced by that higher conversion of the furfural (100%) and acetol (98%) than that of syringaldehyde (84%) when the added NaOH concentration is 12.7%. Moreover, the carbon chain increase of the light carbonyl compounds can also improve the utilisation efficiency of the carbonaceous components in the bio-oil. The removal of the carbonyl functional groups by the based-catalysed aldol condensation during the high-pressure reactive distillation could improve the stability of the product.

The carbonyl compounds are mainly converted via the aldol condensation reaction which could lead to the increase of the average molecular weight of the products as is shown in the Figure 5-12. The DTG peak in the range of 25 - 100 ^{o}C is mainly caused by the evaporation of water and other small molecules such as formic acid. In the range from 100 to 400 ^{o}C, the DTG curves of the products from the high-pressure reactive distillation of pure bio-oil and “Bio-oil - AcOH” have a peak centralized at 200 ^{o}C, whereas the DTG peak of the “Bio-oil - NaOH” system is around 285 ^{o}C. This indicates that the molecular weights of the organic components in the product are increased in the presence of NaOH and the possible reason is that the carbonyl compounds would undergo the base-catalysed aldol condensation reaction to form larger molecules. Even though acid-catalysed aldol condensation would also occur in the high-pressure distillation of “Bio-oil - AcOH”, the production of newly formed carbonyl compounds may let the dimerisation of an aldehyde and/or ketone become the dominant reaction. However, in the “Bio-oil - NaOH”, the formed α,β-unsaturated aldehyde or ketone may continue the aldol condensation due to the lack of newly formed and highly reactive aldehyde and ketone.

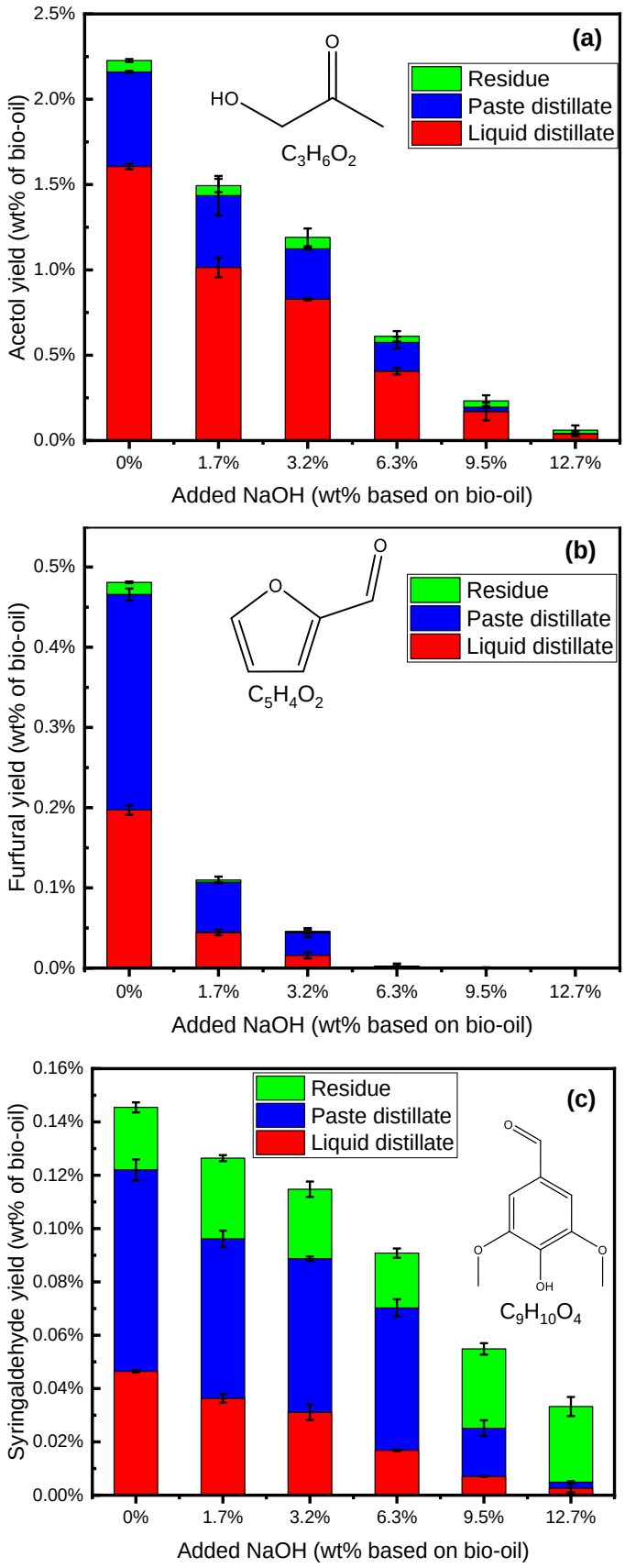


Figure 5-11. Effects of added NaOH concentration (wt% based on bio-oil) on the carbonyl compounds yields (wt% of bio-oil). Distillation was conducted at 200 °C and 40 barg with the holding time of 2 min.

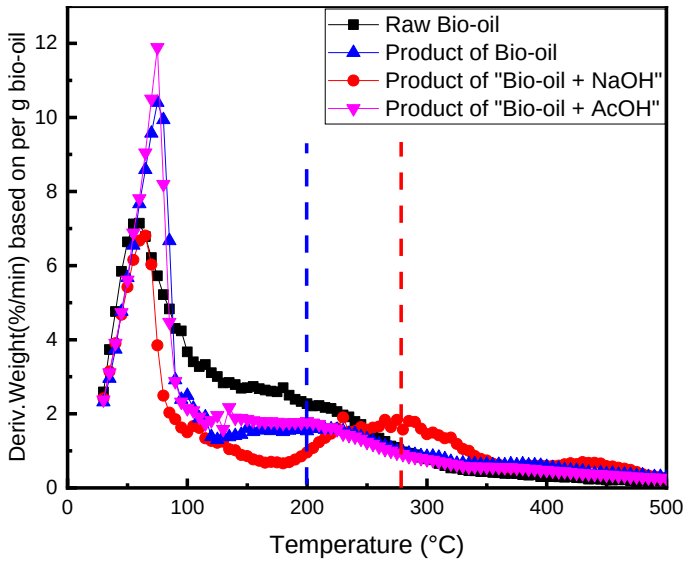


Figure 5-12. DTG curve comparison between the pure bio-oil, "Bio-oil - NaOH" and "Bio-oil - AcOH" systems. AcOH denotes acetic acid. Distillation was conducted at 200 °C and 40 barg with the holding time of 2 min.

5.4 Conclusion

The conversion of carbonyl compounds during the high-pressure reactive distillation of bio-oil was investigated in this study. The light and heavy carbonyl compounds would have different behaviour at high pressure. Pressure could accelerate the conversion of light carbonyl compounds and inhibit the conversion of heavy carbonyl compounds due to the higher reactivity of the light carbonyl compounds. Acetol, as an example of the light carbonyl compound, would undergo aldol condensation reaction with itself and other carbonyl compounds such as furfural. The acid-catalysed reactions would not lead to the significant consumption of carbonyl compounds. NaOH could remove carbonyl compounds by acting as a catalyst to the aldol condensation reaction of aldehydes and ketones and neutralising carboxylic acids.

5.5 References

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Chapter 6 Enrichment of aromatic compounds during the high-pressure reactive distillation of bio-oil

6.1 Introduction

Bio-oil, as a pyrolysis product of the renewable biomass, is a liquid mixture of hundreds of oxygenated compounds and can be either upgraded into biofuels by hydrotreatment or used as a source to produce high-value added chemicals such as aromatic compounds. The aromatic compounds in bio-oil are mainly derived from the decomposition of lignin in biomass (e.g. mainly single ring aromatic compounds) and the reaction of sugar compounds [1]. The aromatic rings of different sizes may have various functional groups substituted, such as the hydroxyl, methoxy and carbonyl groups. The substituted aromatic compounds such as phenolic compounds would also be included in this study.

It has been reported that the aromatic compounds in the bio-oil would contribute to the coke formation during the bio-oil processing. For example, the polymerisation of the aromatic rings during the catalytic hydrotreatment of bio-oil would lead to the high tendency of coke formation and the deactivation of catalysts [2]. In addition, the species derived from the cellulose or hemicellulose would also enhance the polymerisation of aromatic compounds in bio-oil [3].

