

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

**Upgrading of Pyrolysis Bio-oil Through Hydrodeoxygenation and Cracking in a
Continuous Packed-bed Catalytic Reactor**

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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

Depleting petroleum resources, increasing demand for clean and cheap energy and increasing concern on climate have attracted the recent interest in renewable energy. Biomass could be one of the economically competitive renewable energy sources. Pyrolysis converts biomass into bio-oil. But the high content of oxygen, high concentrations of heavy components, high acidity and poor stability of bio-oil prevent it from being used directly as a liquid fuel. The catalytic hydrotreatment of bio-oil appears to be a promising route to make bio-oil a commercially competitive and environmentally friendly liquid biofuel.

A serious issue in the catalytic hydrotreatment of bio-oil is the deactivation of catalyst due to the formation of coke. The fundamental understanding of the hydrotreatment of bio-oil under different process conditions is essential for the optimisation and improvement of biofuel production via hydrotreatment. In this study, the continuous hydrotreatment of bio-oil from mallee tree (wood or whole tree mixed biomass) under different process conditions was carried out. The study was focused on the use of cheap commercial pre-sulphided NiMo/ γ -Al₂O₃ catalyst. The key parameters investigated in this study included the bio-oil liquid hourly space velocity, temperature, reactor configuration and feedstock inlet temperature. The results indicate that high-quality liquid fuels, miscible with petrol and diesel, can be produced from the hydrotreatment of bio-oil.

This study has gained some insights into the mechanisms of reactions during the hydrotreatment of bio-oil. Bio-oil has many reactive structures and functional groups. On entering the hot hydrotreatment reactor, some covalent bonds in bio-oil could be broken, which is followed by a network of many parallel and series reactions. In the absence of sufficient amounts of active hydrogen, radical recombination, i.e. polymerisation, could take place, resulting in the formation of heavy species and finally coke, even if the overall reaction conditions favour hydrogenation and hydrocracking.

Different components in bio-oil would play different roles and follow different reaction pathways. While the light species in bio-oil may become vapour and pass through the catalyst bed very quickly, the heavy species in the same bio-oil feedstock may experience very long residence time in the reactor. The adsorption of heavy species on the catalyst is believed to drastically reduce the activity of catalyst

for the production of active hydrogen and for the hydrotreatment of light species.

Matching the bond breakage with the supply of active hydrogen is a key aspect to minimise the formation of coke. Based on the results from this study, a novel reactor configuration for the hydrotreatment of bio-oil is described. Experiments were carried out to provide the key concept of this novel reactor design. Better results were achieved with using novel design of the reactor including late and less coke formation in the bio-oil hydrotreatment process.

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Chapter 1

Introduction

1.1. Importance of renewable energy

The environmental concerns about pollution and the possible future shortage of petroleum-based fuels have boosted research on alternative liquid fuels [1]. At the beginning of the 20th century, crude petroleum (which was discovered in the U.S.A in 1859) covered only 4% of the world's energy demand. Decades later it became the most important energy source. Currently, crude petroleum covers about 40% of the world's energy demand with 96% of the transportation fuels being produced from it [1,2]. With the world energy demand projected to rise, crude petroleum production will not increase accordingly due to the fast depletion of its reserve. The prediction of world crude petroleum demand is shown in Figure 1-1 [1].

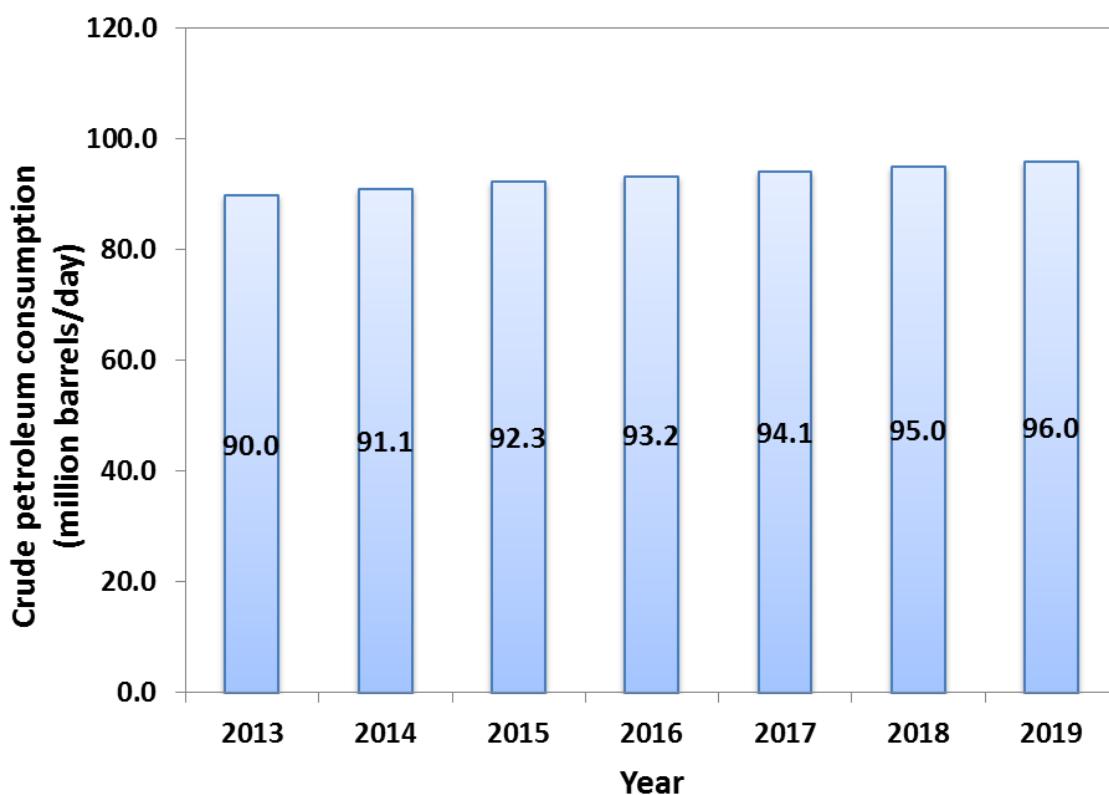


Figure 1-1. Crude petroleum demand outlook in the world [1].

Another issue in the use of petroleum fuels is their environmental effects such as producing huge amounts of carbon dioxide as an important greenhouse gas. This

resulted in calls for an increase in bio-energy usage [1,3]. The world demand outlook for bio-energy is shown in Figure 1-2.

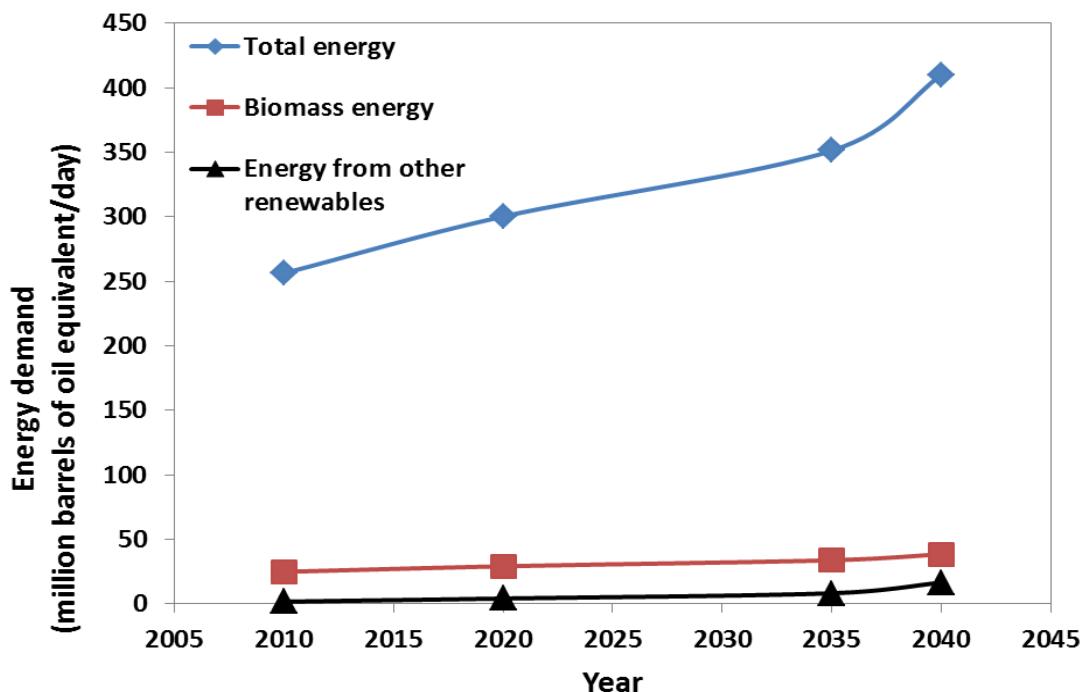


Figure 1-2. Total energy and bio-energy demand outlook in the world [1].

1.1.1. Importance of biomass as a renewable resource

Biomass is one of the main renewable resources that can provide considerable energy. It has some advantages over other renewables resources such as less CO₂, SO_x and NO_x production, more similarities to fossil fuels in terms of its characterisation than other renewable resources [3,4]. Therefore, developing technologies which can convert the biomass into engine fuels is necessary. In Figure 1-2 [1], the demand outlook for biomass energy is shown.

1.1.2. Wood as a main biomass feedstock for bio-energy production

Different types of biomass such as food crops, vegetables, corn and wheat straw were used as a biomass resource to produce energy. However, the high population growth rate and need for more food resources limited the use of food-stock biomass as an energy source. Therefore, lignocellulosic resources such as

straw and wood became the main sources of bio-energy production (2nd generation of biofuels) [4].

Among various types of lignocellulosic biomass, wood has the highest potential for producing energy. Mallee wood was selected in this study because of its easy planting, establishment and high energy content [5,6].

1.1.3. Possible conversion technologies of biomass into bio-energy

Biomass can be used directly as an energy source through combustion or can be converted to gas or liquid products by gasification and pyrolysis technologies, respectively [4]. The gasification converts the biomass into a fuel gas which can be used as a heat source or in electricity generation. On the other hand, by pyrolysis, the biomass can be converted into a liquid fuel which can be used in heating, electricity generation or can be upgraded to biofuels as a replacement of the petroleum-derive liquid fuels [3,4].

1.1.4. From biomass to bio-oil through fast pyrolysis

Biomass is a renewable raw matter that used for heat and fuel production. Properties of solid biomass can be improved by converting it to bio-oil, which can be economically handled, stored and transported. The most common way to produce bio-oil is pyrolysis [4]. Biomass is a mixture of different components like hemicellulose, cellulose, lignin and other organics. During pyrolysis, the thermochemical decomposition of organic matter takes place at elevated temperatures in the absence of oxygen. It typically occurs at operating temperatures above 250°C [4,7]. The rate and extent of decomposition of the organics inside the biomass depends mainly on the pyrolysis temperature, pressure and heating rate [7]. According to heating rate of biomass inside the reactor, pyrolysis is categorised to slow and fast types. Fast pyrolysis is currently the preferred option because the slow process takes longer (up to a couple of days) to complete and results in biochar as the main product. After cooling and condensation of liquid and vapour products from the pyrolysis, a dark brown liquid with considerable heating value (half of fossil crude oil) is formed that is called bio-oil. The bio-oil yield in fast pyrolysis is nearly 60 wt% [7,8].

To produce bio-oil, different reactor configurations have been designed, such as ablative pyrolysis, fluidised-bed and circulating fluid bed pyrolysis, vacuum pyrolysis and grind pyrolysis reactors. Ablative pyrolysis works by pressing biomass against a hot surface. The biomass moves rapidly on the hot surface and leaves a film of oil behind. The important feature of ablative pyrolysis is that it is not limited by the biomass particle size. Moreover, no carrier gas is needed in this process. However, it requires a surface area controlled system not smaller than the fluidised-bed reactors [4]. In fluidised-bed and circulation fluid bed pyrolysis, a carrier gas is used to fluidise the particles. The heat transfer in this type of reactor is efficient and the heat transfers by convection and conduction. The limitation of this system is the particle size of biomass that affects the yield of bio-oil significantly [4].

In vacuum pyrolysis, the reactor is vacuumed and slow heating rates are used. The disadvantages of this type of pyrolysis are the higher cost and also lower bio-oil yield [4].

Grinding pyrolysis reactor is another type of reactor which is used for bio-oil production [8]. In this type of reactor the biomass is in contact with hot metal balls which are mainly with the reactor rotating and continuously touching the biomass. This results in converting the outer layer of biomass into bio-oil and producing a char layer on the biomass. The grinding process by hot balls removes the produced char layer from the surface of biomass and pyrolysis continues. The important advantage of this method is the ability of feeding different particle sizes of biomass from a few millimeters to a few centimeters. Moreover, all biomass types including wood, bark, leave and twigs can be fed into the grinding pyrolysis reactor [8]. In addition, there is no need for high flow of carrier gas. In this study, grinding pyrolysis is used for the production of bio-oil.

