

**Department of Chemical Engineering
Fuels and Energy Technology Institute**

Coke Formation during the Hydrotreatment of Bio-oil

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

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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

Biomass is a renewable and abundantly available feedstock for the production of a liquid transport fuel via pyrolysis resulting in bio-oil followed by hydrotreatment. Coke formation is the biggest challenge in hydrotreatment, which transforms the valuable organic components in bio-oil into coke and leads to catalyst deactivation.

In this study, the importance of active hydrogen in suppressing coke formation was shown. With added C₅-C₆ sugars (except levoglucosan), the coke formation was severe even in the presence of a catalyst. The absence of carbonyl group(s) in levoglucosan disabled it to contribute much to coke formation in the presence of a catalyst. In the absence of a catalyst, levoglucosan could be converted to glucose and would behave similar to glucose during hydrotreatment. C₆ sugars contributed more to coke formation than C₅ sugars as they could form the six-member ring structures, which have some structural similarities to highly aromatic coke. Carbonyl group(s) in the phenolics also made them very reactive towards coke formation. Without carbonyl group(s), the phenolics (e.g. guaiacol and isoeugenol) showed suppressive effects on coke formation by acting as a hydrogen shuttler.

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CHAPTER 1

INTRODUCTION

1.1 BIOMASS AS RENEWABLE RESOURCE OF ENERGY

The fast expansion of the world population causes huge increases in the worldwide energy demand in the last 50 years. Due to the fast depletion of fossil fuels [1] and the associated environmental problems, the development of new technologies for the production of liquid fuels and chemicals from renewable feedstock such as biomass is becoming increasingly more important [2].

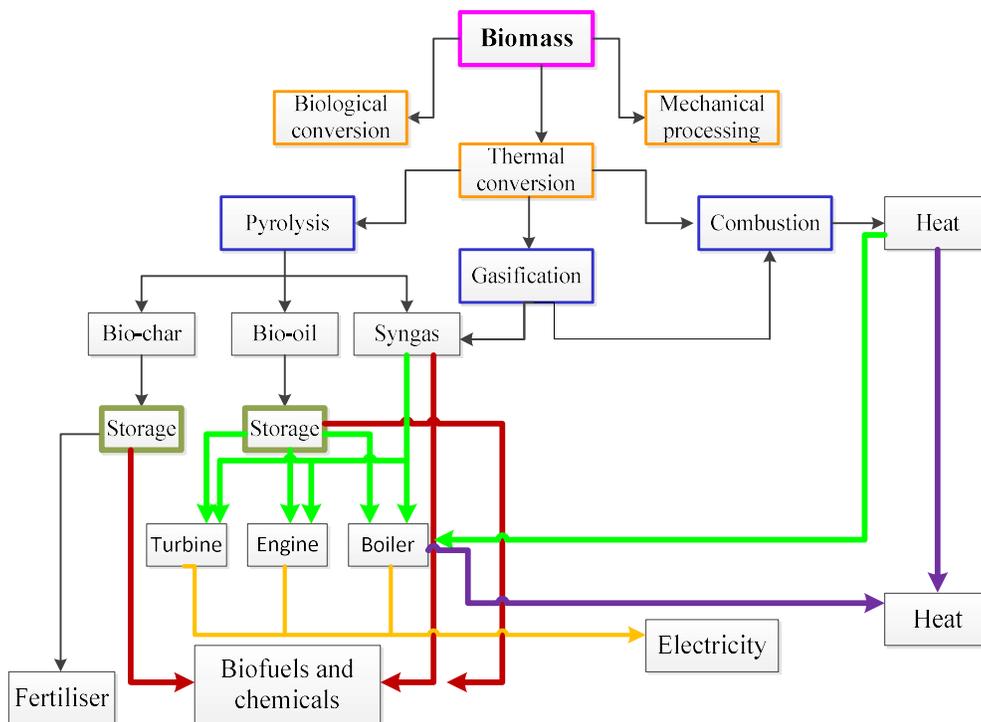


Figure 1-1. A schematic diagram of biomass utilisation to energy, fuels and chemicals [3].

Biomass is one of the most promising energy resources and the only renewable source of carbon. It is abundant and widely available [4]. Biomass has negligible contents of sulphur and nitrogen. It is considered as a clean energy source. Biomass-derived fuels can be carbon neutral [5-7]. Moreover, the use of biomass as an energy source does not have to compete

with food demand [8]. Biomass is thus a very promising energy source [8, 9] and the development of bioenergy industry can contribute to sustainability of development [10].

Biomass can be converted to energy, fuels and platform chemicals via a number of technologies [3], as is shown schematically in Figure 1-1. For example, biomass can be directly burnt to generate heat and electricity or be converted into liquid, gas and solid fuels via several processes such as gasification [1, 11, 12], fermentation [13, 14], bacterial digestion [15-18], liquefaction [19-22], and pyrolysis [3, 11, 23-25].

1.2 PYROLYSIS OF BIOMASS

Pyrolysis is a process of decomposition of (macromolecular) materials thermally at high temperatures in the absence or shortage of oxygen [3, 26, 27]. Pyrolysis is one of the most promising technologies in the conversion of biomass into advantageous products [28]. Pyrolysis of biomass produces gas, bio-oil and bio-char. The bio-oil can be directly used for the substitution of fuels in some applications such as stationary heaters and electricity generators or readily stored and transported for further application [24, 29].

The yields of bio-oil from the pyrolysis process is affected by ash yield and moisture content, reaction conditions (or mode of pyrolysis) and reactor types. In slow pyrolysis mode, a slow heating rate to ~400°C and a long vapour residence time (up to hours) are employed [11, 24, 30]. The slow heating rate favours the production of solid product, often called by bio-char (~35 wt%), and a comparable amount of liquid (~30 wt%) and gas (~35 wt%). A fast heating rate to ~500°C and a very short vapour residence time, normally at the orders of seconds or milliseconds to minimise the secondary reactions, are typically applied in fast pyrolysis [24, 25, 31]. A less homogeneous liquid would be produced from fast pyrolysis due to the short residence time as it would cause an incomplete decomposition of lignocellulosic

macromolecules [24]. The fast heating rate can result in a lower amount of bio-char (~12 wt%) and gas (~13 wt%), and a high yield of bio-oil up [3, 25, 29]. Other modes of pyrolysis process are also known, such as torrefaction and intermediate pyrolysis.

To achieve good product consistency and characteristics, as well as process efficiency, many aspects need to be considered in the pyrolysis of biomass. Reactor configuration, heat transfer, heat supply, feed preparation, process conditions (e.g. reaction temperature, vapour residence time) and post-reaction process (e.g. product recovery) [24] would have important effects on the product quality and process efficiency. Fluidised-bed and circulating fluidised-bed pyrolysis, ablative pyrolysis and vacuum pyrolysis have been developed to produce bio-oil from biomass. In (bubbling) fluidised-bed and circulating fluidised-bed pyrolysis, a carrier gas is used to fluidise the biomass particles. The rate of heating of biomass particles is the rate limiting step. Therefore, the small biomass particles (<2-3 mm) are needed to limit the heat transfer and achieve a high yield of bio-oil [3, 24].

In ablative pyrolysis, the mode of reaction is pressing the biomass particles over the heated surface. The heat is transferred from the hot reactor wall to the pressed biomass in contact. The molten layer of biomass then vaporises to produce a film of oil [24, 32]. This type of pyrolysis does not require a carrier gas. Even though the pyrolysis process is still limited by the heat transfer, the larger biomass particle sizes could be used. In vacuum pyrolysis, the pyrolysis process is performed under vacuum with slow heating rate. Therefore, the process is complex and costly due to high vacuum requirement. The liquid (bio-oil) yield is typically low (35-50 wt%) with higher char yield [3, 24].

A novel grinding pyrolysis technology has been developed by Li *et al.* [33] to overcome a number of problems with the existing pyrolysis technologies. In this technology, the pyrolysis and pulverisation of biomass take place simultaneously [34]. Therefore, biomass with big particle size (magnitudes of centimetres) can be effectively converted into

bio-oil, thus reduce the cost of the process. Furthermore, the need of little or no carrier gases significantly increases the energy efficiency of the process, reduces the process complexity and facilitates the condensation of bio-oil vapour to liquid bio-oil [34]. The bio-oil used in this study [the experiments carried out by (or in collaboration with) others at Fuels and Energy Technology Institute, Curtin University] was produced from the pyrolysis of mallee wood with the grinding pyrolyser.

The rapid heating of biomass feedstock during the pyrolysis at a temperature of 450-500 °C results in the formation of high yield of organics composed of fragments of lignin, hemi-cellulose and cellulose. The analysis by gel permeation chromatography (GPC) showed a high molecular weight of the condensed oil. More than 200 compounds in bio-oil have been identified including aldehydes, hydroxyl aldehydes, hydroxyl ketones, sugars, carboxylic acids and phenolics [35-38].

Bio-oil is the product from the fast quenching and condensing of degradation and dissociation fragments from hemicellulose, cellulose, lignin and other components in biomass. Bio-oil also can be considered as a micro-emulsion of aqueous solution (including the compounds soluble in it) and lignin macromolecules through mechanisms e.g. hydrogen bonding [39]. Bio-oil is a complex mixture of oxygenated compounds (70-75 wt%) and water (~25-30 wt%), which is not miscible with hydrocarbons and petroleum-derived fuels. These oxygen-containing compounds are usually co-condensed with the water that was originally in the biomass feedstock or produced from pyrolysis process as a by-product to form a single-phase oil. The high water content of bio-oil results in the low heating value (HHV) of ~16-18 MJ/kg [40] compared to fossil fuels (HHV ~45 MJ/kg) [3].

The oxygen-containing organics present in bio-oil promoted the aging and instability of bio-oil even at ambient temperature [41]. This phenomenon is caused by continuous and slow secondary reactions in the bio-oil, which result in an increase in bio-oil viscosity with time.

The properties of bio-oil will strongly vary depending on the type of biomass feedstocks and the pyrolysis process.

Despite the above-mentioned disadvantages, bio-oil does show many advantages including easier handling and transportation, higher energy density and more flexibility to be used than the biomass, as well as lower sulphur and nitrogen contents than fossil fuels [42]. Therefore, the technology development in order to make a good use of bio-oil as an energy and fuel resource is important.

1.3 HYDROTREATMENT OF BIO-OIL

Bio-oil produced from the fast pyrolysis of biomass has potential to substitute the non-renewable fossil-based fuels. The bio-oil can be used in many ways [29]. Bio-oil could be directly used as a fuel in boilers and/or turbines [43]. However, the direct use of bio-oil as transport fuels is troublesome. Bio-oil is immiscible with fossil fuels due to the high oxygen content. It is critical to deoxygenate bio-oil to some extent to make it compatible with current fuels and chemical manufacturing infrastructure. Therefore, the upgrading of bio-oil to improve its quality for various applications is crucial. The technologies for upgrading bio-oil includes catalytic hydrodeoxygenation [44-50], upgrading using supercritical alcohols [51-55], zeolite conversions of bio-oil [56, 57] and emulsification [3].

Hydrotreatment is considered to be the most promising technology in bio-oil upgrading. By this way, bio-oil can be converted to gasoline- or diesel-like fuels by hydroprocessing using a hydrotreating catalyst commonly used in petroleum refineries such as CoMo and NiMo supported on alumina [42, 58]. This one-step hydrotreating process was found to be severely coked-up [22] even in the early stage of the process. The two-stage hydrotreating process was then developed [59, 60], consisting of the first stage using noble metal catalysts

such as Ru/C or Pd/C and the temperature of 150-280 °C to stabilise the bio-oil and prevent the excessive coke formation [61]. The partially hydrotreated bio-oil is then processed at the second stage under more severe condition, e.g. (350-450 °C) and high hydrogen pressure (typically 100-200 bar), where a deep deoxygenation could be achieved [62]. In the second stage of the hydrotreatment, the severe condition would allow the elimination of phenolic and furanic compounds, as well as the conversion of heavy molecules. This condition also would enable the total oxygen elimination and high grade hydrocarbon recovery comparable to those obtained from fossil fuel [43]. The main problem of this two-stage process is the high hydrogen consumption (> 800 L/kg feed) to hydrogenate the adjacent aromatic rings [43]. Furthermore, coke formation could not be avoided in this two-stage hydrotreatment and the success for resolving the coke formation problem has not been reported yet. Therefore, an effective hydrotreatment process with lower hydrogen consumption needs to be developed.

Hydrotreatment of the real bio-oil has been studied in the last 30 years. Different reaction parameters, reactor configuration and catalysts have been investigated to achieve efficient processes to produce gasoline- or diesel-like fuels. The commercial hydrotreating catalysts (e.g. presulphided NiMo and CoMo supported on alumina) [49, 63-65], non-noble synthesised catalysts (e.g. Ni-Cu [46]) and noble metal catalyst (e.g. Ru/C and Pd/C) [50, 66, 67] have been used in the hydrotreatment of the real bio-oil. However, the use of easy-regenerated catalyst is favourable for the sustainability of the process in addition to minimise the production cost. Therefore, the use of the commercial hydrotreating catalysts in the hydrotreatment of bio-oil is preferable to maintain the process efficiency and lower the production cost.

The high severity of the hydrotreatment process (high hydrogen pressure and high temperature) is also a challenge in the technology development of hydrotreatment. A hydrotreatment process under a mild condition would be preferred in order to stabilise the

reactive compounds in bio-oil as well as partially deoxygenate it for further treatment. A low-severity (mild) hydrotreatment would not produce fuels with very low oxygen content but this process would provide significant information on the bio-oil behaviour during the hydrotreatment of bio-oil. This process increases the stability of bio-oil by eliminating the reactive functional groups, partially deoxygenates the bio-oil [62]. Furthermore, such process would allow understanding the behaviour of major components in bio-oil (e.g. phenolics or sugar oligomers) during hydrotreatment. Therefore, the hydrotreatment of bio-oil using the commercial non-noble hydrotreating catalysts at low-severity condition is useful to gain insight into the hydrotreatment reactions, especially the contribution of those components to some reactions, e.g. coke formation.

1.4 COKE FORMATION DURING THE HYDROTREATMENT OF BIO-OIL

Bio-oil produced from the pyrolysis of biomass is a complex mixture of organic compounds with a wide range of molecular weights and functionalities [24, 28, 29, 68, 69]. The oxygen-containing functionalities are largely responsible for the properties of bio-oil produced. The reactive oxygen-containing compounds can easily undergo polymerisation during storage [41] and consequently change its physical properties e.g. increase in viscosity. Polymerisation could also take place during the hydrotreatment even under mild conditions [45, 70, 71], leading to coke formation that ultimately causes the catalyst deactivation [50, 72].

Coke formation is one major problem that almost cannot be avoided in the hydrotreatment of bio-oil. Coke formed during hydrotreatment could cause the blockage of reactor system and would immediately stop the process [60, 73, 74]. Therefore, coke formation is one of the biggest challenges in the hydrotreatment of bio-oil. Due to the

complexity of bio-oil constituent, extensive research have been done on individual or mixtures of model compounds [19, 43, 75-95]. Furthermore, the contribution of each class of compounds (e.g. sugars, phenolics, or other classes of compounds) to coke formation during the hydrotreatment has been investigated [87, 92, 96-100]. However, the knowledge about the behaviour of single model compound or mixtures of model compounds during the hydrotreatment as well as their contribution to coke formation cannot be used to predict the behaviour of bio-oil on coke formation during the hydrotreatment of real bio-oil due to the complex interactions between model compounds and other bio-oil components.

Bio-oil consists of widely distributed compounds with different structure and various oxygen-containing functionalities. Due to its complexity, and thus the interactions among the bio-oil components, understanding the behaviour of the components in the bio-oil is troublesome. The studies on the hydrotreatment of bio-oil fractions or bio-oil with the modified composition could provide a better understanding on the contribution of those fractions (with a certain composition) to the coke formation. These compounds with different structures in the bio-oil would behave differently in the hydrotreatment reactions and contribute to coke formation to different extents. Due to their susceptibility towards coke formation, sugar-derived fraction [77] as well as compounds with oxygen-containing functionalities [87, 88] in bio-oil are important bio-oil components in studying the behaviour of the major components of bio-oil during hydrotreatment. However, insufficient information is available to understand the contribution of each to the coke formation during the hydrotreatment of bio-oil [77, 87]. Therefore, understanding the contribution of different compound(s) to the formation of coke during the hydrotreatment of real bio-oil is crucial to minimise the formation of coke.

1.5 PURPOSES OF THIS STUDY

This study aims to investigate the coke formation of bio-oil during hydrotreatment. The bio-oil from mallee woody biomass and commercial hydrotreating catalysts were used in the hydrotreatment experiments. The effects of adding model compounds with different functionalities and types on coke formation during the hydrotreatment of bio-oil were investigated. The transformation of light compounds and aromatic ring structures was investigated to gain a good understanding on the contribution of each individual compound to coke formation.

1.6 SCOPE OF THESIS

The schematic diagram in Figure 1-2 summarises the scope of this thesis as a flowing and integrated story. This thesis will mainly consist of the followings:

Chapter 2 will describe the experimental aspects and methods used in this study. The details will be further described in each chapter.

Chapter 3-5 will describe the results and discussion. Each of these chapters will contain specific introduction and literature review closely related to the topic of the chapter.

Chapter 3 will describe the effects of temperature and levoglucosan concentration on the polymerisation and coke formation during the hydrotreatment of mallee bio-oil.

Chapter 4 will describe the effects of C₅ and C₆ sugars on the coke formation during the hydrotreatment of bio-oil using a commercial pre-sulphided NiMo catalyst.

Chapter 5 will describe the beneficial effects of oxygen-containing functionalities in the phenolic compounds in the bio-oil feedstock in reducing the formation of coke during the hydrotreatment of bio-oil

Chapter 6 will summarise the important findings of this work and recommendations for the future work.

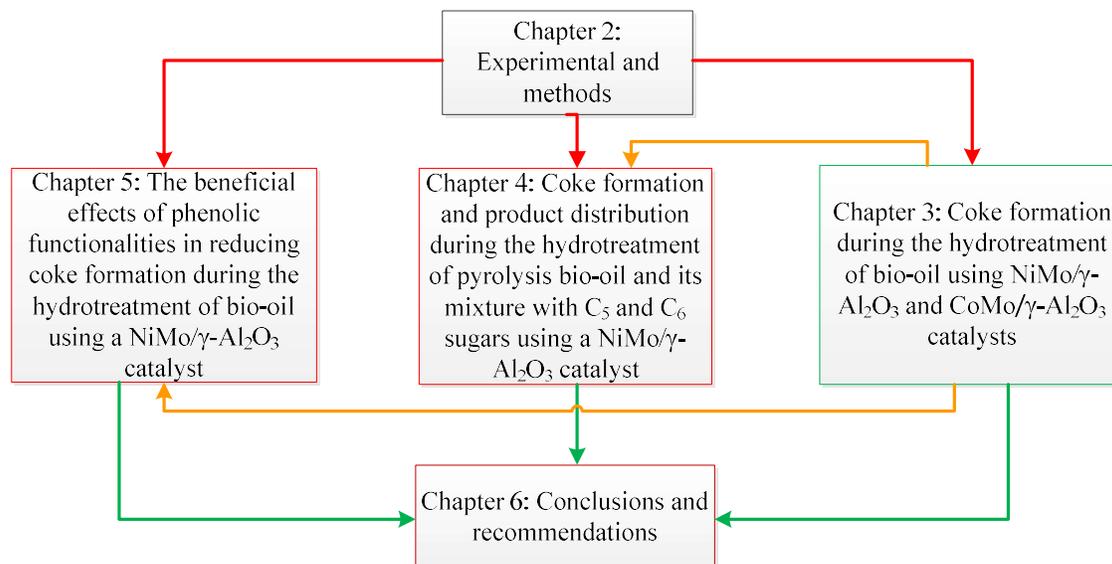


Figure 1-2. A schematic diagram of the scope of this thesis.

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CHAPTER 2

EXPERIMENTAL AND METHODS

2.1 INTRODUCTION

This chapter includes the details of the preparation of bio-oil and catalysts, reactor used in the hydrotreatment experiments and brief procedures of the experiments. The analysis methods of hydrotreatment products including gaseous, liquid, and solid products are also explained in details in this chapter.

2.2 BIO-OIL PREPARATION

The bio-oil from mallee wood was produced by Dr. MD Mahmudul Hasan (Fuels and Energy Institute, Curtin University) using a grinding pyrolyser (up to 20 kg/h in capacity) at 450-465 °C and a constant reactor rotation speed of 54 rpm. Two condensers were used. The first condenser used water for cooling down the vapour from 450 °C to ~40 °C, while the second condenser used dry ice for cooling the vapour that had passed through the water cooling bath to about -75 °C. The bio-oil collected from those two condensers was mixed and filtered with two layers of Whatman filter paper (grade 4). The details of the bio-oil production from mallee wood were explained elsewhere [1, 2]. A single phase bio-oil was obtained and the bio-oil was stored in a fridge at a temperature of -10°C for further use. The characteristics of the produced bio-oil are presented in Table 2-1.

Table 2-1.

Properties of bio-oil produced from mallee wood with a grinding pyrolyser at 450 °C and 54 rpm [2].

Property	Typical value*
Water content (wt%, bio-oil basis)	31.6
Density (kg/dm ³)	1.15
Elemental composition (wt%)	
C	52.5
H	7.5
O	40.3
HHV as produced (MJ/kg)	15.8
Chemical composition (wt%, dry biomass basis)	
Levoglucosan	3.1
Guaiacol	0.1
Methoxy eugenol	0.03

*The data are extracted from Hasan [2].

2.3 PREPARATION OF THE CATALYSTS

The catalysts used in this study, pre-sulphided NiMo and pre-sulphided CoMo supported on γ -Al₂O₃, are commercial hydrotreating catalysts. The pre-sulphided NiMo and CoMo catalysts (purchased from EureCat, France) are hereafter called as the NiMo and CoMo catalysts. The NiMo catalyst has a Ni and Mo metal loading of 3 wt% and 12 wt%, respectively, with a BET surface area of 160-170 m²/g. Whereas, the metal loading of Co and Mo in the CoMo catalyst is 4 wt% and 14 wt%, respectively, with a BET surface area of 170-180 m²/g. They were ground and sieved to obtain the particle size of 250-600 μ m. There was no pre-treatment needed prior to its use in the hydrotreatment experiments.

2.4 HYDROTREATMENT EXPERIMENTS

The hydrotreatment of mallee bio-oil was conducted (at Fuels and Energy Technology Institute, Curtin University) typically at 150-300°C with a total pressure of ≥ 100 bar and a stirring rate of 400 rpm. A stirring rate > 300 rpm did not show a heat transfer limitation as reported in our previous work [3]. The schematic of batch reactor system used in the hydrotreatment experiments is shown in Figure 2-2. The batch autoclave reactor is equipped with a universal reactor controller (labelled as URC in Figure 2-1) and a thermocouple immersed into the reactor to allow the measurement of the process temperature. The reaction mixture was continuously mixed during the experiments using a magnetic stirrer provided with the autoclave reactor to minimise heat and mass transfer limitation. The inlet of the reactor was connected to a hydrogen cylinder to supply the hydrogen for hydrotreatment reaction. The details of the procedure were similar to those specified in our previous work [4].

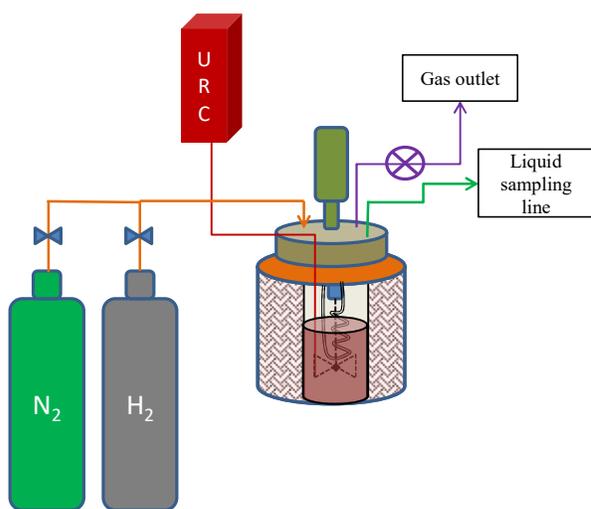


Figure 2-1. The schematic diagram of the batch reactor system used in the hydrotreatment experiments.

Typically, in each experiment, 40 g of bio-oil was introduced together with 4 g of the catalyst (pre-sulphided NiMo or CoMo supported on alumina) and 1.5 g of zinc oxide (to prevent the corrosion of the reactor vessel due to the possible release of H₂S gas formed from the pre-sulphided catalysts during the experiment). In a typical experiment investigating the effects of model compounds, 5 or 10 g of model compound was added in the reaction mixture. Non-catalytic experiments were also performed for comparison by feeding bio-oil and hydrogen in the absence of a catalyst. The initial hydrogen pressure was 50 bar at room temperature. When reaction starts (at pre-set temperature), the pressure of the system was maintained at minimum 100 bar. More hydrogen was added periodically during the experiments to maintain the total pressure in the reactor at the minimum 100 bar. The holding time of the experiments with mallee bio-oil was 3 h for all experiments. After experiment, the hydrotreatment products including gaseous products, liquids (oil phase and aqueous phases) and solids were recovered for further analysis.