To inhibit the polymerisation of aromatic compounds during the subsequent application, it is necessary to separate the aromatic compounds from other reactive compounds in bio-oil. Moreover, the enriched aromatic compounds from a bio-oil could be further hydrotreated into value-added fuels or directly used as useful chemicals. For example, the bio-oil that is rich in aromatic compounds could be hydrotreated into cycloalkanes and aromatic hydrocarbons [4]. In addition, many phenolic structures in bio-oil could be isolated or recovered from bio-oil as valuable chemicals and used directly for the polymer production [5, 6].

Currently, phenolic compounds are enriched or separated from bio-oil mainly by solvent extraction and distillation [6]. Mantilla and co-workers extracted phenolic compounds from bio-oil by the two-step liquid-liquid extraction using dichloromethane and ethyl acetate as the solvents [7]. Jean and co-workers used the steam distillation to separate phenolic compounds into the light fraction [8]. However, the tedious extraction and distillation (at either atmospheric or vacuum pressure) are usually restricted by the consumption of extra solvent and the low distillate yield, respectively.

High-pressure reactive distillation could achieve high distillate yield separation of bio-oil with reduced polymerisation and it might be used to separate aromatic compounds from bio-oil because the polymerisation of the reactive components in bio-oil could be inhibited [9, 10]. In this study, the distribution and reaction of aromatic compounds during the high-pressure reactive distillation of bio-oil are investigated to intensify the transfer of aromatic compounds. First, the effects of pressure on the distribution of aromatic compounds are discussed. Then, the reaction of aromatic compounds in

the high-pressure and high-temperature environment is investigated in terms of process parameters and the light component. Finally, $Ca(OH)_2$ is used to intensify the transfer of aromatic compounds to the paste distillate fraction based on the acidity of phenolic compounds.

6.2 Experimental

6.2.1 Materials

The pyrolysis bio-oil was acquired from Renergi Pty Ltd [11] by grinding pyrolysing mallee wood at 400 °C. After filtration, the bio-oil was stored at –10 °C to avoid the undesired degradation. Tetrahydrofuran (THF, ≥99.9%), methanol (≥99.9%), calcium hydroxide (⩾ 95.0%), chloroform (≥99.8%), phenol (⩾99%), guaiacol (⩾98.0 %), and syringol (99%) were bought from Sigma-Aldrich and used without further purification.

6.2.2 Distillation experiments

The high-pressure reactive distillation was conducted using a 100 mL autoclave (Autoclave Engineers) coupled with two sequential 150 mL condensers (made of Swagelok sample cylinders) as in [10]. 50 mL bio-oil mixed with other reactants was first loaded into the reactor. N_2 was utilised to expel the air in the reactor before heating. When the reactant was heated to the pre-set temperature, the reactor would be pressurised with high-pressure nitrogen to the desired value. If the reactor pressure exceeded the desired pressure before reaching the pre-set temperature, the extra pressure would be slowly released to maintain the reactor at the desired pressure. After holding the reactor at desired temperature and pressure for a pre-set time, the pressure would be released quickly to achieve the flash distillation by opening the valve between the reactor and condensers. The vapour phase would be condensed in the condensers as the distillate fraction that could be divided into liquid distillate and paste distillate by decanting. The liquid distillate would have higher water concentration than the paste distillate. The liquid/solid phase retained in the reactor would be the residue.

6.2.3 UV-fluorescence spectroscopy

The wavelength and intensity of the UV-fluorescence spectroscopy could be used to characterise the size and abundance of the aromatic ring, respectively. The samples were first dissolved in the mixture of chloroform and methanol (volume ratio being 4:1) and then diluted with methanol to 4 ppm (wt). The synchronous fluorescence spectra were acquired using a Perkin-Elmer LS50B spectrometer at a scan speed of 200 nm/min, with a constant energy difference of -2800 cm^{-1}

and slit widths of 2.5 nm [3]. The fluorescence intensity is expressed based on per g bio-oil by multiplying the intensity with the corresponding yield of the distillation fraction.

6.3 Results and discussion

6.3.1 Enhanced transfer of aromatic compounds to paste distillate by elevating pressure

Bio-oil contains various kinds of aromatic compounds of different sizes and substituted functional groups. The UV fluorescence spectroscopy could be utilised to indicate the overall changes of the aromatic compounds. During the bio-oil distillation, some reactions (e.g. polymerisation) of aromatic compounds would take place and lead to the structure change. Moreover, aromatic compounds of different sizes or boiling points would also be transferred into different fractions during the distillation. Pressure is a vitally important parameter for the phase equilibrium of bio-oil and could affect the distillation behaviours of the aromatic compounds. According to the UV-fluorescence spectroscopy in Figure 6-1, most of the aromatic compounds is transferred into the paste distillate during the high-pressure reactive distillation (Figure 6-1a) and retained in the residue during the atmospheric pressure distillation (Figure 6-1b). Apparently, the application of high pressure would intensify the transfer of aromatic compounds to the paste distillate from the residue during the distillation. This could also be supported by the effects of pressure on the synchronous spectra of the paste distillate (Figure 6-1c) and residue (Figure 6-1d).

The raw bio-oil is featured with two peaks at 280 nm and 340 nm as is shown in Figure 6-1a. The peak centred at 280 nm is mainly caused by the aromatic compounds with a single ring, such as phenol (See Section 6.3.2 for more detail). After distillation, the total intensity of the distillation products decreased at both 280 nm and 340 nm and increased at 400 nm when compared to the intensity of the original bio-oil. This indicates that the aromatic compounds of smaller sizes would polymerise into larger ring structures. However, the polymerisation of aromatic compounds would be reduced during the high-pressure reactive distillation compared to the atmospheric pressure distillation. According to the DTG curves in Figure 6-2, the second peak after 100 ^{o}C would shift to left with increasing pressure, which indicates that the application of pressure could reduce the polymerisation of bio-oil. In addition, the residue of the high-pressure reactive distillation was in the form of paste whereas the residue of the atmospheric pressure distillation was a hard solid. This could also prove the severe polymerisation during the atmospheric pressure distillation.

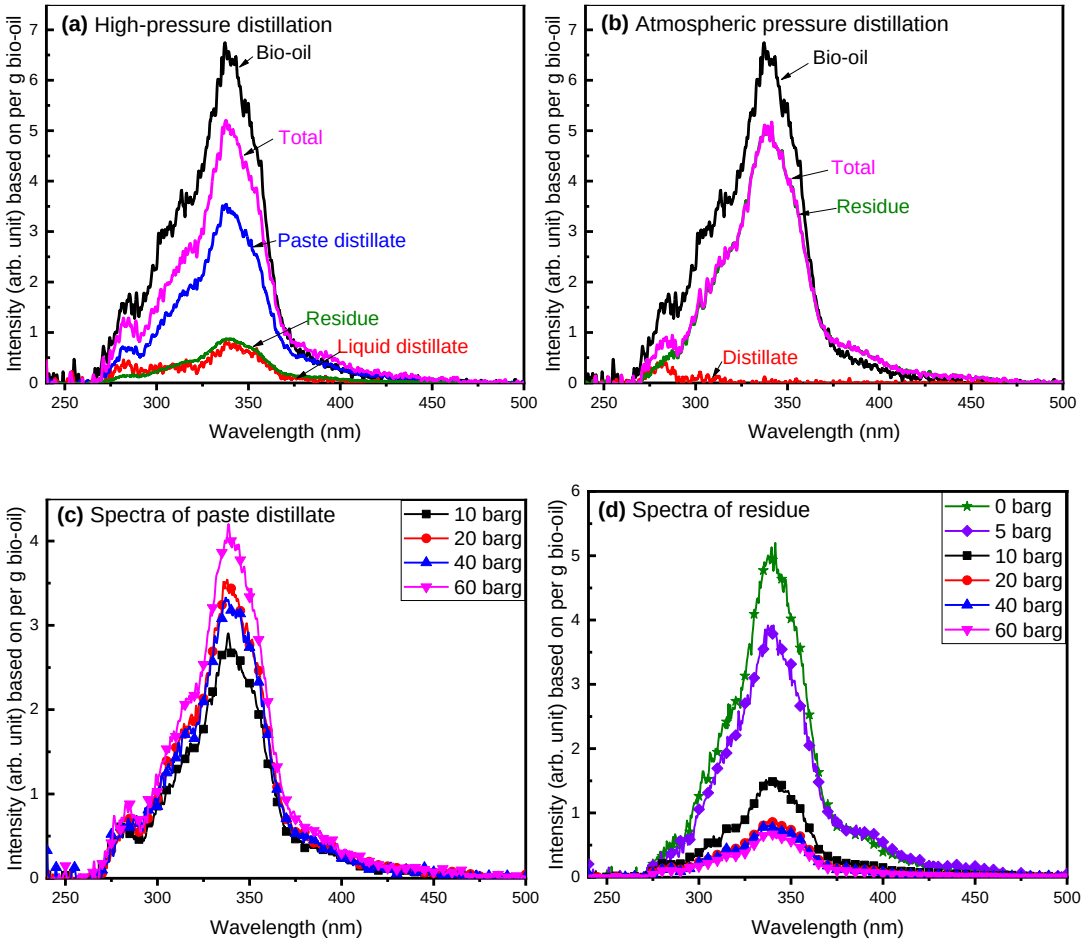

Figure 6-1. Constant energy (-2800 cm^{-1}) synchronous spectra of products from (a) high-pressure reactive distillation (P = 40 barg), (b) atmospheric pressure distillation (P = 0 barg), (c) paste distillate from distillation at different pressure and (d) residue from distillation at different pressure. The distillation experiment was conducted at 200 ^{o}C and the holding time of 2 min.