Bio-oil is an attractive alternative energy source for many reasons. Most notably, it is renewable and easily created from common forestry and agriculture waste products. In the short term, bio-oil can be used to replace traditional fuel oil in conventional furnaces and boilers with little modification. However, it has dissimilarities with fuels from crude petroleum, preventing it to be used as a transportation fuel. The high acidity, instability and high oxygen content are the major challenges in the direct use of bio-oil as an engine fuel. Some of the physical properties of bio-oil and fossil fuels are reported in Table 1-1 [9-11].

Table 1-1. Typical physical properties of bio-oil and fuel oils [9-11]

Oil name	Oxygen content (Moisture free, wt%)	Water content (wt%)	Sulphur content (wt%)	Viscosity at 40°C (cSt)	pH
Bio-oil	38	20-30	0-0.05	15-35	2-3
Fossil fuel	1	0.025	0.2	3.0-7.5	Neutral

Therefore, it needs upgrading. Bio-oil can be upgraded to replace petrol or diesel fuels via hydrogenation to remove the excessive oxygen [9,10].

In the long term, the development of large scale bio-oil refining processes will be required to commercialise the biofuel production. The bio-oil refineries can also open up a wide range of other applications. Chemicals, organic fertilisers and fuel additives can all be produced from bio-oil [11,12]. A schematic of biofuel production from mallee wood is shown in Figure 1-3.

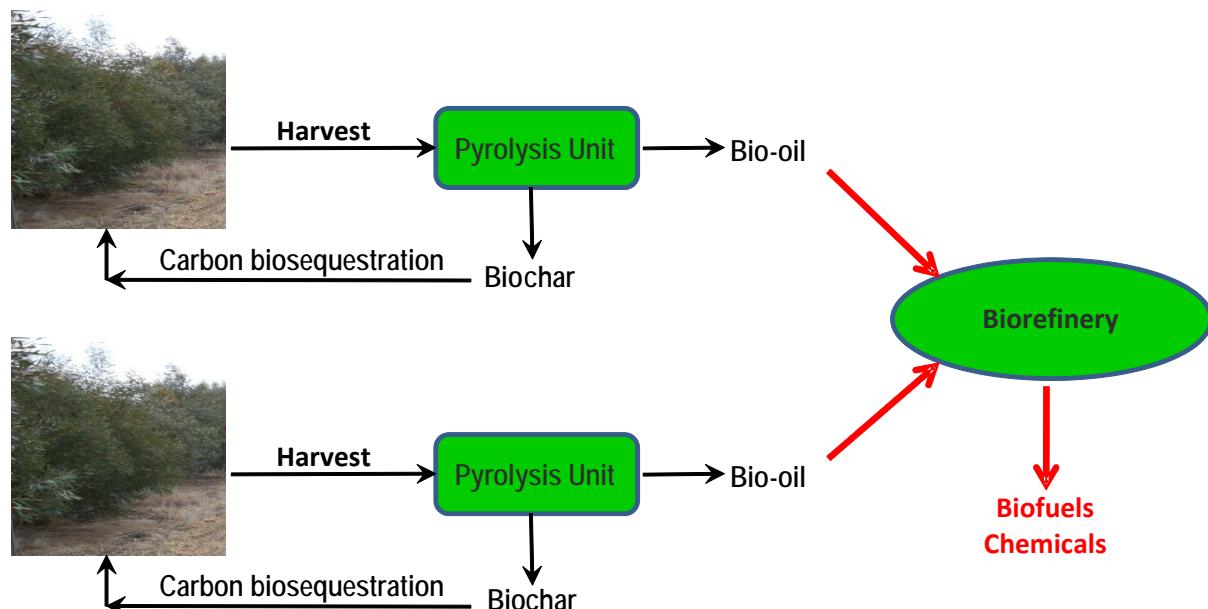


Figure 1-3. Schematic of upgrading pyrolysis bio-oil from biomass.

1.1.5. Bio-oil upgrading

As was noted above, the bio-oil produced from pyrolysis has some disadvantages. Its high content of oxygen results in low heating values. The abundance of heavy components makes it unstable [13,14]. Therefore it needs to be upgraded. There are two main ways to upgrade the bio-oil; (1) catalytic cracking (2) catalytic hydrodeoxygenation (HDO). Catalytic cracking needs the use of high

temperature (500-550°C) with acidic zeolite catalysts. This results in the formation of high amount of coke (> 20 wt%) and it also lowers the yield of biofuel, which is not desirable [15]. Because of higher coke formation amounts and lower yields of produced biofuel in the cracking process, the most promising method to upgrade the bio-oil is HDO over a catalyst. In this process, the ultimate goal is to eliminate the reactive functionalities by removing oxygen and crack large molecules [10,16]. Bio-oil HDO can be performed in batch and continuous reactors. The continuous HDO is more likely used in commercial operations.

The earliest paper on the HDO of bio-oil appeared in 1984 [16]. In this trial, apparent similarities between hydrodesulphurisation (HDS) of crude petroleum in the refinery and HDO were taken as a starting point. As a result, the commonly applied catalysts were HDS catalysts, either NiMo/Al₂O₃ or CoMo/Al₂O₃. From these trials, it was concluded that NiMo/Al₂O₃ or CoMo/Al₂O₃ is inappropriate for HDO due to quick and severe coke formation [16].

A two-stage process using mild conditions was developed and patented by Battelle [17]. In this attempt, the bio-oil was stabilised at low temperature (< 280°C) and then followed by severe hydrotreatment at higher temperature range of 370-400°C. This process extended the experiment time length. However, coke formation was still reported as the main problem.

Noble metal catalysts such as Ru and Pd were tested [3,18]. In the continuous set-ups, the noble metal catalysts in general showed better performance than the HDS catalysts. In the recent work by Chaiwat [19], the effect of liquid hourly space velocity (LHSV) on residence time of heavy and light species at the pressure of 100-150 bar and temperature below 300°C using Pd/C catalyst in one stage process has been studied. A serious deactivation of catalyst due to the formation of coke was seen during first hours of the experiments.

In 2009, Elliott et al reported a successful run of two-stage bio-oil hydrotreatment for 102 h using Pd/C and commercial catalysts in the first and second stages, respectively. They could achieve 98 to 99% of oxygen removal. The temperature in their process was between 250-410°C. Moreover, operation pressure of 140 bar and LHSV 0.15 h⁻¹ were chosen [10]. However, still coke formation and product deterioration with prolonged time were limiting the experiment.

As the price of the noble metal catalysts is much higher than the HDS catalysts, some researchers endeavored to work on HDS catalysts and use sulphur to keep

the catalyst active. The result of their research showed that coke formation cannot be avoided even by using sulphur. A few different methods have been applied to sulphidise the catalyst such as using H₂S, dimethyl disulphide (DMDS) or ditertiary butyl disulphide (DTBDS) as a sulphur source [20,21].

The effect of LHSV on the hydrotreatment of bio-oil was studied by Elliot et al [22]. The temperature was kept constant in the range of 148-157°C and 349-435°C in the first and second stages, respectively. The commercial catalysts were used and LHSV varied between 0.1 and 0.5 h⁻¹. Their result showed that increasing LHSV resulted in increases in the oxygen content in the hydrotreated bio-oil from nearly zero to 30 wt%. Baldauf also studied the effect of LHSV on oxygen content in the hydrotreatment of bio-oil [23]. The temperature in their experiments was kept at 350-370°C. They varied weight hourly space velocity (WHSV) from 0.15 to 0.80 (kg oil/kg of catalyst) h⁻¹ and as a result the oxygen content of the oil changed slightly from 0.02 up to 3.06 wt%. They also studied the effect of LHSV on the weight of heavy components (boiling points > 500°C) remaining inside the reactor after the experiment. Their result showed that the increase of LHSV resulted in the increase of heavy components remaining inside the reactor. In short, they found that LHSV has a significant impact on the cracking of large molecules inside the bio-oil.

An important parameter that can affect the deoxygenation reaction rate is temperature. Baldauf and Elliot investigated the effect of temperature change on deoxygenation in the hydrotreatment process. Their main finding was that the deoxygenation of bio-oil was improved by increasing temperature [22,23].

Mainly packed-bed reactors with down-flow operation were used for hydrotreating pyrolysis oil. The chosen reaction conditions were the temperature of 200-400°C, the pressure of 50-200 bar and the LHSV varied from 0.05 up to 2 h⁻¹. The findings from these works showed a severe reactor blockage due to the charring of the bio-oil to form coke [11]. This indicates that the down-flow packed-bed reactors are not suitable for HDO process of bio-oil or might needs some improvement in the design.

In general, the fuels from the hydrotreatment of bio-oil can be used in two ways. Hydrotreated bio-oils can be co-fed into a conventional refinery or it can be used directly as an engine fuel [24,25].

After HDO, the upgraded bio-oil might still contain some heavy components that should be further cracked prior to use as a transportation fuel. The most obvious

way is co-processing the upgraded bio-oil with one of the petroleum refinery mid products in cracking process. However, choosing a suitable mid product of petroleum with an optimised mixing ratio with HDO bio-oil for co-feeding is challenging due to high tendency of bio-oil for coke formation [26,27].

Generally, the flow schematic diagram of a common petroleum refinery together with its mid products is shown in Figure 1-4 [2].

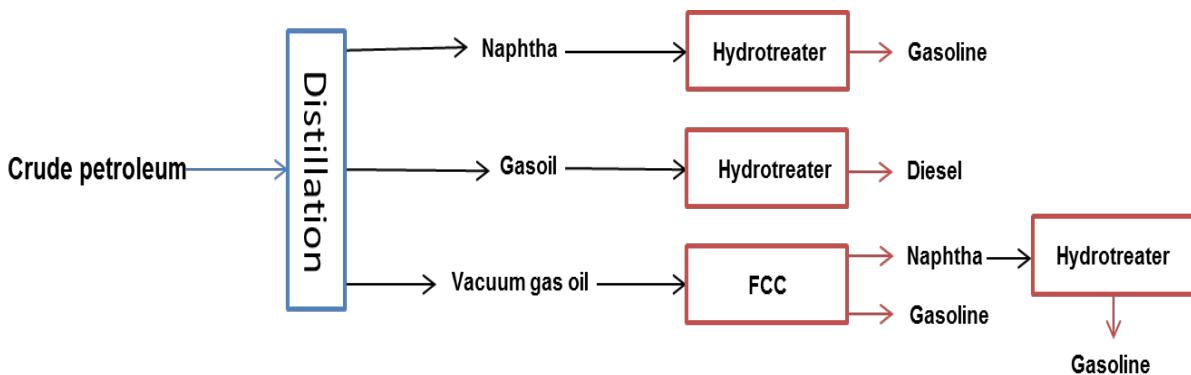


Figure 1-4. The general process operation diagram of a petroleum refinery [2].

In a general point of view, a petroleum refinery is an industrial process where crude petroleum is processed and refined into more useful products such as gasoline, diesel fuel, asphalt base, heating oil, kerosene and liquefied petroleum gas. Petroleum refineries are typically large sprawling industrial complexes with extensive piping running throughout and carrying streams of fluids between large chemical processing units [2]. Fluid catalytic cracking (FCC) and hydrodesulphurisation units can be considered as the most important parts of the refinery. In these two consecutive units by using hydrogen gas at high temperature, the heavy components are cracked and nitrogen and sulphur are separated. Most of the researchers used vacuum gasoil (VGO) as a proper petroleum mid product for mixing with hydrotreated bio-oil [26-28]. In comparison with only VGO cracking, low yields of gasoline production and high concentration of coke, aromatics and paraffins were obtained when 20 wt% of hydrotreated bio-oil was co-processed with VGO [28]. As a result, the direct use of hydrotreated bio-oil as an engine fuel or drop-in biofuels is more desired.

From the above trials, it is clear that HDO is the main way to improve the bio-oil properties and convert the bio-oil to an engine fuel. However, fundamental

knowledge in this area is still scarce. The studies of HDO process is mainly done in batch reactors while the continuous process is not well investigated. Moreover, in term of coke formation, the study of bio-oil hydrotreatment with using commercial catalysts needs more investigation, specially the effects of different process parameters on the coking of bio-oil inside the reactor. Therefore, there is a need for better fundamental understanding of continuous HDO process by using commercial catalysts. The effects of the parameters like LHSV, temperature and reactor configuration on the production of hydrotreated bio-oil should be studied in detail. These parameters can significantly change the coke formation inside the reactor and also deoxygenation of the bio-oil.

1.2. Purpose of this study

To overcome the mentioned above issues, a bench scale continuous HDO system using NiMo/Al₂O₃ and Pd/C catalysts is developed to study the effect of different process conditions on the producton of hydrotreated bio-oil. Packed-bed reactors were used in HDO of bio-oil. New configuration of reactor suitable for the hydrotreatment of bio-oil was designed and tested. These are the focus of this study.

1.3. Scope of thesis

To achieve the optimum HDO process conditions and study the effect of different parameters on the HDO of bio-oil, this research will focus on laboratory experimental investigation. The research work will consist mainly of the following aspects:

Chapter 2 will describe the details of the experimental set-up. The procedure for carrying out hydrotreatment will be described. Also it will include the analytical methods to characterise the product samples.