2.5 CHARACTERISATION OF HYDROTREATMENT PRODUCTS

2.5.1 Gas chromatography (GC)

The gas sample was collected in a gas bag after reactor was cooled down to room temperature. The residual pressure at room temperature after each experiment was recorded to determine the yield of each gas and calculate the total gas yields. The gaseous products after each hydrotreatment experiment were analysed by using a gas chromatograph (GC, Agilent 6890) equipped with flame ionisation detector and methaniser to allow the identification of CO₂, CO and hydrocarbon gases as the hydrides. For gas analysis, the oven in the GC instrument was set at 40 °C and held for 4 min. It was then ramped up to 180 °C with a rate of

40 °C/min and held for 2 min. The temperature of the oven was then brought to 80 °C with a rate of 100 °C/min and held at 80 °C for 6.5 min. The standard gases were injected prior to an analysis to have reproducible response factors for the quantification of the gases. The example of the calibration curve for methane is presented in Figure 2-2. The yields of gaseous products were expressed on a basis of per gram of organics in the feedstocks (bio-oil plus added model compound, if any).

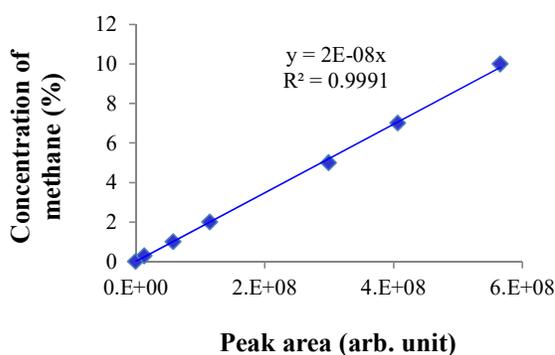


Figure 2-2. The standard curve for methane in the GC analysis.

2.5.2 UV-fluorescence spectroscopy

The aromatic structural features of the hydrotreated products were analysed using a Perkin-Elmer LS50B UV-fluorescence spectrometer. Due to the negligible fluorescence intensity of the aqueous phase of the hydrotreated products, the synchronous spectra shown in this study are the spectra of the bio-oil feedstock and the corresponding produced oil phases. The samples were diluted in methanol (Uvasol for spectroscopy, purity >99.9%) to a concentration of 4 ppm to avoid the self-absorption effect [5, 6]. This concentration was in the linear range of the relationship between the concentration of the samples in methanol and the fluorescence intensity, as is shown in Figure 2-3. The synchronous spectra presented are the average of four scans which were recorded with a constant energy difference of -2800 cm^{-1} ,

slit widths of 2.5 nm and a scan speed of 200 nm min⁻¹. The relative concentration of aromatic ring systems in the samples was reflected by the intensity of peaks at a certain wavelength range. The big aromatics (multiple fused benzene rings) have a centre at a wavelength of 380-390 nm [5]. The synchronous spectra were expressed on a moisture free basis per gram organics in the bio-oil feedstocks to allow for a fair comparison by multiplying the measured intensity from the spectrometer with the yield of the organics in the oil phase on a moisture free basis.

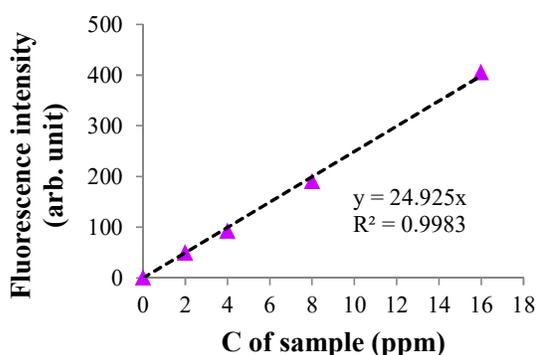


Figure 2-3. The relationship between the concentration of the samples and the fluorescence intensity in the analysis using UV-fluorescence spectroscopy.

2.5.3 Gas chromatography-mass spectroscopy (GC-MS)

The GC-MS analysis of the bio-oil feedstock and the liquid hydrotreatment products was performed using an Agilent 5973 MSD attached to an Agilent 6890 GC, equipped with a 30 m × 0.25 mm × 0.25 μm HP-Innowax (cross-linked polyethylene glycol) column. 1 μL of acetone containing 5-10 wt% (accurately known) of sample was injected into the injection port set at 250 °C. A split ratio of 50:1 was used in the analysis. The parameters used in the GC-MS analysis in this study were similar to those in our previous work [4, 7, 8]. The oven temperature was kept at 40 °C for 3 min then increased to 260 °C at a rate of 10 °C/min. The oven was then

held at 260 °C for 5 min. Identification of compounds was based on NIST library software and also the injection of the standard solutions. For quantifying the compounds in the bio-oil feedstocks and the corresponding hydrotreatment products, standard solutions (including water standards) were analysed to obtain reproducible response factors. The example of the standard curve used for water quantification using the GC-MS is presented in Figure 2-4.

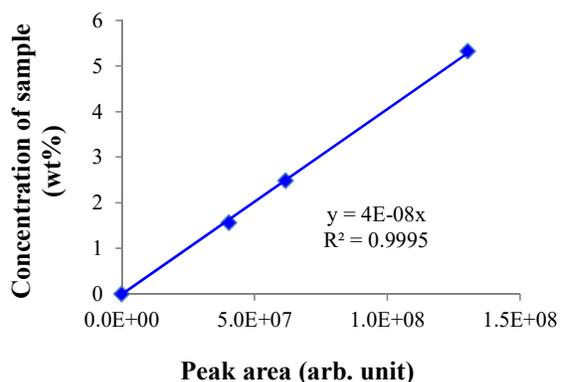


Figure 2-4. The standard curve of water sample in the GC-MS analysis.

2.5.4 Thermogravimetric analysis (TGA)

The TGA experiments were carried out using a TGA-Q5000 and SDT Q600 in nitrogen atmosphere. The TGA instruments were calibrated for the weight and temperature. These two instruments were used based on their availability and there was no significant difference of the results measured by the two TGA instruments. 5-10 mg (accurately known) sample was heated from room temperature up to 500 °C in nitrogen atmosphere with a ramping rate of 10 °C/min. The residue left behind at 500 °C is defined as the potential coke yields. The example of the TGA curve for bio-oil itself is presented in Figure 2-5.

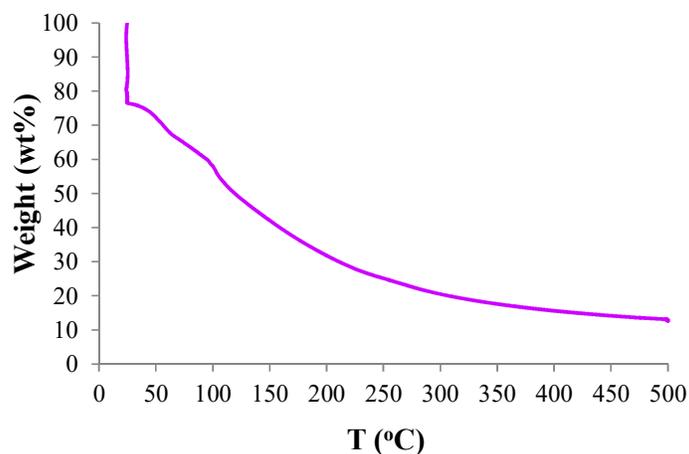


Figure 2-5. The TGA curve of the raw bio-oil heated at 25-500 °C in nitrogen atmosphere.

2.5.5 Elemental analysis

Elemental composition (C, H, N and S) of the hydrotreated oils was determined with a Flash 2000 Interscience elemental analyser. The elemental analysis of the hydrotreated oils presented in this study (Chapter 3) was done by Dr. Ferran de Miguel Mercader (Scion, New Zealand). The oxygen content was determined by difference. The content of elements in the hydrotreated oils was expressed on a moisture free basis.

The elemental composition of the solids was determined at Fuels and Energy Technology Institute, Curtin University. It was determined by a Thermo-Fischer Flash 2000 equipped with a thermal conductivity detector. The elemental analyser was calibrated with 2,5-(Bis(5-tert-butyl-2-benzo-oxazol-2-yl) thiophene (BBOT) each time prior to an analysis. Ultra-high purity oxygen (purchased from BOC) was used in the process. 2-3 mg (accurately known) of the solid samples was encapsulated in a tin capsule and carefully folded. The sample was then put in the sample chamber of the elemental analyser for analysis. The oven was set at 950 °C to allow a complete oxidation during burning. Once the sample was dropped into the reactor, it would be converted to gases. The gases produced would be separated in a GC column and detected based

on their thermal conductivity. The measured elemental contents were then corrected from the ash yield and the moisture content. The content of elements was calculated on the basis of the weight of the coke on a moisture and ash free basis. The oxygen content was calculated by difference.

2.5.6 FT-Raman spectroscopy

To investigate the changes in the coke structural features during the hydrotreatment of the bio-oil feedstocks, the solids recovered after the hydrotreatment experiments were analysed using FT-Raman spectrometer. In this study, a Perkin-Elmer Spectrum GX FT-IR/Raman spectrometer equipped with a Nd:YAG laser at 1064 nm as its light source was used to record the Raman spectra. To avoid the sample degradation during analysis under laser irradiation [9], the solid samples were diluted with spectroscopic grade KBr to a concentration of 1 wt%. This concentration reached a plateau in the relationship between the concentration of the sample and the total Raman area from the deconvoluted spectra at a wavenumber range of 800-1800 cm^{-1} , as is presented in Figure 2-6. A InGaAs detector was used at room temperature and a laser power of 100 mW was selected. Each spectrum represents 400 scans with a spectral resolution of 4 cm^{-1} . The Raman spectra were deconvoluted into 10 Gaussian bands using a GRAM/32AI version 6.0 provided with the Perkin-Elmer instrument as discussed in details elsewhere [10]. The example of the deconvolution of the Raman spectra into 10 bands is presented in Figure 2-7. The assignment of the deconvoluted bands is presented in Chapter 3 of this thesis.

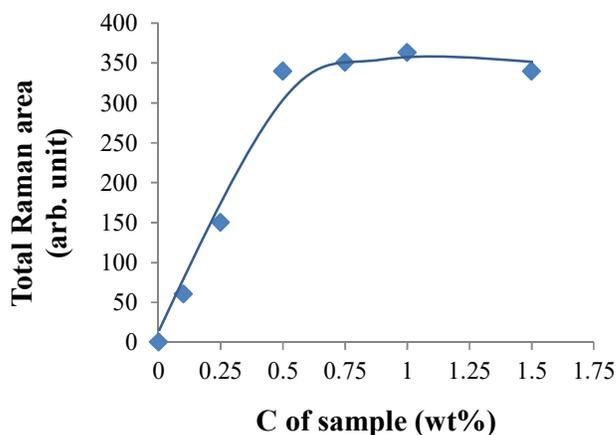


Figure 2-6. The relationship between the concentration of the sample and the total Raman area of the deconvoluted spectra at a wavenumber of 800-1800 cm^{-1} .

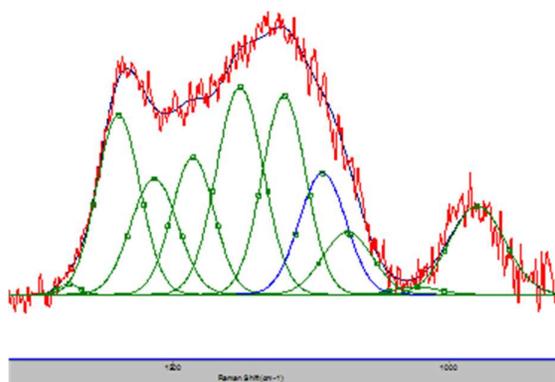


Figure 2-7. The example of the deconvoluted Raman spectrum for “NiMo-BO” after heating in nitrogen at 600 °C. “NiMo-BO” represents the coke from the catalytic hydrotreatment of bio-oil alone at 300 °C.

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CHAPTER 3

COKE FORMATION DURING THE HYDROTREATMENT OF BIO-OIL USING NiMo/ γ -Al₂O₃ AND CoMo/ γ -Al₂O₃ CATALYSTS

3.1 INTRODUCTION

Pyrolysis of biomass is a promising method to produce bio-oil that is easier to store and transport than the bulky solid biomass. However, upgrading is required before the bio-oil can be used as a transport fuel due to its adverse properties such as high acidity, high water content and high instability. Hydrotreatment has been shown to be a promising method to overcome these problems [1-3]. However, when bio-oil is heated up, many compounds become very reactive and tend to form coke [4-6]. This leads typically to reactor fouling and product deterioration. An additional stabilisation step has been suggested to suppress or prevent the coke formation by stabilising bio-oil [7, 8]. In such approach, bio-oil is first stabilised by using a noble metal catalyst prior to full deoxygenation of the oil in a second stage with conventional commercial catalysts [8] such as sulphided NiMo/ γ -Al₂O₃ or CoMo/ γ -Al₂O₃ catalyst (referred hereafter as CoMo and NiMo catalysts). The use of noble catalysts would greatly increase the overall costs of biofuel production. Furthermore, coke formation is still a problem even when the noble catalysts are used to stabilise the bio-oil [9, 10].

Coke formation is a complicated process. During the hydrotreatment, a break-down of the chemical bonds in the bio-oil is first required. The breakage of these chemical bonds would generate radicals. The radicals may further break down or be hydrogenated to form stable molecules, or re-combine to form larger molecules towards coke [11]. Herein, active hydrogen plays an essential role in suppressing coke formation [11, 12]. The active hydrogen would react with and terminate those radicals. Otherwise, significant amounts of coke could form during the hydrotreatment at elevated temperature due to the lack active hydrogen supply, which cannot match the demand of the broken bonds [11-15].

Catalysts play an important role in providing adequate hydrogen supply in a catalytic reaction [9, 11, 12]. Although the commercial CoMo and NiMo catalysts are commonly used

at high temperatures of typically >350 °C, they might still be sufficiently active in providing active hydrogen at lower temperatures. However, little information is currently available about the coke formation at low temperature using non-noble catalysts such as NiMo and CoMo catalysts. The knowledge about coke formation at low temperature during bio-oil heating up is essential. Therefore, this study aims to gain insights into the coke formation during the hydrotreatment of bio-oil at low temperature using NiMo and CoMo catalysts.

Bio-oil has an exceedingly complex composition, having thousands of compounds. Various catalysts including NiMo, CoMo and noble metal catalysts have been used in the hydrotreatment of model compounds such as furfural and acetic acid [16], various phenolic compounds [17-19] including guaiacols [19, 20], ketones and carboxylic compounds [17, 19] and carbohydrate fraction [21] to understand their hydrotreatment behaviour. Special attention has been given to sugars and its model compounds [4, 21]. These sugars have the tendency to react towards coke formation when heated [4, 22]. Due to their high concentration in bio-oil, they are an important fraction determining the tendency of bio-oil towards coke formation. It is important to understand how the sugars in bio-oil contribute to the coke formation.

This chapter presents the effects of the NiMo and CoMo catalysts on the coke formation during the hydrotreatment of bio-oil under mild conditions (150 - 300 °C and ≤ 100 bar hydrogen pressure). Since levoglucosan is always found in high concentrations in bio-oil, its role in the coke formation has been studied. Blank experiments were also performed in order to get the information on the catalyst activity and the importance of the non-catalytic thermal reactions.

3.2 EXPERIMENTAL

3.2.1 Materials

The bio-oil used as the feedstock in the hydrotreatment experiments was produced from the pyrolysis of mallee wood in a grinding pyrolyser operated at 450 °C [23]. The details of the pyrolysis procedures can be found elsewhere [23]. The commercial hydrotreating catalysts, pre-sulphided NiMo and CoMo catalysts (containing 3-4 wt% of Ni or Co and 12-16 wt% of Mo) were purchased from EureCat. They were ground to 250-600 µm before use. The chemicals used as standards in the GC-MS analyses were obtained from Sigma-Aldrich. Hydrogen and nitrogen (high purity grade, 99.99%) were obtained from BOC.

3.2.2 Experimental procedures

The catalytic hydrotreatment experiments were performed in a batch autoclave reactor system as described in our previous work [9]. Briefly, in each experiment, 4.0 g of NiMo or CoMo catalyst, 1.5 g of zinc oxide (to prevent the corrosion of the batch reactor by H₂S gas possibly formed from the pre-sulphided catalysts) and raw bio-oil (40.0 g) were introduced into the reactor. For comparison, blank experiments (feeding bio-oil and hydrogen but without a catalyst) were conducted. For some experiments, levoglucosan was added to the bio-oil so that the final concentration of levoglucosan in the bio-oil was 21.5 wt% (called NiMo-LGA) or 31.6 wt% (called NiMo-LGB). It was observed that this amount of levoglucosan is soluble in bio-oil. The reactor was flushed with N₂ prior to the experiment and was subsequently pressurised with H₂ (100 bar) at room temperature to check for possible leakage. The reactor was then pressurised with hydrogen (50 bar) at room temperature and heated to the desired

reaction temperature (150–300 °C) under continuous agitation at a stirring rate of 400 rpm. After the system reached the desired temperature, the total pressure was kept constant at 100 bar by feeding additional hydrogen when needed. An exception is the experiments at 300 °C in which the pressure was 120 bar.

After the pre-set reaction time (3 h), the reactor was rapidly cooled to room temperature by cooling water running through a coil in the reactor. The produced gases were quantified by a gas chromatograph (GC, Agilent 6890) equipped with a methaniser and a flame ionisation detector. The residual pressure was recorded from which, together with the gas composition, the gas yields and hydrogen consumption could be determined.

After an experiment, the products (oil and aqueous phases) and the solids (catalyst, zinc oxide and coke) were separated and collected. The aqueous phase was on the top, while the oil phase was in the middle, and the solids were at the bottom of the reactor. Firstly, the aqueous phase and the oil phase were taken out. The reactor was then rinsed thoroughly using tetrahydrofuran (THF). The THF mixture of solids and remaining oil was then filtered and weighed. Knowing the weight of the filtrate and the concentration of THF (determined using GC-MS), extra oil yield could be added to the already collected oil phase. The amount of solids (filter residue) subtracted by the total weight of the catalyst and ZnO loaded into the reactor was defined as the amount of coke (solids) formed during hydrotreatment. The water content of the oil and aqueous phase was determined using GC-MS. The total water produced was determined by the difference between the water in the hydrotreated products (oil and aqueous phases) and that in bio-oil. The mass balance was then expressed on a moisture free basis (per gram of bio-oil).

3.2.3 Analyses

3.2.3.1 *Gas chromatography-mass spectroscopy (GC-MS)*

The GC–MS analyses of the liquid products were performed using an Agilent 5973 MSD attached to an Agilent 6890 GC, equipped with a 30 m × 0.25 mm × 0.25 μm HP-Innowax (cross-linked polyethylene glycol) column. The parameters were similar to those specified in our previous work [24-26]. Briefly, 1 μL of acetone solutions containing 5-10 wt% (accurately known) of sample was injected into the injection port set at 250 °C. A split ratio of 50:1 was used in the analysis. The temperature of the oven was 40 °C at the initial stage of analysis and kept isothermal for 3 min. The oven temperature was then ramped up to 260 °C at a rate of 10 °C/min and then held at that temperature for 5 min. Identification of compounds was based on the NIST library as well as the injection of standard solutions. For quantifying the compounds in bio-oil and hydrotreatment products, standard solutions (including water standards) were analysed to obtain reproducible response factors.

3.2.3.2 *UV-fluorescence spectroscopy*

In this study, the synchronous UV-fluorescence spectra of hydrotreated oil and the bio-oil feedstock were recorded using a Perkin-Elmer LS50B spectrometer [9, 27]. The solution of oil phase was diluted with methanol (Uvasol for spectroscopy; purity ≥ 99.9%) to 4 ppm. The synchronous spectra were recorded with a constant energy difference of -2800 cm⁻¹. The slit widths were 2.5 nm and the scan speed was 200 nm min⁻¹. At the same concentration, the fluorescence intensity was multiplied by the yield of organics in the oil phase on a moisture free basis to express the fluorescence intensity on the basis of per gram of organics in bio-oil.

3.2.3.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of bio-oil and hydrotreated oils was performed by using a SDT Q600 instrument over the temperature range of 25-500 °C at a heating rate of 10 °C/min in nitrogen (flow rate of 50 mL/min). In each run, 5-10 mg (accurately known) of sample was loaded into a crucible in the TGA instrument. The residue left behind after the experiment was referred as the “potential coke” following our previous work [9].

3.2.3.4 Elemental analysis

Elemental composition of C, H, and N was measured by using a Flash 2000 Interscience elemental analyser and oxygen content was calculated by difference. The elemental composition of bio-oil and the hydrotreated oils presented in this chapter was expressed on a moisture free basis by excluding the water concentration in the hydrotreatment products [28]. The analysis was done in collaboration with Scion, New Zealand.

The elemental composition of the non-catalytic coke from the hydrotreatment of bio-oil and the bio-oil with added levoglucosan in the absence of a NiMo catalyst was done at Fuels and Energy Technology Institute, Curtin University. A Thermo-Fischer Flash 2000 equipped with a thermal conductivity detector was used in the analysis. A 2-3 mg (accurately known) of the solid samples was used in each analysis and was encapsulated in a tin capsule before introducing in a pre-heated sample chamber set at 950 °C. The gases produced from the burning process would be separated in a GC column and detected by a thermal conductivity detector. The elemental composition was expressed on an ash and moisture free basis. The oxygen content was calculated by difference.

3.2.3.5 *FT-Raman spectroscopy*

Raman spectra of the spent catalysts and/or coke obtained from the hydrotreatment experiments were recorded at room temperature using a Perkin–Elmer Spectrum GX FT–IR/Raman spectrometer with a back-scattered configuration. A Nd:YAG laser at 1064 nm was used as the light source. A laser power of 100 mW was selected. An InGaAs detector was used. To reduce the heat up of the sample, the solid samples were mixed and ground with spectroscopic grade potassium bromide (KBr, purchased from Sigma-Aldrich). The concentration of 1 wt% has reached the plateau in the relationship between Raman area and the concentration of the sample. The well ground KBr-solid mixture was then loaded (hand pressed) into the sample cell to record a Raman spectrum. Each spectrum presented in this study was the average of 400 scans with a spectral resolution of 4 cm^{-1} . After the raw spectrum has been baseline corrected by an interactive method provided with the Perkin–Elmer instrument software, it was then curve-fitted with 10 Gaussian bands using the GRAMS/32 AI software (version 6.0). The integrated peak area between 800 and 1800 cm^{-1} is used as a measure of the Raman total intensity. The band assignments of deconvoluted spectra [29, 30] are listed in Table 3-1.

Table 3-1.

Summary of Raman peak/band assignment [30].

Band Position (cm ⁻¹)	Band Name	Description	Bond Type
1700	G ₁	Carbonyl group C=O	sp ²
1590	G	Graphite E_{2g}^2 ; aromatic ring quadrant breathing; alkene C=C	sp ²
1540	G _r	Aromatics with 3-5 rings; amorphous carbon structures	sp ²
1465	V ₁	Methylene or methyl; semicircle breathing of aromatic rings; amorphous carbon structures	sp ² , sp ³
1380	V _r	Methyl group; semicircle breathing of aromatic rings; amorphous carbon structures	sp ² , sp ³
1300	D	D band on highly ordered carbonaceous materials; C–C between aromatic rings and aromatics with not less than 6 rings	sp ²
1230	S ₁	Aryl–alkyl ether; para-aromatics	sp ² , sp ³
1185	S	C _{aryl} –C _{alkyl} ; aromatic (aliphatic) ethers; C–C on hydroaromatic rings; hexagonal diamond carbon sp ³ ; C–H on aromatic rings	sp ² , sp ³
1060	S _r	C–H on aromatic rings; benzene (ortho-di-substituted) ring	sp ²
960-800	R	C–C on alkanes and cyclic alkanes; C–H on aromatic rings	sp ² , sp ³

3.3 RESULTS AND DISCUSSION

3.3.1 The activity of pre-sulphided NiMo and CoMo catalysts

3.3.1.1 *Yields of the oil and aqueous phases, gas and coke*

The activity of pre-sulphided NiMo and CoMo catalysts was examined in the hydrotreatment of bio-oil under the mild conditions (temperatures of 150-300 °C and ≤ 100 bar initial hydrogen pressure) at a constant holding time of 3 h. The mass balance closure of the experiments performed was always above 90 wt%. Yields are reported on a moisture free basis (g organic product per phase/g organics in bio-oil). To check the reproducibility, experiments under identical conditions were repeated and the results are summarised in Table 3-2. The hydrotreatment products consisted of an oil phase, a water-rich (aqueous) phase, a solid residue (coke) and gas. The trends for the hydrotreatment using NiMo and CoMo catalysts are quite similar except the higher coke yields for CoMo and correspondingly lower oil yields at lower temperatures (150-200 °C). Figure 3-1 shows that the organic yields in both oil and aqueous phases decreased with increasing temperature. The decreases in the organics yields in both phases can be explained by the removal of oxygen via the water formation and by the production of CO and CO₂. The decrease in organics in the aqueous phase can also be partly due to the phase transfer from the polar aqueous phase into the less polar oil phase when oxygen was removed.

Table 3-2.

Reproducibility of mild hydrotreatment experiments at 100 bar total pressure and 3-h reaction time.