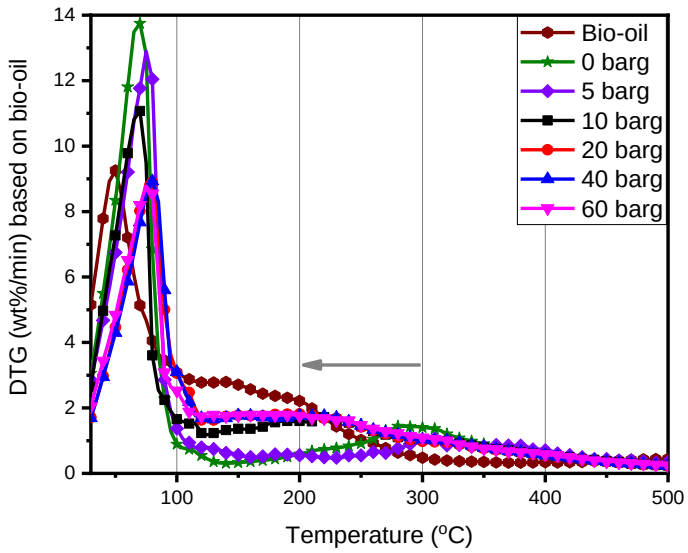

Figure 6-2. Effects of pressure on the DTG (wt%/min based on bio-oil) of distillation products. Distillation was performed at 200 °C and the holding time of 2 min.

To understand the distribution of aromatic compounds, the typical aromatic compounds were analysed by GC-MS. The effects of pressure on the yield (wt% of bio-oil) of aromatic compounds are shown in Figure 6-3. Yield, wt% of bio-oil, is the product of the component concentration in a fraction and the yield of the corresponding fraction. During the atmospheric pressure distillation (P = 0 barg), most of the phenol and guaiacol are distributed into the distillate as is shown in Figure 6-3a and Figure 6-3b, whereas most of the syringol is retained in the residue and converted to solid as is illustrated in Figure 6-3c. During the high-pressure distillation (P ≥ 10 barg), the majority of the three aromatic compounds are transferred into the distillate, especially into the paste distillate. With the increase of pressure, the aromatic compound yield in the residue decreases and that in the paste distillate increases. The paste distillate at 5 barg was too little to be collected. Therefore, the application of pressure would help transfer the aromatic compounds from the residue to distillate. Moreover, the aromatic compounds would mainly be distributed into the nonpolar paste distillate after the liquid-liquid phase separation of the distillate because the benzene ring on the aromatic compounds would decrease the molecular polarity [10]. In addition, the increase of pressure would slightly increase the overall yield (wt% of bio-oil) of these aromatic compounds. It also supports that the pressure might reduce the polymerisation of aromatic compounds.

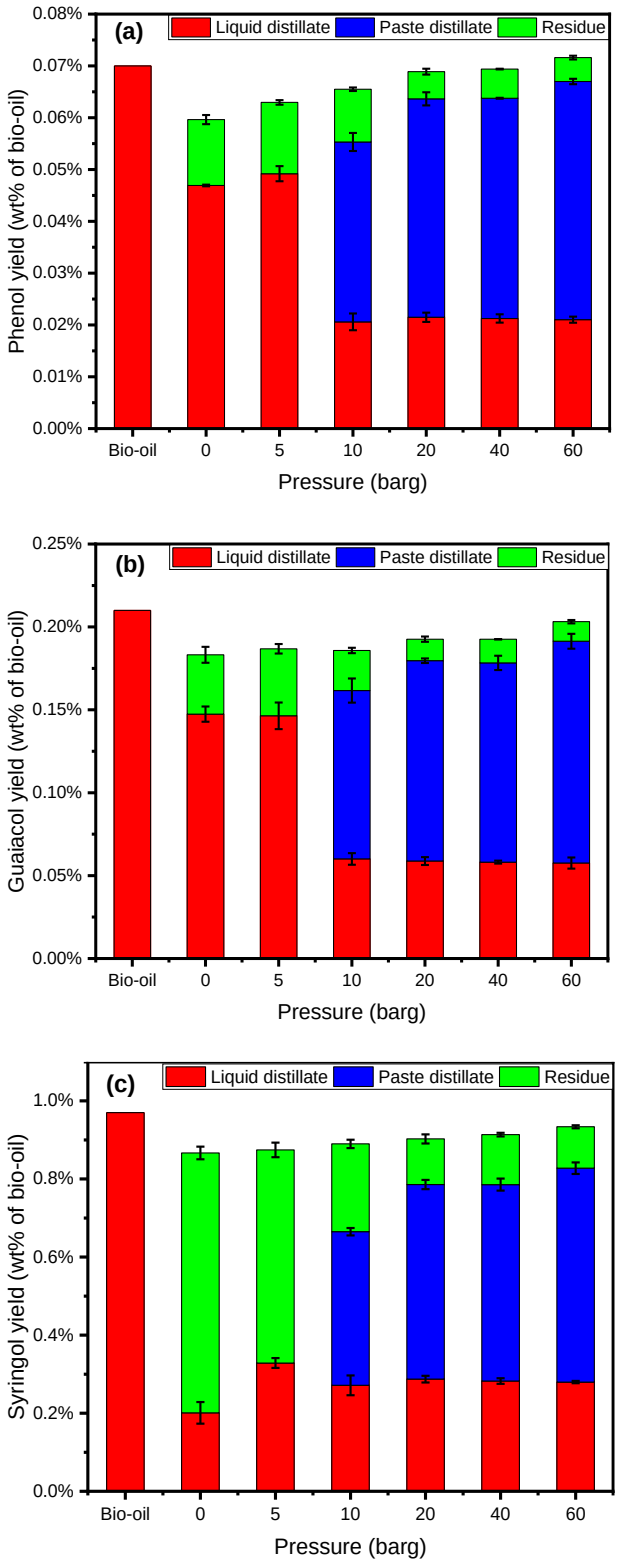

Figure 6-3. Effects of pressure on the yields (wt% of bio-oil) of (a) phenol, (b) guaiacol and (c) syringol. Distillation was conducted at 200 °C and the holding time of 2 min.

The effects of pressure on the aromatic compound concentration in different fractions are shown in Figure 6-4. During the atmospheric pressure distillation (P = 0 barg), phenol and guaiacol

have the highest concentration in the distillate and syringol has the highest concentration in the residue. The distillate from the atmospheric pressure distillation is an aqueous phase similar to the liquid distillate from the high-pressure reactive distillation [10]. During the high-pressure distillation, phenol and guaiacol have the highest concentration in the paste distillate and syringol has the highest concentration in the residue. The difference of syringol concentration between the paste distillate and residue is not significant. It can be seen that phenol and guaiacol are mainly transferred from liquid distillate to paste distillate and syringol is mainly transferred from residue to paste distillate. The concentration of the aromatic compounds in different fractions would mainly be determined by the boiling point and solubility. In the presence of pressure, the small aromatic compounds are mainly transferred from liquid distillate to paste distillate (Figure 6-3a and 6-3b) whereas the large aromatic compounds are mainly transferred from residue to paste distillate (Figure 6-3c). In addition, during the high-pressure distillation, the pressure has less effect on the concentration of aromatic compounds in different fractions, especially when the pressure is higher than 20 barg.