Chapters 3-6 will present the experimental results and discussion. Each chapter contains introduction and relevant literature review.

Chapter 3 will present the HDO of bio-oil with different LHSV. The noble metal catalyst (Pd/C) and industrial catalyst (NiMo/γ-Al₂O₃) were used in the cold and hot zones of the reactor, respectively. The effects of LHSV on the reaction behaviour of

light and heavy species, product deterioration, coke formation and oxygen content will be discussed in detail.

Chapter 4 will present the effect of temperature on hydrotreatment process and product quality. The reaction temperature was changed from 375 up to 450°C to study its effects on the behaviour of bio-oil during hydrotreatment, including product quality, cracking and coking of the bio-oil. Oxygen content, potential coke and coke yield on the different parts of the reactor will be discussed.

Chapter 5 will present the effect of pre-heating of feed hydrogen on the coke formation, product yield and water formation in the hydrotreated bio-oils.

Chapter 6 will present a new configuration of the reactor to tackle the formation of coke and energy recovery inside the reactor during the HDO of bio-oil.

The conclusions and future work recommendation will be summarised in **Chapter 7**.

The summary of the scope of this thesis is presented in Figure 1-5.

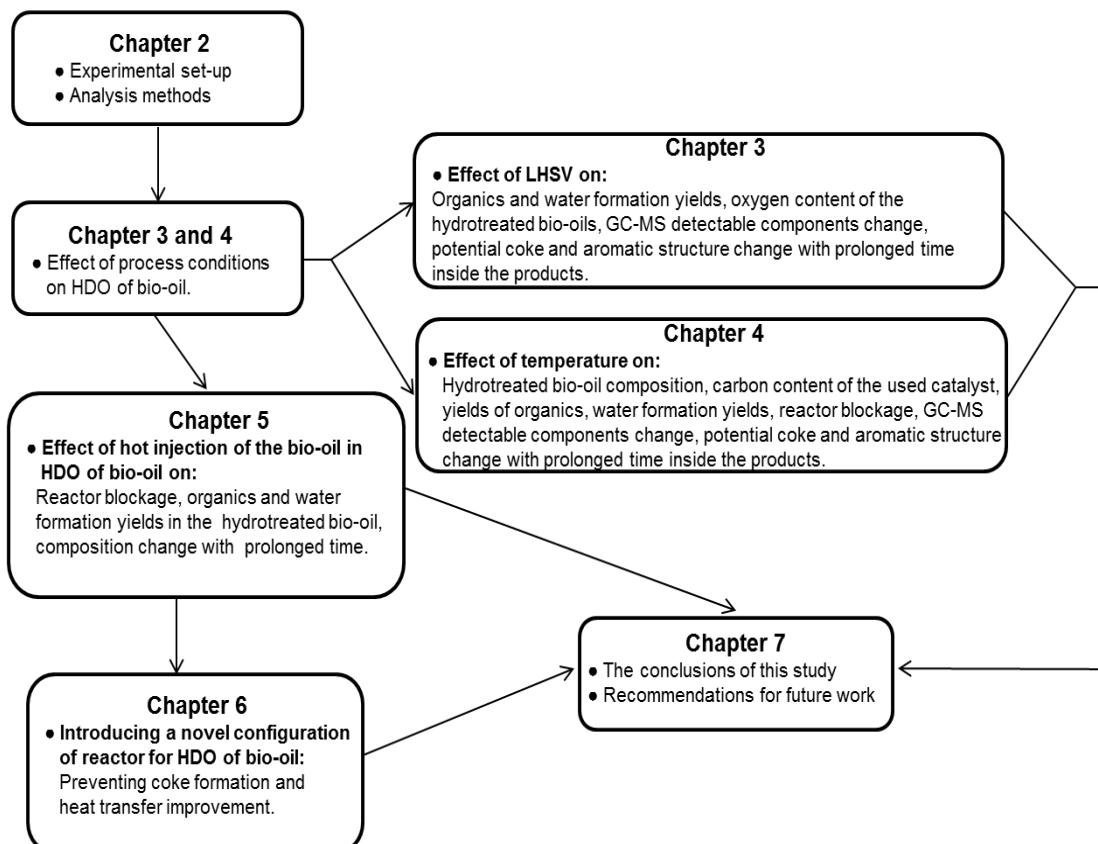


Figure 1-5. A flow chart showing the scope of this thesis.

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Chapter 2

Experimental methods

2.1. Introduction

The hydrotreatment set-up, reactor design and process conditions are described in this chapter together with the analysis of bio-oil and the products.

2.2. Pyrolysis experiment

The bio-oil used in this study was produced in a grind pyrolysis reactor from mallee biomass (wood or wood/bark/leaves mixture). The detailed procedure for production of the bio-oil via the grinding process was described elsewhere [1]. Briefly, the bio-oil was produced at the temperature in the range of 450 to 465°C with a rotation rate of the grinding pyrolyser at 54 rpm. The grinding pyrolyser has the electrical heating mats outside the reactor wall for heating up the biomass fed from two hoppers connected in series in a continuous mode. Some steel balls were filled inside the pyrolyser for grinding the biomass fed by rotation of the reactor at the elevated temperature. By this way, the chunk biomass particles can be crushed into small particles and simultaneously pyrolysed, releasing volatiles and the solid product, biochar. The mixture of the solid product and the volatiles was then separated via two cyclones connected in tandem. After separation, the volatiles were condensed and collected by a series of condensers including a water condenser and two dry-ice condensers. Some very fine biochar particles may still be mixed with the condensable liquid (bio-oil), which was then removed via filtration with filter paper with the pore size of 0.2 um. The filtered bio-oil was stored in fridge before use.

2.3. Hydrotreatment experiment

For hydrotreating the bio-oil, a bench scale reactor system was designed and used, configuration of which is shown in Figure 2-1. The whole system consists of gas cylinders for providing hydrogen and nitrogen, mass flow controllers for adjusting gas flow rate, high-pressure dual syringe pumps for feeding bio-oil, a fluidised-sand bath furnace for heating up the hydrotreating reactor, hydrotreating reactor loaded with hydrogenation catalyst, back pressure regulator to control the system pressure, and a sampling system. The whole reactor system was placed in a room purposely designed for the high-pressure systems. An exhaust fan was used to remove any

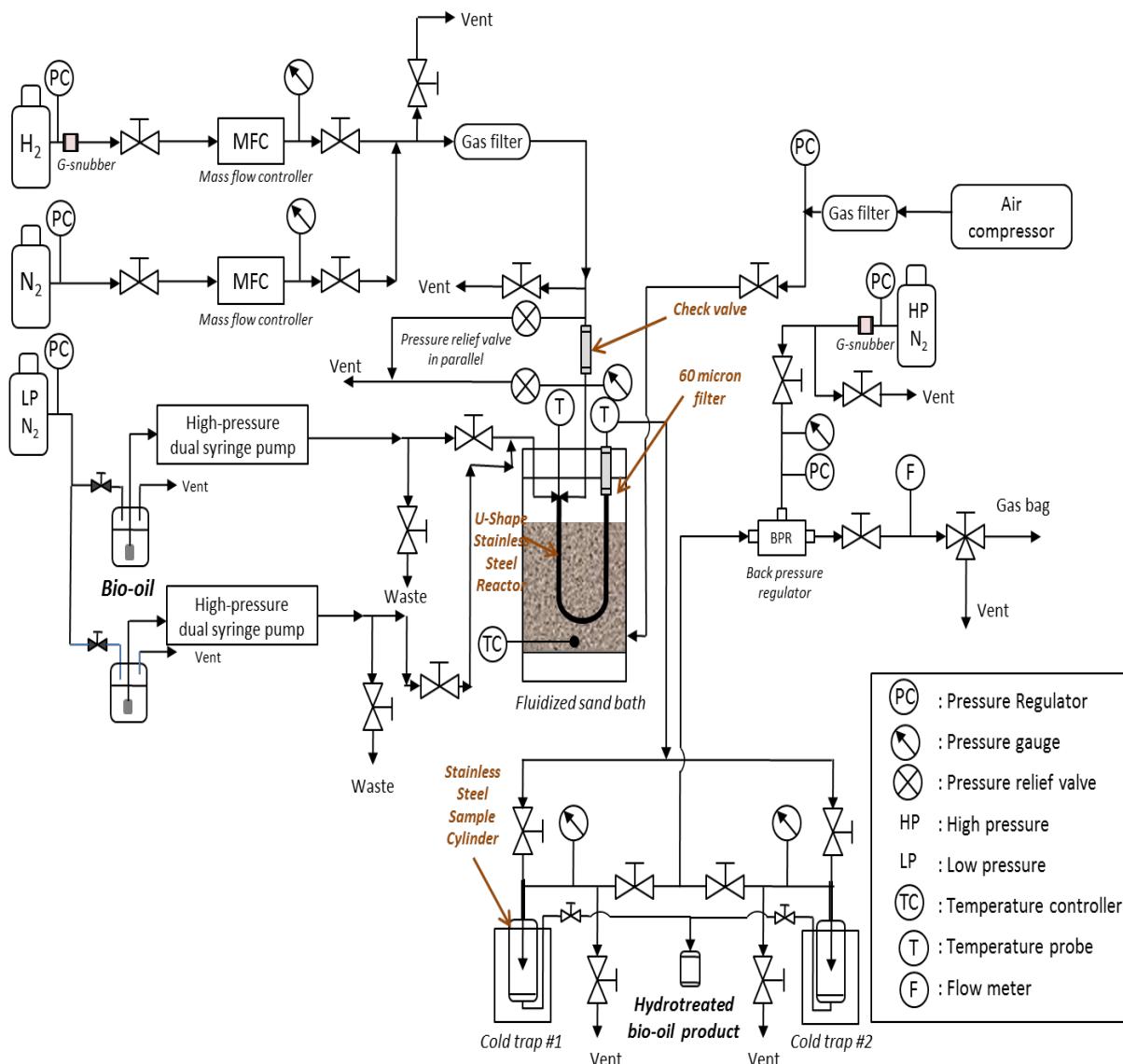


Figure 2-1. A process flow diagram of the continuous catalytic hydrotreating [3].

reactive/explosive gases leaked while a number of detectors were installed as well to detect any leakage from the high-pressure system.

The reactor was made from stainless steel 316 tubing with varied diameters, which depends on the requirements of the specific experiments. Generally, the diameters of the reactors range from 3/4 to 2 inch with the length ranging from 30 to 40 cm.

The reactors were heated up in a fluidised-bed sand bath furnace pre-set at the temperature in the range 375 to 450°C to achieve uniform temperature distribution and high heat transfer rate. As is shown in Figure 2-1, part of the reactor is outside the sand bath, temperature of which is not the same as that of the sand

bath. In some specific experiments, the actual temperatures of the reactor outside of the sand bath were measured with thermocouples inside the reactor. For the part of the reactor which is inside the sand bath, the temperature in theory should be similar to the temperature of the sand bath. However, during our hydrotreatment experiments, we found the actual temperature of the reactor might be different to the sand bath temperature in some circumstances, due to some exothermic reactions in the hydrotreating of bio-oil. The temperature was thus measured as well by installing thermocouples inside the reactor.

The bio-oil sample was pumped into the reactor with a syringe pump (Teledyne Isco, 500D). The specifications of the syringe pump was detailed below in Section 2.3.2. The feeding rate of bio-oil ranges from 0.1 to 85 mL/min, depending on size of the reactor. The LHSV of bio-oil ranges from 0.5 to 12 h⁻¹, depending on size of the reactor. The LHSV here was defined as the ratio of volume of bio-oil to volume of the catalyst(s) loaded.

Hydrogen was supplied from cylinders via mass flow controllers with the feeding rate of 0.1 to 20 L/min, depending on purposes of the specific experiment. Hydrogen is a reactant and also serves as a carrier gas. In some experiments hydrogen was fed directly into the reactor. In others, hydrogen was pre-heated before feeding into the reactor. The feeding of cold or pre-heated hydrogen has a significant effect on the hydrotreating process and the product distributions, which will be detailed in Chapter 5.

The pressure used for all the hydrotreating experiments performed for this study is 60 to 70 bar, which was controlled with a back pressure regulator (BPR, Equilibar and EB1HP2) installed in the downstream of the reactor. However, due to blockage of the reactor resulting from such as coke formation on catalyst bed, the inlet pressure of the reactor system can go above 100 bar. In this circumstance, the experiment was forced to be stopped because of the safety considerations.

Catalyst(s) were/was used for all the hydrotreating experiments, which are commercially available pre-reduced Pd/C catalyst and sulphided Nickel-Molybdenum on alumina (NiMo/ γ -Al₂O₃). The Pd/C catalyst was purchased from Sigma-Aldrich Australia while the NiMo/ γ -Al₂O₃ catalyst was obtained from Eurecat France. In some experiments, only the NiMo/ γ -Al₂O₃ catalyst was used while in others both were used, which will be specified in the following Chapters.

During the hydrotreating experiments, sampling was performed at a certain time interval to measure progress of the experiments. A cold trap system (two parallel stainless steel sample cylinders immersed in water–ice coolers) was used to cool down and recover the products for the sampling.