T (°C)	Catalyst		Yields (wt%, moisture free basis)				
			Gas	Coke	Organics in oil phase	Organics in aqueous phase	Produced water
150	CoMo	(1)	0.8	8.9	59.5	25.7	1.0
		(2)	0.7	10.2	57.4	26.4	0.5
250	NiMo	(1)	2.4	5.7	65.1	18.0	5.3
		(2)	2.4	5.9	64.6	18.8	4.9

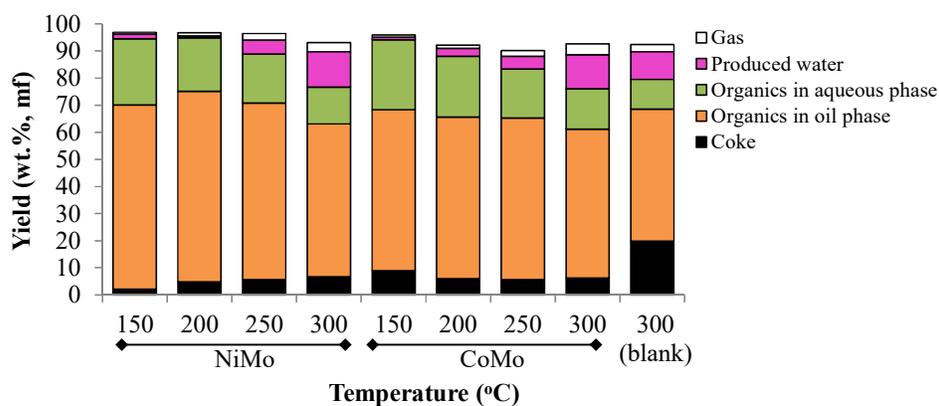


Figure 3-1. Mass balance closure on a moisture free basis in the hydrotreatment of bio-oil using NiMo and CoMo catalysts. The yields are expressed on a moisture free basis per gram bio-oil.

The high water production can also be partially ascribed to the dehydration of sugars [21]. This becomes clear when the results of catalytic hydrotreatment and non-catalytic thermal treatment (further marked as blank) at 300 °C were compared with each other. Indeed, a large

amount of water was produced from the thermal hydrotreatment (blank experiment), which was accompanied with the coke formation. On the other hand, the thermal hydrotreatment (in the absence of the catalyst) at 200 °C gave a negligible coke formation and gas production (below 1 wt%). This result was comparable with that of the hydrotreatment in the presence of the catalyst at low temperatures (150-200 °C).

Figure 3-1 shows that coke formation did occur under all applied conditions. However, coke formation was unequivocally more severe in the thermal hydrotreatment (blank) in the absence of the catalyst at 300 °C. The hydrotreated oils produced during the hydrotreatment experiments were a viscous and paste-like liquid. The large molecules formed via the condensation of the organics was further analysed using TGA. The yields of the residue from the TG experiments are defined as potential coke yields. The potential coke yields increased from 15.3 wt% for original bio-oil to 28.1 wt% for the hydrotreated oil produced at 300 °C using the NiMo catalyst. Clearly, the content of heavy fraction in the hydrotreated oils increased during the hydrotreatment, which was obviously due to polymerisation and in turn related to the coke formation [9, 31, 32]. In this work, the characterisation of the catalytic coke (collected together with the spent catalyst) was not presented due to the unknown changes on the catalyst surface during the hydrotreatment, thus caused an immature translation on what was happening during the hydrotreatment.

Figure 3-2 shows the gas yields as a function of the hydrotreatment temperature for the NiMo and CoMo catalysts. The production of CO was exclusively observed for the blank experiment. CO could be transformed into CO₂ via the water-gas-shift reaction under the conditions employed: the hydrotreatment catalysts possibly have catalysed the water-gas-shift reaction to convert CO into CO₂. This provides a plausible explanation for the near absence of CO and the increases in the CO₂ yields with increasing temperature in the catalytic hydrotreatment. The production of CO₂ and CO reduced the oxygen content of the oil and

hence enhanced the energy density. However, deoxygenating via this pathway was accompanied with the loss of carbon. As can be seen in Figure 3-2, the CO₂ production in the presence of the NiMo catalyst was similar to that for the CoMo catalyst at temperatures of 150-200 °C, and became higher at temperature of 250 °C. However, the CO₂ production of the former was slightly lower than that of the latter with increasing temperature to 300 °C. In addition, more considerable hydrocarbon gases were produced at higher temperatures, resulted from the catalytic or thermal cracking of side chains and the hydro(deoxy)genation of light organic molecules to form gases. In particular, CH₄ gas could be produced from the hydrocracking of side chains and/or from the catalytic conversion (methanation) of CO/CO₂ in the presence of H₂ under the conditions employed.

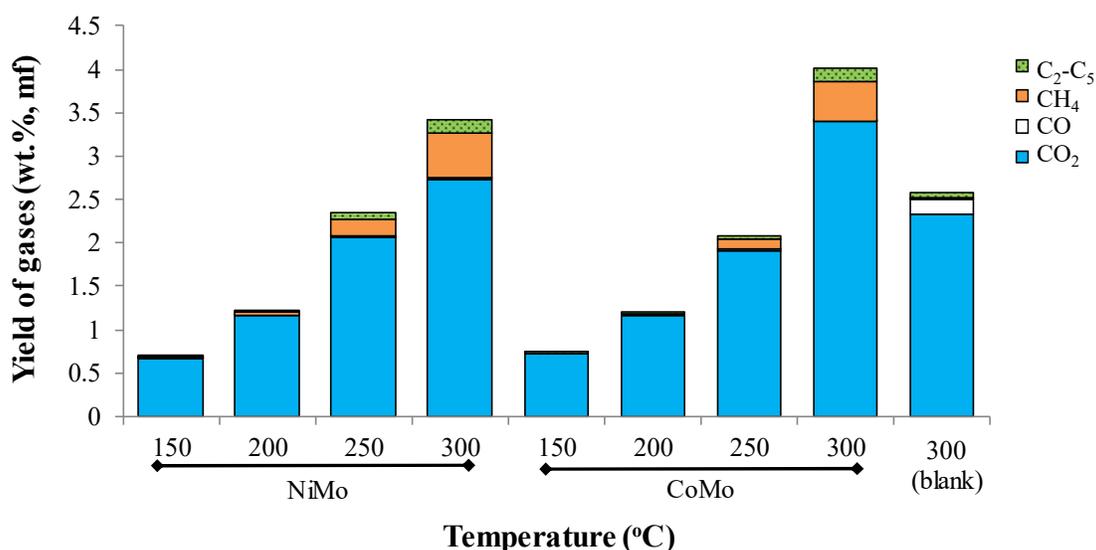


Figure 3-2. Gas yields as a function of hydrotreatment temperature using NiMo and CoMo catalysts. The yields are expressed on a moisture free basis per gram bio-oil.

Figure 3-3 shows the hydrogen consumption as a function of the reaction temperature. The hydrogen consumption of blank experiment and that with extra levoglucosan in bio-oil are also presented in this graph. The blank experiment (without catalyst but with hydrogen) did reveal

that there were negligible amounts of hydrogen consumed, as is shown in Figure 3-3. With increasing temperature, more hydrogen was consumed. The hydrogen consumption was almost doubled from 250 to 300 °C, showing an increasing activity of the catalysts. Interestingly, the CO₂ production kept increasing together with the hydrogen consumption. Despite of the addition of levoglucosan, which contains many oxygen groups, less hydrogen was consumed. This is probably due to the high amount of water and gases produced (further explained in section 3.2), which pushed the reactor pressure to its limit and hence no additional hydrogen could be added to promote further hydrotreatment.

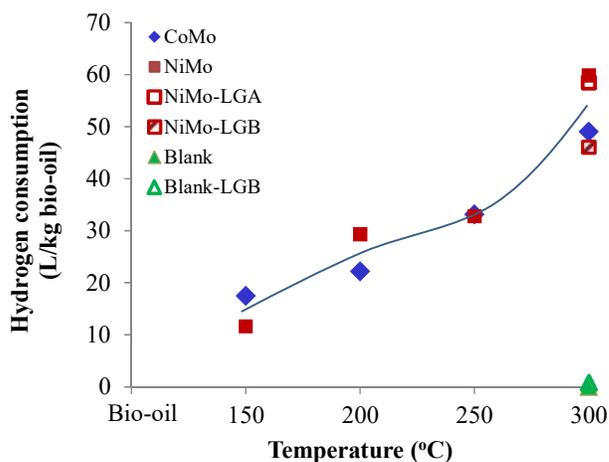


Figure 3-3. Hydrogen consumption as a function of the hydrotreatment temperature.

The elemental composition (hydrogen, carbon, nitrogen and oxygen) of bio-oil and hydrotreated oils are shown in Table 3-3 as a function of hydrotreatment temperature. After hydrotreatment at 200, 250, and 300 °C, the oxygen contents decreased significantly compared to that in the bio-oil. Together with the data on hydrogen consumption (Figure 3-3), it implies that the NiMo catalyst was active in the deoxygenation at mild temperatures and pressure. Hydrotreatment became more pronounced at temperatures ≥ 250 °C, evidenced by the increase in the production of the hydrocarbon gasses and the decrease in the oxygen content (by 45.5%

compared to the bio-oil at 250 °C). However, this was accompanied by the formation of increasing amounts of coke. It is, therefore, important that, in a continuous operation, the bio-oil do not experience very long residence time in the temperature regime where the catalyst was not very active and where the coke formation was already severe (200-250 °C). At 300 °C the degree of deoxygenation was ca. 55.5%. Higher temperatures are thus needed to achieve deeper deoxygenation (ca. 10 wt% oxygen).

Table 3-3.

Elemental composition of bio-oil and hydrotreated oils using the NiMo catalyst.

T(°C)	Elemental composition (wt%, moisture free basis)			
	N	C	H	O
Raw bio-oil	1.0	54.8	6.7	37.5
200	0.4	65.8	6.5	27.3
250	0.4	70.2	6.8	22.6
300	0.5	75.5	7.2	16.7

3.3.1.2 *Changes in individual compounds measured by GC-MS*

To study in details the catalytic performance of the NiMo or CoMo catalyst, individual compounds in the oil and aqueous phases were analysed using GC-MS. The results are shown in Figures 3-4 to 3-9. The results from the blank experiment were also included in the graphs for comparison (shown as open symbols). The reported compound yields are the sums of those in the aqueous and oil phases on a moisture free basis. The results generally showed that the

trends for NiMo or CoMo catalyst were quite similar but in some cases the absolute values were somewhat different.

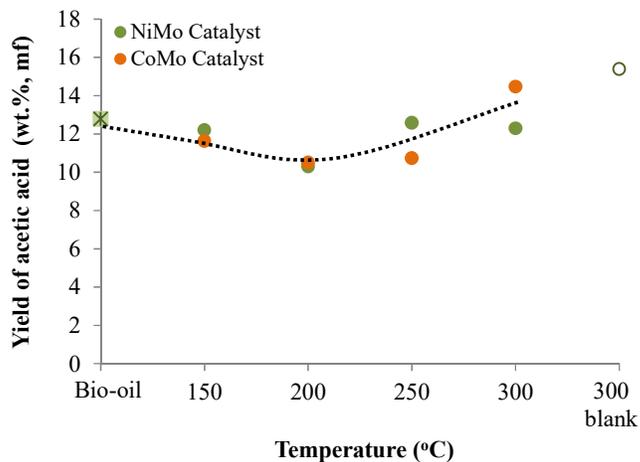


Figure 3-4. Yields of acetic acid as a function of hydrotreatment temperature using the NiMo and CoMo catalysts. The yields are expressed on a moisture free basis.

A small decrease in the yields of acetic acid in the hydrotreatment of bio-oil using the NiMo and CoMo catalysts was observed at lower temperatures (150-200 °C), which can be seen in Figure 3-4. The yields of acetic acid slightly increased at higher hydrotreatment temperatures, possibly due to the formation of acetic acid from the breakdown of oligomers in the bio-oil. More severe conditions are required to fully hydrogenate carboxylic acids [16, 17, 33].

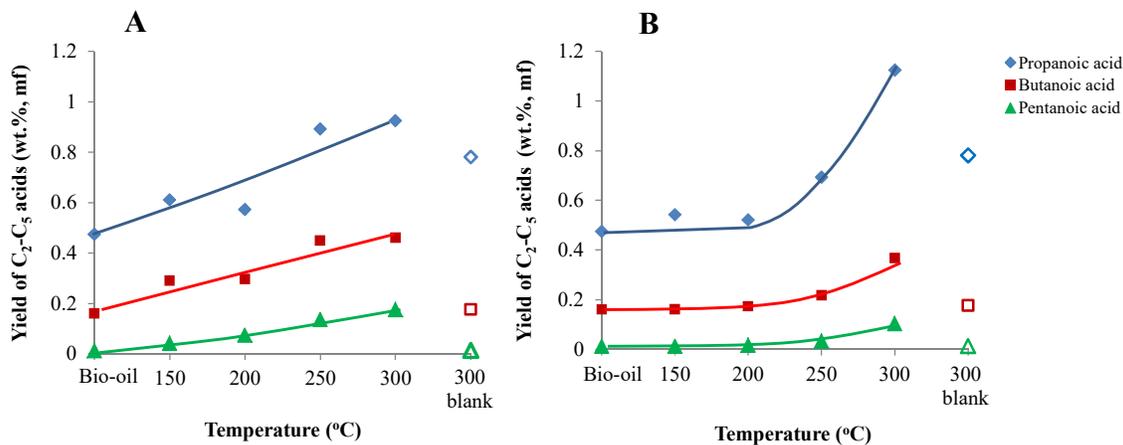


Figure 3-5. Yields of C₃-C₅ carboxylic acids as a function of hydrotreatment temperature using the (A) NiMo and (B) CoMo catalysts. The yields are expressed on a moisture free basis.

On the other hand, propanoic, butanoic and pentanoic acids were produced with increasing hydrotreatment temperature, as is shown in Figure 3-5. The yields of those three acids were almost doubled in the hydrotreatment products at 300 °C compared to that in original bio-oil. They could be produced from the cracking of side chains of sugar-derived oligomers [34]. These results are in line with the results obtained with noble metal catalysts [34]. As is shown in Figure 3-5, the trends for the NiMo and CoMo catalysts are slightly different. It might be due to the different activity of these catalysts during hydrotreatment. The CoMo catalyst is more active in cracking reactions, whereas NiMo catalyst is more active in hydro(deoxy)genation reactions [17]. The blank experiment showed lower production of the carboxylic acids at 300 °C.

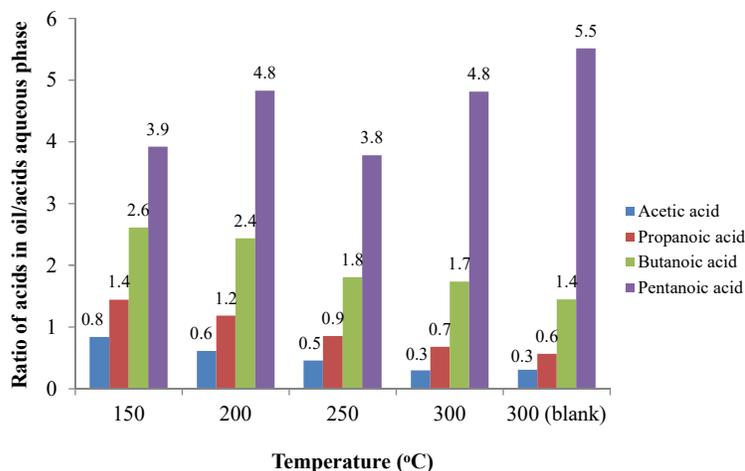


Figure 3-6. The distribution of acids in the oil and aqueous phases as a function of the hydrotreatment temperature using the NiMo catalyst.

The information about how the acids distribute in the hydrotreatment products is a key to understand the pathway of the hydrotreatment process. Hydrotreatment process changed the polarity of bio-oil. It is the reason for the formation of a two-phase hydrotreatment product, i.e. a viscous dark-brown oil phase and brown to light-yellow aqueous phase. The compounds in the hydrotreatment products will distribute among the two phases depending on their polarity. Figure 3-6 shows the ratios of C₂-C₅ carboxylic acids in the oil phase and aqueous phase produced in the hydrotreatment of bio-oil using the NiMo catalyst as a function of reaction temperature. The ratio of acids in oil phase to those in aqueous phase is defined as the ratio of the yields of particular acid found in oil phase to that in aqueous phase expressed on a moisture free basis. The decrease in the ratio of acids in oil to aqueous phase by increasing temperature was due the decrease in the water content of the oil phase, thus the dissolved organic compounds in it were very low (<1 wt%) and could therefore not account for the "high" concentration of acids in it.

It can be seen from Figure 3-6 that, with a higher hydrotreatment temperature, the oil became less polar and, as a result, more acids tend to be distributed more to the aqueous phase.

An exception is pentanoic acid due to its longer carbon chain length. Generally, the relative change (decreasing ratio) in the distribution of acids over the two phases, with increasing hydrotreatment temperature, became more pronounced for smaller acids because of their higher polarity and thus better solubility in water. From the data, it is clear that, at higher hydrotreatment temperature and the resulting lower polarity of the oil, more acids are transferred to the aqueous phase and are therefore removed from the oil product, which is beneficial. Nevertheless, it is very well possible that a major part of the acids could become gases at higher hydrotreatment temperatures [16].

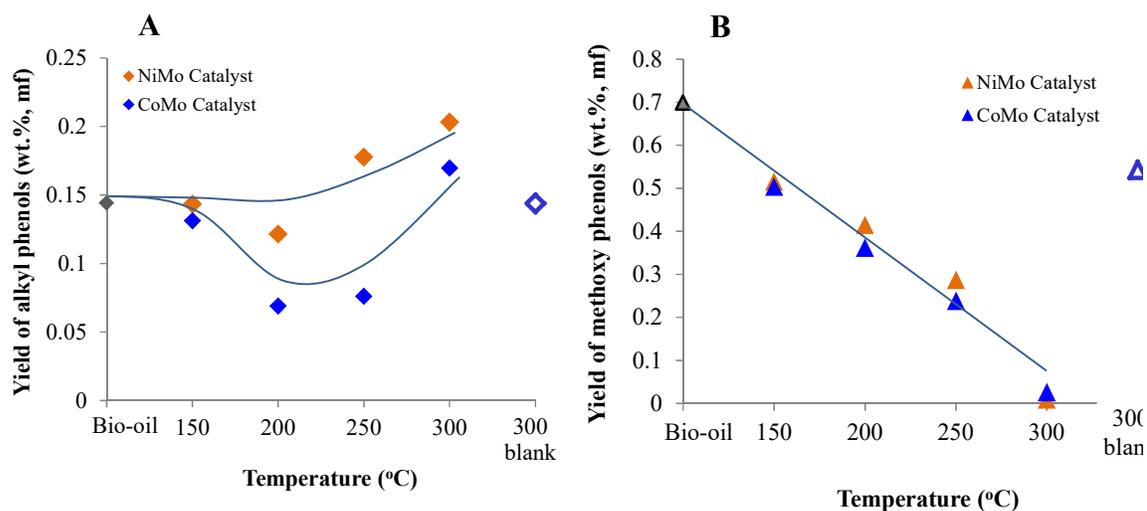


Figure 3-7. Yields of (A) alkyl and (B) methoxy phenols as a function of hydrotreatment temperature using the NiMo and CoMo catalysts. The yields are expressed on a moisture free basis.

The yields of alkyl phenols (*m*-, *p*- and *o*-cresol and ethyl-phenol) decreased at lower temperature and started to increase when the hydrotreatment temperature became higher (Figure 3-7A). On the other hand, the yields of methoxy phenols (guaiacol, methyl guaiacol, syringol, syringaldehyde and methoxy eugenol) considerably decreased with increasing

hydrotreatment temperature. It is most likely due to the hydrogenation of methoxy phenols such as syringol and guaiacol at higher temperature to form, amongst others, *o*-cresol [16, 35]. Methoxy phenols seemed more reactive compared to alkyl phenols due to the presence of reactive $-O-CH_3$ functional groups.

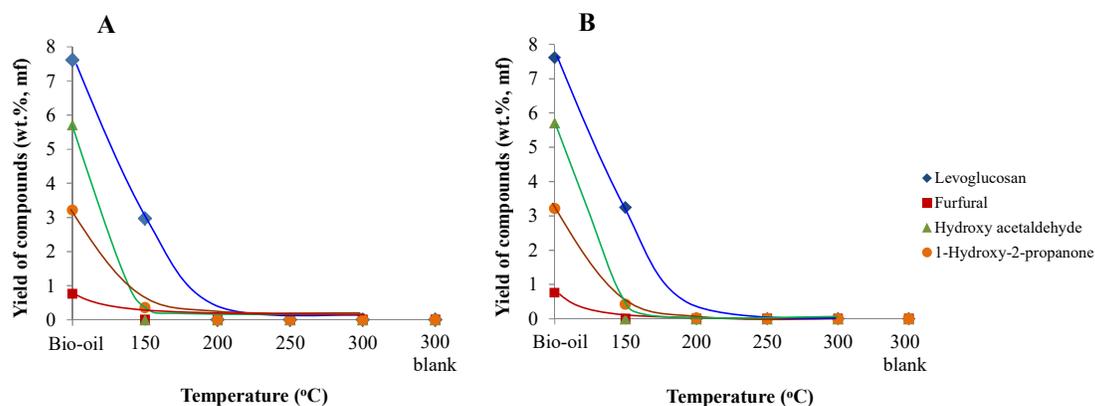


Figure 3-8. Yields of levoglucosan, furfural, hydroxy acetaldehyde, and 1-hydroxy-2-propanone as a function of hydrotreatment temperature using the (A) NiMo and (B) CoMo catalysts. The yields are expressed on a moisture free basis.

Furfural, hydroxyl acetaldehyde and 1-hydroxy-2-propanone (Figure 3-8) were almost completely converted already at 150 °C for both catalysts, while levoglucosan was not completely converted at 150 °C. Levoglucosan started to disappear already at 150 °C and disappeared completely at 200 °C. Levoglucosan could be hydrolysed to form glucose and be further hydrogenated [21] or converted into coke. Aldehydes and ketones such as hydroxy acetaldehyde and 1-hydroxy-2-propanone are very reactive and could be readily hydrogenated to produce alcohols [2]. Even though not in a stoichiometric conversion, our measurement did confirm the increases in the yields of ethanol and 1-propanol with increasing temperature.

Furfural can be hydrogenated to form relatively stable cyclopentanone [34]. In this work, the yields of 2-methyl cyclopentanone (Figure 3-9) tended to increase at elevated temperatures

(except at 300 °C with the NiMo catalyst for unknown reasons). It might be formed from furfural through hydrogenation followed by alkylation [36]. It also could be formed from the compounds with similar structures to furfural such as 2-cyclopent-1-ones [34]. Furfural can also polymerise to form some larger polymeric products at low temperatures (> 110 °C) [4] and react with phenolic compounds (e.g. syringol, guaiacol) at high temperature and in acidic medium via electrophilic substitution to form a phenolic resin [4].

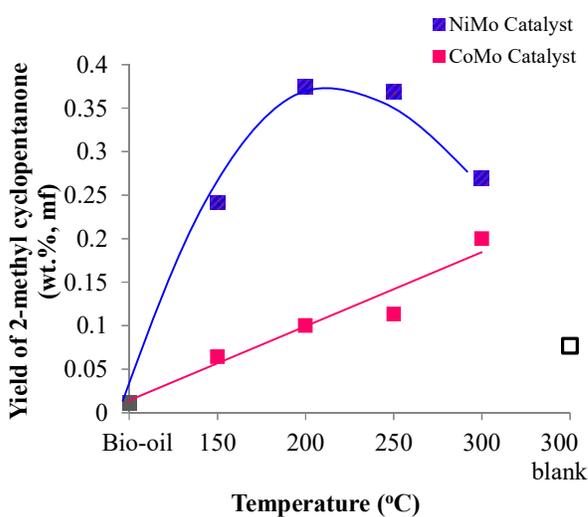


Figure 3-9. Yields of 2-methyl cyclopentanone as a function of hydrotreatment temperature using the NiMo and CoMo catalysts. The yields are expressed on a moisture free basis.

3.3.1.3 Changes in aromatic ring structures during the hydrotreatment of bio-oil

Figure 3-10 shows the fluorescence intensity of bio-oil and hydrotreated oils expressed on a moisture free basis. The UV-fluorescence spectroscopy is an analytical technique used to identify different sizes of aromatic ring structures [37]. The trends for both catalysts were similar; the fluorescence intensity of the hydrotreated oils at 150 and 200 °C was similar with the starting bio-oil and a clear increase was observed at the higher hydrotreatment

temperatures. Generally, the bio-oil shows two peaks centred at 270-290 nm and 310-340 nm in the synchronous spectra. The latter peak has higher fluorescence intensity than the former one. The data show an increase in the large aromatic ring system (two or more fused benzene rings) when the hydrotreatment conditions became more severe. The corresponding increases in new peaks at 350-360 nm and 380-390 nm showed the formation of large aromatic ring structures. These larger ring structures might have formed from lignin-derived oligomers in bio-oil [6, 38]. Cracking of oligomers and ring fusion may also happen at the same time. The large aromatic ring structures are believed to be the precursors of coke formation.