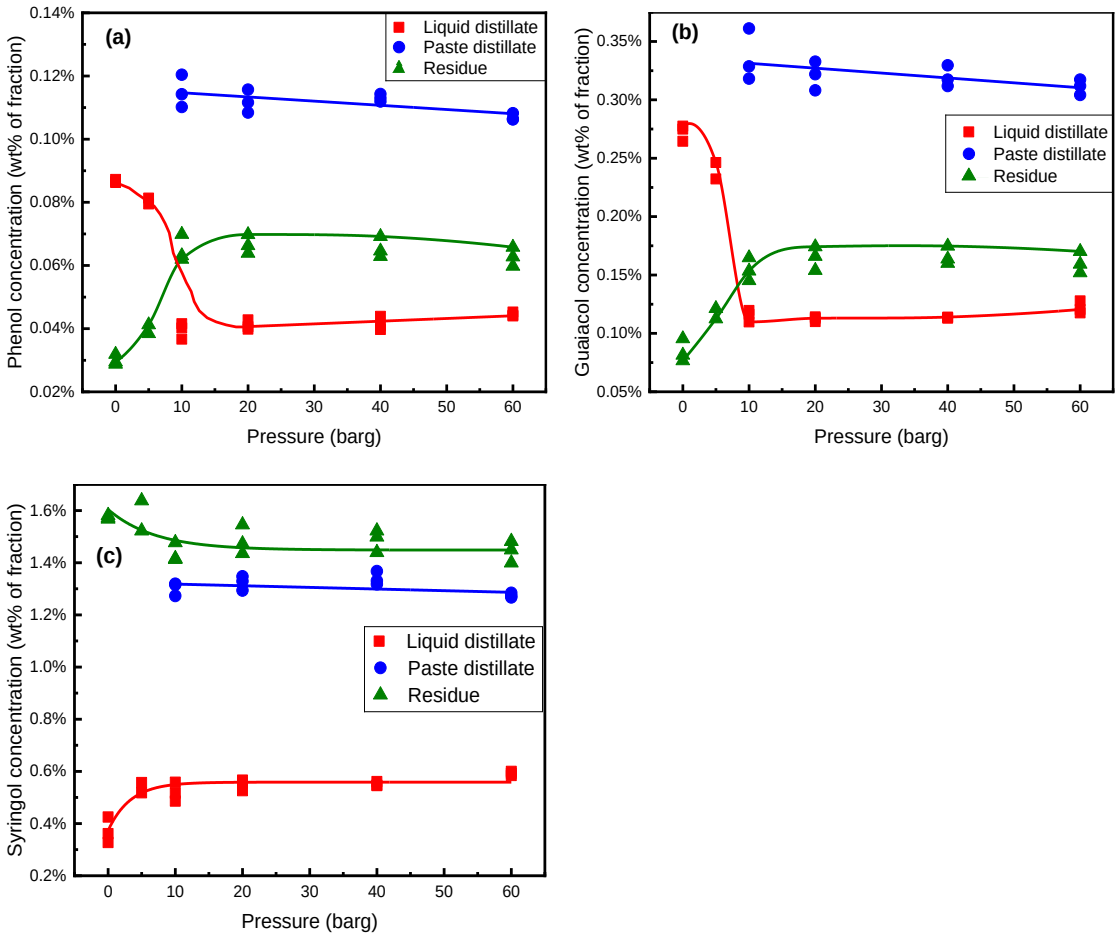

Figure 6-4. Effects of pressure on the absolute concentration of (a) phenol, (b) guaiacol and (c) syringol in different fractions. Distillation was performed at 200 °C and the holding time of 2 min.

6.3.2 Reactions of aromatic monomers under the hydrothermal condition

To investigate the reactions of the aromatic compounds, the high-pressure reactive distillation of bio-oil was conducted at different reaction temperature and holding time. The reactive distillation was conducted from 140 to 280 °C with the holding time being 2 min. As is shown in Figure 6-5, the increasing temperature would lead to the increase of larger aromatic ring systems at 400 nm. This may be caused by the polymerisation of the aromatic compounds at 280 nm and 340 nm. The intensified polymerisation could be also confirmed by the increased PCY in Figure 6-6a and the shifted peak (after 100 °C) in Figure 6-6b with increasing temperature. In Figure 6-6b, the DTG peaks < 100 °C are mainly caused by H_2O and other light compounds such as formic acid. The peaks after 100 °C are mainly caused by the large molecules, such as aromatic compounds. The shift of the DTG peaks (> 100 °C) to higher temperature would indicate that more large molecules would be formed by the polymerisation of aromatic compounds.

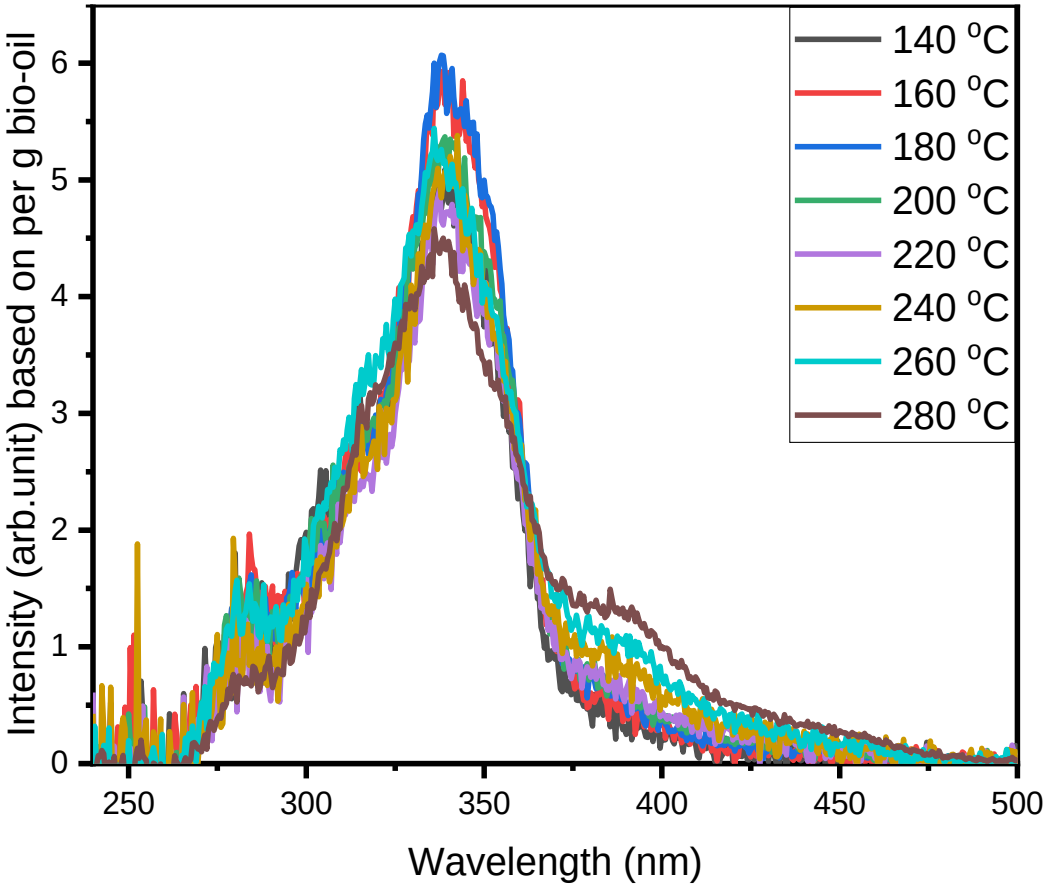

Figure 6-5. Constant energy (-2800 cm^{-1}) synchronous spectra of products from different temperature. Distillation was conducted at autogenous pressure and the holding time of 2 min. The intensity was acquired by adding up all the intensities of different fractions.