All major equipment being used in the system is considered to be workable under designed extreme conditions as listed below with their specifications.

2.3.1. High-pressure mass flow controller (Bronkhorst MFC F-231M-AGD-22-V (EL-FLOW 400 bar)):

- Flow Range: 0.2-10 L/min.
- Pressure: 7-300 barg.
- Temperature: 24°C.
- Connections: 1/4 inch OD SS Swagelok compression fittings.

2.3.2. High-pressure dual syringe pump (Teledyne Isco 500D):

- Refill or depressurisation rate is 1.0 µL/min to 204 mL/min at any pressure from 0 to 25.8 MPa.
- Pressure range is 0.07 to 25.8 MPa.
- Cylinder capacity for every individual pump is 507.38 mL.

2.3.3. Fluidised sand bath (Techne SBL-2D):

- Ability to heat up from 20 to 600°C.
- Heat up from 20 to 600°C takes 1 hour and 45 min.
- Cool down to 200°C takes 5 hours and 30 min.
- Air supply should have the pressure of 21 kPa (3 psi) and maximum flow rate of 57 L/min.

2.3.4. Back pressure regulator (EQUILIBAR, EB1HP2):

- The body and diaphragm made from stainless steel 316.
- Maximum pressure control is 344 bar (5000 psig).

2.3.5. Swagelok fittings

The 316 stainless steel Swagelok fittings, tubing, valves and reactors being used in the experimental set-up can be safely operated under high pressure and high temperature conditions.

2.4. Characterisation of bio-oil and hydrotreated bio-oils

2.4.1. UV-fluorescence spectroscopy

To characterise the relative size and concentration of aromatic ring systems in the bio-oil and its hydrotreated bio-oils, UV-fluorescence spectroscopy was used. In this study, a Perkin-Elmer LS50B spectrometer was used for measuring the UV-fluorescence spectra of the samples. The samples were diluted with methanol [Uvasol for spectroscopy; purity \geq 99.9%] to 4 weight ppm (on weight basis including water in the sample). A constant energy difference of -2800 cm^{-1} was used for recording synchronous spectra. The scan speed of 200 nm/min and 2.5 nm slit widths were used. The aromatic ring sizes can be indicated by recorded wavelength (e.g. < 290 nm is for mono-rings). For having the data on the basis of consumed organic, the recorded fluorescence intensity was multiplied by the corresponding organic phase yield [2].

The yield (η_i), on wet basis is expressed as the mass of sample collected divided by the mass of oil fed during the above mentioned time intervals:

$$\eta_i(\text{wet}) = \frac{M_i}{M_{\text{feed oil}}} \quad (1)$$

The product yields are always expressed on moisture free basis (formula 2).

$$\eta_i(\text{dry}) = \frac{\eta_i(\text{wet}) * (1 - (H_2O_i))}{1 - (H_2O_{\text{feed oil}})} \quad (2)$$

2.4.2. GC-MS analysis

The bio-oil and hydrotreated bio-oils were analysed with an Agilent 6890/5973 GC-MS. The instrument was equipped with a capillary column (HP-INNOWax) (length, 30 m; internal diameter, 0.25 mm; film thickness, 0.25 µm). Before injecting the samples, they were diluted with acetone. The injection amount was 1 µL. The sample was injected into the injection port having a splitless configuration at the temperature of 250°C. The carrier gas through the column was helium. The initial temperature of the column was 40°C and the heating rate was 10°C/min. The final temperature was 260°C. The standard solutions were injected to GC-MS for identifying the peaks in the chromatogram [3,4].

2.4.3. Thermogravimetric (TGA) analysis

The volatility and DTG curves of bio-oil and the hydrotreated bio-oil samples were measured using a thermogravimetric analyser (TGA, TA Instruments Q5000 or Q600). For this aim, the samples were heated to 500°C with a 10°C min⁻¹ heating rate. Nitrogen gas at the flow rate of 50 ml min⁻¹ was used during the analysis. The residue remaining after 500°C was considered as potential coke and it was measured by subtracting the starting weight of the sample crucible from the weight of the sample crucible at the end of the experiment [5-8].

2.4.4. Gas chromatography (GC) analysis

Agilent 6890 gas chromatograph equipped with flame ionisation and thermal conductivity detectors was used to analyse the gaseous products from burning of the used catalyst for measuring the amount of coke formed on catalyst. The instrument is also equipped with capillary "plot U" and molecular sieve 5A columns for separating different components in the gas. Argon gas was used as the carrier gas. The standard gas was injected before and after the injection of samples to identify the peaks in the recorded chromatogram. The peak area of the relevant gas in the chromatograph from GC was measured relative to a constructed baseline for quantification. To calculate the gases concentration, the measured area was

multiplied to the response factor from the calibration of GC with the standard gases with the concentration in the range of analysed samples [9].

2.4.5. Raman analysis

A Perkin–Elmer GX FT-IR/Raman spectrometer with a back-scattered configuration was used to characterise the carbonaceous materials (especially ring distribution) in the catalyst samples. The Raman spectrometer was equipped with a Nd:YAG laser at 1064 nm as its light source. For fitting the curve with 10 bands, the FT-Raman spectral range of 800–1800 cm⁻¹ was chosen [10].

2.4.6. Elemental analysis

For measuring the elemental composition, a Thermo Flash 2000 CHNS-O was used. The C, H and N elements of the samples were recorded directly while the oxygen content can be calculated by difference [11].

2.4.7. Carbon content in the catalysts

The carbon content of fresh and used NiMo/Al₂O₃ catalysts from the reactor was measured by a combustion process in a quartz reactor (Figure 2-2). For this aim, the sample was ground very finely. 4-5 milligram (accurately weighted) was loaded into the reactor and burnt by flowing 15-20 ml/min UHP oxygen (purity = 99.999 v%) through the reactor in the combustion furnace. The furnace had the set temperature of 900°C to ensure the complete oxidation of the formed coke into CO₂. A porosity 4 (pore size: 4-5.5 micron) sintered disc was used in the reactor to prevent the catalyst from being blown away. The collected product gas was injected to gas chromatograph (GC) to measure the CO₂ content. For this aim, standard gases with certain concentrations of CO₂ in the range of CO₂ content of the product gas sample were injected to the GC to calibrate it. The volume of produced CO₂ was calculated based on the calibration using an internal gas standard, which was methane with ultra-high purity. For this, certain volume of methane gas was injected to the collected gas bag before experiment and its content was measured by GC after collecting the produced gas from burning of the catalyst. Consequently, the

volume of the produced gas from combustion was calculated and as a result the produced CO₂ volume can be measured. The carbon content of the catalyst was calculated according to the produced CO₂ gas amount.

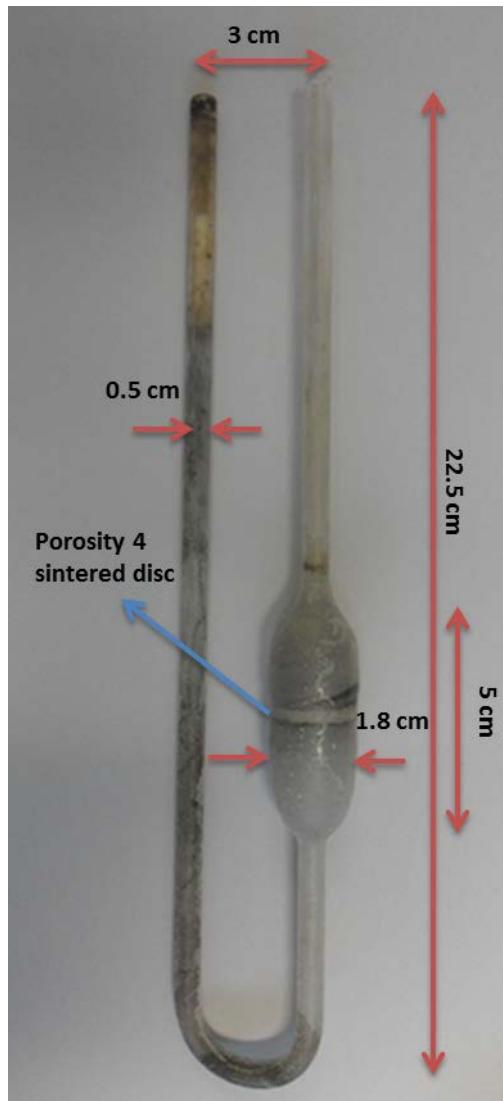


Figure 2-2. A photograph of the reactor used for determine the carbon content of the catalyst using a combustion method.

2.5. References

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Chapter 3

**Differences in the reaction behaviour of light
and heavy species during the hydrotreatment
of pyrolysis bio-oil in a continuous pack-bed
reactor**

3.1. Introduction

Increasing concerns about climate change and increasing demand for energy as a result of wide economic development, including that in rural and remote regions, have stimulated the development of various renewable energy technologies. Biomass holds a special position because biomass is the only carbon-containing renewable resource that can be used to produce liquid fuels to replace the petroleum-derived conventional ones. Pyrolysis of biomass would produce gases, biochar and bio-oil with their yields strongly depending on the feedstock and pyrolysis conditions [1-3]. Compared with the bulky biomass, bio-oil is a liquid that can be transported relatively easily and economically. This allows for the pyrolysis to be carried out in a modular and “distributed” mode, saving the costs to transport the wet bulky biomass over a long distance and greatly improving the economic competitiveness of biofuel production.

However, bio-oil is acidic and contains water and high molecular mass components [3-5]. Therefore, bio-oil cannot be used directly as a replacement of petrol and diesel. Bio-oil must be upgraded, e.g. via hydrotreatment [6-15]. During the hydrotreatment of bio-oil, a significant fraction of its oxygen will be removed in the forms of H₂O, CO and CO₂. The hydrotreatment could also result in decreases in molecular mass.

In order to improve the commercial feasibility of the hydrotreatment of bio-oil, the LHSV must be high so that the hydrotreatment reactor size can be reduced. The pressure of hydrogen should be as low as possible. LHSV, i.e. the rate at which bio-oil is fed into the hydrotreatment reactor, can significantly affect the formation of coke on the hydrotreatment catalyst, which would ultimately result in the deactivation of the catalyst. Unfortunately, little information is available in the literature about the effect of LHSV on the product quality and coke formation, lagging behind the requirement of technology development.

As a product from the random thermal breakdown of macromolecular networks and other species in biomass, bio-oil has an inherently complicated composition with abundant reactive functional groups. More importantly, the bio-oil components would have a very wide molecular mass distribution with light species such as formic acid and heavy species that are the products from the partial thermal breakdown of the polymeric structures in biomass. During hydrotreatment, the

residence time for bio-oil species could vary over an extremely wide range [15]. While some heavy bio-oil species would exist in the liquid phase in the hydrotreatment reactor, some would become vapour on entering the reactor. The overall LHSV value does not describe in any way the true residence time of various species in the reactor. This situation is worsened when operation is carried out at low pressures.

This study aims at investigating the hydrotreatment behaviour of bio-oil in a continuous reactor using a commercial pre-sulphided NiMo/Al₂O₃ catalyst at a moderate temperature (375°C) and a relatively low hydrogen pressure (70 bar). The study is focused on the effect of the overall LHSV on the hydrotreatment behaviour of lighter and heavier species in bio-oil. The hydrotreated products (termed as biofuel) were characterised with a wide range of analytical techniques in order to gain insights into the important processes taking place during hydrotreatment.

3.2. Experimental

3.2.1. Bio-oil sample

Bio-oil was produced in a grinding pyrolysis pilot plant [16,17] from the pyrolysis of mallee wood (*Eucalyptus loxophleba*, ssp *lissophloia*) grown in the wheatbelt of Western Australia [18,19]. Briefly, a mixture of wood chips having a wide range of particle sizes from microns to centimetres was continuously fed into a rotating reactor at 450°C in which the pyrolysis and particle size reduction took place simultaneously. After the separation of biochar particles in two cyclones, bio-oil vapour was condensed to give the liquid bio-oil sample used in this study. The bio-oil sample was stored in a freezer (-18°C) until use. The bio-oil was filtered (0.2 µm) before the hydrotreatment experiments.

3.2.2. Hydrotreatment

The hydrotreatment of bio-oil was carried out in a U-shape continuous packed-bed reactor, as is shown in Figure 3-1. The reactor was made of stainless steel 316 and had a diameter of 3/4 inch with a total reactor length of 40 cm. The reactor was

partly (about half, see “the sand bath level” shown in Figure 3-1) immersed in a hot fluidised sand bath that was heated to 375°C.