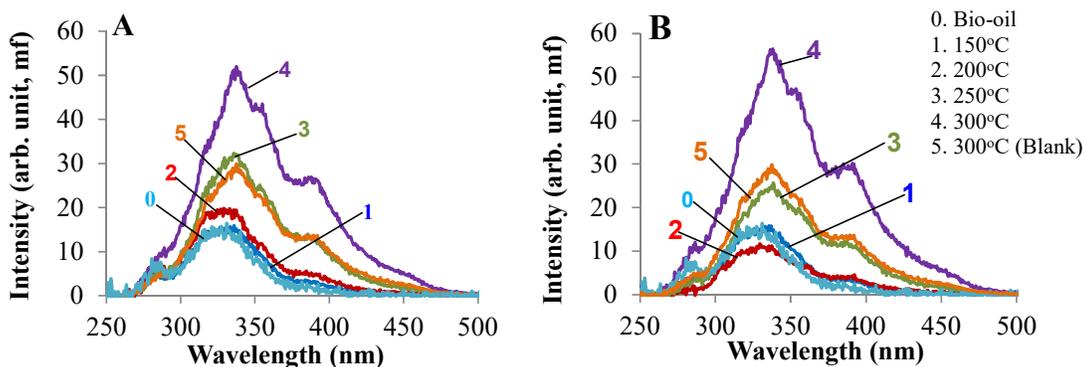


Figure 3-10. Synchronous spectra with a constant energy difference of -2800 cm^{-1} in the hydrotreatment of bio-oil using (A) NiMo and (B) CoMo catalysts. The data are expressed on a moisture free basis per gram bio-oil.

In the absence of a catalyst, the fluorescence intensity is much lower than that in the presence of a catalyst. It indicates that the formation of aromatic ring structures soluble in the liquid phases in the absence of a catalyst was suppressed due to the severe coke formation (see Figure 3-1).

3.3.2 Effect of adding levoglucosan on the coke formation during hydrotreatment

The cellulose-derived sugar fraction is an abundant and reactive fraction in bio-oil and therefore an important source of coke formation in the bio-oil upgrading [21, 39, 40]. During hydrotreatment, competition takes place between two kinds of reactions, i.e. thermal non-catalytic reactions and catalytic hydrogenation [9, 17, 34, 41]. To study this competition, levoglucosan, the most abundant sugar in bio-oil detected by GC-MS, was added into the bio-oil. The NiMo and NiMo-LGA experiments refer to the feedstock containing 7.7 wt% (raw bio-oil) and 21.5 wt% levoglucosan, respectively, while NiMo-LGB and Blank-LGB experiments refer to 31.6 wt% levoglucosan.

Figure 3-11 shows the yields of the hydrotreatment products produced at 300 °C for the oils with the different amounts of levoglucosan. All yields including the ones with added levoglucosan are expressed on a moisture free basis. There are a few observations to be made in the data in Figure 3-11. Firstly, adding levoglucosan in the presence of the NiMo catalyst did not result in any increases (in fact, minor decreases) in the yield of coke. These data indicate that the presence of the NiMo catalyst has provided enough active hydrogen to stabilise the reactive intermediates formed from levoglucosan without the formation of additional solid coke. Secondly, adding levoglucosan in the absence of the NiMo catalyst (Blank and Blank-LGB) resulted in massive coke formation. A detailed analysis of the data would in fact reveal that the amount of additional coke formed due to added levoglucosan was at least the same as or even more than the amount of levoglucosan added. Given that not all levoglucosan molecules would turn into coke, these data thus indicate that the reactive intermediates formed from levoglucosan would probably have cross-linked with other lighter bio-oil components to turn them into part of the coke observed. While the exact reaction pathways remain unknown,

one possibility is that levoglucosan could undergo hydrolysis in acidic aqueous medium to form glucose [25], which in turn could condense together with other components in bio-oil [4].

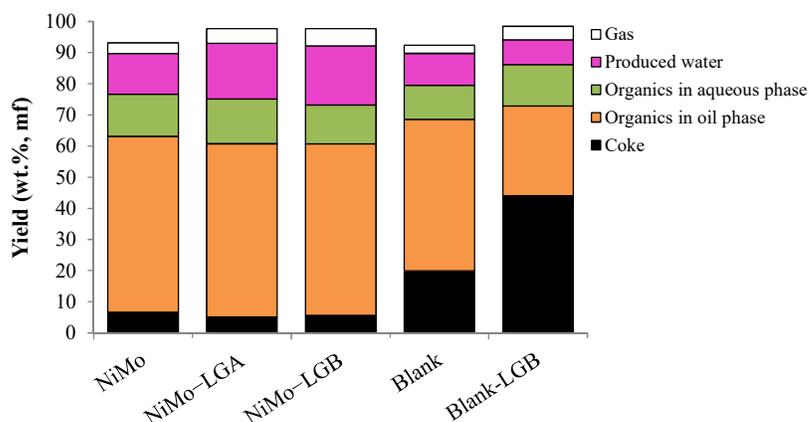


Figure 3-11. Mass balance of hydrotreatment products as a function of the levoglucosan concentration in bio-oil with and without NiMo catalyst at 300°C. NiMo and NiMo-LGA experiments correspond with 7.7 wt% and 21.5 wt% levoglucosan, respectively, while NiMo-LGB and Blank-LGB experiments correspond with 31.6 wt% levoglucosan. The yields are expressed on a moisture free basis per gram (bio-oil + added levoglucosan).

The coke formed from the catalytic and non-catalytic hydrotreatment in the presence and absence of a NiMo catalyst at 300 °C was characterised with FT-Raman spectroscopy to study the structural features of the coke. The total Raman areas (Figure 3-12A) are used to represent the observed Raman intensity. It is mainly affected by the presence of oxygen-containing functionalities and aromatic ring systems [29, 30, 42-45]. The presence of oxygen-containing functionalities would increase the Raman intensity due to their resonance effect with the aromatic rings to which they are attached [44]. On the other hand, the increases in the number of fused aromatic rings would weaken the Raman intensity due to the increases in the light absorptivity [44].

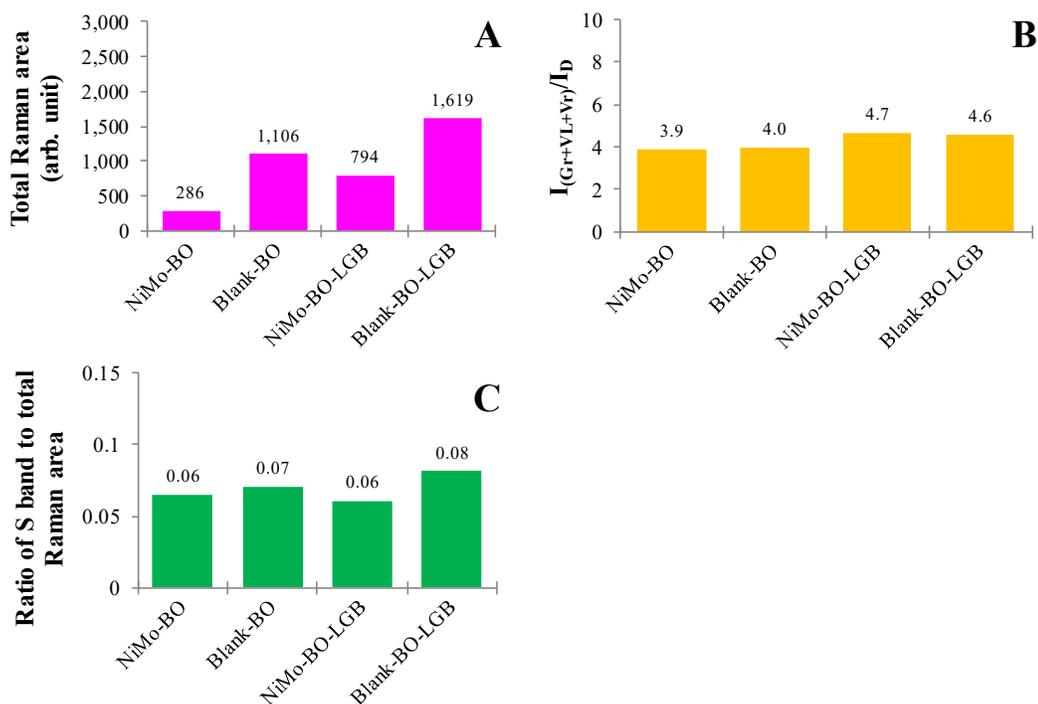


Figure 3-12. (A) Total Raman area, (B) ratio of small to big rings and (C) ratio of the S band area to the total Raman area of the spent NiMo catalysts after hydrotreatment of bio-oil itself and bio-oil with added levoglucosan using a NiMo catalyst at 300 °C.

In the presence of the NiMo catalyst, the Raman areas (Figure 3-12A) of the coke from the hydrotreatment of bio-oil with added levoglucosan (“NiMo-BO-LGB) were significantly higher than those of the coke from the “NiMo-BO”, the catalytic hydrotreatment without added compounds. This reflects the formation of highly oxygen-containing coke in the presence of added levoglucosan. The data indicated that the oxygen-containing functionalities (mainly due to the addition of levoglucosan) contributed to the formation of coke. The similar phenomenon was observed from the hydrotreatment of bio-oil itself and the bio-oil with added levoglucosan in the absence of the NiMo catalyst (blank experiments); an increase in the total Raman areas was observed due to the addition of levoglucosan. Under mild hydrotreatment conditions in

this study (at 300 °C, ≥ 100 barg total pressure), the formation of coke may be largely due to the polymerisation of various bio-oil fragments as well as the added levoglucosan without drastic ring condensation at low temperature. A simplified reaction scheme for the formation of coke during the hydrotreatment of bio-oil with and without added levoglucosan is presented in Figure 3-13.

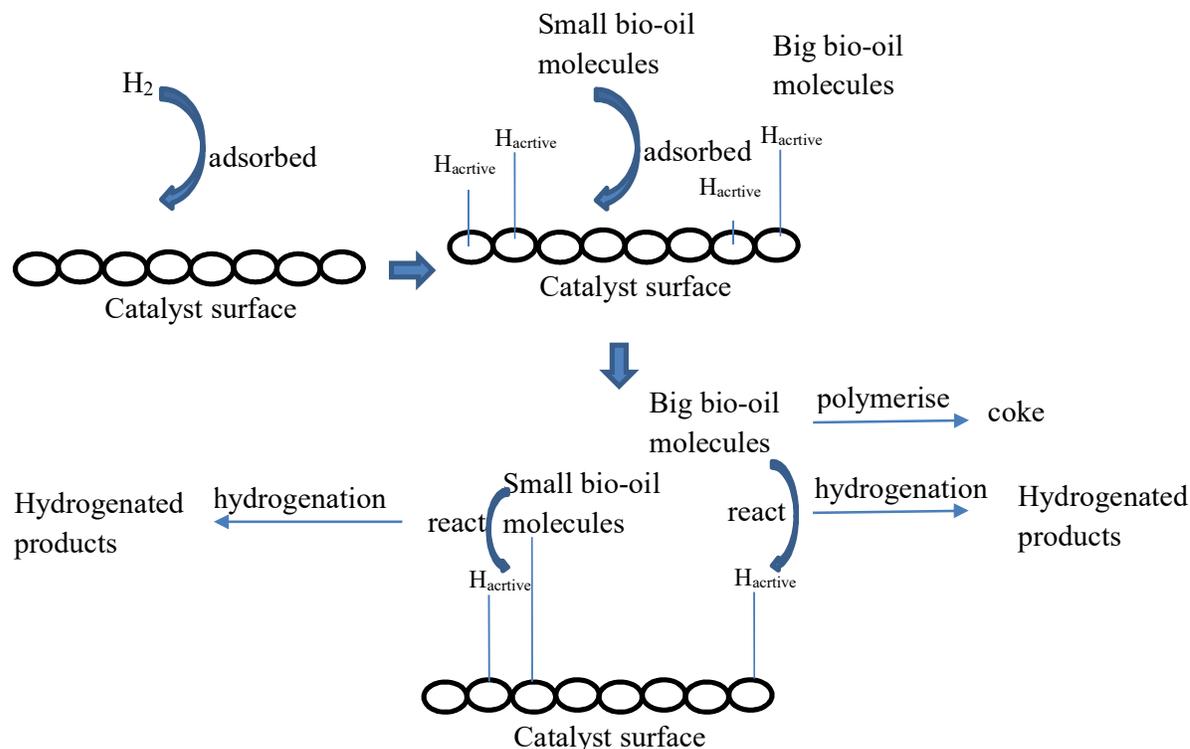


Figure 3-13. A simplified reaction scheme for coke formation during the hydrotreatment of bio-oil.

In addition to the total Raman area, the ratios among the intensities of some major Raman bands would allow a semi-quantitative reflection of changes in coke structures. The G_R , V_L and V_R bands, i.e. the ‘overlap’ between the G and D bands, represent the typical structures found in amorphous carbon materials with relatively small (3–5 fused) aromatic ring systems [29, 30, 44]. On other hand, D band refers to “defect” in the carbonaceous materials, representing the

disordered structure in highly ordered materials and more importantly aromatic ring systems with >6 fused rings. Figure 3-12B shows the ratio of the intensity of G_R , V_L and V_R bands to D band of the solids. This ratio reflects the ratio between small (3-5 fused) and big (≥ 6 fused) rings [42]. It is shown in Figure 3-12B that a slight increase in relative amount of small rings was observed, regardless if the NiMo catalyst was used.

Another important structural feature of the coke is the extent of the cross-linking in the coke structures, as is reflected by the ratios of the S band area to the total Raman area in Figure 3-12C. The S band represents sp^3 -C connected to aromatic ring structures. It gives an indication of the extent of cross-linking and the level of substitution in the coke structures [30]. With and without added levoglucosan, a low level of cross-linking was observed for all coke, regardless if the NiMo catalyst was used.

Table 3-4.

Elemental composition of the non-catalytic coke from the hydrotreatment of bio-oil itself and the bio-oil with added levoglucosan.

Coke from experiment:	Elemental composition (wt.%)			
	N	C	H	O
Blank-BO	0.3	77.9	4.3	17.4
Blank-BO-LGB	0.2	77.9	4.5	17.4

The elemental composition of the non-catalytic coke with and without levoglucosan is presented in Table 3-4. Surprisingly, the elemental composition of the coke formed from the blank experiments with and without added levoglucosan was similar. It showed that the amount of oxygen-containing functionalities between those two cokes was quite similar. However, adding levoglucosan in “Blank-BO-LGB” caused the increase in the small rings in the coke

structures (see Figure -12B), thus sharpened the intensity of the Raman intensity observed (see Figure 3-12A). In short, the amount of oxygen in the two cokes was quite similar but with different coke structures; with added levoglucosan, the coke was less condensed and dominated by the small ring structures.

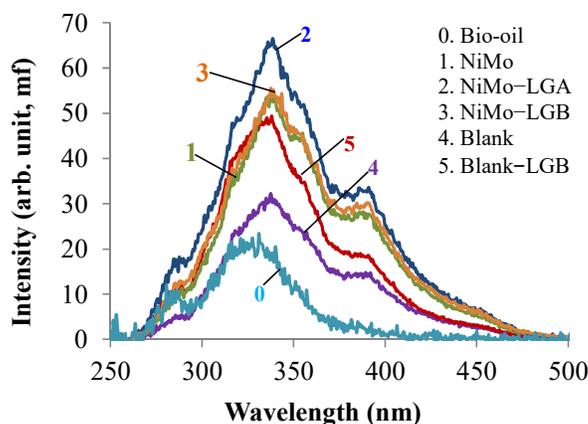


Figure 3-14. Synchronous spectra with a constant energy difference of -2800 cm^{-1} as a function of the levoglucosan concentration with and without NiMo catalyst at 300°C . The data are expressed on a moisture free basis per gram (bio-oil + added levoglucosan).

Considering that large aromatic ring systems may be the precursors of coke formation, further efforts were made to trace the formation of large aromatic ring systems due to the addition of levoglucosan. The synchronous spectra of the hydrotreated oils are shown in Figure 3-14. In the presence of the NiMo catalyst, hydrotreatment of the bio-oil with added levoglucosan did not show significant effects on the fluorescence intensity of aromatic ring structures. In other words, the presence of NiMo catalyst could prevent the formation of additional large aromatic ring systems when levoglucosan was added. The growth of aromatic ring structures also could be suppressed. This is in good agreement with the data on coke formation (Figure 3-11). On the other hand, in the absence of a catalyst, the fluorescence

intensity of the liquid products in the Blank and Blank-LGB experiments was lower than that of the hydrotreated oils from the catalytic experiments. This is possibly due to the transformation of the large aromatic ring structures in the blank experiments into coke.

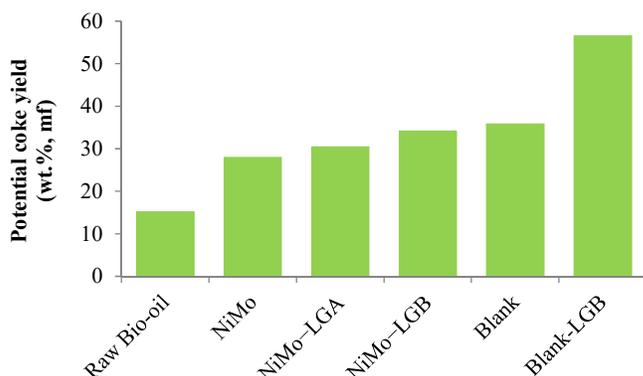


Figure 3-15. The potential coke yields of hydrotreated oils at 300 °C with and without added levoglucosan measured by TGA at 500 °C.

However, the hydrotreated oils with added levoglucosan showed somewhat higher potential coke yield as indicated in Figure 3-15 than that from the hydrotreated oil without extra levoglucosan at 300 °C. It was found that the potential coke yield increased from 28.1 to 30.5 wt% when the concentration of levoglucosan increased from 7.7 to 21.5 wt%. Furthermore, the increase in the levoglucosan concentration further to 31.6 wt% did cause the increase in potential coke formation to 34.3 wt%. It is believed that the high potential coke yield was due to bigger molecules in the oil which corresponds to the high viscosity of the oil with the higher levoglucosan content.

3.4 CONCLUSIONS

Reducing the coke formation during the hydrotreatment of bio-oil at low temperatures (150-300 °C) by the presence of pre-sulphided NiMo and CoMo catalysts was demonstrated in a batch reactor. Under the reaction conditions employed, deoxygenation occurred, which reduced the oxygen content by ca. 55.5% at 300 °C. However, severe coke formation also took place, which was accompanied by the formation of large aromatic ring structures and the higher tendency of the hydrotreated oils towards coke formation. The role of levoglucosan on the coke formation was also investigated by adding levoglucosan into the bio-oil feedstock. It was found that the catalysts were active in reducing the formation of solid coke and large aromatic ring systems in liquid products from bio-oil or the bio-oil with added levoglucosan (at 300 °C with the NiMo catalyst). In the absence of the hydrotreating catalyst, adding levoglucosan to the bio-oil induced severe coke formation. The coke formed in the presence of added levoglucosan was more oxygenated with a smaller size ring structures. The amount of the extra coke produced due to the addition of levoglucosan at least equalled to or even exceeded the amount of the levoglucosan added to bio-oil. The results proved that levoglucosan or its reactive intermediates could cross-link with other compounds in the bio-oil, leading to severe coke formation.

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CHAPTER 4

**COKE FORMATION AND PRODUCT DISTRIBUTION
DURING THE HYDROTREATMENT OF PYROLYSIS
BIO-OIL AND ITS MIXTURE WITH C₅ AND C₆ SUGARS
USING A NiMo/ γ -Al₂O₃ CATALYST**

4.1 INTRODUCTION

Lignocellulosic biomass is the most abundant resources of renewable carbon, and is therefore suitable for the large scale production of liquid fuels and chemicals [1-3]. Bio-oil from the pyrolysis of biomass is a complex mixture of various components, including acids, aldehydes, ketones, alcohols, phenols, sugars, oligomers and water [4]. The high oxygen content (20-50 wt%), low pH value (1.5-3.8), low energy density and high thermal instability of bio-oil make its direct use troublesome. Therefore, the upgrading of bio-oil is crucial for it to be used as a liquid transport fuel.

Hydrotreatment is a promising method to remove the oxygen in bio-oil in the forms of water, CO and CO₂ through the catalytic reactions of bio-oil with hydrogen. Typically, the process is carried out separately from the pyrolysis of biomass, at a high pressure (up to 20 MPa) and high temperature (300-450 °C) with an abundant hydrogen supply [5]. Coke formation is one of the biggest challenges during the hydrotreatment of bio-oil due to the complex but reactive composition of bio-oil.

Sugars are one of the main fractions of bio-oil. Sugars can contribute up to ca. 30 wt% of bio-oil in various forms [6, 7]. The presence of sugars in bio-oil may raise several issues in a subsequent refining process such as coke formation, catalyst deactivation and high hydrogen consumption due to its highly oxygenated nature [8]. The sugars in bio-oil are mostly in water-soluble fraction [9], mainly in the form of cellulose-derived sugars such as levoglucosan. Levoglucosan is the most abundant GC-detectable sugar in bio-oil. Other C₆ sugars (e.g. glucose, galactose and mannose) and C₅ sugars (e.g. xylose and arabinose) are also present in bio-oil [7].

To understand how sugars behave during the hydrotreatment, extensive research have been done by using model compounds. The hydrotreatment of sugars such as *D*-glucose [10-

17], fructose [16], levoglucosan [17, 18], *D*-cellobiose [10] and other sugars has been extensively studied to gain insight into the hydrotreatment of carbohydrate fractions. However, the knowledge about the behaviour of model compounds during hydrotreatment may not be the same as they are in bio-oil during hydrotreatment. Hundreds of compounds in bio-oil could have a very complicated interaction among them and with the added sugar model compounds.

To understand how the sugars in bio-oil contribute to coke formation, the hydrotreatment of the bio-oil with added sugars was performed in a batch reactor system at 300 °C using a commercial NiMo/ γ -Al₂O₃ catalyst. The coke formation as well as the changes in bio-oil in the presence of added sugars during hydrotreatment have been investigated and traced by the formation and transformation of light compounds and aromatic ring structures in the hydrotreated products. The results for the hydrotreatment of sugars in aqueous medium under identical conditions were also presented for comparison. The cross-polymerisation of the added sugars with the components in bio-oil was correlated with their molecular structures.

4.2 EXPERIMENTAL

4.2.1 Materials

The bio-oil used in this study was produced from the pyrolysis of mallee woody biomass in a grinding pyrolyser by Dr. MD Mahmudul Hasan. The details of the pyrolysis procedures can be found elsewhere [19, 20]. Briefly, the mallee woody biomass (1-2 centimetres in size) was pyrolysed at a temperature range of 450-465 °C in a rotating reactor (with a constant rotation speed of 54 rpm) filled with steel balls. The biomass particles were

“ground” into smaller particles once in contact with the steel balls while they are simultaneously pyrolysed. The vapour produced in the pyrolysis process was condensed into bio-oil using condensers cooled with water and dry ice. The produced bio-oil was then filtered and stored at ca. -10 °C.

The catalyst used in the hydrotreatment experiments was a commercial hydrotreating catalyst, pre-sulphided NiMo supported on γ -Al₂O₃ (EureCat, France). It contains 3-4 wt% of Ni and 12-16 wt% of Mo. The particle size of 250-600 μ m was used in all hydrotreatment experiments. The catalyst is hereafter referred to as the “NiMo catalyst”. Levoglucosan (Carbosynth, \geq 99%), *D*-(+)-xylose (Sigma-Aldrich, \geq 99%), *D*-(+)-glucose (Sigma-Aldrich, \geq 99.5% GC) and sucrose (Sigma-Aldrich, \geq 99.5% GC) were added into bio-oil as feedstocks for the hydrotreatment experiments. The individual compounds used as standards in the GC-MS analyses were purchased from Sigma-Aldrich. Hydrogen and nitrogen (BOC, high purity grade, 99.99%) were used in the hydrotreatment experiments.

4.2.2 Hydrotreatment

The hydrotreatment of bio-oil with added C₅-C₆ sugars were studied in a batch autoclave reactor system. The experimental details were described in our previous work [21] and in Chapter 3 [22]. The assignment of the experiments is based on the catalytic/non-catalytic conditions followed by the specific added sugars. For example, “NiMo-BO” and “Blank-BO” represent the catalytic (NiMo as a catalyst) and non-catalytic experiment without added sugars, respectively. Furthermore, “NiMo-BO-Levoglucosan” and “Blank-BO-Levoglucosan” refer to the catalytic and non-catalytic hydrotreatment of bio-oil with added levoglucosan, respectively. Some experiments reported here were the same experiments as

reported previously in Chapter 3 [22], namely the experiments assigned as “NiMo-BO”, “Blank-BO”, “NiMo-BO-Levogluconan” and “Blank-BO-Levogluconan”.

Before starting each experiment, 40.0 g of mallee bio-oil, together with a sugar compound (10.0 g of each sugar in each experiment), 4.0 g of the NiMo catalyst and 1.5 g of ZnO (to prevent the corrosion of the reactor vessel by the corrosive H₂S gas possibly formed from the NiMo catalyst) were introduced into the reactor vessel at room temperature. Blank experiments (having bio-oil with and without added sugars and hydrogen in the absence of the NiMo catalyst) were performed as well for comparison. The reactor was flushed with nitrogen several times prior to an experiment to remove the air. The reactor was then pressurised with hydrogen (100 bar) at room temperature to check for any leakage. To start the experiment, the reactor was pressurised with 50 bar hydrogen at room temperature and heated to 300 °C at a stirring rate of 400 rpm. Based on the previous work [23-25], there was no mass transfer limitation observed at a stirring rate > 300 rpm. Feeding additional hydrogen was possible during the experiment to keep the total pressure at minimum 100 bar.