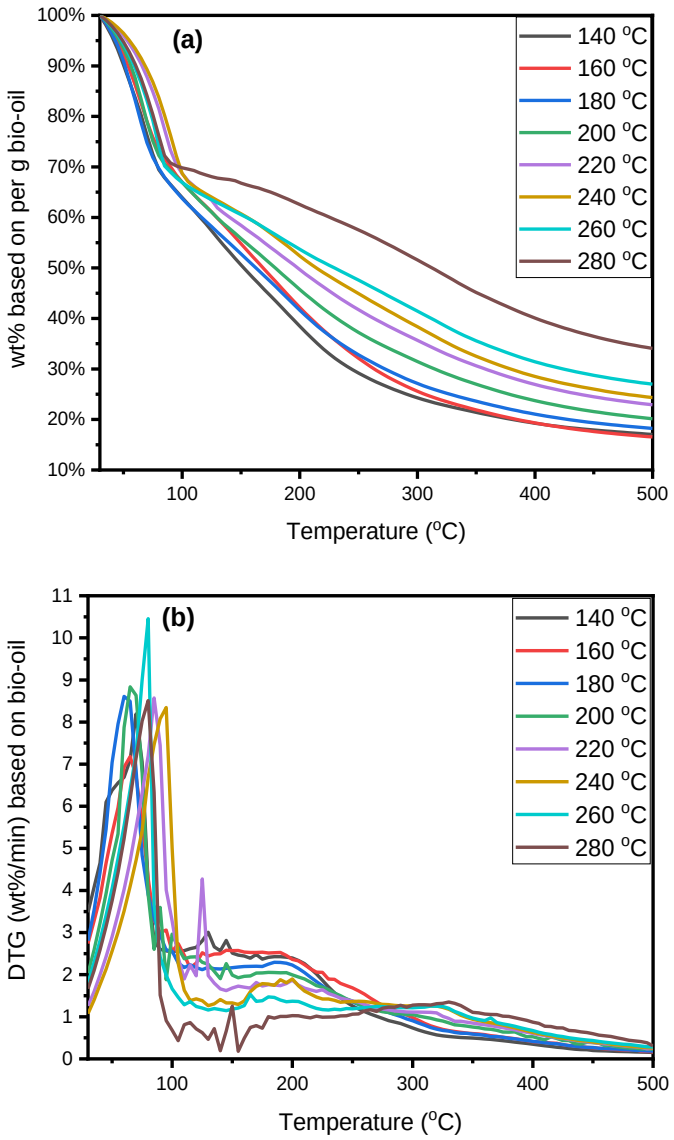

Figure 6-6. Effects of temperature on the TGA (a) and DTG (b) of the distillation products. Distillation was conducted at autogenous pressure and the holding time of 2 min. Both the TGA and DTG were calculated by adding up all the fractions.

As is shown in Figure 6-7, when the temperature is higher than 200 °C, more aromatic monomer is produced. The possible reason is that high temperature would accelerate the production of aromatic monomers because the application of high pressure and the elevated temperature would create a hydrothermal environment in which the aromatic compounds may also be produced by the hydrothermal reaction of sugar compounds and their derivatives [12]. This could be supported by the abrupt consumption of sugar compounds when temperature is higher than 200 °C [See in Chapter 4]. In addition, the disintegration of lignin-derived oligomers might also contribute to the formation of aromatic monomers in the hydrothermal environment.

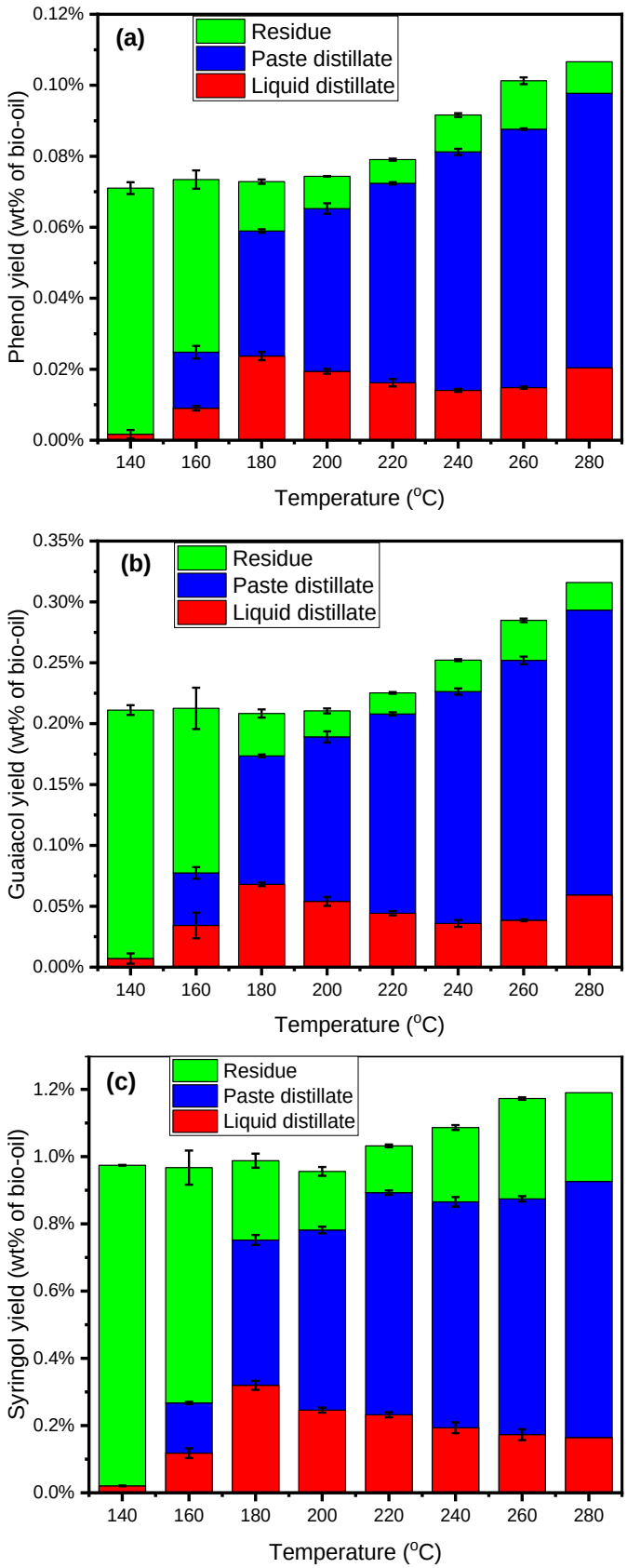

Figure 6-7. Effects of temperature on the yield (wt% of bio-oil) of aromatic monomers: (a) phenol, (b) guaiacol and (c) syringol. Distillation was conducted at autogenous pressure and the holding time of 2 min.

To investigate the effects of holding time on the reaction of aromatic compounds, high-pressure reactive distillation was conducted from 2 min to 30 min at 200 °C. As is shown in Figure 6-8, with the increase of holding time, more aromatic monomers would be produced because the hydrothermal conversion of sugar compounds would gain more reaction time. Besides affecting the yields of aromatic compounds, the holding time could also change their distribution. As it can be seen from Figure 6-8, with the increase of holding time, more aromatic compounds are transferred into the paste distillate from the residue and liquid distillate. This could also be confirmed by the synchronous spectra of paste distillate and residue in Figure 6-9. Thus, it could be concluded that longer holding time is advantageous for the enrichment of aromatic compounds into the paste distillate.