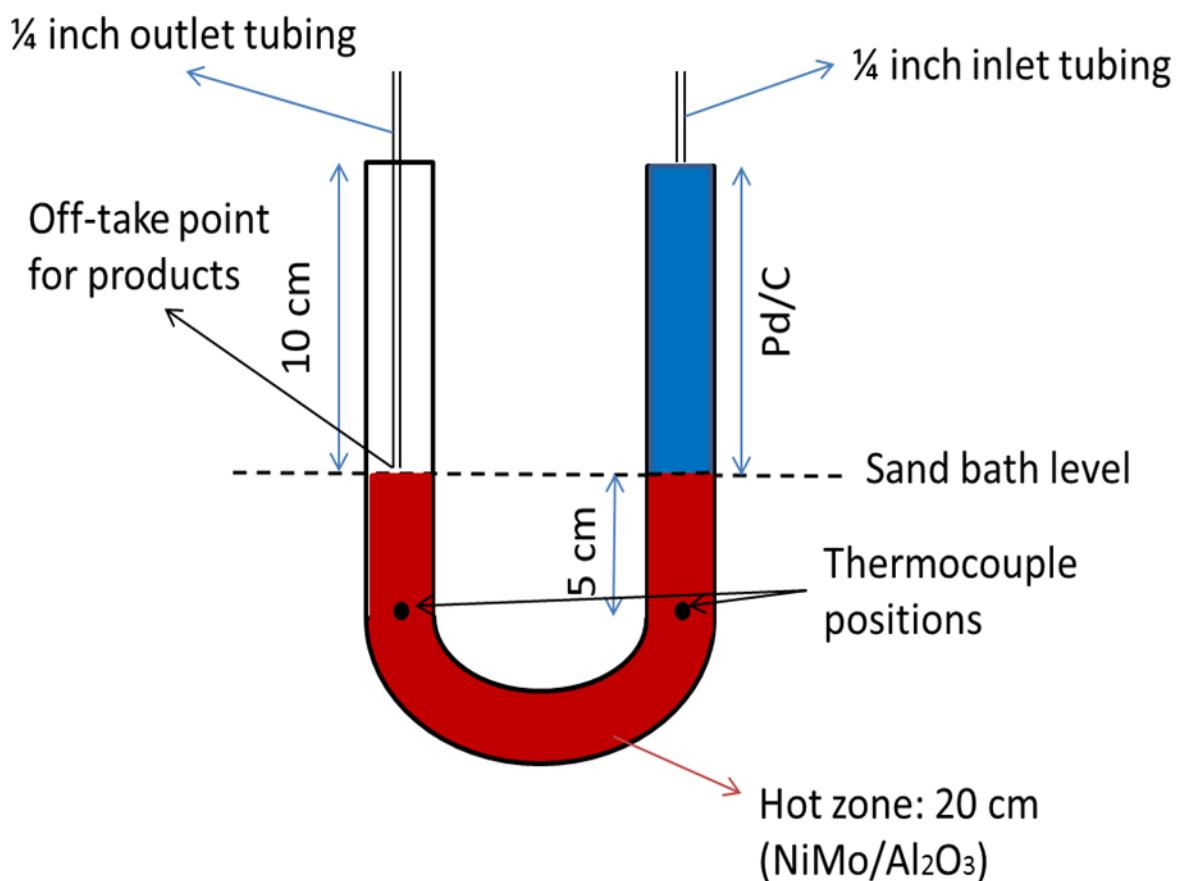


Figure 3-1. A schematic diagram showing the reactor configuration.

The packed-bed reactor contains two zones of catalysts. In the first zone (10 cm), 5% palladium supported on activated carbon (Pd/C, Bioscientific) catalyst was used. It was outside the sand bath. This section would have undergone a temperature transition ranging from room temperature to < 250°C, aiming to stabilise the incoming bio-oil based on the finding in the literature [20]. However, as will be demonstrated later in this paper, the use of Pd/C catalyst was marginally, if any, successful in avoiding coke formation. In the second zone, a commercial pre-sulphided NiMo/Al₂O₃ catalyst (from Eurecat, hereafter referred as “NiMo catalyst”) was used. This section of the catalyst was immersed in the hot fluidised sand bath. The steady-state temperature at the border of the Pd/C and NiMo catalyst beds was between 235 and 270°C under current experimental conditions.

The process flow diagram of this hydrotreatment set up has been shown elsewhere [15]. The bio-oil and hydrogen was pre-mixed before being fed into the reactor. The bio-oil was pumped, at a pre-set constant flow rate, into the reactor using a syringe pump (Teledyne Isco, 500D). The LHSV was increased by increasing the bio-oil feeding rate and was defined as the ratio between the bio-oil feeding rate and the volume of the catalyst bed (i.e. the volume of the reactor occupied by the catalyst). The LHSV for the NiMo catalyst was varied between 1 and 3 h⁻¹ in separate experiments. The LHSV for the Pd/C catalyst would be twice that for the NiMo catalyst for the same experiment. Hydrogen was supplied in large excesses via a mass flow controller at a constant flow rate of 4 L/min (measured under ambient conditions) for all experiments.

Two thermocouples were inserted into the catalyst bed to measure the catalyst temperature during the experiments. The tip of the first one was placed 5 cm at the inlet side below the surface level of the fluidised sand bath. The tip of the second thermocouple was also 5 cm, but at the outlet side, below the surface level of the fluidised sand bath. The distance between the tips of the two thermocouples was 10 cm.

The pressure at the outlet of the reactor was maintained at 70 bar by using an accurate back pressure regulator (Equilibar EB1HP2) installed after the condenser system of two parallel traps. The temperature of the condenser system at its outlet was maintained below 10°C by cooling the traps with ice water. The hydrotreated liquid products were collected into fractions every 45 min (LHSV_{NiMo} = 2), 60 min (LHSV = 3) or 90 min (LHSV = 1). The samples were then stored at -18°C and were de-frozen prior to analysis.

The hydrotreated product was normally separated into two phases. The total water production is calculated as the sum of water in the aqueous and oil phases minus the water in the feed bio-oil. The yield of each product is expressed as the mass of product (e.g. the whole biofuel product or certain fraction) divided by the mass of bio-oil fed into the reactor over the same time interval. The product yields are always expressed on the basis of moisture-free (mf) bio-oil feedstock.

3.2.3. Product characterisation

UV-fluorescence spectroscopy. UV-fluorescence spectroscopy was used to

understand the transformation of aromatic structures during hydrotreatment. A Perkin-Elmer LS50B spectrometer was used to measure the UV-fluorescence spectra of bio-oil and its hydrotreated products. Samples were diluted with UV grade methanol (purity \geq 99.9%) to 4 ppm (wet basis). The energy difference for recording synchronous fluorescence spectra was -2800 cm^{-1} with slit widths of 2.5 nm (excitation and emission) and a scanning speed 200 nm/min. The fluorescence intensity was multiplied by the product oil yield to express the fluorescence intensity on the basis of bio-oil (moisture-free) to allow for comparison [21].

GC-MS. The raw bio-oil and the product oil phase were analysed with an Agilent 6890/5973 GC-MS equipped with a capillary column (HP-INNOWax) (length, 30 m; internal diameter, 0.25 mm; film thickness, 0.25 μm of cross linked polyethylene glycol) [4,5,22]. The samples were diluted with acetone prior to analysis [10,15]. The following compounds were quantified: acetic acid, phenol, 2-ethylphenol, 2,4,6-trimethylphenol, 2,4-xylenol, 4-(1-methylpropyl)phenol and 3,4,5-trimethylphenol. The phenolic type of compounds are summed together and hereafter referred to as phenolics. Another group of compounds quantified included ethylbenzene, 1,3-xylene, 1,2-xylene, 1,4-xylene, propylbenzene, 1-ethyl-2-toluene, 1,2,3-trimethylbenzene and (1-methylpropyl)benzene, which are summed together and referred to as benzene compounds. Cyclopentane and methylcyclohexane were also quantified.

Thermogravimetric analysis (TGA) was used to gauge the volatility of hydrotreated products, which partially reflects the molecular mass distribution. The weight loss and differential thermogravimetric (DTG) curves of hydrotreated bio-oils (biofuels) were measured using a TGA (TA Instruments Q5000). The samples were heated from 25 to 500°C at a heating rate of $10^\circ\text{C min}^{-1}$ in a flow of nitrogen (50 mL min^{-1}) [3-5,23]. After the experiment the residue, as a result of the evaporation of light species and polymerisation, was measured and is referred to as “potential coke”.

Elemental analysis. A Thermo Flash 2000 analyser was used for the elemental analysis (C, H and N) of the bio-oil and biofuel samples. The oxygen content was calculated by difference [24].

3.3. Results and discussion

3.3.1. General observation

Reproducibility. To check the reproducibility of our experiments, one set of two experiments under identical conditions ($LHSV = 1\text{ h}^{-1}$) were performed. It was found that both the temperature and pressure profiles were almost identical. The product yields on the moisture-free basis from these two repeated experiments were as follows after feeding 256 ml of bio-oil into the reactor: organics in the oil phase 23.8 and 20.8 wt%, organics in the aqueous phase 9.5 and 6.6 wt%, the production of water 31.9 and 37.2 wt%, the sum of gas and coke was 34.8 and 35.4 wt%, respectively.

Despite of the use of Pd/C catalyst at the beginning of the catalyst bed (Figure 3-1), the pressure drop across the reactor would remain low (< 4 bar) initially and then increased rather rapidly. Once the pressure increased very significantly (e.g. > 110 bars), the experiments were terminated. Contrary to the reports in the literature [20,25] that the Pd/C catalyst could stabilise the bio-oil to reduce coke formation, these experiments demonstrated that the stabilisation of bio-oil using the Pd/C catalyst was rather limited, certainly not to the extent to ensure long-term continuous operation using the NiMo catalyst, at least under the current experimental conditions. In fact, separate experiments [15,17] also showed that the use of Pd/C alone (i.e. without the NiMo catalyst) would also result in the blockage of reactor and the deactivation of catalyst.

Exothermic peaks. As is shown in Figure 3-1, two thermocouples were placed in the NiMo catalyst bed: one at 5 cm into the NiMo catalyst bed in the fluid flow direction and another one at 15 cm into the bed. The bed temperatures measured at 15 cm into the NiMo catalyst bed for the three different LHSV values are shown in Figure 3-2a.

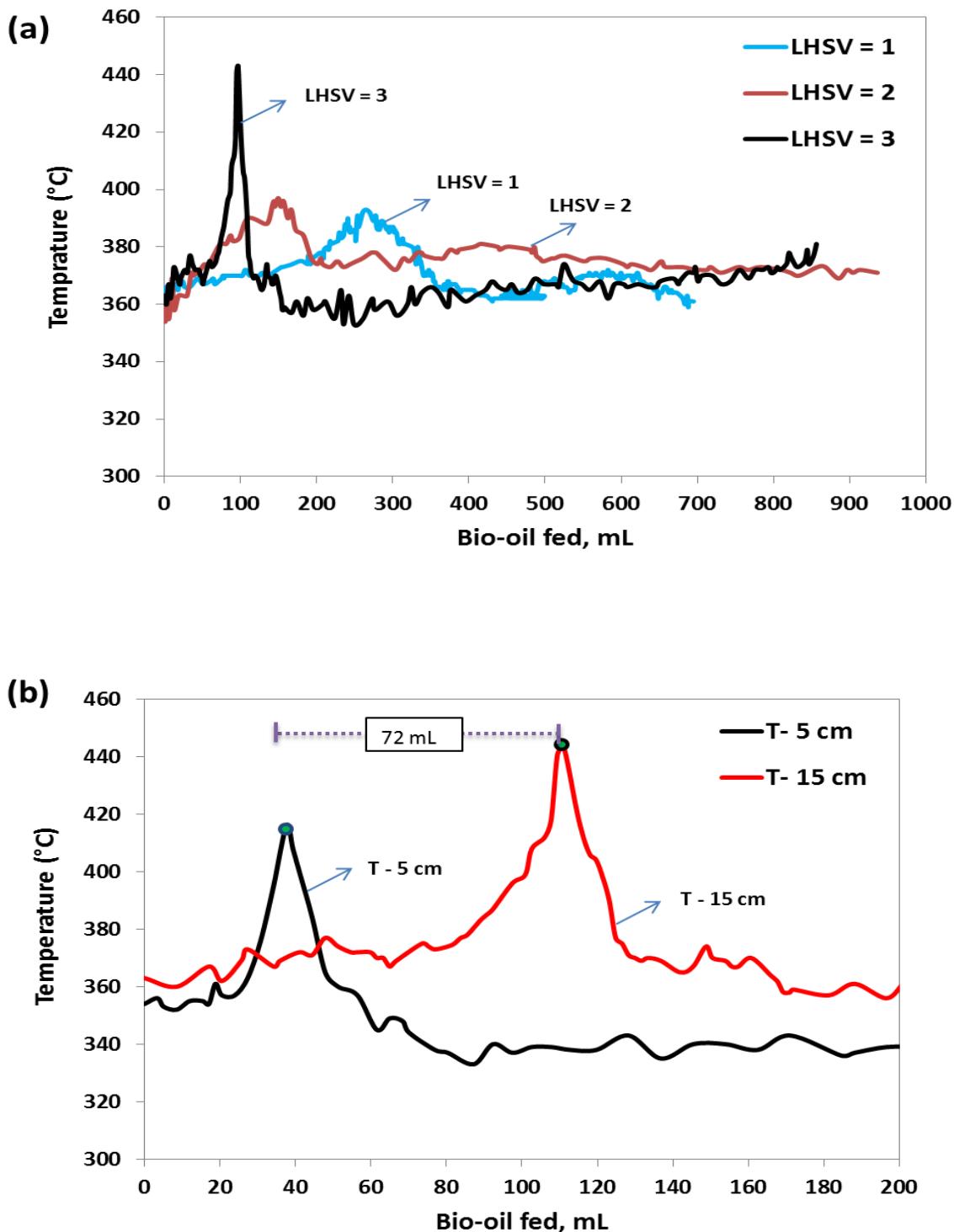


Figure 3-2. (a) The temperature profiles measured at the location 15 cm into the NiMo/Al₂O₃ catalyst bed as a function of LHSV. (b) The temperature profiles measured at 5 cm and 15 cm into the NiMo/Al₂O₃ catalyst bed for LHSV = 3 h⁻¹.