All hydrotreatment experiments were conducted with the same holding time (3 h) at 300 °C. After 3 h, the reactor was rapidly cooled to room temperature by a cooling coil inside the reactor. After each experiment, the residual pressure (at room temperature) was recorded, from which the gas composition could be determined to calculate the gas yields. The gas sample (consisting of the gaseous products together with the unconsumed hydrogen) was collected into a gas bag and analysed by a gas chromatograph (GC, Agilent 6890). The GC was equipped with a methaniser and a flame ionisation detector to allow the quantification of CO, CO₂ and light hydrocarbon gases.

After opening the reactor, the hydrotreatment products, including oil phase, aqueous phase and solids (catalyst, ZnO and coke) were recovered for further analysis. The aqueous phase was first taken out, followed by the oil phase. Subsequently, the solids at the bottom of

the reactor were then thoroughly rinsed using tetrahydrofuran (THF). The recovered solids were further washed using THF until a clear THF solution was observed in the filtrate. The solids then were dried at 50 °C under reduced pressure of -50 kPa. Assuming that no change in the catalyst took place, the amount of coke produced during the hydrotreatment was defined as the difference between the amount of total solids after drying and the amount of solids (the NiMo catalyst and ZnO) initially loaded into the reactor. The water content of each of the hydrotreated products (the oil and aqueous phases) was determined using GC-MS. The amount of water produced during the hydrotreatment was defined as the difference between the water in the products (both the oil and aqueous phases) and that in the original bio-oil. The mass balance was expressed on a moisture free basis of bio-oil plus the added sugar (i.e. excluding water in the bio-oil only).

The catalytic (using the NiMo catalyst) and non-catalytic hydrotreatment of the sugars alone (levoglucosan, sucrose and xylose) in aqueous medium were also performed for comparison. The procedure of the hydrotreatment experiments was the same as the above-explained hydrotreatment of bio-oil with the added sugars. The weight of water used was the same as the weight of bio-oil.

4.2.3 Analyses

4.2.3.1 Gas chromatography-mass spectroscopy (GC-MS)

An Agilent 6890 GC equipped with a 30 m × 0.25 mm × 0.25 μm HP-Innowax (cross-linked polyethylene glycol) column was used in the GC-MS analysis of the hydrotreated products (the oil and aqueous phases) with similar parameters to those in our previous work [17, 22, 26, 27]. The Agilent 5973 MS detector was attached to the GC instrument to allow

the identification of single compounds in the hydrotreated products based on their fragmentation patterns. A certain amount of sample was diluted in acetone to prepare a 5-10 wt% (accurately known) acetone solution. A 1 μL of solution was then injected into the GC with a split ratio of 50:1. The temperature of the injection port was 250 $^{\circ}\text{C}$. The oven temperature was kept at 40 $^{\circ}\text{C}$ for 3 min, and then ramped up to 260 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$. The oven was then held at 260 $^{\circ}\text{C}$ for 5 min. The GC-MS instrument was equipped with a NIST library, which allows the identification of each individual compound in addition to the injection of standard solutions. Standard solutions (including water standards) were analysed to obtain reproducible response factors ($R^2 \geq 0.9$) to allow the quantification of the compounds in bio-oil and the hydrotreatment products.

4.2.3.2 UV-fluorescence spectroscopy

A Perkin-Elmer LS50B spectrometer was used to record the synchronous UV-fluorescence spectra of the bio-oil feedstocks (bio-oil with and without added sugars) and the corresponding hydrotreated oils with a constant energy difference of -2800 cm^{-1} [21, 28]. Due to the negligible intensity of the aqueous phase, the spectra shown in this study are only for the oil phases. The solution of the oil phase was diluted with methanol (Uvasol for spectroscopy; purity $\geq 99.9\%$) to 4 ppm to minimise the self-absorption effect [29, 30]. The analysis was performed with the slit widths of 2.5 nm and the scan speed of 200 nm min^{-1} . The fluorescence intensity presented in this study was expressed on the basis of per gram of organics in feedstock by multiplying the intensity by the yield of organics in the oil phase on a moisture free basis.

4.2.3.3 Thermogravimetric analysis (TGA)

A TGA-Q5000 instrument was used in thermogravimetric analysis (TGA) of the bio-oil feedstocks (bio-oil with and without added C₅-C₆ sugars) and the corresponding hydrotreated oils. A temperature range of 25-500 °C with a heating rate of 10 °C/min was applied in each TGA run in nitrogen atmosphere. 5-10 mg (accurately known) of sample was used in each of TGA runs. The residue left in the pan after each run at 500 °C was defined as the potential coke yield as described in our previous work [21, 22]. The aqueous phases showed a very low potential coke and therefore not presented here.

4.3 RESULTS AND DISCUSSION

4.3.1 Effects of C₅ and C₆ sugars on coke formation

4.3.1.1 Hydrotreatment of sugar model compounds

The hydrotreatment of sugar model compounds (levoglucosan, xylose and sucrose) in aqueous medium was performed in order to study their behaviour especially their effect on coke formation. The hydrotreatment of pure sugars resulted in the formation of one liquid phase, gaseous products and coke. The yields of the coke produced from the hydrotreatment of pure sugars were expressed on a basis of the feedstock (sugar model compound and water mixture), as detailed in Table 4-1. In the presence of NiMo catalyst, the coke formed during hydrotreatment of sugar model compound alone was suppressed, ranging from 1.3 to 3.2 wt%. In contrast, the coke formed in the absence of catalyst was higher (8.5 to 10.1 wt%).

The hydrotreatment of the pure sugars produced a low yield of the gaseous products (1.1–2.1 wt%). CO₂ was the predominant gaseous products both in the catalytic and non-catalytic hydrotreatment. Hydrocarbon (C₁-C₅) gases were also produced, exclusively in the catalytic hydrotreatment. CO was exclusively produced in the blank experiments, mainly from the decarbonylation of the carbonyl groups of the sugars.

Table 4-1.

Yields of coke produced during the hydrotreatment of pure C₅-C₆ sugars, bio-oil alone and the bio-oil with added C₅-C₆ sugars using the NiMo catalyst at 300 °C.

Catalyst	Model compound	Coke yield (wt%)			
		From pure model compound	From bio-oil	From BO + model compound	Predictive coke from BO + model compound
NiMo	Levoglucofan	3.2	6.7	5.7*	9.9
Blank	Levoglucofan	8.5	19.9	44.1*	28.4
NiMo	Xylose	1.3	6.7	23.3	8.0
Blank	Xylose	10.1	19.9	34.6	30.0
NiMo	Sucrose	2.3	6.7	18.7	9.0
Blank	Sucrose	8.8	19.9	45.1	28.7

*The data were from our previous work reported earlier in Chapter 3 [22].

4.3.1.2 Hydrotreatment of bio-oil with added C₅-C₆ sugars

In order to better understand the coke formation during the hydrotreatment of bio-oil with added C₅ or C₆ sugars, the hydrotreatment products including oil and aqueous phases, coke and gaseous products were quantified and analysed.

Table 4-1 also compares the coke produced from hydrotreatment of pure sugars with the hydrotreatment of bio-oil alone and bio-oil with added sugars in the presence and the absence of the NiMo catalyst. It was clear that the coke formed from the catalytic hydrotreatment of bio-oil with the added sucrose and xylose was higher than the sums of coke formed from the catalytic hydrotreatment of bio-oil alone and that of sugars alone under identical conditions. Different phenomenon was found for the catalytic hydrotreatment of bio-oil with added levoglucosan. It showed a lower coke formation than was predicted, indicating the negligible contribution of levoglucosan to coke formation. Furthermore, the coke formation in the non-catalytic hydrotreatment of bio-oil with the added sugars was higher than the predictive coke ideally formed from the non-catalytic hydrotreatment of sugars alone and the bio-oil alone. In the absence of the NiMo catalyst, levoglucosan behaved like sucrose and glucose (see Figure 4-1) since it will be first hydrolysed to form glucose in an acidic aqueous medium (such as bio-oil) [18, 31]. The results clearly show that the added C₅ and C₆ sugars interacted with other bio-oil components during hydrotreatment, promoting severe coke formation.

Figure 4-1 shows the mass balance closure of the bio-oil and bio-oil with added sugars during hydrotreatment expressed on a moisture free basis. The hydrotreatment of bio-oil without added sugars in the absence of a catalyst (labelled as “Blank-BO”) was performed for comparison. The comparison was also made by the hydrotreatment of bio-oil in the presence of ZnO alone (labelled as “ZnO-BO”) to provide direct evidence that ZnO did not catalyse hydro(deoxy)genation during hydrotreatment. The hydrotreatment of bio-oil with added xylose in the absence the NiMo catalyst (labelled as “Blank-BO-Xylose”) was conducted in duplicate as presented in Figure 4-1. It can be seen that the reproducibility of the experiments was good.

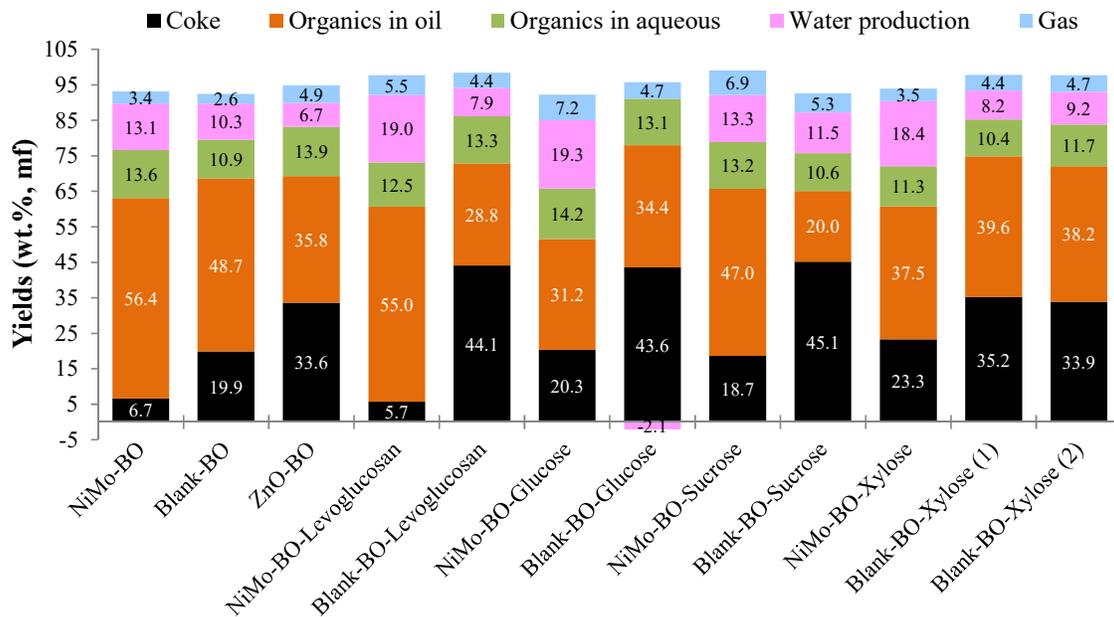


Figure 4-1. Mass balance closure of bio-oil and added C₅-C₆ sugars in the hydrotreatment of bio-oil using the NiMo catalyst at 300 °C. The data labelled as “NiMo-BO”, “Blank-BO”, “NiMo-BO-Levogluconan” and “Blank-BO-Levogluconan” were reported earlier in Chapter 3 [22]. Water consumption (shown as a negative value) was observed for “Blank-BO-Glucose”.

As can be seen in Figure 4-1, without adding any sugars, the yields of hydrotreated liquid and gaseous products for “NiMo-BO” were higher than those for “Blank-BO”. As expected, the coke formation in “NiMo-BO” was lower than that in “Blank-BO”. The generation of active hydrogen must have occurred in the presence of the NiMo catalyst [21]. This active hydrogen would further react with the components (or fragments) of bio-oil (and added compounds) adsorbed at the active sites of the catalyst [21] or in the fluid phase to undergo hydro(deoxy)genation.

During the catalytic hydrotreatment with added levogluconan, “NiMo-BO-Levogluconan” did not show a significant change in the yield of organics in both oil and aqueous phase compared to “NiMo-BO”. In contrast, the yield of organics in the oil phase for

“Blank-BO-Levogluconan” drastically decreased. The addition of other sugars (sucrose, xylose and glucose) did significantly decrease the yields of organics in the oil phase but not those in the aqueous phase, regardless if the NiMo catalyst was used.

With added sugars (levogluconan, glucose, sucrose and xylose) and in the presence of the NiMo catalyst, the water production of “NiMo-BO-Levogluconan”, “NiMo-BO-Glucose” and “NiMo-BO-Xylose” increased remarkably compared to “NiMo-BO”. In the case of “NiMo-BO-Sucrose”, there was no (or very little) increase in the water production. On the other hand, in the absence of the NiMo catalyst, the water production of “Blank-BO-Levogluconan”, “Blank-BO-Glucose”, “Blank-BO-Sucrose” and “Blank-BO-Xylose” was a bit lower than that of the corresponding catalytic hydrotreatment. It is interesting to note that the water consumption was observed for “Blank-BO-Glucose”, as shown by a negative yield value in Figure 4-1.

The data in Figure 4-1 also indicate that the decreases in the yields of the organics in the oil phase were mainly due to the formation of coke. As also shown in Table 4-1, the hydrotreatment of bio-oil with added sugars (except levogluconan, see below) showed drastic increases in coke formation even in the presence of the NiMo catalyst. Sugar compounds would intend to react in acidic aqueous environment like bio-oil to yield humic substances of non-defined composition [32]. These humic substances are coke-like material. Moreover, the added C₅-C₆ sugars with abundant oxygen-containing functional groups would limit the adsorption of hydrogen on the catalyst surface, thus limiting the active hydrogen supply in the reaction system. This is because oxygen would be easier to be adsorbed on the active sites of the catalyst than hydrogen, which would be dissociatively adsorbed on the active sites of the catalyst [33]. As this trend was similar for all the sugars, the mechanism of coke formation with added different sugars might be similar, as is shown in the simplified reaction scheme in Figure 4-2. Furthermore, the C₆ sugars (glucose and sucrose) tended to form more

coke than the C₅ sugars (xylose), as the C₆ sugars could form a six membered ring, which resembles to the structures of the highly aromatic coke. In comparison, the formation of the five-membered ring structures in coke is relatively difficult.

The only exception was the “NiMo-BO-Levoglucosan”. It showed a similar extent of coke formation to “NiMo-BO”. Levoglucosan is an anhydrous sugar, which could not be transformed to an open-chain structure with the formation of carbonyl groups, whereas xylose, glucose, and sucrose could. It appears [34] that the carbonyl functional groups may be particularly reactive in the formation of coke. Without the formation of the open-chain structure and thus a carbonyl, levoglucosan was probably stabilised quickly in the presence of the NiMo catalyst and did not contribute much towards the coke formation.

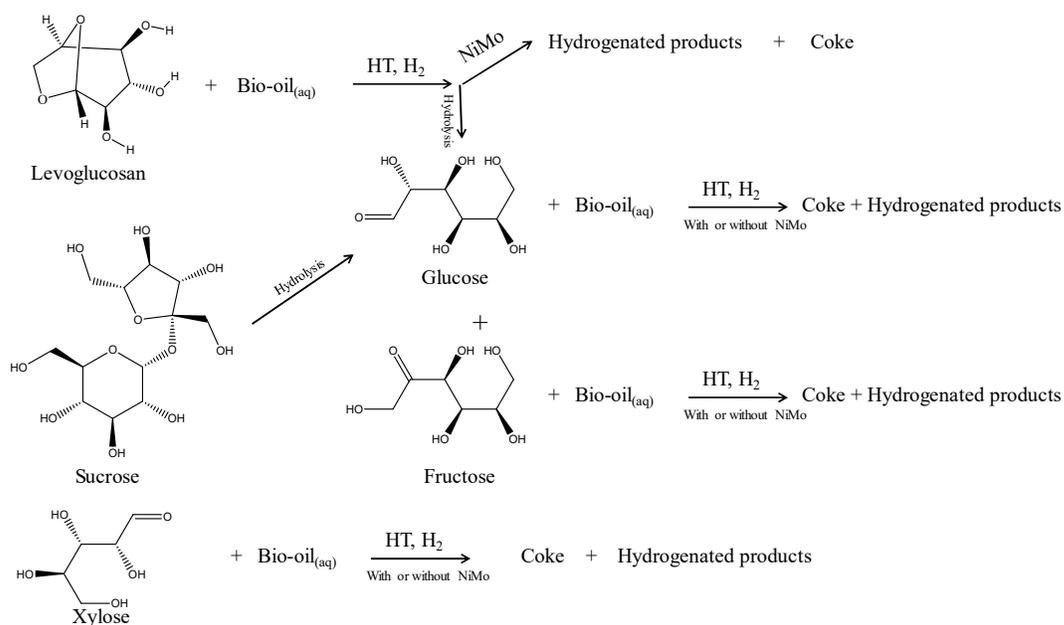


Figure 4-2. A simplified reaction scheme for the coke formation during the hydrotreatment of bio-oil with added C₅ and C₆ sugars.

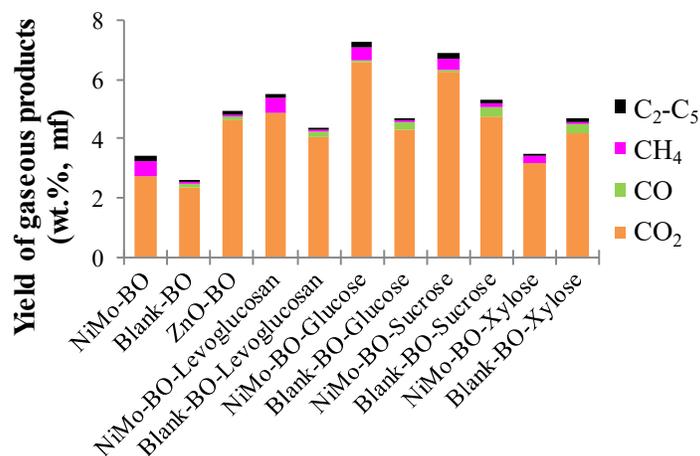


Figure 4-3. Yields of gaseous products in the hydrotreatment of bio-oil and bio-oil with added C₅-C₆ sugars using the NiMo catalyst at 300 °C. The data labelled as “NiMo-BO”, “Blank-BO”, “NiMo-BO-Levogluconan” and “Blank-BO-Levogluconan” were reported earlier in Chapter 3 [22].

The yields of the gaseous products produced during hydrotreatment are separately presented in Figure 4-3. It seems that the abundant oxygen-containing groups in the added C₅-C₆ sugars tended to promote the production of gaseous products during both catalytic and non-catalytic hydrotreatment. The gas production of “NiMo-BO-Levogluconan”, “NiMo-BO-Glucose”, “NiMo-BO-Sucrose” and “NiMo-BO-Xylose” was higher than that of “NiMo-BO”, whereas the gas production of “Blank-BO-Levogluconan”, “Blank-BO-Glucose”, “Blank-BO-Sucrose” and “Blank-BO-Xylose” was higher than that of “Blank-BO”. The gas production during the hydrotreatment of bio-oil with added C₅ sugar like xylose (“NiMo-BO-Xylose” and “Blank-BO-Xylose”) was somewhat lower than that with added C₆ sugars (sucrose, glucose and levogluconan).

CO₂ was the most abundant gas produced during the hydrotreatment of bio-oil with and without added sugars for both catalytic and non-catalytic hydrotreatment. A possible explanation is the occurrence of decarboxylation to produce CO₂ possibly from acids and

esters present in the bio-oil. In addition, the high abundance of oxygen-containing functional groups in the bio-oil allowed the catalytic and non-catalytic decarbonylation to form CO. However, insignificant production of CO was observed for the catalytic hydrotreatment, whereas the non-catalytic hydrotreatment showed a much higher production of CO. It might be due to the conversion of CO produced in the presence of the NiMo catalyst to CO₂ via the water-gas-shift reaction, leading to a predominant production of CO₂. Furthermore, the production of significant amounts of CH₄ in the catalytic hydrotreatment was observed, suggesting that the NiMo catalyst used possibly also catalysed the methanation of CO/CO₂ in the presence of hydrogen at 300 °C. Another explanation is the possible cracking of side chains of the large components and hydro(deoxy)genation of the light components of bio-oil.

The coke-forming propensity of bio-oil and the hydrotreated products might be indicated by the potential coke yields measured at 500 °C with TGA. The heavy fractions derived from hemicellulose, cellulose and lignin in bio-oil could contribute a significant portion to coke formation [21] during the TGA experiment. Figure 4-4 shows the potential coke yields for bio-oil itself, bio-oil with added C₅-C₆ sugars (e.g. “BO- Levoglucosan”) and their corresponding hydrotreated oils (e.g. “NiMo-BO-Levoglucosan”), and expressed on a moisture free basis by excluding the amount of water in the sample. The potential coke yields of the feedstocks (bio-oil itself and bio-oil with added sugars) represent a special case of reactions, i.e. the thermal reactions in the absence of hydrogen, catalyst and pressure. The pressure seemed to be an important factor in the coke formation. A pressurised reactor like in the hydrotreatment experiments would allow volatiles stay in the liquid phase, creating more chance to their cross-reactions. In the TGA experiment, in contrast, the light components would evaporate before they could react with other components in bio-oil to form heavy molecules. Thus, during the TGA experiment, the thermal treatment of the bio-oil/sugar feedstock did not give high yields of coke as compared to that using autoclave reactor.

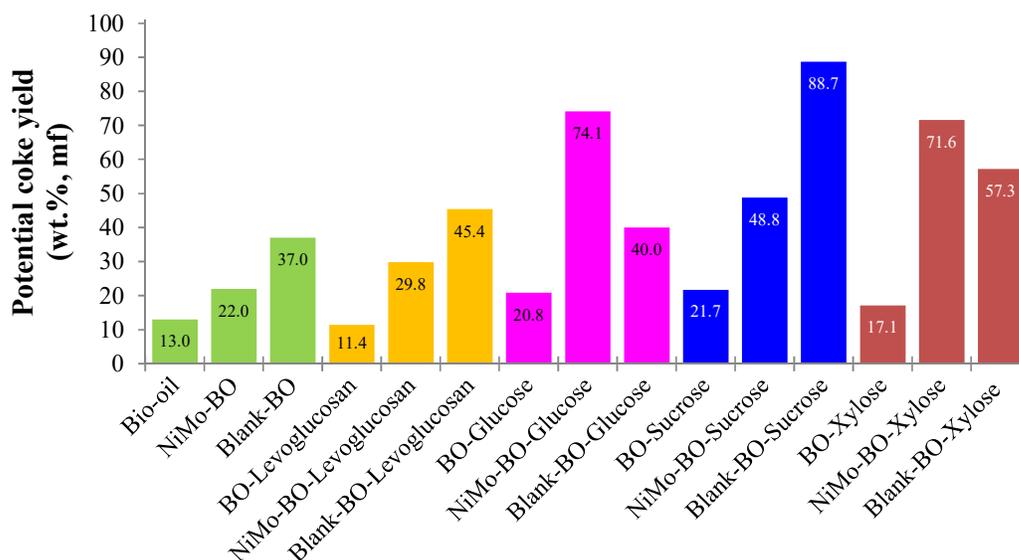


Figure 4-4. Potential coke yields for bio-oil, bio-oil with added C₅-C₆ sugars and their corresponding hydrotreated oils measured at 500 °C using TGA. The data labelled as “NiMo-BO”, “Blank-BO”, “NiMo-BO-Levoglucosan” and “Blank-BO-Levoglucosan” were reported earlier in Chapter 3 [22].

After hydrotreatment with added C₅-C₆ sugars to bio-oil, the potential coke yields all increased significantly regardless if the NiMo catalyst was used, indicating the contribution of the added sugars on the formation of heavy products. Possibly, the hydrotreatment of bio-oil/sugars led to the formation of more heavy components, which has not been transformed into coke yet, but were present in the liquid products. After the thermal treatment of bio-oil in the blank experiment, the potential coke yield increased from 13 wt% (“Bio-oil”) to 37 wt% (“Blank-BO”), indicating the occurrence of the polymerisation reactions. A noticed phenomenon was observed for the “Blank-BO-Sucrose”; the potential coke yield drastically increased to 88.7%. Sucrose is an oligomer. The cross-polymerisation of sucrose with the components in bio-oil probably decreased the volatility of the products.

Coke could be formed from the recombination of radicals and the condensation of compounds with reactive functional groups e.g. carbonyl groups. Via radical mechanism, the radicals could be generated through any bond cleavage of the bio-oil components as well as the added sugars. The radicals could undergo two different types of reaction to form more stable molecules: either (1) hydrogenation, (hydro)cracking and (hydro)deoxygenation, or (2) recombination to form molecules with higher molecular weight. The latter would likely occur if the supply of active hydrogen in the reaction system is not adequate to terminate the radicals [35], especially in the absence of a catalyst. The continued recombination would lead to the formation of coke [30, 36].

On the other hand, the formation of coke via aldol condensation during the hydrotreatment of bio-oil could also take place as bio-oil consists of various species containing carbonyl groups. Glucose and xylose (as well as sucrose, as it would be hydrolysed into glucose and fructose) are able to form two types of structures, i.e. open and ring structures. The open structure of those sugars contains carbonyl group. Those two structures are in dynamic equilibrium. If the open structure is consumed via the polymerisation or other reactions, the ring structure will instantly shift to the open form until all the sugars are consumed.