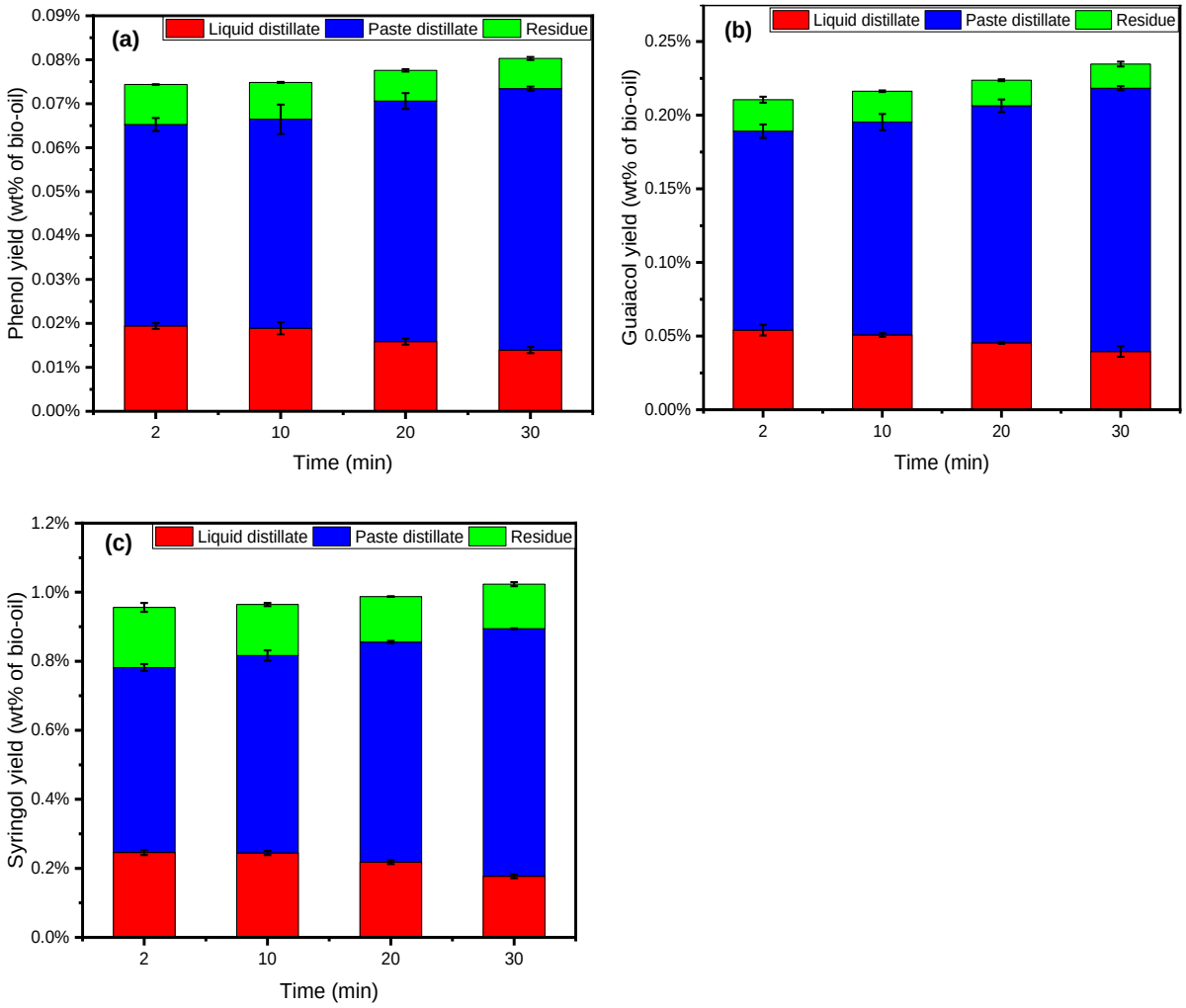

Figure 6-8. Effects of holding time on the aromatic compound yield, wt% of bio-oil: (a) phenol, (b) guaiacol and (c) syringol. Distillation was conducted at 200 °C and autogenous pressure.

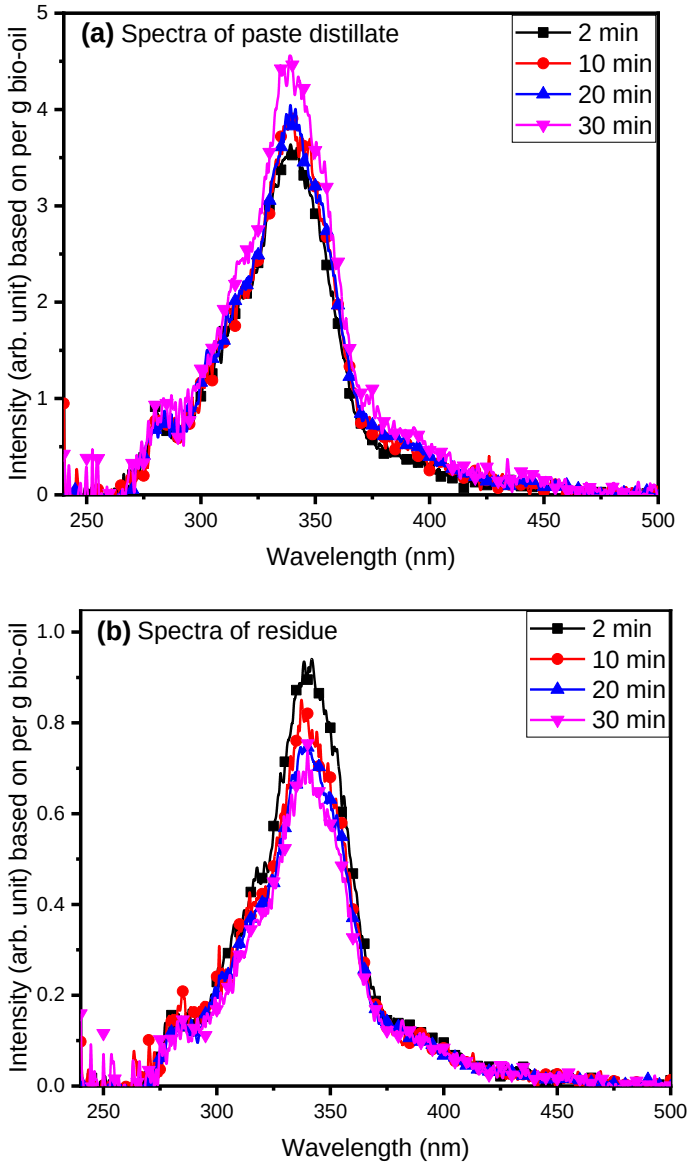

Figure 6-9. Constant energy (-2800 cm^{-1}) synchronous spectra of the (a) paste distillate and (b) residue from different holding time. Distillation was conducted at 200 °C and autogenous pressure.

Based on the above analysis, it could be concluded that the increase of pressure, temperature and holding time would all contribute to the production of aromatic monomers because the elevated pressure and temperature would provide a hydrothermal environment for the conversion of sugar compounds. However, to achieve high distillate yield, the optimal condition for the high-pressure distillation of the investigated bio-oil is at the temperature range of 180 – 220 °C and short holding time because the polymerisation reaction of other reactive components such as sugars and aldehydes could also be accelerated at the same time when the temperature is increased to higher than 220 °C [10].

Even though the process parameters are limited by the reactive components, the light components such as methanol might be advantageous for the inhibition of the polymerisation of aromatic monomers. The original methanol concentration in the investigated bio-oil was 0.99 wt%. The methanol has been reported to inhibit the polymerisation of phenol and formaldehyde during the production of phenolic resin [13]. To examine the effects of methanol on the aromatic compounds during the reactive distillation of bio-oil, extra methanol of 5 wt% and 10 wt% (based on bio-oil) was added to conduct the high-pressure reactive distillation at 200 °C. As is shown in Figure 6-10, with the increase of added methanol, the total yield of aromatic monomers increases slightly. The methanol in the bio-oil would inhibit the polymerisation of the aromatic monomers under the current experimental condition.

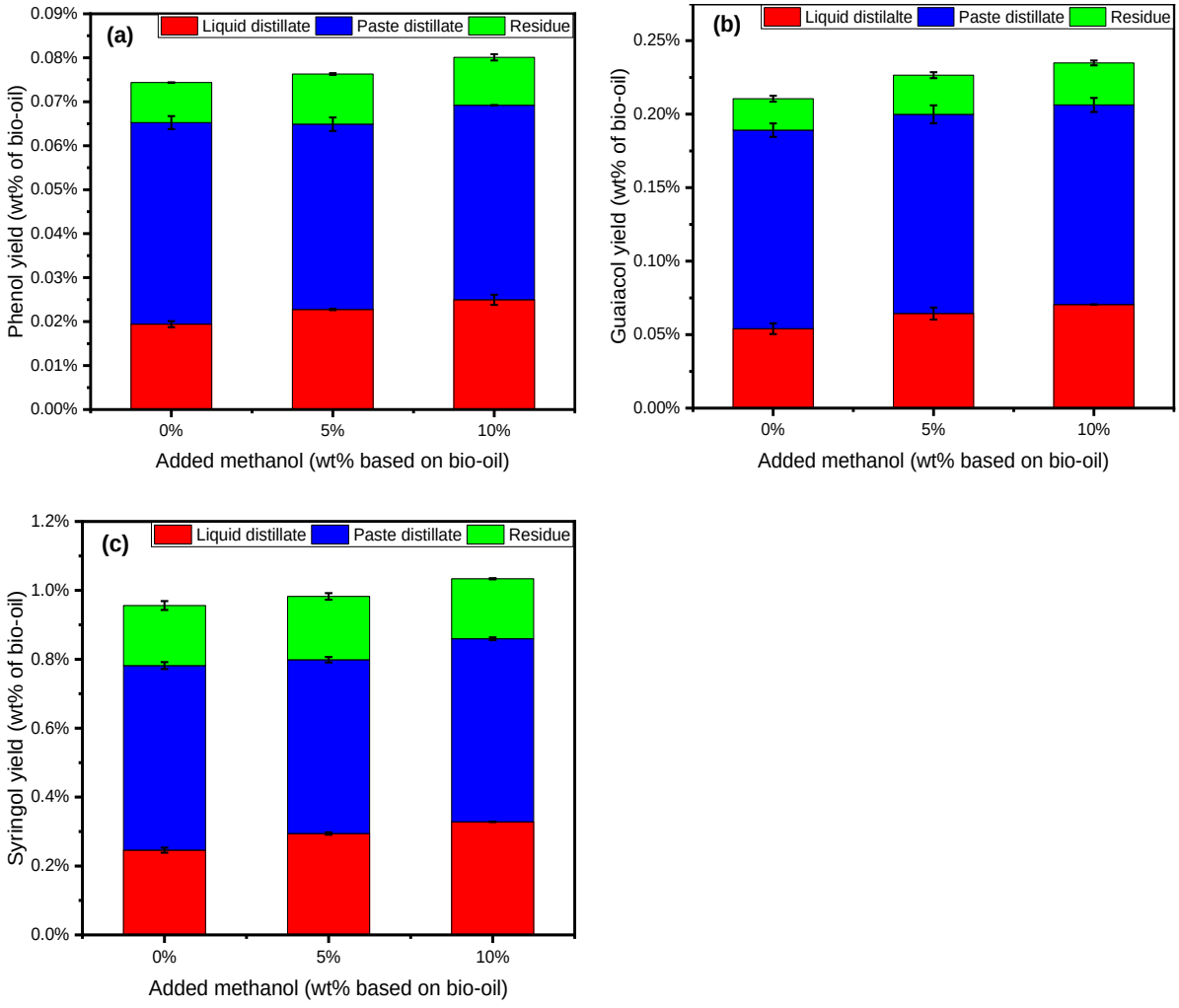

Figure 6-10. Effects of added methanol (wt% based on bio-oil) on the yield (wt% of bio-oil) of aromatic monomers: (a) phenol, (b) guaiacol and (c) syringol during the high-pressure reactive distillation of bio-oil. Distillation was conducted at 200 °C and autogenous pressure.