The x-axis refers to the total amount of bio-oil that had been fed into the reactor, which facilitates a better comparison of the experiments with different bio-oil

feeding rates. It is an indirect indication of the time that has passed since the start of the feeding of bio-oil. Figure 3-2b shows the temperature profiles measured at 5 and 15 cm into the NiMo catalyst bed at the same LHSV value of 3 h^{-1} .

The most striking feature of Figure 3-2 is the presence of huge exothermic peaks. Temperature increases as high as 80°C were observed. Under the present experimental conditions ($> 350^\circ\text{C}$ and > 70 bar), many light species (e.g. acetic acid) would exist in the gas/vapour phase. Carried by the excess supply of hydrogen, the residence time of these light species could be at the order of seconds, in fact < 0.8 s in this particular case. However, the data in Figure 3-2 indicate that, at 5 cm in the catalyst bed, it took many min for the exothermic peaks to appear. Therefore, it is fair to conclude that the exothermic peaks were not due to the hydrotreatment of light species that would travel through the reactor in the gas/vapour phase. Instead, these exothermic peaks were due to the hydrotreatment of the bio-oil species that largely travelled through the catalyst bed in the reactor in the liquid phase.

The presence of a peak in Figure 3-2 would mean that the exothermic reactions at the given location where the thermocouple was present underwent increases and decreases in reaction rates (i.e. the heat generation rate) with time. However, bio-oil was always continuously fed into the reactor at a pre-set constant flow rate in each experiment in the continuous excess supply of hydrogen. Any hydrotreatment reactions at a given location in the catalyst bed would be expected to show increases in reaction rates (as the reactants were supplied to, i.e. reached, the catalyst at that given location) and then level off (i.e. not to decrease). In other words, the reaction rates at a given location in the catalyst bed should have shown a monotonic increase and then approached a plateau value without showing a maximum. The only plausible explanation to this obvious contradiction between the observed reaction rate peaks (exothermic peaks) and the expected monotonic-plateau trends is that (part of) the catalyst was almost instantly deactivated to result in decreases in the reaction rate (i.e. heat generation rate). As will be shown later, the bio-oil was continuously hydrotreated well beyond the time scale of the exothermic peaks shown in Figure 3-2. Therefore, the catalyst deactivation associated with the exothermic peaks in Figure 3-2 was very selective. In other words, only a (small) fraction of the hyperactive sites in the catalyst were instantly deactivated as soon as they came into contact with (some components of) the bio-oil.

A further observation can be made from the data in Figure 3-2a. As the bio-oil feeding rate was increased (i.e. as the LHSV was increased), the liquid components reached the location at 15 cm in the NiMo catalyst bed increasingly rapidly. While the exothermic peak appeared after 270 mL of bio-oil was fed into the reactor (470 min) at a LHSV of 1 h^{-1} , the exothermic peaks showed at about 150 mL (130 min) and 110 mL (65 min) for LHSVs of 2 and 3 h^{-1} respectively. In other words, the exothermic peak did not show after the same amount of bio-oil was fed into the reactor at different bio-oil feeding rates. The exothermic peak became increasingly narrow and high as the LHSV was increased from 1 to 3 h^{-1} . Clearly, the hydrotreatment reactions would take place as soon as the bio-oil and hydrogen came into contact with the catalyst. In addition to, or simultaneously with, the removal of oxygen from bio-oil, the molecular sizes would also decrease, which combine to turn more bio-oil components into vapour. With decreasing LHSV value, the residence time of bio-oil in the reactor would increase for more hydrotreatment reactions to take place. The net result is that the actual liquid flow rate in the downstream decreased more than the decreases in the bio-oil feeding rate. Another reason for the exothermic peak not to appear after the same amount of bio-oil was fed at different feeding rates was due to the need for the liquid to fill the pores in the catalyst. Certain amount of liquid must be required to fill the pores within the catalyst particles. Once the liquid molecules went into pores, they were less carried ("blown") by the gas and liquid and thus moved through the reactor slowly. Once the pores are filled, the extra liquid would be forced by the flowing hydrogen through the reactor more rapidly.

It then follows that the composition of liquid/vapour reaching the catalyst downstream, e.g. at the location of 15 cm into the catalyst bed in Figure 3-2a, would be different when LHSV value was increased. Nevertheless, the exothermic peak always appeared. As will be shown later (Figure 3-5), the overall oxygen content of the liquid passing through the catalyst bed at 15 cm would be very different as the LHSV value was increased. While the hyperactive sites in the catalyst at that location (15 cm) would complete the deactivation only after the residual liquid from about 150-200 mL (peak width in Figure 3-2a) of bio-oil had passed by at an LHSV of 1 h^{-1} , the peak width was only about 70-80 mL in the case of LHSV of 3 h^{-1} . All results combine to indicate that the deactivation of hyperactive sites in the catalyst, as was evidenced by the exothermic peaks, is related both to the catalyst itself

(heterogeneity in terms of the presence of some hyperactive sites) and to the bio-oil composition.

3.3.2. Overall product yields

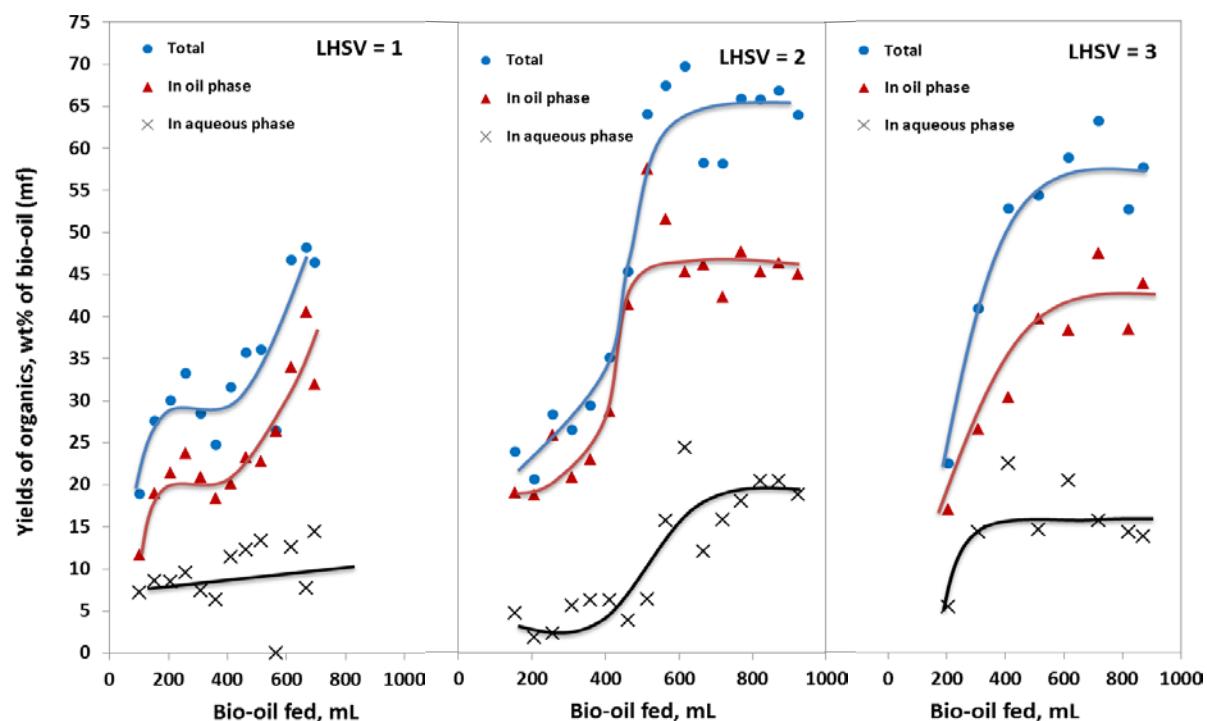


Figure 3-3. The yields of organics from the hydrotreatment of bio-oil as a function of the volume of bio-oil fed into the reactor and LHSV.

The effects of LHSV on the yield of organic products from the hydrotreatment of bio-oil are shown in Figure 3-3. The product stream from the hydrotreatment reactor went alternatively into one of two traps to condense the liquid products. The product was thus collected into time-on-stream-resolved fractions. Each datum point in Figure 3-3 (and other figures) represented the yield of product collected in one trap, which was defined as the amount of product in the trap divided by the amount of bio-oil (on the moisture-free basis) fed into the reactor over the same period of time. To determine the amount of product in a trap, the trap contents were then transferred into a container where the product separated into two phases: one oil phase rich in organic product and one aqueous phase rich in water. The amount of each phase was weighed following decanting. The water content in each phase was determined to calculate the amount of organics in each phase (shown as “in oil phase” and “in

aqueous phase" in Figure 3-3). The total yield of organics in the whole trap is also shown in Figure 3-3. The product in the first trap contained impurities (e.g. the solvent residue used to clean the feeding line) and thus was not considered in plotting the data in Figure 3-3. The transfer of the contents in a pressurised trap into another container at atmospheric pressure was a difficult operation and did not always ensure 100% transfer of all materials in the trap. This contributed significantly to the observed scatters in the data shown in Figure 3-3.

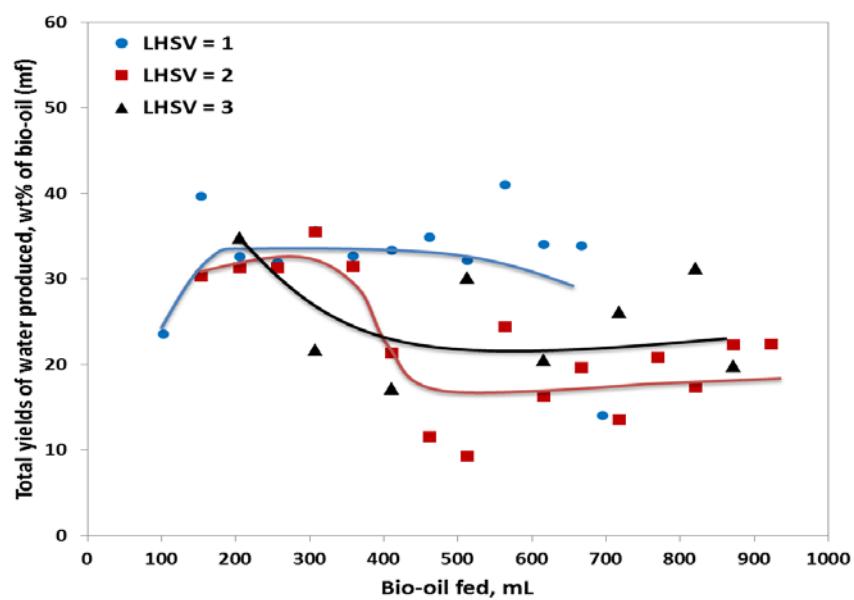


Figure 3-4. The total water produced as a function of the amount of bio-oil fed into the reactor and LHSV.

The total yields of organic products during the initial periods of hydrotreatment were low, often < 30%. The low liquid product yields were neither due to the formation of coke nor due to the formation of gases. Massive formation of coke at this level would have blocked the reactor: the observed pressure drop increases were in fact minimal. Furthermore, the analysis of gases using a gas chromatograph did not give evidence of massive gas formation. When the total yield of water formation was considered (Figure 3-4), the total yield of organics and water was far smaller than 90%. The main reason must be due to the hold up of liquid in the catalyst bed in the reactor. In fact, little product (although difficult to quantify accurately, see above) was collected in the first trap. Significant amounts of heavier bio-oil components, as liquid, filled the pores in the catalyst particle and the inter-

particle voids in the reactor. The hold up of bio-oil components in the reactor has been observed and discussed in detail in our previous study [15].

It follows then that the organic products observed in the first couple of traps are mainly the light species (also see discussion below) that travelled through the reactor in the gas/vapour phase. These species were well hydrotreated to form water (Figure 3-4) and to give products with low oxygen contents (Figure 3-5). Irrespective of the LHSV values used in the range of 1 to 3 h^{-1} , the oxygen contents of the products in the oil phase at the initial stages of the experiments (low amount of bio-oil fed into the reactor) were very low (Figure 3-5). It can thus be concluded that the NiMo catalyst was very active to hydrodeoxygenate the species in the gas/vapour phase, at least under the current experimental conditions.