4.3.2 Transformation of light components

As was explained above, the added C₅-C₆ sugars are very reactive with other components in the bio-oil, promoting coke formation. The transformation of light GC-detectable compounds might provide specific information on which types of compounds would contribute to coke formation during hydrotreatment. Therefore, the transformation of individual light compounds was studied and the data are presented in Figure 4-5 to 4-7. The

yields presented here are the sums of the yield of compound(s) in both aqueous and oil phases of the hydrotreated products. These yields are expressed on the basis of the feedstock (bio-oil plus the added sugar) on a moisture free basis.

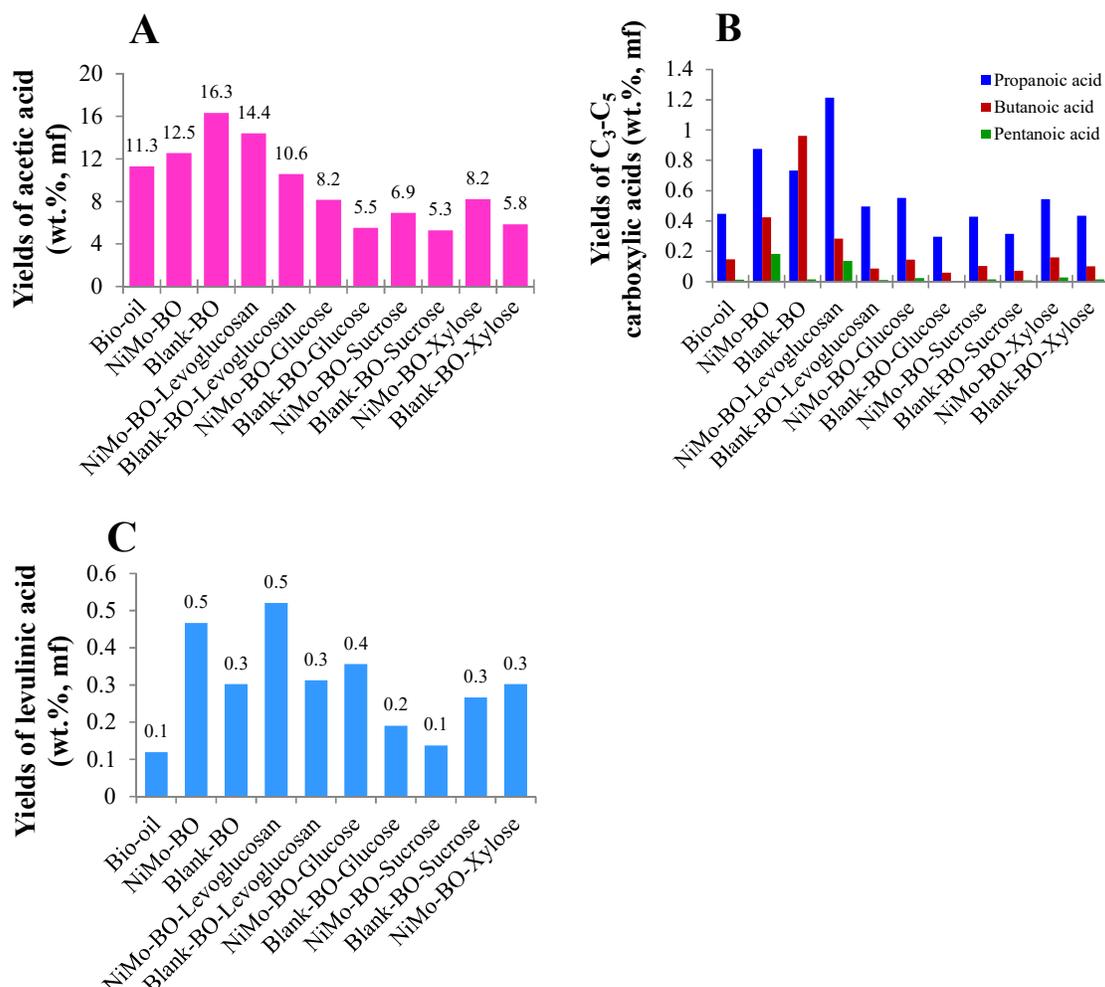


Figure 4-5. Yields of (A) acetic acid, (B) C₃-C₅ carboxylic acids and (C) levulinic acid from the hydrotreatment of bio-oil with added C₅-C₆ sugars using the NiMo catalyst at 300 °C. The data labelled as “NiMo-BO”, “Blank-BO”, “NiMo-BO-Levoglucoosan” and “Blank-BO-Levoglucoosan” were reported earlier in Chapter 3 [22].

The deoxygenation of acetic acid was reported to be difficult [37, 38]. Therefore, it is important to study the change in the yields of acetic acid during the hydrotreatment, as presented Figure 4-5A. Acetic acid was produced in “NiMo-BO” and “Blank-BO”, the catalytic and non-catalytic hydrotreatment of bio-oil without added sugars, respectively. Acetic acid might be produced from the cracking of side chains of sugar-derived oligomers in the bio-oil. With the added levoglucosan, acetic acid was only produced in “NiMo-BO-Levoglucosan”, but not in the “Blank-BO-Levoglucosan”. On the other hand, the yields of acetic acid considerably decreased during the catalytic and non-catalytic hydrotreatment with added other sugars (i.e. sucrose, xylose and glucose). Therefore, there must be reactions consuming acetic acid in the original bio-oil. Such reactions could be between acetic acid and sugars, or involving acetic acid in the interactions between sugars and other bio-oil components.

It was reported that C₃-C₅ carboxylic acids were produced during the hydrotreatment of bio-oil [22, 38] from the aliphatic chains connecting lignin-derived oligomers and/or with sugar-derived oligomers in bio-oil. Figure 4-5B shows the yields of C₃-C₅ carboxylic acids during the hydrotreatment of bio-oil and bio-oil with the added C₅-C₆ sugars. These acids were produced in appreciable amount in “NiMo-BO”, “Blank-BO” and “NiMo-BO-Levoglucosan”. With the added other sugars (glucose, sucrose and xylose), the yields of those acids slightly increased in the presence of the NiMo catalyst, but tended to be slightly consumed in the absence of the NiMo catalyst. From the results, it could be noticed that the production of C₃-C₅ carboxylic acids was a catalytic process. The C₃-C₅ carboxylic acids might take a part in the formation of coke during the hydrotreatment of bio-oil with the added sugars, except levoglucosan.

The production of levulinic acid came from the hydrolysis of sugars or sugar oligomers in the bio-oil [17, 39]. From Figure 4-5C it can be seen that the yields of levulinic acid was

far too small compared to the theoretical yields of levulinic acid from the sugars [39]. Apparently, those C₆ sugars were first cross-polymerised before they can be converted into levulinic acid.

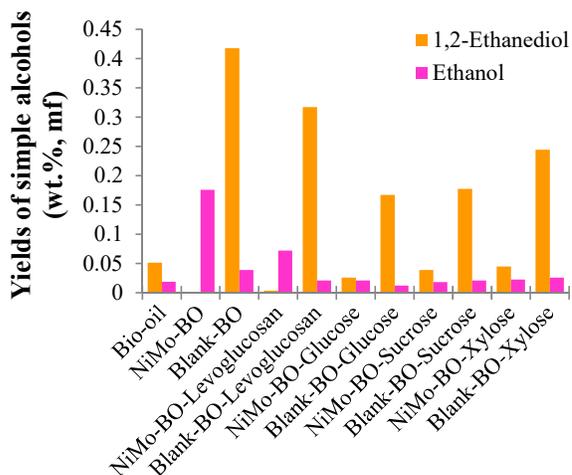


Figure 4-6. Yields of simple alcohols from the hydrotreatment of bio-oil with added C₅-C₆ sugars using the NiMo catalyst at 300 °C. The data labelled as “NiMo-BO”, “Blank-BO”, “NiMo-BO-Levoglucoosan” and “Blank-BO-Levoglucoosan” were from the same experiments reported earlier in Chapter 3 [22].

Hydroxyl acetaldehyde (glycoaldehyde), which is found in the bio-oil, is a very reactive compound. In our previous work [22], hydroxyl acetaldehyde was almost totally consumed even at 150 °C. In this study, hydroxyl acetaldehyde was also totally consumed (not shown here) during the hydrotreatment of bio-oil or bio-oil with added sugars due to its high reactivity. Aldehydes such as hydroxyl acetaldehyde are very easy to be hydrogenated to produce alcohols such as ethanol or 1,2-ethenediol [40]. Although not in a stoichiometric ratio, the increases in the yields of those two simple alcohols were observed (as is shown in Figure 4-6). In addition, the aldehydes possibly also contributed to coke formation due to its high reactivity [18].

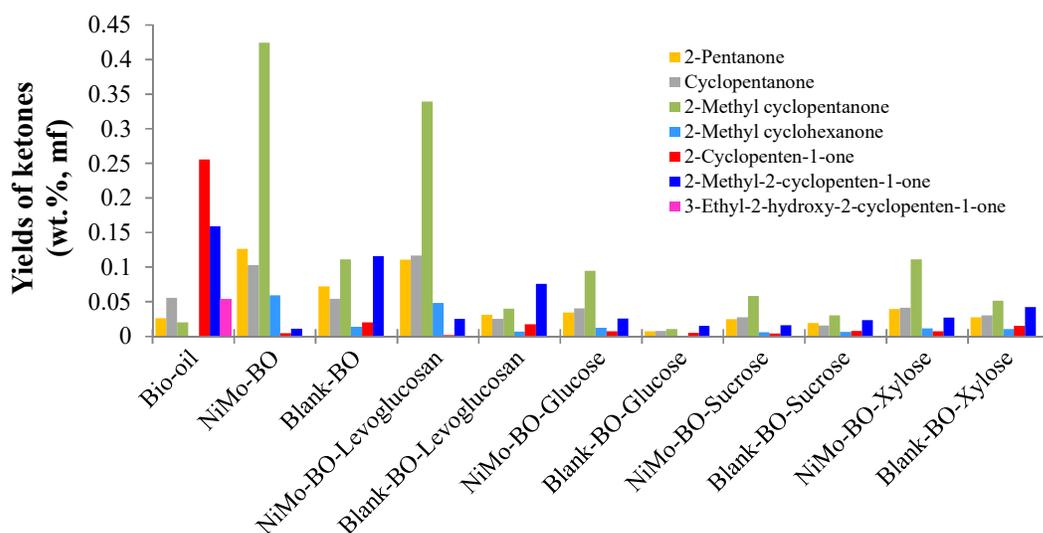


Figure 4-7. Yields of ketones from the hydrotreatment of bio-oil with added C₅-C₆ sugars using the NiMo catalyst at 300 °C. The data labelled as “NiMo-BO”, “Blank-BO”, “NiMo-BO-Levogluconan” and “Blank-BO-Levogluconan” were reported earlier in Chapter 3 [22].

In addition, furfural is very reactive and was also totally consumed at 300 °C as previously reported in Chapter 3 [22]. It can be converted to cyclopentanone through the reaction with hydrogen and can further form cyclopentanol and 1-pentanol [38]. 2-methyl cyclopentanone, which was produced during the hydrotreatment in this study, can also be formed from the hydrogenation of compounds with a molecular structure similar to furfural such as cyclopenten-1-ones. Subsequently, the yields of cyclopentanones (Figure 4-7) increased significantly. It was also noticed that the production of ketonic compounds in the presence of added C₅-C₆ sugars was not significant. These data also support the previous explanation that the added sugars (except levogluconan) possibly strongly interacted with other components in bio-oil and changed their reaction pathways.

4.3.3 Transformation of aromatic ring structures

UV-fluorescence spectroscopy with a constant energy difference of -2800 cm^{-1} was used to characterise the aromatic ring structures of the feedstocks and the corresponding hydrotreated products from the hydrotreatment experiments. Due to negligible fluorescence intensity of the aqueous phase, the synchronous spectra presented in Figure 4-8 are only for the oil phases. The synchronous spectra were expressed on a moisture free basis of the bio-oil plus added sugars (feedstock). The synchronous spectra of the bio-oil with added sugars are not shown in Figure 4-8 because it shows exactly the same spectra but only slightly different intensity as bio-oil itself without added sugars. As expected, sugars are not showing any fluorescence intensity in the current fluorescence method.

The raw bio-oil from the pyrolysis of mallee wood itself is a complex mixture, ranging from simple molecules such as water and acetic acid to cellulose-, hemicellulose- and lignin-derived oligomers. The catalytically hydrotreated oils clearly show a much stronger intensity in the synchronous spectra than the feedstocks. This intense peak indicates the presence of abundant large aromatic ring structures. This also provided a direct evidence for the ring condensation (ring growth) to form larger aromatic ring systems during hydrotreatment under very mild conditions in this study. This ring growth in the hydrotreated oils could be related to the potential coke yields (e.g. formation of large molecules, see Figure 4-4) and the highly aromatic coke possibly formed from the hydrotreatment.

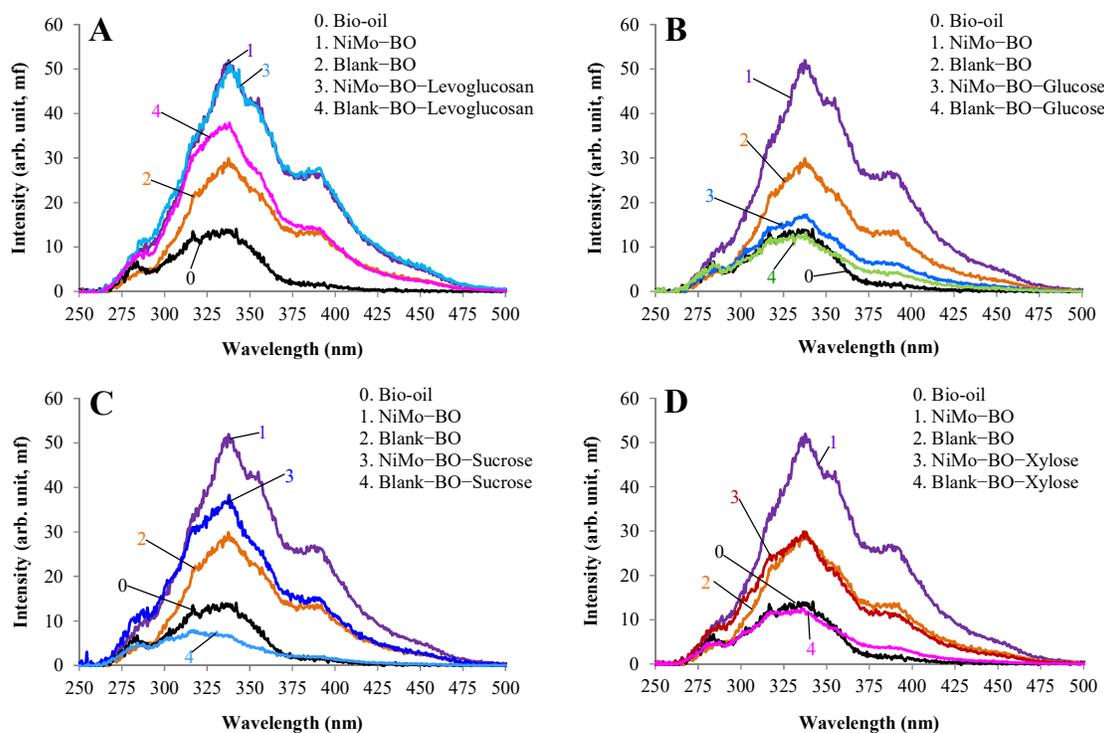


Figure 4-8. Synchronous spectra of the oil phases at a constant energy difference of -2800 cm^{-1} after the hydrotreatment of bio-oil with added (A) levogluconan, (B) glucose, (C) sucrose and (D) xylose using the NiMo catalyst at $300\text{ }^{\circ}\text{C}$. The data labelled as “NiMo–BO”, “Blank–BO”, “NiMo–BO–Levogluconan” and “Blank–BO–Levogluconan” were reported earlier in Chapter 3 [22].

It can also be clearly seen in Figure 4-8 that the growth of the aromatic ring systems was observed for all of the catalytically hydrotreated oils compared to the original bio-oil/feedstock. The catalytically hydrotreated oils not only showed the higher fluorescence intensity in the range of 320-330 nm, but also gave higher fluorescence intensity at wavelengths higher than 360 nm, indicating the formation of bigger aromatic ring structures. It appears that abundant ring systems with various sizes could be produced via the cracking and recombination of large molecules (such as large oligomers) [21] as well as the

condensation of small aromatic ring structures under the hydrotreatment conditions employed.

In most cases, the catalytically hydrotreated oils showed higher fluorescence intensity than those from the non-catalytic ones. It might indicate that in the absence of a catalyst, the condensation of small ring systems into extremely large ones and/or coke severely occurred. These extremely large ring systems might be beyond the detection limit of the current synchronous spectral method [21]. This is supported by the data on coke formation in Figure 4-1 and the potential coke yields in Figure 4-4. Two reactions possibly simultaneously took place during the hydrotreatment under very mild conditions (at 300 °C and \leq 100 bar hydrogen pressure), i.e. rapid formation of aromatic ring structures, and hydrogenation leading to the competition between polymerisation/coke formation and hydro(deoxy)genation.

Furthermore, the fluorescence intensity of the hydrotreated oils from blank experiments (except “Blank-BO-Levogluconan”) was surprisingly lower than that of “Blank-BO”. It could suggest the severe coke formation in the presence of sugars so that what was left in the liquid phase (being analysed) become less aromatic. This is also in a good agreement with the data of coke formation in Figure 4-1. Of four added sugars to bio-oil, bio-oil with added glucose (“NiMo-BO-Glucose” and “Blank-BO-Glucose”) showed the lowest fluorescence intensity both in the presence and the absence of the NiMo catalyst. It suggested that, with added glucose, the polymerisation leading to extremely high molecular weight compounds that cannot be seen in UV-fluorescence method occurred even in the presence of the NiMo catalyst.

4.4 CONCLUSIONS

C₅ and C₆ sugars, which have different numbers of oxygen-containing functional groups and thus different structures, was found to tend to form coke during the hydrotreatment of pure sugars. They also involved in the coke formation during the hydrotreatment of bio-oil to different extents. C₆ sugars contributed more to the coke formation compared to C₅ sugars due to their structures being close to highly aromatic coke. Sucrose and glucose showed similar reactivity and thus similar effect on the coke formation during the hydrotreatment i.e. showed a higher coke formation. The reaction behaviours of sucrose are similar to those of the C₆ sugars such as glucose, as sucrose could be hydrolysed to form fructose and glucose during the hydrotreatment in the aqueous acidic bio-oil. On the other hand, xylose showed a lower reactivity and thus relatively lower tendency towards coke formation. Sugars strongly interacted with other components in bio-oil, significantly promoting coke formation.

An exceptional phenomenon was observed for levoglucosan. In the presence of the NiMo catalyst, it did not contribute much to the coke formation since it does not have carbonyl group(s), although the formation of heavy molecules took place significantly. In contrast, in the absence of the NiMo catalyst, the coke formation of the hydrotreatment of bio-oil with added levoglucosan was similar to that in glucose and sucrose. Levoglucosan could be hydrolysed to glucose, and thus its reaction behaviours became similar to that of glucose, promoting the coke formation. The added sugars strongly reacted with the reactive components in the bio-oil, leading to the cross-polymerisation reactions. In addition, in the hydrotreatment of bio-oil with added sugars, there are abundant heavy products formed, which, however, could not be seen by the fluorescence method.

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CHAPTER 5

**THE BENEFICIAL EFFECTS OF PHENOLIC
FUNCTIONALITIES IN REDUCING COKE FORMATION
DURING THE HYDROTREATMENT OF BIO-OIL
USING A NiMo/ γ -Al₂O₃ CATALYST**

5.1 INTRODUCTION

Pyrolysis has been considered as a promising technology to convert renewable biomass to bio-oil [1, 2]. Bio-oil is a potential candidate to replace fossil fuel. However, bio-oil cannot be directly used as a liquid transport fuel due to its high oxygen content (30-40 wt%) [2] leading to low energy density (HHV of 16-18 MJ/kg), instability, corrosiveness and immiscibility with petrol or diesel [1-5]. Therefore, upgrading of bio-oil to a high quality liquid transport fuel is imperative.

Catalytic hydrotreatment is one of the promising technologies for bio-oil upgrading into fuels and chemicals [6-9]. However, coke formation is one of the biggest challenges, currently an almost unavoidable problem in the hydrotreatment of bio-oil. It affects the stability of the hydrotreatment catalysts and thus the process operability and efficiency [2, 10, 11]. Various methods have been tried to reduce coke formation. For example, the pre-treatment using methanol through the esterification of bio-oil prior to hydrotreatment has been shown effective to eliminate the reactive oxygen-containing functional groups and reduce coke formation [12-14]. However, the coke-related problem remains to be significant, hindering the commercialisation of bio-oil hydrotreatment.

Due to the complex composition of bio-oil and the complicated reaction network during hydrotreatment, studies on model compounds have been extensively performed to deal with the complexity of bio-oil. The hydrotreatment of phenolic compounds [15-25] has been used to gain insights into the behaviour of bio-oil during hydrotreatment. Model compound studies are useful to understand the reactivity of some simple components in bio-oil. However, the behaviour of single model compound or mixture of model compounds would be too simple to reflect the actual behaviour of bio-oil due to the complex interaction among the components in the bio-oil during hydrotreatment.

In general, bio-oil contains acids, aldehydes, ketones, sugars, phenols and other organics with multiple functionalities [26]. Phenolic compounds are derived from lignin in biomass [27], which constitute c.a. 30 wt% of bio-oil [1, 3, 28] and have been considered as a potential source for the production of useful products [2, 29]. However, the high reactivity of the oxygen-containing functionalities in the phenolics compounds, leading to relatively low stability [30, 31], is troublesome during the hydrotreatment of bio-oil.

The reactivity of phenolic compounds is strongly related to their chemical structure. For instance, the presence of a methoxy group attached to a phenol molecule (found in guaiacol) would affect the reactivity of the corresponding phenolic compounds. It has been shown that O-CH₃ bond in guaiacol would be easier to break down than C_{aryl}-O bond in phenol [22, 30], which was the reason of the higher reactivity of guaiacol than phenol. Furthermore, the presence of an extra alkenyl group (e.g. in isoeugenol) or an extra carbonyl group (e.g. in vanillin) attached to guaiacol would greatly affect the reactivity of the corresponding phenolic compounds. The alkenyl group (with one C=C double bond) in isoeugenol would be relatively more reactive than O-CH₃ in guaiacol. Likewise, the carbonyl group in vanillin would be expected to be much more reactive than the O-CH₃ group.

The presence of the phenolic compounds with such different reactivity could significantly affect the behaviour of the components in the bio-oil during hydrotreatment. Their contribution to coke formation might vary, depending on their functional groups, thus on their reactivity. However, very little information is available in the literature on the behaviour of different phenolic compounds on coke formation during the hydrotreatment of the real bio-oil. Such information would be very useful in the development of hydrotreatment technologies.

In this study, the contribution of different functional groups in the phenolic compounds to coke formation was investigated. Guaiacol, isoeugenol and vanillin were added

individually to the bio-oil and their behaviour during the hydrotreatment was examined. The hydrotreatment of bio-oil with added methanol was also conducted to understand its roles in suppressing coke formation e.g. through esterification. The transformation of aromatic ring structures and light components during the hydrotreatment were also studied to gain insight into the roles of the phenolic functionalities in reducing or promoting coke formation. In addition, the hydrotreatment of model compounds in aqueous medium under identical conditions was also conducted for comparison.

5.2 EXPERIMENTAL

5.2.1 Materials

Grinding pyrolysis is a novel pyrolysis technology to convert biomass into bio-oil [32, 33]. In this study, the bio-oil used in the hydrotreatment experiments was produced from the pyrolysis of mallee wood in a grinding pyrolyser, and was done by Dr. MD Mahmudul Hasan. The details of the pyrolysis procedures were described elsewhere [32]. The pyrolysis experiment was conducted at temperature of 450-465 °C with a constant reactor speed rotation of 54 rpm. Two condenser systems were installed downstream the pyrolysis unit, i.e. the water condenser and dry ice condenser. The oil condensed in those two condensers was collected and mixed before filtration. The filtered bio-oil was then stored in a fridge at -10 °C before use.

In this study, pre-sulphided NiMo supported on γ -Al₂O₃ was used in the hydrotreatment experiments, hereafter is referred to as “NiMo catalyst”. The catalyst was purchased from EureCat, France. It typically contains 3-4 wt% of Ni and 12-16 wt% of Mo and was ground to 250-600 μ m before use. Guaiacol (Sigma-Aldrich, \geq 99.5%), isoeugenol (Sigma-Aldrich, \geq

99.5%), vanillin (Sigma-Aldrich, $\geq 99.5\%$ GC) and methanol (Sigma-Aldrich, $\geq 99.5\%$ GC) were added into the bio-oil to form modified bio-oil feedstocks for the hydrotreatment experiments. Hydrogen and nitrogen (high purity grade, 99.99%) used in all hydrotreatment experiments were purchased from BOC.

5.2.2 Hydrotreatment experiments

The hydrotreatment experiments were performed in a batch reactor system described earlier in Chapter 3 [34] and 4. The hydrotreatment experiments included hydrotreatment of bio-oil, bio-oil with added phenolic compounds and pure phenolic compounds. The structure of the phenolic compounds used in this study is specified in Table 5-1. Hydrotreatment of bio-oil with added methanol was also conducted for comparison.