To determine the role of aromatic compounds, extra phenol was added to the bio-oil to conduct the high-pressure reactive distillation at 200 °C and 40 barg with the holding time being 2 min. As is shown in Figure 6-11, with the increase of phenol content from 0 to 1.5 wt% (based on bio-oil), the levoglucosan yield decreases and the yields of acetol and furfural increase. This indicates that increasing phenol would elevate the acidity which can intensify the hydrolysis reaction of sugar components (e.g. levoglucosan) and the production of carbonyl compounds (e.g. furfural and acetol).

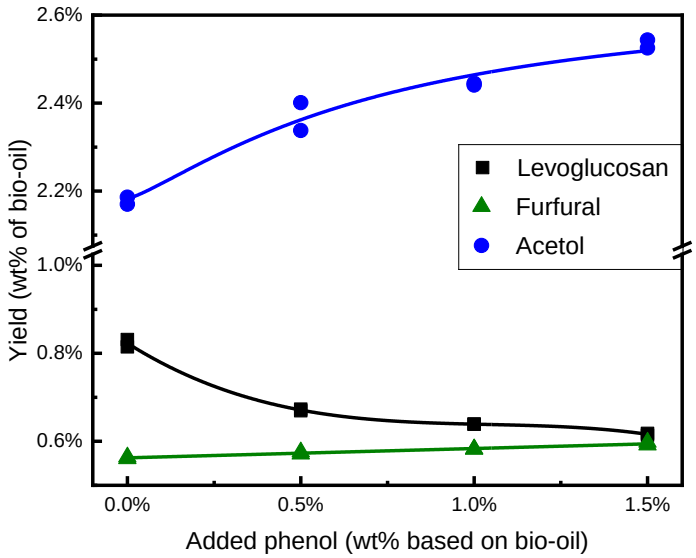

Figure 6-11. Effects of added phenol concentration on the yield (wt% of bio-oil) of levoglucosan, furfural and acetol. Distillation was conducted at 200 °C and 40 barg with the holding time of 2 min.

The effects of added phenol on the UV synchronous spectra of the distillation products are shown in Figure 6-12. The increasing intensity of peaks at 280 nm is obviously caused by the increase of phenol as a single ring aromatic compound. Furthermore, the intensity increase of peaks at 340 nm is largely due to the polymerisation of phenol.

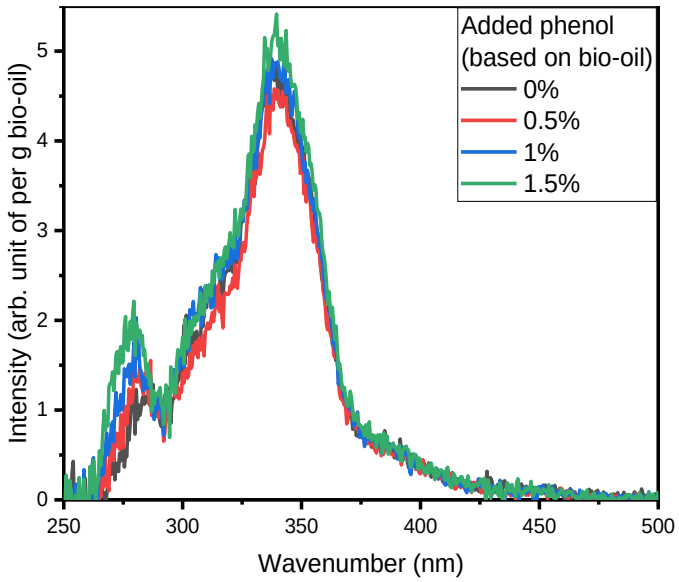

Figure 6-12. Effects of added phenol (wt% based on bio-oil) on the UV synchronous spectra (constant energy: -2800 cm^{-1}) of products. High-pressure reactive distillation was conducted at 200 °C and 40 barg with the holding time of 2 min.

6.3.3 Intensified transfer of aromatic compounds to paste distillate by base

Many aromatic compounds in bio-oil would have hydroxyl functional group on the aromatic ring, which would enable the phenolic compounds to have the acidic properties as discussed in Section 6.3.2. Based on the acidity, base may be used to enhance the transfer of aromatic compounds to the paste distillate. $Ca(OH)_2$ of 1.5 wt%, 4.4 wt% and 5.9 wt% (based on bio-oil) was added to the bio-oil to study the effects of base on the reaction and distribution of phenolic compounds. As is shown in Figure 6-13, with the increase of $Ca(OH)_2$ concentration, the phenolic compound yield (wt% of bio-oil) in the paste distillate increases.

The phenolic compounds would be transferred into the paste distillate due to their nonpolarity and the change of the environment. Generally, the phenolic compounds might form hydrogen bonds with the abundant carboxylic acids in bio-oil, which would inhibit the transfer of phenolic compounds from liquid distillate to paste distillate [14]. The consumption of carboxylic acids by the neutralisation reaction with $Ca(OH)_2$ would reduce the interaction between the carboxylic acid and the phenolic compounds. The $Ca(OH)_2$ in the product is mainly in the form of calcium carboxylate (mainly calcium acetate and formate) based on the potential coke yield (PCY) result as is shown in Table 6-1. The increase of the total PCY is a combination of the increases in the form of calcium acetate and calcium formate. Evidently, the neutralisation of the carboxylic acids by $Ca(OH)_2$ would favour the transfer of phenolic compounds into the paste distillate fraction from the liquid distillate.

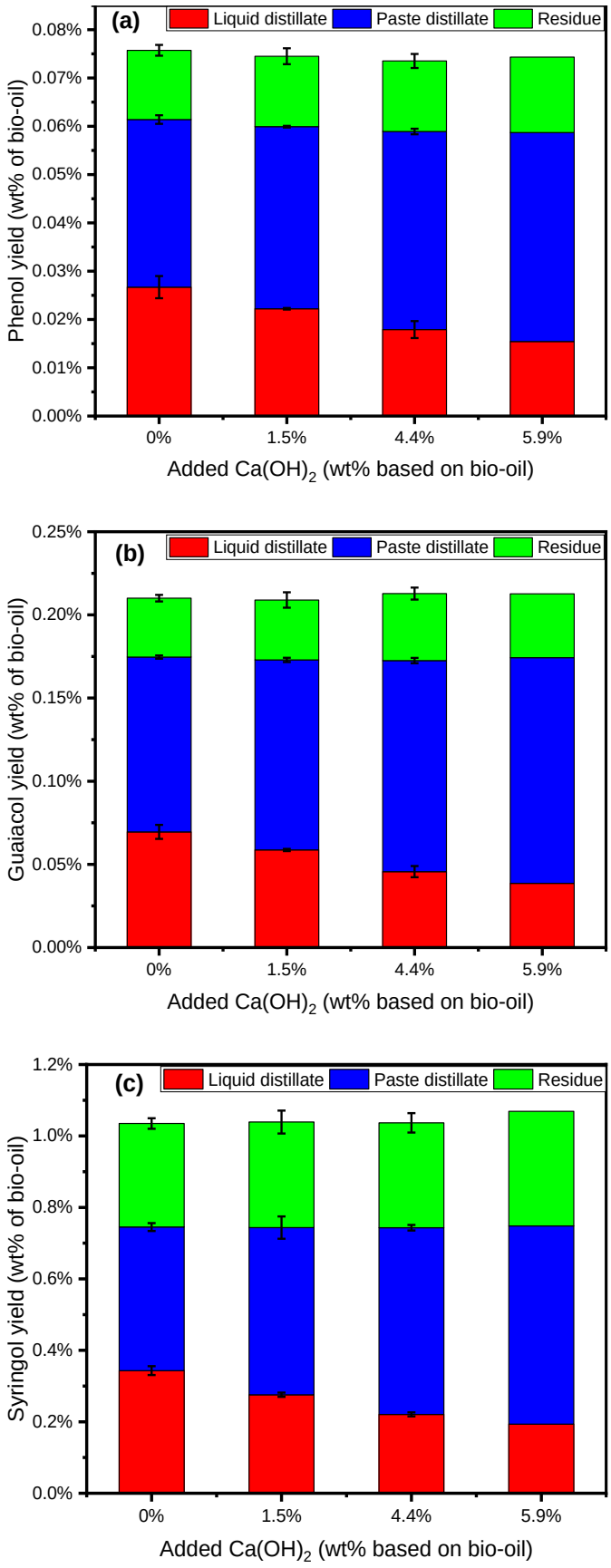

Figure 6-13. Effects of added $Ca(OH)_2$ concentration on the yields (wt% of bio-oil) of (a) phenol, (b) guaiacol and (c) syringol. Distillation was conducted at 200 °C and 40 barg.