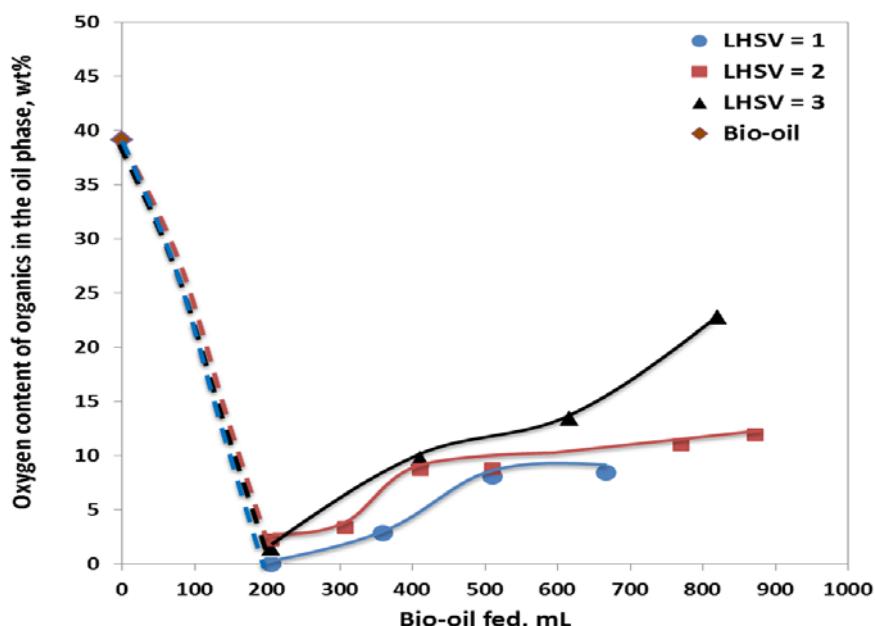


Figure 3-5. The oxygen content of the organics in the oil phase as a function of the amount of bio-oil fed into the reactor and LHSV.

At a LHSV value of 1 h^{-1} , the observed yield of organics, mainly that in the oil phase, increased rapidly to about 30 wt% of bio-oil fed into the reactor (on the moisture-free basis). This is at least partly due to the appearance of heavier species in the product stream when the catalyst bed had been saturated with the heavy liquid. The yield of organic product and the production of water remained almost unchanged (within the scatters) until after ~500 mL of bio-oil had been fed into the reactor. Beyond 500 mL of bio-oil feed, the yield of organic product increased (Figure

3-3), which was accompanied by the increases in its oxygen content (Figure 3-5) and somewhat by the decreases in the production of water (Figure 3-4). This signals the deactivation of catalyst for reduced hydrodeoxygenating activities.

When the LHSV value was increased to 2 and 3 h⁻¹, the yield of organic products appeared to increase more rapidly and to a higher value (to 60-70 wt%) than at 1 h⁻¹, with less water production and higher oxygen content in the oil phase.

These data would indicate that the NiMo catalyst used in the present study appeared to have less ability to handle heavy bio-oil components than the lighter ones. The behaviour of lighter and heavier species will be discussed below.

3.3.3. The transformation and formation of lighter compounds in the vapour phase

The total ion chromatograms for typical oil phase of hydrotreated bio-oil are shown in Figure 3-6. The compounds identified are listed in Table 3-1.

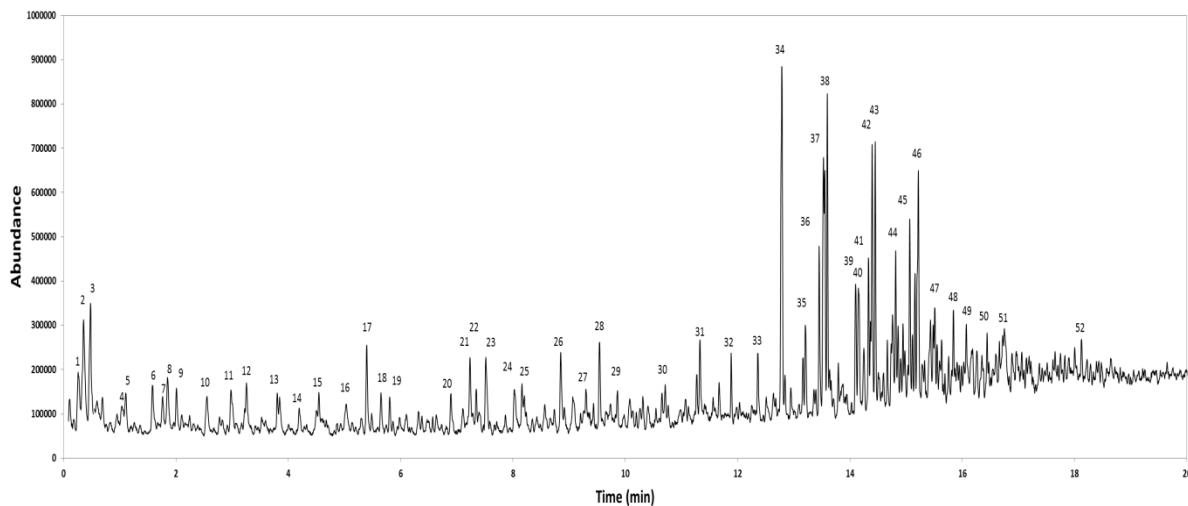


Figure 3-6. Total ion chromatograms of typical hydrotreated bio-oil.

Figure 3-7 shows the yields of various classes of lighter species in the products. In each case, those found in the aqueous and oil phases were summed up to give the total yields shown in Figure 3-7. The datum points at “0 mL” of bio-oil fed into the reactor indicates the contents of these species in the raw bio-oil. Due to the complexity of bio-oil composition, many species may be formed and consumed simultaneously during hydrotreatment. For simplicity, all species have been shown

as “yield”, which should simply be taken as a ratio of their mass flow rate at the reactor exit to the bio-oil feeding rate.

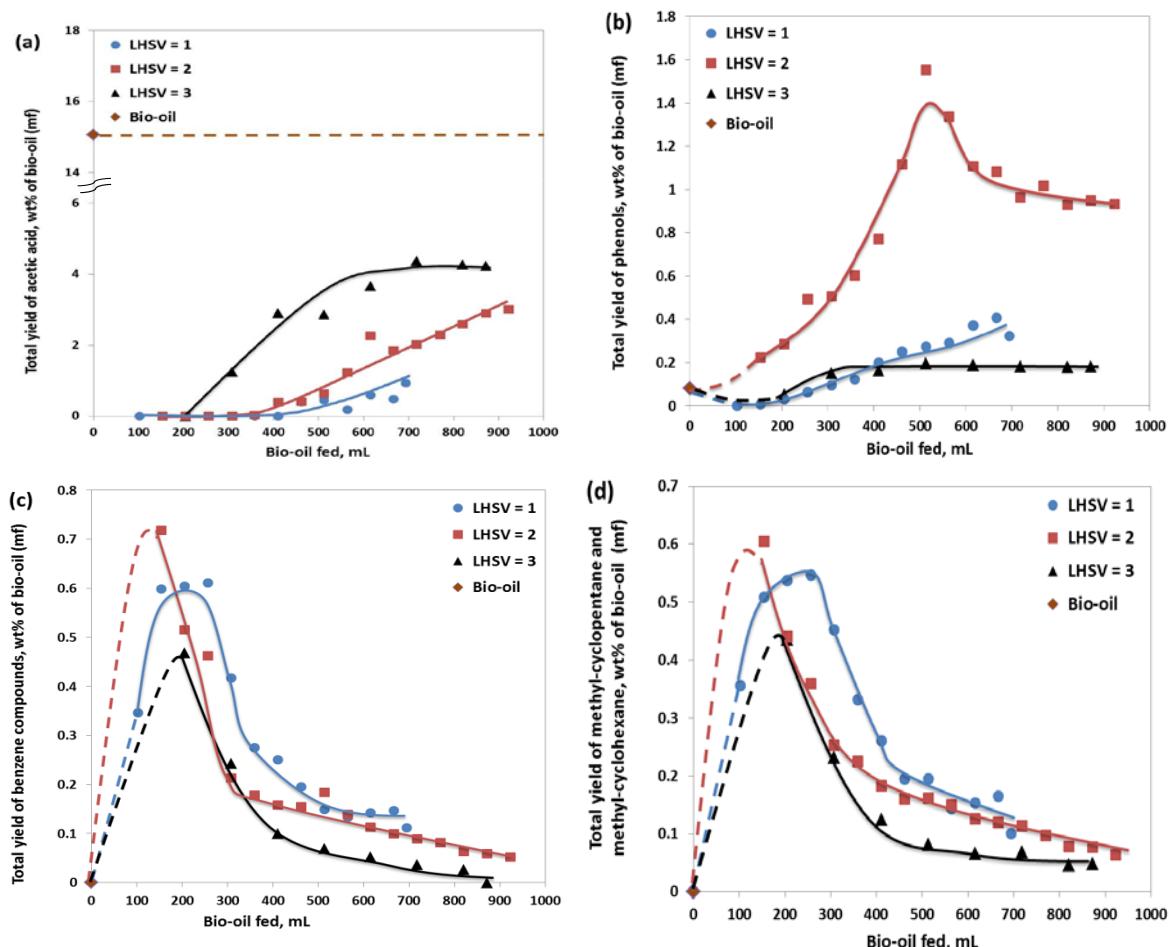


Figure 3-7. The yields of lighter species from the hydrotreatment of bio-oil as a function of the amount of bio-oil fed into the reactor and LHSV.

Acetic acid is the most abundant (15 wt%) organic acid in bio-oil, contributing to the high acidity of the unhydrotreated bio-oil. The data in Figure 3-7a show that acetic acid can be destroyed during hydrotreatment, improving the biofuel product quality. At all LHSV values used, acetic acid was nearly completely destroyed during the initial periods of the experiments. It is believed that acetic acid would exist in the vapour form under the present experimental conditions and thus would travel through the reactor rapidly. This means that the fresh NiMo catalyst was very active in removing acetic acid. However, the concentration (reflected as “yield”) of acetic acid increased as the experiment progressed, increasing more rapidly at a higher

LHSV value than at a lower LHSV value. At a LHSV value of 1 h^{-1} , significant amounts of acetic acid were observed after $> 400\text{ mL}$ of bio-oil had been fed into the reactor. This appears to coincide with the exothermic peak shown in Figure 3-2a: by extrapolation, the exothermic peak would appear at the end of the NiMo bed at $> 400\text{-}500\text{ mL}$. Even at the end of that experiment, the concentration of acetic acid in the product was never as high as its concentration in the raw bio-oil. This is taken to mean that the destruction of acetic acid can take place both at the hyperactive sites and at the “normal” active sites of the catalyst. However, the occupation of the reactive sites by heavy liquid species did greatly reduce the accessibility of these active sites to acetic acid.

Table 3-1. Identification of compound labelled in Figure 3-6

Peak no	Compound	Retention time (min)
1	Cyclododecanol	0.258
2	Toluene	0.357
3	Water	0.479
4	Cyclohexane,butyl-	1.033
5	1H-indene,octahydro-,cis-	1.107
6	Ethylbenzene	1.581
7	Benzene,1,3-dimethyl-	1.761
8	Benzene,1,2-dimethyl-	1.849
9	1-butanol	2.008
10	P-xylene	2.556
11	Benzene,propyl-	2.981
12	Benzene,1-ethyl-3-methyl-	3.256
13	Benzene,1-ethyl-2-methyl-	3.804
14	Benzene,1,2,3-trimethyl-	4.194
15	Benzene,(1-methylpropyl)-	4.545
16	Benzene,1-ethyl-3,5-dimethyl-	5.028
17	Benzene,2-propenyl-	5.395
18	2,4-dimethylstyrene	5.654
19	Indan,1-methyl-	5.806
20	1H-indene,2,3-dihydro-5-methyl-	6.897
21	1H-indene,2,3-dihydro-4-methyl-	7.235
22	Benzene,2-ethenyl-1,3,5-trimethyl-	7.351
23	Naphthalene,1,2,3,4-tetrahydro-	7.516
24	Naphthalene,1,2,3,4-tetrahydro-2-methyl-	8.023
25	Naphthalene,1,2,3,4-tetrahydro-1-methyl-	8.161
26	Naphthalene,1,2,3,4-tetrahydro-6-methyl-	8.857
27	Naphthalene,1,2,3-tetrahydro-2,7-dimethyl-	9.304

28	Naphthalene,1,2,3,4-tetrahydro-5-methyl-	9.543
29	Naphthalene,5-ethyl-1,2,3,4-tetrahydro-	9.861
30	Naphthalene,1,2,3,4-tetrahydro-5,7-dimethyl-	10.712
31	Naphthalene,1,2,3,4-tetrahydro-6,7-dimethyl-	11.334
32	Phenol,2,6-dimethyl-	11.887
33	Phenol,2-ethyl-5-methyl-	12.361
34	Phenol,3-propyl-	12.791
35	Phenol,2,4,6-trimethyl-	13.208
36	Phenol,2-ethyl-	13.453
37	Phenol,4-methyl-	13.529
38	Phenol,3-methyl-	13.598
39	Phenol,3-ethyl-5-methyl-	14.096
40	Phenol,4-ethyl-3-methyl-	14.148
41	Phenol,2-ethyl-3-methyl-	14.332
42	Phenol,2,4-dimethyl-	14.394
43	Phenol-3-ethyl-	14.452
44	Phenol,3,4-dimethyl-	14.815
45	Phenol,4-(1-methylpropyl)-	15.066
46	Phenol,3-propyl-	15.218
47	Phenol,3,4,5-trimethyl-	15.51
48	Phenol,3-methyl-6-propyl-	15.845
49	Benzene,1-ethyl-2,4,5-trimethyl-	16.073
50	Phenol,nonyl- 1-cyclohexene-1-acrylic acid,2,6,6-trimethyl-3-oxo,methyl	16.444
51	ester	16.749
52	2,3-2H-benzofuran-2-one,3,3,4,6-tetramethyl-	18.125

When the LHSV was increased to 2 h^{-1} , acetic acid started to appear in the product stream just after 350 mL of bio-oil had been fed into the reactor. At the LHSV value of 3 h^{-1} , acetic acid appeared in all product samples except in the product in the first trap. These again correspond to Figure 3-2a that the exothermic peaks appeared earlier with increasing LHSV. These results confirm the importance of availability of active sites to the destruction of acetic acid, which could be occupied by the heavy species.