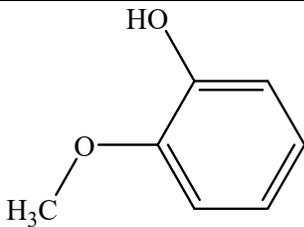
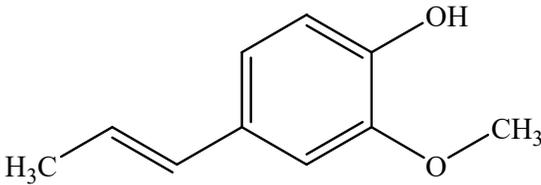
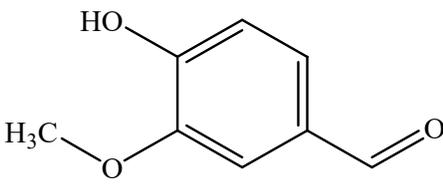
The experiments are labelled by the experimental conditions followed by the added model compound. For example, the catalytic and non-catalytic hydrotreatment of bio-oil with added guaiacol are labelled as “NiMo-BO-Guaiacol” and “Blank-BO-Guaiacol”, respectively.

The detail procedures of the experiments were the same as those reported earlier in Chapter 3 [34] and 4. Briefly, raw bio-oil (40.0 g), phenolic compounds (10.0 g of one phenolic compound in each experiment), the NiMo catalyst (4.0 g) and ZnO (1.5 g; to prevent the corrosion of the batch reactor as mentioned earlier in Chapter 3 [34] and 4) were introduced into the reactor. For comparison, blank experiments (having bio-oil with added phenolic compounds and hydrogen) in the absence of the NiMo catalyst were also conducted. All experiments were conducted at the same temperature and holding time (300 °C for 3 h) with a stirring rate of 400 rpm. The initial hydrogen pressure at room temperature was 50 bar. During the experiments, the total pressure was kept at minimum 100 bar. Therefore, feeding

additional hydrogen during experiments when the pressure reduced due to the consumption of hydrogen was possible.

Table 5-1.

Chemical structure of the phenolic compounds added into the bio-oil as feedstocks in the hydrotreatment experiments.

Name of compound	Chemical structure
Guaiacol	
Isoeugenol	
Vanillin	

After 3 h, the experiment was stopped and the reactor was rapidly cooled to room temperature. A water cooling system running through a coil inside the reactor was used. After reaching room temperature, the residual pressure was recorded from which, the gas composition could be determined to calculate the gas yields. The gas sample was then taken into a gas bag and immediately injected into a GC instrument (GC, Agilent 6890, equipped with a methaniser and a flame ionisation detector) to allow the quantification of the gaseous products.

After an experiment, the products (oil and aqueous phases and the solids including catalyst, zinc oxide and coke) were separated and collected. In the case of catalytic and non-catalytic hydrotreatment of bio-oil with added guaiacol and isoeugenol (labelled as “NiMo-BO-Guaiacol”, “Blank-BO-Guaiacol”, “NiMo-BO-isoeugenol” and “Blank-BO-isoeugenol”, respectively), the oil phase and the aqueous phase were separated using a centrifuge. In the case of the hydrotreatment of bio-oil with added vanillin (labelled as “NiMo-BO-Vanillin” and “Blank-BO-Vanillin” for the catalytic and non-catalytic hydrotreatment, respectively), the aqueous phase was at the top, the oil phase was in the middle and the solids were at the bottom of the reactor. After the oil phase and the aqueous phase were taken out, the solids remaining at the bottom of the reactor was then rinsed thoroughly using tetrahydrofuran (THF). The recovered solids were then washed with THF until a colourless filtrate was obtained. They were then dried under reduced pressure of -50 kPa at 50 °C. The amount of solids after drying subtracted by the total weight of the solids initially put into the reactor was defined as the amount of cokes formed during hydrotreatment.

The GC-MS was used to quantify the water contents in both oil and aqueous phases. The water production was defined as the total amount of water in the hydrotreated products (oil and aqueous phases) subtracted by the water in the original bio-oil. The mass balance was then expressed on a moisture free basis per gram of organics in the feedstock.

The hydrotreatment experiments of model compounds were conducted under identical conditions as the hydrotreatment of bio-oil except the use of water instead of bio-oil with the same amount (weight). The yields of products in the hydrotreatment of pure phenolics in aqueous medium were expressed on a basis of per gram of phenolic compounds plus water. The hydrotreatment experiments of pure phenolic compounds were labelled as follows. “NiMo-Guaiacol-Water” and “NiMo-Vanillin-Water” refer to the catalytic hydrotreatment of guaiacol and vanillin in water, respectively. The experiments of pure guaiacol and vanillin in

the absence of the NiMo catalyst are labelled as “Guaiacol-Water” and “Vanillin-Water”, respectively.

Some experiments reported here were from the same experiments reported previously in Chapter 3 [34], namely the catalytic and non-catalytic hydrotreatment of bio-oil alone labelled as “NiMo-BO” and “Blank-BO”.

5.2.3 Analyses

5.2.3.1 *Gas chromatography-mass spectroscopy (GC-MS)*

The liquid products from the hydrotreatment of bio-oil, bio-oil with added phenolics and individual phenolics were analysed using GC–MS to study the transformation of the light GC-detectable compounds with the parameters similar to those in our previous work [12, 35, 36]. An Agilent 6890 GC equipped with a 30 m × 0.25 mm × 0.25 μm HP-Innowax (cross-linked polyethylene glycol) column was used in the analysis. An Agilent 5973 MS detector was attached to the GC instrument to allow the identification of the individual compounds in the samples. 5-10 wt% (accurately known) of sample in acetone solution was used in the analysis. 1 μL of the acetone solutions was injected into the injection port set at 250 °C. The split ratio used was 50:1. The temperature of the oven was kept at 40 °C for 3 min, heated up to 260 °C at a rate of 10 °C/min and then kept isothermal for 5 min. The NIST library as well as the injection of standard solutions was used to qualitatively identify the individual compounds. For the quantification of the individual compounds in the bio-oil and the corresponding hydrotreated products, the injection of standard chemicals was conducted to obtain reproducible response factors (R^2 of ≥ 0.9).

5.2.3.2 *UV-fluorescence spectroscopy*

In this study, the bio-oil feedstocks and the corresponding hydrotreated oils were analysed with a Perkin-Elmer LS50B spectrometer to record the synchronous UV-fluorescence spectra at a constant energy difference of -2800 cm^{-1} [37, 38]. Methanol (Uvasol for spectroscopy; purity $\geq 99.9\%$) was used to dilute the samples to 4 ppm prior to analysis. The analysis was done with a scan speed of 200 nm min^{-1} and the slit widths of 2.5 nm. Each spectrum presented was the average of 4 scans. To have a fair comparison, the fluorescence intensity was expressed on the basis of per gram of organics in the feedstock by multiplying the intensity with the yields of organics in the oil phase on a moisture free basis.

5.2.3.3 *Thermogravimetric analysis (TGA)*

The bio-oil feedstocks and the corresponding hydrotreated products also underwent a thermogravimetric analysis (TGA) in inert atmosphere. A TGA-Q5000 instrument was used in the analysis. Firstly, 5-10 mg (accurately known) of sample was loaded into a sample pan in the TGA instrument and then heated in nitrogen atmosphere at a temperature range of 25-500 °C with a heating rate of 10 °C/min. The amount of material left in the pan after the experiment at 500 °C was referred to as the potential coke yield [14, 38, 39]. The potential coke yields were expressed on a moisture free basis.

5.3 RESULTS AND DISCUSSION

5.3.1 Beneficial roles of phenolic compounds with different functionalities in reducing coke formation

5.3.1.1 *Hydrotreatment of model phenolic compounds*

In order to gain a better understanding of the behaviour of phenolic compounds, the hydrotreatment of model phenolic compounds themselves at 300 °C with and without the NiMo catalyst was performed in the aqueous medium. It is believed that water is a suitable solvent allowing the selective hydrogenation of the phenolic compounds [40-43]. Figure 5-1A shows the yields of products in the hydrotreatment of model compounds only. The hydrotreatment of guaiacol and vanillin in water medium resulted in the formation of one single phase, except for the non-catalytic hydrotreatment of guaiacol (shown as “Guaiacol-Water” in Figure 5-1A). “Guaiacol-Water” resulted in two phases: yellowish liquid at the top and paste-like brown liquid at the bottom. The yields of the products were determined based on the weight of the model compound plus water in each run. The catalytic hydrotreatment of pure guaiacol in water was done in duplicate to show the good reproducibility of the data, as is shown in Figure 5-1.

All hydrotreatment experiments of individual phenolic compounds resulted in a very low (< 1 wt%) gaseous products. Methane and CO₂ were the predominant gases produced. The hydrotreatment of guaiacol (shown as “NiMo-Guaiacol-Water” and “Guaiacol-Water” in Figure 5-1A) did not result (or very low) in coke formation. In contrast, the hydrotreatment of vanillin (shown as “NiMo-Vanillin-Water” and “Vanillin-Water”) resulted in a significant amount of coke regardless if the NiMo catalyst was used. The formation of coke was possibly

much quicker than hydrogenation during the hydrotreatment of vanillin under the present experimental conditions (300 °C, \leq 100 bar initial hydrogen), indicated by the significant coke formation.

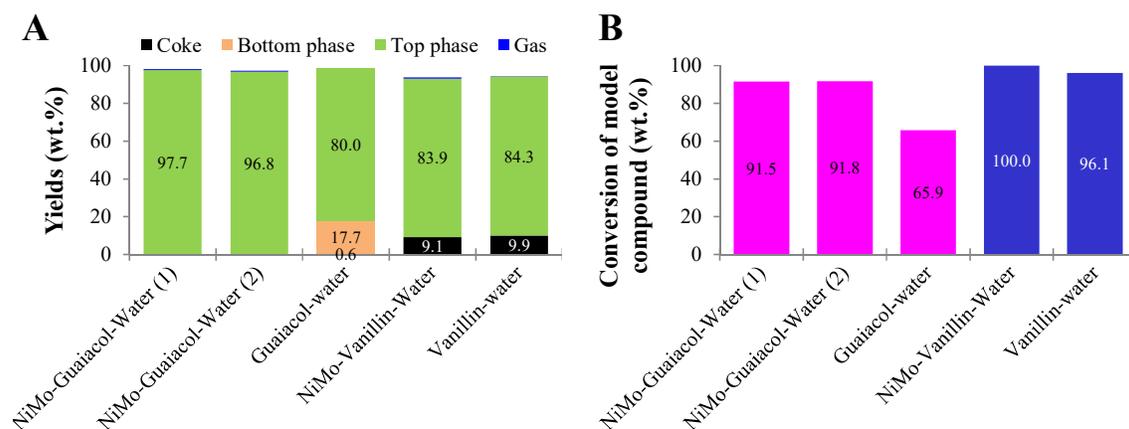


Figure 5-1. (A) Mass balance closure and (B) conversion of the individual model compound in the hydrotreatment of model phenolic compounds in the aqueous medium using the NiMo catalyst at 300 °C.

The conversion of vanillin was higher than that of guaiacol as presented in Figure 5-1B, regardless if the NiMo catalyst was used. The presence of the carbonyl group in vanillin might be the reason for the higher reactivity of vanillin in comparison to guaiacol. It was found that the carbonyl group was very reactive during the hydrotreatment as no compound with carbonyl group was detected in the product.

The yields of the products (as is shown in Table 5-2) was defined as the weight of a certain product divided by the weight of the individual model compound initially loaded in the hydrotreatment experiments. 1,2-benzenediol was observed as the major product and considered as important intermediate in the catalytic conversion of guaiacol and substituted guaiacols (e.g. vanillin). It might be produced through the breakage of the $-\text{OCH}_3$ group [22].

The produced 1,2-benzenediol could be subsequently converted to cyclohexanone either via dehydration followed by hydrogenation, or via hydrogenation followed by the dehydration of cyclohexane-1,2-diol [44, 45]. In addition, it also could be transformed to phenol by the elimination of hydroxyl group [22, 46], and then converted to cyclohexane and benzene.

Table 5-2.

Yields of the products in the hydrotreatment of phenolics model compounds at 300 °C using the NiMo catalyst.

Yield (wt%, g/g model compound)	NiMo-Guaiacol-Water	Guaiacol-Water	NiMo-Vanillin-Water	Vanillin-Water
Methanol	21.1	5.0	18.4	15.6
Guaiacol	8.4	34.1	0.7	3.6
Vanillin	–	0.1	–	3.9
1,2-benzenediol	59.9	3.3	10.6	–
Phenol	2.0	0.1	0.2	–
Methyl guaiacol	–	–	0.1	0.1
2-Methyl phenol	0.1	–	–	–
3-Methyl phenol	0.1	–	0.1	–
4-Methyl phenol	–	–	0.1	–
Cyclohexanone	2.4	–	–	–
<i>Cis</i> -1,2-cyclohexanediol	–	–	–	–

It is important to highlight that methanol was produced in the hydrotreatment of both vanillin and guaiacol in different extents regardless if the NiMo catalyst was used, with the hydrotreatment of vanillin (“NiMo-Vanillin-Water” and “Vanillin-Water”) showing much higher yields of methanol. Interestingly, the presence of produced methanol could not suppress the formation of coke as is evidenced by a high coke formation in “NiMo-Vanillin-Water” and “Vanillin-Water”. In contrast, a negligible coke formation was observed for “NiMo-Guaiacol-Water” and “Guaiacol-Water”. The detail species involved in the reactions

resulting in the coke suppression remain unknown and should be part of the future’s investigation. Because methanol was produced in significant quantity, the subsequent experiments with the bio-oil included methanol as a “model compound”.

5.3.1.2 Hydrotreatment of bio-oil with added phenolic compounds

The hydrotreatment of bio-oil with added phenolic compounds and methanol was conducted under identical conditions (300 °C, 3 h, total pressure of ≥ 100 bar). The yields of gaseous products, oil phase, aqueous phase and coke as well as water production are shown in Figure 5-2. The yields from the hydrotreatment of bio-oil alone (labelled as “NiMo-BO” and “Blank-BO”) are presented for comparison.

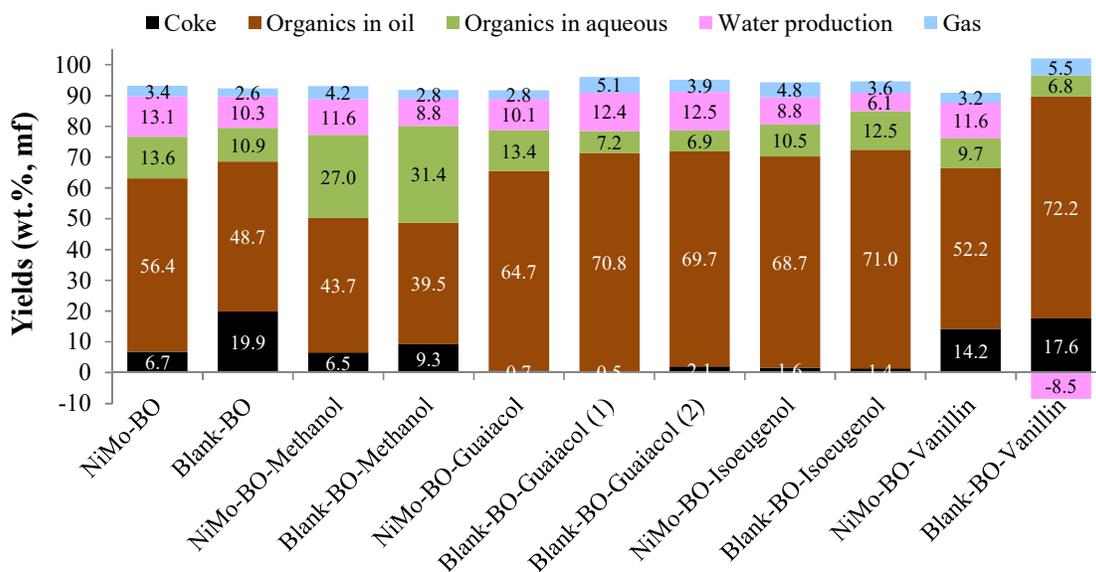


Figure 5-2. Mass balance closure in the hydrotreatment of bio-oil with added phenolic compounds and methanol using the NiMo catalyst at 300 °C. The data labelled as “NiMo-BO” and “Blank-BO” were reported earlier in Chapter 3 [34]. Water consumption was observed for “Blank-BO-Vanillin” (shown as a negative value).

In the absence of added phenolics and methanol, the yields of organics in the oil phase for “NiMo-BO” were higher than that for “Blank-BO” (56.4 wt% versus 48.7 wt%, respectively). This trend was also observed for “NiMo-BO-Methanol” and “Blank-BO-Methanol”, the catalytic and non-catalytic hydrotreatment of bio-oil with added methanol, respectively. On the other hand, with added phenolic compounds, the yields of organics in the oil phase from the catalytic hydrotreatment were lower than that from the non-catalytic one. The deeper hydrogenation, which would reduce the yield of organics and increase the formation of water, could be a reason for this phenomenon.

In most cases, there was a minor decrease in the yields of organics in the aqueous phase in the blank experiments compared to the corresponding catalytic experiments (“NiMo-BO” vs “Blank-BO”, “NiMo-BO-Guaiacol” vs “Blank-BO-Guaiacol, etc.). However, with added methanol and isoeugenol, a slight increase in the yields of organics in the aqueous phase for the “Blank-BO-Methanol” and “Blank-BO-Isoeugenol” compared to those for the “NiMo-BO-Methanol” and “NiMo-BO-Isoeugenol”, respectively, was observed. Methanol in “NiMo-BO-Methanol” was slightly consumed (ca. 3.5 wt%), whereas no consumption of methanol was observed in the “Blank-BO-Methanol”. The presence of the very polar organic solvent like methanol changed the distribution of organics throughout oil and aqueous phases. Likewise, the changes in the polarity of the bio-oil due to the catalytic hydrotreatment would also change the distribution of the organics in both the oil and aqueous phases. On the other hand, in the absence of the NiMo catalyst, the more amount of light polar compounds was not removed from the “Blank-BO-Isoeugenol”, remaining in the polar aqueous phase. This might be the reason for the higher yield of organics in the aqueous phase for “Blank-BO-Isoeugenol”, in comparison to “NiMo-BO-Isoeugenol”.

The formation of C–C bonds during hydrotreatment involving oxygen-rich components like bio-oil is typically accompanied by the production of water in large quantities [47] due to hydrodeoxygenation, which further contributes to oxygen removal. Dehydration, polymerisation and coke formation are possible other reactions producing water during hydrotreatment. It was noticed that the water production in the non-catalytic hydrotreatment was always slightly lower than the catalytic one. The low water production during the non-catalytic hydrotreatment might be due to the much lower level of hydrotreatment, leading to dehydrogenation and polymerisation to form coke.

The coke formation for “Blank-BO” was higher than that for “NiMo-BO” due to the lack of the supply of active hydrogen in the absence of the NiMo catalyst. It is likely that the formation of coke during the hydrotreatment in the absence of the NiMo catalyst involved the formation of radicals formed during the reactions. The radicals then would react with other compounds to promote polymerisation and aromatisation [47] to form polymeric or oligomeric species in the absence of active hydrogen [48].

The hydrotreatment by adding methanol to bio-oil was also conducted to understand the role of methanol in reducing coke formation during the hydrotreatment of the real bio-oil. With added methanol, the coke formation was observed even in the presence of the NiMo catalyst. The coke formation for “NiMo-BO-Methanol” was similar to that for “NiMo-BO”. It is shown that methanol could not significantly suppress the coke formation during the hydrotreatment of bio-oil. In contrast, in the absence of the NiMo catalyst, the coke formation of “Blank-BO-Methanol” was considerably lower than that of “Blank-BO”. To some extent, the esterification might take place in the mixture of acidic bio-oil and methanol in the absence of the NiMo catalyst, causing the lower tendency of the bio-oil to form coke [12, 13, 38, 49]. Furthermore, the presence of light oxygenates such as methanol could possibly suppress the formation of coke [50]. The data on the coke formation of “NiMo-BO-

Methanol” and “Blank-BO-Methanol” indicated that the effects of chemical functionalities in reducing coke formation, which were observed for the added guaiacol and isoeugenol (see below), were not due to the production of methanol from phenolic compounds during hydrotreatment.

Surprisingly, the coke formation for “NiMo-BO-Guaiacol” and “NiMo-BO-Isoeugenol” was significantly lower than that of “NiMo-BO-Vanillin”, and even lower than that of “NiMo-BO-Methanol”. Guaiacol and isoeugenol were able to suppress coke formation. They possibly solubilised the coke formed into solution, thus minimised the overall coke formation. It should be noted that guaiacol molecules are much smaller than the heavy component in bio-oil, which can be easily adsorbed on catalyst surface and rapidly hydrogenated. The hydrogenated compound acted as a hydrogen donor, supplying hydrogen to the compounds in bio-oil. The overall effect would be to speed up the hydrotreatment reactions. The dehydrogenated compounds, after donating hydrogen, can then be hydrogenated again. Thus, guaiacol could act as a shuttler for hydrogen during hydrotreatment, and therefore minimising the coke formation.

In the absence of the NiMo catalyst, the suppressive effect of guaiacol on coke formation was still observed. There must be “species” in the reaction system of “Blank-BO-Guaiacol” acting in stabilisation of bio-oil. In that way, the coke formation could be minimised. These species could be intermediates, possibly from guaiacol.

In the case of isoeugenol (“NiMo-BO-Isoeugenol” and “Blank-BO-Isoeugenol”), its alkenyl ($-\text{CH}=\text{CH}-\text{CH}_2$) group would generate hydrogen radicals via the acid-catalysed cracking [51] and provide the hydrogen to the reaction system and react with other components in bio-oil. This could be another route of hydrogen shuttling, similar to that of guaiacol. By providing hydrogen radicals, isoeugenol could minimise the coke formation by terminating other radicals generated during hydrotreatment. In short, the generation of

hydrogen *in situ* during hydrotreatment promoted the suppressive effect of isoeugenol on coke formation.

In contrast, “NiMo-BO-Vanillin” and “Blank-BO-Vanillin” showed a significantly higher coke formation than “NiMo-BO-Guaiacol”, “Blank-BO-Guaiacol”, “NiMo-BO-Isoeugenol” and “Blank-BO-Isoeugenol”. It is clearly shown that the functionalities attached to the phenolic structures played an important role during the hydrotreatment of bio-oil. Vanillin has one carbonyl ($-C=O$) group attached to the benzene ring. Importantly, this carbonyl group can participate or initiate polymerisation reactions to lead to coke formation. The reactions of vanillin alone (Figure 5-1) also resulted in the formation of large amounts of coke regardless if the NiMo catalyst was used. Taken together, it appears that the thermal reaction involving this carbonyl group must have been rather rapid and must have taken place at a low temperature before the catalyst had become active to supply active hydrogen. A simplified reaction scheme for the role of the hydrogen shuttler during the hydrotreatment of bio-oil in the presence of phenolic compounds is presented in Figure 5-3.

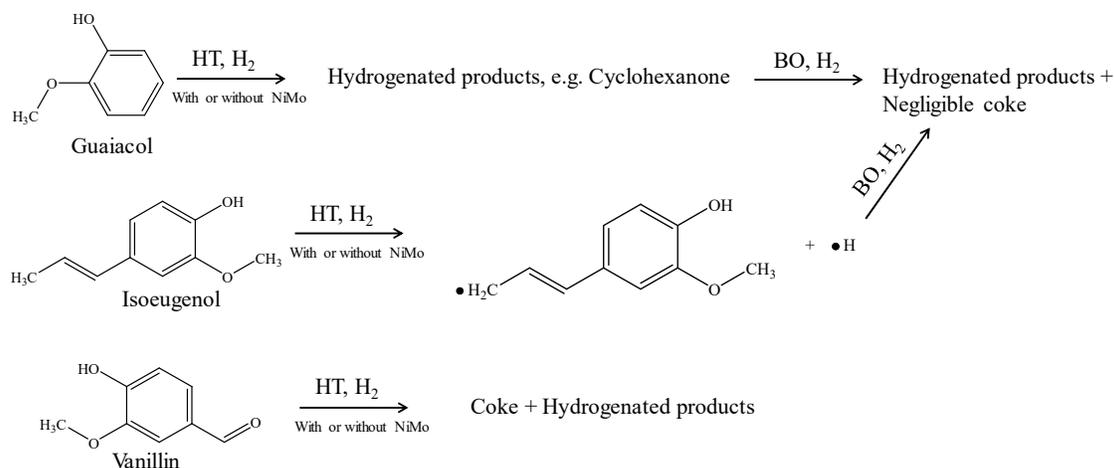


Figure 5-3. A simplified reaction scheme during the hydrotreatment of bio-oil with added phenolic compounds.