Table 6-1

PCY of distillation products and the form of calcium carboxylates

$Ca(OH)_2$ concentration (wt% based on bio-oil)	Total PCY (wt%)	Increase of total PCY(wt%)	wt% increase in the form of $Ca(CH_3COO)_2$	wt% increase in the form of $Ca(HCOO)_2$
0.0%	15.5%		0.0%	0.0%
1.5%	18.8%	3.4%	3.1%	2.5%
4.4%	23.4%	8.0%	9.1%	7.5%
5.9%	25.2%	9.8%	11.9%	9.8%

6.4 Conclusion

In this study, the distribution and reaction of aromatic compounds during the high-pressure reactive distillation of bio-oil are investigated to achieve the enrichment to paste distillate fraction. The pressure could not only enhance the transfer of aromatic compounds from the residue and liquid distillate fractions to the paste distillate fraction, but also reduce their polymerisation. Moreover, high temperature would lead to the severe polymerisation of the aromatic compounds even though some aromatic monomers could be produced due to the enhanced hydrothermal reaction of sugar compounds and their derivatives when the temperature is higher than 200 ^{o}C. Longer holding time can also help produce more aromatic monomers and transfer aromatic compounds to paste distillate fraction. Besides the process parameters, methanol in the bio-oil could also help reduce the polymerisation of aromatic compounds. Furthermore, the phenolic compounds would act as an acid catalyst to accelerate the hydrolysis of sugar and the production of carbonyl compounds. Based on the acidity, $Ca(OH)_2$ could also help transfer phenolic compounds to the paste distillate fraction.

6.5 References

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Chapter 7 Conclusions and recommendations

7.1 Conclusions

This study aims to achieve bio-oil upgrading via high-pressure reactive distillation by investigating the roles of process parameters especially pressure and the major components in the high-pressure reactive distillation of bio-oil produced from the pyrolysis of mallee woody biomass. The distillation at elevated pressures is advantageous over distillation at atmospheric pressure in terms of high distillate fraction yields, reduced polymerisation and improved distillate properties. Besides the effects of process parameters, the distribution and reaction behaviours of the major components, including levoglucosan, carbonyl compounds and aromatic compounds, were also investigated to gain insight into the coupling between reaction and distillation. The main conclusions are as below.

7.1.1 High-pressure reactive distillation of bio-oil for reduced polymerisation: effects of process parameters

- High-pressure reactive distillation can achieve high yield of distillate with reduced polymerisation compared to the atmospheric pressure distillation because high pressure could change the phase behaviour of the light species of the bio-oil.
- The presence of high pressure could retain H_2O and other light components in the liquid phase to reduce the polymerisation and favour such reactions as hydrolysis that would tend to decrease the molecular sizes.
- The distillate yield is 90% when the distillation is conducted at 200 ^oC and a pressure not lower than 20 barg.
- Additional water would be produced during the high-pressure reactive distillation, probably by dehydration reaction and most of the water is transferred into the liquid distillate.
- The lower water concentrations (~15 wt%) and higher organic content could render the paste distillate as the desired product for further upgrading to high-value added fuels or chemicals.
- The optimal condition for the investigated bio-oil is at pressure not lower than 20 barg and temperature of 180 – 220 ^oC.

7.1.2 Reaction and distribution of levoglucosan during the high-pressure reactive distillation of bio-oil

- Levoglucosan would mainly undergo hydrolysis reaction during the high-pressure distillation whereas thermal polymerisation would dominate during the atmospheric pressure distillation.

- The reaction environment would play an important role for levoglucosan reaction. The increases in pressure, water and acetic acid concentrations could all accelerate levoglucosan conversion during bio-oil distillation, especially via hydrolysis reaction.
- Most of the levoglucosan could be converted into small molecules and distilled out during the high-pressure reactive distillation and would be mainly retained as the levoglucosan-derived products in the heavy residue during the atmospheric pressure distillation.
- The liquid distillate could be recirculated to intensify the hydrolysis of levoglucosan because of its high water and acetic acid concentrations.

7.1.3 Conversion of carbonyl compounds in bio-oil via catalysed reactive distillation at high pressure

- High pressure could affect the distribution of carbonyl compounds in the bio-oil to accelerate the reaction of light carbonyl compounds and inhibit the reaction of heavy carbonyl compounds due to the higher reactivity of the light carbonyl compounds.
- During the atmospheric pressure distillation, most of the light carbonyl compounds are distilled to the condensers and the heavy carbonyl compounds are retained in the liquid phase and converted into solid in the reactor. However, during the high-pressure distillation, both the light and heavy carbonyl compounds would be retained in the liquid phase, especially when pressure is higher than 20 barg.
- The acid can help catalyse the aldol condensation of carbonyl compounds and produce more carbonyl compounds by accelerating the hydrolysis of sugar compounds. The acid-catalysed reaction would not lead to the significant consumption of carbonyl compounds.
- The base (e.g. NaOH) could remove carbonyl compounds more effectively than the acid by acting as a catalyst to the aldol condensation reaction of the aldehydes and ketones and neutralising the carboxylic acids during the high-pressure reactive distillation.

7.1.4 Enrichment of aromatic compounds during the high-pressure reactive distillation of bio-oil

- High pressure could help transfer aromatic compounds into the paste distillate fraction from the heavy residue and liquid distillate fraction and reduce the polymerisation of the aromatic compounds.
- High temperature would cause the severe polymerisation of the aromatic compounds even though some aromatic monomers could be produced due to the enhanced hydrothermal reaction of sugar compounds and their derivatives when temperature is higher than 200 ^{o}C.

- Methanol could be used to inhibit the polymerisation of aromatic compounds during the high-pressure reactive distillation of bio-oil.
- $Ca(OH)_2$ could be used to intensify the transfer of aromatic compounds to paste distillate fraction by neutralising the carboxylic acids to decrease the interaction between the carboxylic acids and phenolic compounds.

7.2 Recommendations

This study mainly focused on the effects of the process parameters and bio-oil composition on the yield and properties of the distillate fractions during the high-pressure reactive distillation. High distillate yield and improved properties have been achieved by the high-pressure reactive distillation. Future work about the high-pressure reactive distillation operated in the continuous mode could be investigated based on the reaction and distribution behaviour of the components in the batch distillation. The reaction and separation behaviours of the bio-oil from other biomass sources could also be investigated. Based on the investigation of different bio-oils in both batch and continuous modes, the high-pressure reactive distillation at bench scale could be scaled up to industrial application. In addition, the paste distillate fraction that is featured with high organic compounds concentration and low water concentration could be further upgraded into valued-added fuels or chemicals, for example, through the hydrotreatment. Moreover, the high-pressure reactive distillation could be directly integrated with the hydrotreatment.

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High-pressure reactive distillation of bio-oil for reduced polymerisation

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Appendix II Co-author attribution statement

Chapter 3:

Paper "High-pressure reactive distillation of bio-oil for reduced polymerisation, Fuel Processing Technology, 211 (2021) 106590."

	Conception & design	Experiments conduction & data acquisition	Data processing & analysis	Interpretation & discussion	Manuscript writing, revision & finalisation	Final approval
Hongqi Wang	X	X	X	X	X	X
I acknowledge that these represent my contribution to the above result outp Signed						
Richard Gunawan					X	X
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Zhitao Wang	X				X	X
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Lei Zhang					X	X
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Yurong Liu					X	X
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Shuai Wang					X	X
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M.D. Mahmudul Hasan		X			X	X
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Chun-Zhu Li	X		X	X	X	X
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