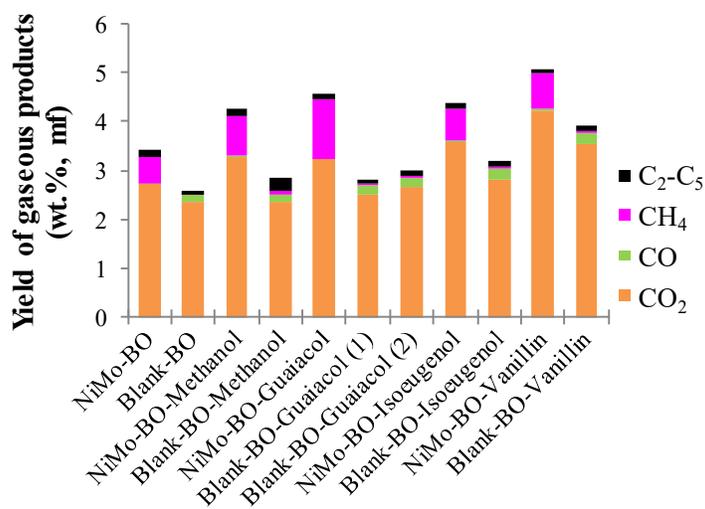


Figure 5-4. Yields of gaseous products from the hydrotreatment of bio-oil with added phenolic compounds and methanol using the NiMo catalyst at 300 °C. The data labelled as “NiMo-BO” and “Blank-BO” were reported earlier in Chapter 3 [34].

The gas production, as presented in Figure 5-4, from the hydrotreatment of bio-oil with added phenolic compounds and methanol was higher than that of bio-oil alone. In the hydrotreatment with added methanol, guaiacol and isoeugenol, there were increases in the yields of CO₂, even though there was no extra carbonyl group in the system. It might indicate that the added methanol or guaiacol or isoeugenol were possibly promoting the carboxylation, carbonylation, methanation and cracking to form more gaseous products from bio-oil molecules. The presence of an extra carbonyl group in vanillin indeed promoted the decarbonylation to form CO, which further could be converted to CO₂ via the water-gas-shift reaction in the presence of the NiMo catalyst.

As the methyl–aryl ether bond can be easily broken, the production of CH₄ could also take place through the demethylation of –O–CH₃ group of the added phenolic compounds and/or the originally present in the bio-oil [52]. The exclusively higher production of CH₄ in

the hydrotreatment of bio-oil with added guaiacol might be due to the demethylation of guaiacol.

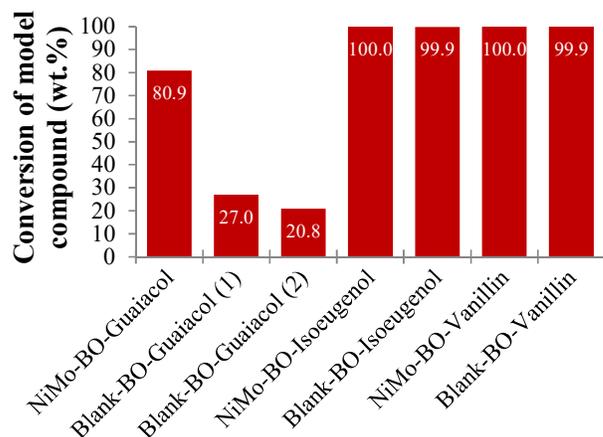


Figure 5-5. The conversion of model compounds added to the bio-oil in the hydrotreatment of bio-oil with added phenolics using the NiMo catalyst at 300 °C.

Figure 5-5 shows the conversion of the added phenolics during the hydrotreatment of bio-oil with added phenolics. It was clearly shown that isoeugenol and vanillin were very reactive during the hydrotreatment regardless if the NiMo catalyst was used. The presence of reactive alkenyl double bond in isoeugenol and carbonyl group in vanillin, promoted their higher reactivity during the hydrotreatment. However, isoeugenol and vanillin showed different effects on coke formation; isoeugenol could largely suppress coke formation, whereas vanillin promoted the coke formation, which is due to the presence of one carbonyl group in its molecular structure. As mentioned above, isoeugenol could probably terminate the radicals to form the more stable molecules. On the other hand, guaiacol showed a lower conversion during the hydrotreatment of bio-oil, due to its lower reactivity, although it still showed a suppressing effect towards coke formation. As mentioned above, guaiacol could

play as a hydrogen shuttling role in the hydrotreatment reactions. During hydrogen shuttling, there would always be some amounts of non-hydrogenated form such as guaiacol itself.

5.3.2 Changes in aromatic ring structures

The transformation of aromatic ring structures during hydrotreatment can be investigated by using UV-fluorescence spectroscopy recorded at a constant energy difference of -2800 cm^{-1} [53, 54]. The relative size of the aromatic ring structures could be indicated by the range of wavelength at which the peaks appear: broadly speaking mono rings would appear at $< 290\text{ nm}$, aromatics with two-fused rings would appear at $290\text{-}320\text{ nm}$, etc. [31, 53].

Due to the negligible intensity of the aqueous phase of the hydrotreated products, the spectra shown here are only for the oil phases, as are presented in Figure 5-6. Some of the data shown here were reported earlier in Chapter 3 [34], i.e. the synchronous spectra of hydrotreated oils from “NiMo-BO” and “Blank-BO” experiments. The spectra are expressed on the basis of per gram of organics in the feedstock.

The hydrotreatment of bio-oil alone in the presence and absence of the NiMo catalyst (“NiMo-BO” and Blank-BO”) showed an increase in the abundance of aromatic ring structures in comparison to the bio-oil feedstock, due to the polymerisation, leading to bigger aromatic ring structures. In the absence of the NiMo catalyst, the severe coke formation would cause the less increase in the fluorescence intensity as observed for “Blank-BO”. The formation of the compounds that cannot be seen in the UV-fluorescence method could be another reason.

With added guaiacol (that appeared at $260\text{-}290\text{ nm}$ in Figure 5-6A), the “NiMo-BO-Guaiacol” resulted in the intensity quite similar to that of “NiMo-BO”. The fluorescence

intensity of the peak at a wavelength range of 300-360 nm increased significantly in comparison to the bio-oil feedstock. It indicates that the polymerisation and ring condensation took place for “NiMo-BO-Guaiacol” even though the coke formation was largely suppressed. Only insignificant differences in the fluorescence spectra of “NiMo-BO-Guaiacol” and “Blank-BO-Guaiacol” were observed. In addition, “Blank-BO-Guaiacol” showed higher fluorescence intensity than “Blank-BO” did. Guaiacol possibly promoted the formation of bigger aromatics in the absence of the NiMo catalyst while suppressing the coke formation.

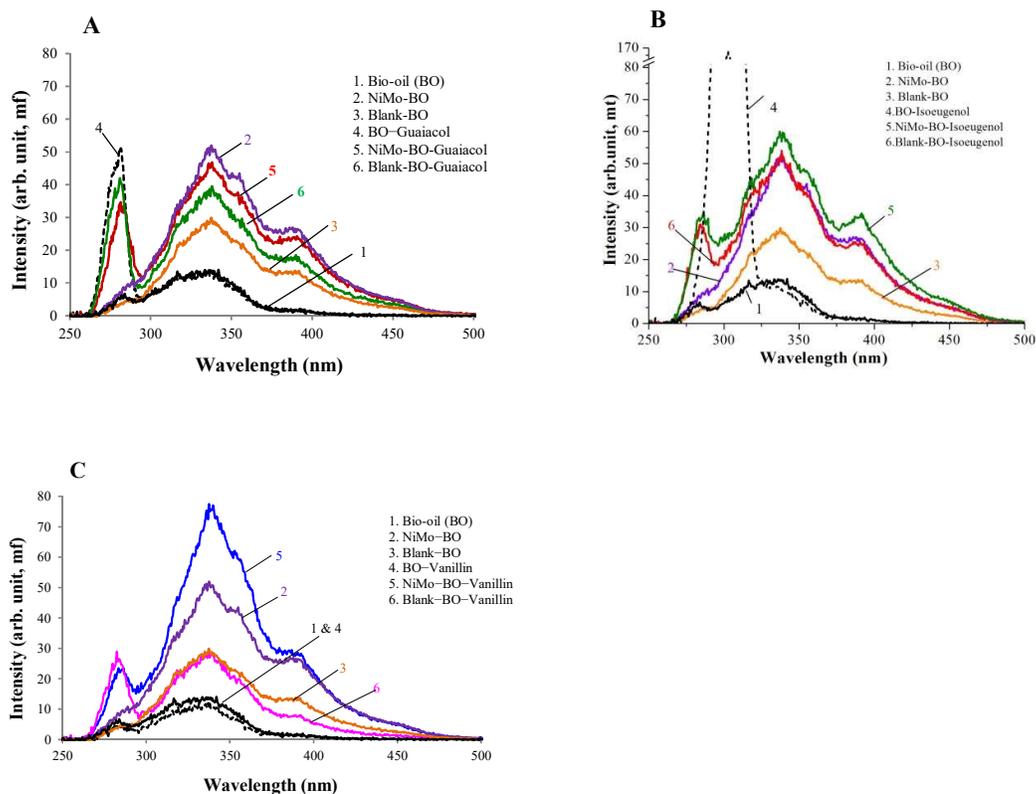


Figure 5-6. Synchronous spectra of the bio-oil feedstocks and the corresponding hydrotreated oils at a constant energy difference of -2800 cm^{-1} from the hydrotreatment of bio-oil with added (A) guaiacol, (B) isoeugenol and (C) vanillin using the NiMo catalyst at $300\text{ }^{\circ}\text{C}$. The data labelled as “NiMo-BO” and “Blank-BO” were reported earlier in Chapter 3 [34].

In the same way, “NiMo-BO-Isoeugenol” and “Blank-BO-Isoeugenol” (Figure 5-6B) showed increases in both peaks (300-360 nm and ≥ 360 nm) with similar intensity. “NiMo-BO-Isoeugenol” and “Blank-BO-Isoeugenol” also only made insignificant differences in the fluorescence spectra. As expected, the peak at a wavelength lower than 300 nm responsible for added isoeugenol drastically decreased due to its reactivity, indicating the hydrogenation of the unsaturated bond of isoeugenol during the hydrotreatment.

A totally different pattern of fluorescence spectra was shown with “NiMo-BO-Vanillin” and “Blank-BO-Vanillin” (Figure 5-6C). Vanillin (in bio-oil and vanillin mixture) did not show a fluorescence peak in the UV-fluorescence spectrometry used in this study. The “NiMo-BO-Vanillin” gave significantly higher fluorescence intensity than that from “NiMo-BO”. The growth of aromatic ring structures was observed in “NiMo-BO-Vanillin”. Vanillin might contribute to the formation of big aromatic structures in the presence of the NiMo catalyst when the hydrogen supply was inadequate. The increase in fluorescence intensity at a wavelength shorter than 300 nm was also observed, which might due to (hydro)cracking big aromatics (mainly from lignin-derived oligomers) from the bio-oil to smaller ones.

On the other hand, the “NiMo-BO-Vanillin” showed significantly higher fluorescence intensity than “Blank-BO-Vanillin”. This was similar to “NiMo-BO” vs “Blank-BO”. The fluorescence intensity of “Blank-BO-Vanillin” was comparable to that of “Blank-BO”. The lower fluorescence intensity for “Blank-BO-Vanillin” and “Blank-BO” was possibly due to severe ring growth leading to coke formation.

The potential coke yields of the oil feedstocks and the corresponding hydrotreated oils measured by using TGA are presented in Figure 5-7. It could provide the direct proof of the volatility of the oils. Furthermore, it can be a good measurement to evaluate whether the oils

contain heavy or light compounds. If the oils contain heavy compounds, it would not be easy to decompose in nitrogen atmosphere at 500 °C.

In general, there was no significant difference in the potential coke yields between bio-oil alone and the bio-oil with the added phenolics; the potential coke yields of “BO-Guaiacol”, “BO-Isoeugenol” and “BO-Vanillin” were a bit lower than that of the bio-oil itself due to the dilution effect by adding the phenolics. Furthermore, there was also no significant difference in the potential coke yields of “NiMo-BO-Guaiacol”, “Blank-BO-Guaiacol”, “NiMo-BO-Isoeugenol” and “Blank-BO-Isoeugenol”. A high potential coke yield was observed for “Blank-BO”. A distinct phenomenon was observed for “NiMo-BO-Vanillin” and “Blank-BO-Vanillin”; both showed a high potential coke yield due to polymerisation reaction. It was well-confirmed with the data of fluorescence spectra (Figure 5-5C) and mass balance closure (Figure 5-1).

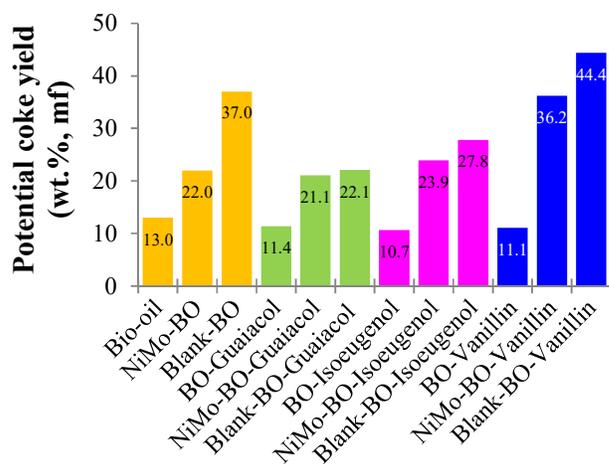


Figure 5-7. Potential coke yields of bio-oil, bio-oil with added phenolic compounds and corresponding hydrotreated oils using the NiMo catalyst at 300 °C, measured at 500 °C using TGA. The data labelled as “NiMo-BO” and “Blank-BO” were reported earlier in Chapter 3 [34].

5.3.3 Transformation of light components

The conversion of the GC-detectable compounds during the hydrotreatment with added phenolics was also investigated, as is summarised in Table 5-3. Compared to that in raw bio-oil, more acetic acid was produced in “Blank-BO”, which might come from the continuous pyrolysis of some components in bio-oil like sugar-derived oligomers. However, acetic acid was consumed during the hydrotreatment of bio-oil with the added phenolics. The phenolics are alcohols, which possibly reacted with acetic acid via esterification reactions. The consumption of acetic acid in the “Blank-BO-Vanillin” was the most significant. Vanillin, which is similar to either guaiacol or isoeugenol, has one hydroxyl group. The potential esterification between vanillin and acetic acid should have the similar effects to that of guaiacol and isoeugenol on acetic acid conversion. However, as discussed above, the yield of acetic acid in “Blank-BO-Vanillin” was just half of that with guaiacol and isoeugenol as the added phenolics. It was possibly vanillin not only reacted with acetic acid via esterification, but also cross-polymerised with the precursors of acetic acid, like some sugar oligomers, leading to the diminished formation of acetic acid.

Vanillin also showed the similar negative effects on the formation of other carboxylic acids such as C₃-C₅ carboxylic acids (Table 5-3). The mechanism was believed the same as that on the formation of acetic acid. In addition to the simple carboxylic acids, it was found that the production of levulinic acid, a main acid from the hydrolysis of C₆ sugars and furans [55, 56], was also the lowest in the “Blank-BO-Vanillin”. Sugars and furans are very reactive towards polymerisation [55]. Possibly, vanillin underwent cross-polymerisation with sugars and furans, preventing their conversion to levulinic acid. The effects of vanillin on the production of carboxylic acid were related to the carbonyl group of vanillin.

The components with carbonyl groups in bio-oil were also very reactive. It can be seen in Table 5-3, where almost all furfural and the cyclopentanones were consumed during the catalytic or non-catalytic hydrotreatment of bio-oil with adding vanillin, guaiacol or isoeugenol. As discussed above, vanillin has a carbonyl group, which made it very reactive towards polymerisation itself or cross-polymerisation with other components in bio-oil. The compounds like furfural or cyclopentanones with the carbonyl or ketone groups also made them very reactive towards polymerisation.

The phenolics, which have no carbonyl or ketone groups, were relatively stable during the catalytic or non-catalytic hydrotreatment of bio-oil. Generally, during the hydrotreatment, adding guaiacol and isoeugenol to bio-oil did not lead to drastic decrease of the abundance the phenolics in the products, while adding vanillin has more negative effects on their production. Obviously, the carbonyl group gave vanillin the capacity for potential cross-polymerisation of the phenolics during the catalytic or non-catalytic hydrotreatment of bio-oil with added vanillin. To summarise, vanillin has a carbonyl group, which activated it for the polymerisation and cross-polymerisation reactions. Guaiacol has no carbonyl group, and it could suppress the polymerisation reactions, and has relatively limited tendency to cross-polymerise with the components in bio-oil. Compared with guaiacol, isoeugenol has additional carbon double bonds on the side chain of the benzene ring, which, however, did not activate isoeugenol for the polymerisation or cross-polymerisation. Isoeugenol also could help suppress the polymerisation of bio-oil. Although both carbonyl group and carbon double bonds are unsaturated functional groups, they had very distinct contribution towards the polymerisation.

Table 5-3.

Yields of individual compounds from the hydrotreatment of bio-oil with added phenolic compounds at 300 °C using the NiMo catalyst. The data labelled as “NiMo-BO” and “Blank-BO” were from our experiments reported earlier in Chapter 3 [34].

Name of compound	Yield (wt%, mf) of compound in the experiment of								
	BO	NiMo-BO	Blank-BO	NiMo-BO-	Blank-BO-	NiMo-BO-	Blank-BO-	NiMo-BO-	Blank-BO-
				Guaiacol	Guaiacol	Isoeugenol	Isoeugenol	Vanillin	Vanillin
Acetic acid	11.3	12.5	16.3	8.4	9.9	8.5	8.0	8.0	4.0
C ₃ -C ₅ carboxylic acids	0.6	1.5	1.7	0.9	0.8	0.8	0.6	0.8	0.3
Levulinic acid	0.2	0.1	0.5	0.2	0.4	0.3	0.3	0.1	0.1
Furfural	0.9	–	–	–	–	–	–	–	–
Glycoaldehyde	4.4	–	–	–	–	–	–	–	–
Syringaldehyde	0.1	–	–	–	–	–	–	–	–
Cyclopentanone	0.1	0.1	0.1	0.1	–	0.1	–	–	–
2-Methyl-2-cyclopenten-1-one	0.2	–	0.1	–	0.2	0.1	0.1	–	–
2-Cyclopenten-1-one	0.3	–	–	–	0.0	–	–	–	–
1,2-Benzenediol	–	–	–	7.4	1.3	–	–	–	–
Guaiacol	0.2	–	0.1	5.0	22.1	1.0	2.0	0.9	0.6
Alkyl guaiacols	0.1	–	0.2	0.2	0.5	0.9	3.9	0.4	0.5
Phenol	0.1	0.2	0.1	0.6	0.1	0.1	0.4	0.2	–
Alkyl phenols	0.4	0.7	0.5	0.4	0.3	0.2	0.2	0.4	0.1
Methoxy phenols	0.8	–	0.6	5.1	22.8	1.9	6.1	1.3	1.1
Syringol	0.4	–	0.4	–	0.4	–	0.2	–	0.1

5.4 CONCLUSIONS

The beneficial effects of phenolic functionalities in reducing coke formation during the hydrotreatment of bio-oil were studied by adding phenolic compounds in the bio-oil to modify the bio-oil feedstocks. It was found that the functionalities of phenolic compounds played an important role in reducing coke formation. Guaiacol and isoeugenol could suppress the coke formation to a significant extent by supplying active hydrogen to the fluid phase to hydrogenate the heavy molecules that could not be adsorbed on the catalyst surface. Guaiacol and isoeugenol appears acting as a hydrogen shuttler: obtaining hydrogen on the catalyst surface and releasing hydrogen in the fluid phase. Moreover, guaiacol even showed remarkably higher activity than methanol for suppressing coke formation. In contrast, vanillin seemed promoted the formation of coke and the growth of aromatic ring structures. The presence of one carbonyl group attached to the benzene ring might promote the polymerisation, leading to severe coke formation even in the catalytic hydrotreatment.

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CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 INTRODUCTION

The study focused on coke formation during the hydrotreatment of bio-oil using commercial hydrotreating catalysts. The hydrotreatment experiments were conducted in a single step hydrotreatment at low temperatures (150-300 °C). The effects of the externally adding C₅-C₆ sugars and phenolic compounds on coke formation were investigated.

6.2 CONCLUSIONS

6.2.1 Coke formation during the hydrotreatment of bio-oil using NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ catalysts

The presence of a hydrotreating catalyst such as pre-sulphided CoMo and NiMo supported on alumina could reduce the coke formation in the hydrotreatment of mallee bio-oil at low temperatures (150-300 °C) to a large extent. However, the formation of large aromatic ring structures was observed, accompanied with the increases in the potential coke yields of the hydrotreated oils. With increasing levoglucosan concentration in the bio-oil, coke formation as well as the formation of large aromatic ring structures could still be suppressed in the presence of the NiMo catalyst but the potential coke yields increased. In contrast, adding levoglucosan to the bio-oil induced severe coke formation in the absence of the NiMo catalyst. The amount of the coke produced due to the addition of levoglucosan exceeded the amount of the levoglucosan added to bio-oil. The cross-polymerisation of levoglucosan with other compounds in the bio-oil took place, leading to severe coke formation.

6.2.2 Coke formation and product distribution during the hydrotreatment of pyrolysis bio-oil and its mixture with C₅ and C₆ sugars using NiMo/ γ -Al₂O₃ catalyst

The effects of C₅-C₆ sugars on coke formation during the hydrotreatment of mallee bio-oil were studied in a batch reactor at 300 °C in the presence of the NiMo catalyst. Bio-oil produced from mallee woody biomass with added C₅ and C₆ sugars was used as reactants. It was shown that C₅ and C₆ sugars involved in the coke formation to different extents. Their distinct contribution to coke formation was correlated to their different numbers of oxygen-containing functional groups and thus their different structures. The sugars did cross-polymerise with other components in bio-oil, significantly promoting coke formation. The capacity of C₆ sugars to form six-member-ring structures was possibly the reason of their higher contribution to the coke formation than C₅ sugars. Furthermore, the sucrose and glucose showed the similar effect on the coke formation during the hydrotreatment as sucrose could be hydrolysed to form fructose and glucose during the hydrotreatment. Xylose, as a C₅ sugar, showed a lower reactivity and thus relatively lower contribution towards coke formation. An exceptional phenomenon was observed for levoglucosan. The absence of carbonyl group(s) in levoglucosan molecules (an anhydrous) might be the reason for its low contribution to the coke formation during the hydrotreatment in the presence of the NiMo catalyst. However, the coke formation considerably enhanced during the hydrotreatment of bio-oil with added levoglucosan in the absence of the NiMo catalyst. Levoglucosan could be hydrolysed to glucose, and its reaction behaviour thus became similar to that of glucose, showing high contribution to coke formation in the absence of the NiMo catalyst.

6.2.3 The beneficial effects of phenolic functionalities in reducing coke formation during the hydrotreatment of bio-oil using a NiMo/ γ -Al₂O₃ catalyst

The beneficial effects of the oxygen functionalities in the phenolic compounds on coke formation were studied in a batch reactor in the presence of the NiMo catalyst. Their effects on coke formation during the hydrotreatment of mallee bio-oil were studied by adding phenolic compounds (guaiacol, isoeugenol and vanillin) into the bio-oil as feedstocks. Different functional groups attached to the benzene ring of the phenolic compounds affected the formation of coke to different extents. For comparison, a model compound study on vanillin and guaiacol was also conducted to investigate the reaction behaviour of single phenolic compounds. It was shown that the presence of hydroxyl and methoxyl group in guaiacol and additional alkenyl group in isoeugenol showed a suppressive effect on the coke formation to a significant extent. During the hydrotreatment of bio-oil, guaiacol and isoeugenol possibly acted as a source of hydrogen donors among other possible ways to reduce coke formation. This active hydrogen would hydrogenate the heavy molecules and/or terminate the radicals and minimise the coking reactions. Moreover, guaiacol showed a higher suppressive effect on coke formation than methanol did under identical conditions. In contrast, the presence of one carbonyl group in vanillin made it much more reactive in promoting the polymerisation, leading to severe coke formation even in the presence of the NiMo catalyst.

6.3 RECOMMENDATIONS

This study focused on coke formation during the hydrotreatment of bio-oil. Various compounds in bio-oil have been studied to investigate their behaviour during the

hydrotreatment in order to gain a better understanding on the coke formation. Experimental observations on coke formation from bio-oil itself and bio-oil with added various compounds with different chemical structures did reveal the different behaviours of the feedstock during hydrotreatment, and thus different effects on coke formation. However, the reactions in hydrotreatment of these real feedstocks were very complex, and the reaction network for coke formation was difficult to be formulated. The future work should cover an ultimate objective in formulating the reaction network of coke formation. The study particularly on the specific role of the carbonyl group during the hydrotreatment of bio-oil could provide a better understanding on the most part of the reaction network of coke formation.

This study has been mainly carried out at relatively low temperatures to understand the coke formation during the initial stage (including heating up) of hydrotreatment. Future work should also extend the reaction conditions to higher temperatures and continuous operation, e.g. in a fixed-bed reactor, to better understand the coke formation under condition pertinent to commercial operation.

The reaction conditions did greatly affect the hydrotreatment process. The reaction system that could provide an excessive hydrogen supply (e.g. with higher initial hydrogen pressure) should be in the part of the future work. Such process would make sure that the effects shown in the hydrotreatment of bio-oil with added sugars was not due to lack of hydrogen. A process with excessive hydrogen would provide a clear picture about what is truly happening during the hydrotreatment in the presence of abundant active hydrogen supply. Furthermore, the hydrotreatment of bio-oil over various catalysts under various conditions should be taken into account as a part of the future work to achieve a catalyst development for hydrotreatment.