Figure 3-7b shows the yield of phenolics including phenol and substitutional phenols. Figure 3-7c shows the yields of benzene and substituted benzenes, shown as “benzene compounds”. Bio-oil is rich in phenol structures both as light components and as heavy components, including lignin-derived oligomers [3,4,21]. However, many phenol structures in bio-oil were embedded in large molecules that would not have gone through the GC column to be quantified. Therefore, light

phenolics could be converted, e.g. to produce benzene and substitutional benzenes, or formed from the breakdown of lignin-derived oligomers. Indeed, the content of GC-quantified light phenolics in bio-oil was higher than the yield of phenolics in the oil phase products produced at the earlier stages at LHSV^s of 1 or 2 h⁻¹ but lower than the yields under all other conditions. The data in Figures 3-7b and 3-7c indicate that the fresh NiMo catalyst at the initial periods of experiments was active in converting light vapour phenolics (Figure 3-7b) into benzene compounds. At the later periods of experiments, this conversion was a lot less effective. This must again have been due to the occupation of the catalyst active sites by the heavy species. In some cases, e.g. LHSV of 2 h⁻¹, when the catalyst was significantly deactivated at later stages of experiments, the observed yields of GC-quantified phenolics decreased, apparently owing to the reduced conversion of phenol structures in large molecules into GC-quantified light phenolics. In the case of LHSV of 3 h⁻¹, the low yields of GC-quantified phenolics must have been due to the low activities of the catalyst that were in contact with abundant bio-oil liquids even at the earlier periods of experiments. To produce high yields of benzene compounds, the catalyst must be sufficiently active to produce light phenolics and also convert light phenolics into benzene and substitutional benzenes, explaining the trends in Figure 3-7c. For example, at a LHSV value of 3 h⁻¹, the active sites were not sufficiently available to convert the phenol structure in large molecules into light phenolics (Figure 3-7b) or to convert the light phenolics into benzene compounds, with the exception at the beginning of the experiment.

Substituted cyclopentanes and cyclohexanes are the hydrogenation products. As is shown in Figure 3-7d, their production was favoured at the fresh catalyst surface, mostly from the hydrogenation of light species in the gas/vapour phase, and decreased with the occupation of the catalyst by liquid and the deactivation of the catalyst.

3.3.4. Transformation of structure and properties of bio-oil during hydrotreatment

Observation based on TGA. Thermogravimetric analysis was used to characterise the thermal properties of the hydrotreated products. A small amount of the oil phase product was heated up in a TGA to 500°C at a heating rate of

10°C/min. The weight loss was a result of combined physical (evaporation) and chemical (decomposition) processes, which in turn is partly related to the molecular mass distribution (see below). The residue at 500°C was termed as “potential coke”, reflecting the potential amount of coke that would form when the oil is heated to 500°C. Figure 3-8 shows the typical DTG curves and the potential coke yields of the hydrotreated oil products (in the oil phases) in comparison with those of the raw bio-oil. The TGA was carried out only with the oil phase products because of the difficulties in getting accurate data with the aqueous phases that had very high water contents.

The data in Figure 3-8a show that, at a LHSV value of 2 h⁻¹, the product collected initially (after only 205 mL of bio-oil was fed) was relatively light, all evaporated at < 225°C in TGA with almost no solid residue (potential coke) left at 500°C in TGA (Figure 3-8b). With the progress in hydrotreatment, the product became heavier, requiring higher temperature to evaporate in TGA. Some solid residue started to appear (Figure 3-8b) for the product collected after 350 mL of bio-oil was fed into the hydrotreatment reactor; the potential yield increased rapidly thereafter. Nevertheless, the potential coke yields of the hydrotreated oil products were always less than that of the raw bio-oil. In fact, the data in Figure 3-8a show that the hydrotreated oil phase contained species heavier than those in the raw bio-oil, as is evidenced by the high DTG intensity at > 400°C in TGA. However, caution must be exercised in interpreting the DTG data at high temperatures (e.g. > 300°C). Bio-oil is exceedingly reactive and will polymerise once it is heated up to elevated temperatures [26]. At high temperatures, these species would tend to polymerise instead of being evaporated, giving very high potential coke yield. On the other hand, many O-containing functional groups responsible for the high reactivity of bio-oil would have been hydrodeoxygenated. Therefore, the data in Figure 3-8 indicate that the hydrotreated bio-oils, even at the later stages of experiments when the catalyst has been partially blocked or even partially deactivated, have much less tendency to polymerise than the raw bio-oil. Some species in the hydrotreated bio-oil could still evaporate at > 450°C instead of forming coke.

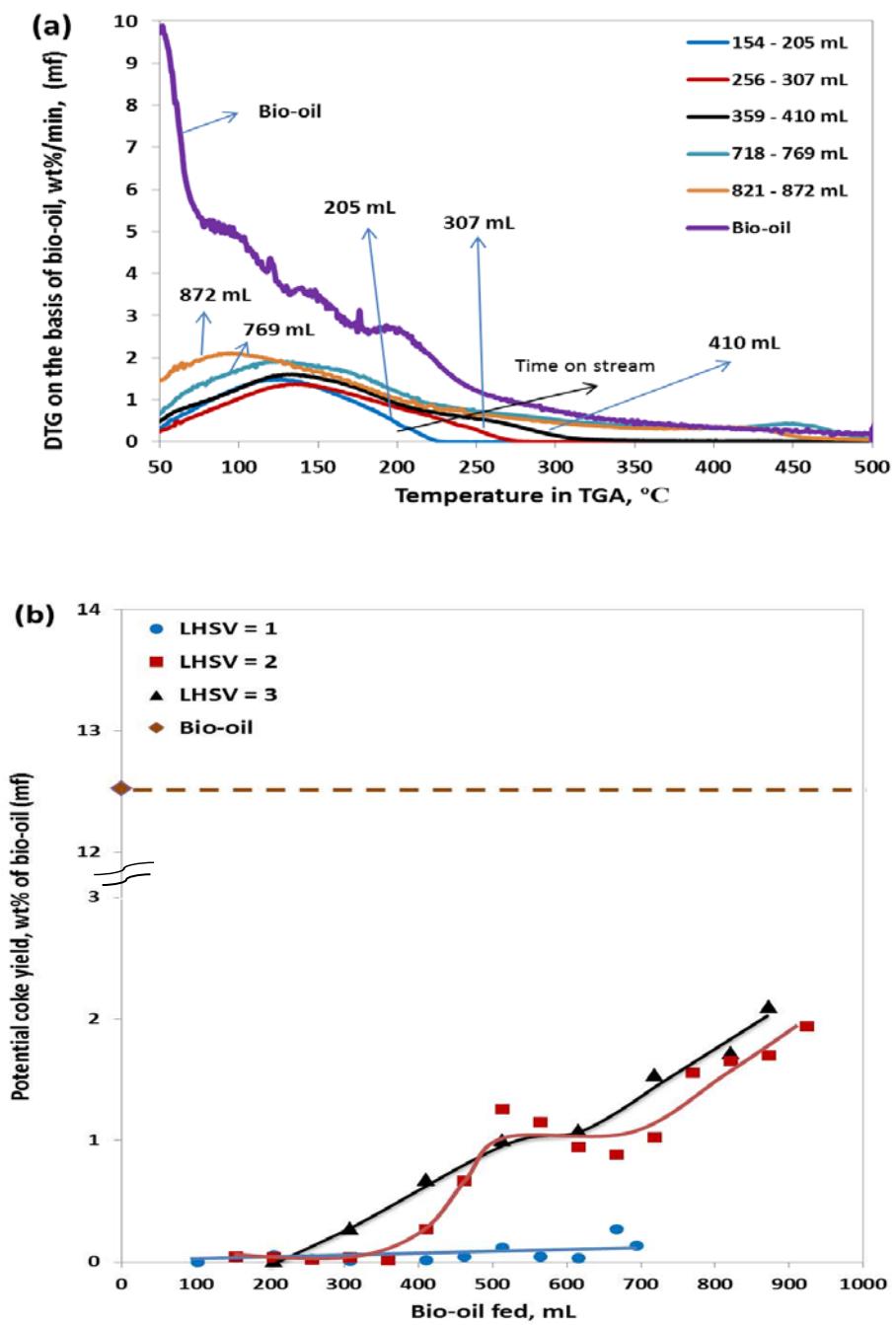


Figure 3-8. (a) DTG curves of the hydrotreated bio-oils (oil phases) produced at a LHSV of 2 h⁻¹ as a function of the catalyst time-on-stream (reflected by the amount of bio-oil fed into the reactor with intervals labelled in the figure). (b) The potential coke yields of the hydrotreated bio-oils (oil phases) measured by TGA as a function of the catalyst time-on-stream (reflected by the amount of bio-oil fed into the reactor) and LHSV.

The data in Figure 3-8b indicate that the potential coke yield determined in TGA was always low for the LHSV value of 1 h^{-1} . Increasing LHSV resulted in rapid increases in the potential coke yield. This is at least due to two reasons. Firstly, the residence time decreased with increasing LHSV, giving less time for hydrotreatment reactions to take place. Secondly, the concentration of heavy liquid in the reactor increased with increasing LHSV, limiting the access of active sites to hydrogen. In the absence of abundant active hydrogen, the relative importance of polymerisation would increase over the hydrogenation and hydrocracking reactions, favouring the formation of heavy species and coke.

Transformation of aromatic structures as reveal by UV-fluorescence spectroscopy. Figure 3-9 shows the synchronous spectra of hydrotreated bio-oils (oil phases). As was stated in Experimental, the fluorescence intensity has been expressed on the basis of moisture-free bio-oil to allow for comparison under different experimental conditions. The spectrum for the raw bio-oil is shown for comparison. At the initial stages of hydrotreatment (Sample 1, Figure 3-9a), the fluorescence intensity was generally very low. Little intensity was observed at wavelengths longer than 320 nm, signalling the absence of ring structures with more than 2 (equivalent) fused benzene rings. The lack of oxygen in the hydrotreated bio-oil also would not give high quantum yields, contributing to the observed low intensity. These data are taken to indicate that the gas-phase-dominated hydrotreatment product was well hydrotreated. This is in agreement with the visual observation that these samples were lightly coloured.

With the progress of experiments (e.g. Sample 2 in Figure 3-9b), the fluorescence intensity increased, at least partly due to the appearance of liquid that had travelled through (most of) the catalyst bed. In particular, at the LHSV value of 3 h^{-1} , there was a significant increase in fluorescence intensity at wavelengths longer than 300 nm, most likely due to the aromatic structures with more than 2 (equivalent) fused benzene rings.

At the later stages of experiments (Samples 3 and 4 in Figures 3-9c and 3-8d), the observed fluorescence intensity of the hydrotreated bio-oils were similar to or higher than those of the raw bio-oil. However, the similarities in the spectral features between the raw and hydrotreated bio-oils (e.g. the shoulder peaks at around 385 nm) indicate the similarities in their aromatic structure features. The

explanation of these data must consider the importance of intra-molecular energy-transfer to the observed fluorescence intensity for this type of samples [27]. Due to the intra-molecular energy transfer, very large aromatic ring systems in large molecules in bio-oil are not well represented by the observed fluorescence [27]. As these large molecules are broken down as a result of thermal or hydrocracking or removal of oxygen, the efficiency of intra-molecular transfer is lowered to result in a better representation of these large aromatic ring systems in the observed fluorescence. This explains why the fluorescence intensity of hydrotreated bio-oil can be higher than that of the raw bio-oil, but having similar spectral features. The possible formation of additional aromatic structures during the later stage of hydrotreatment cannot be ruled out but our data do not give conclusive evidence for this possibility.

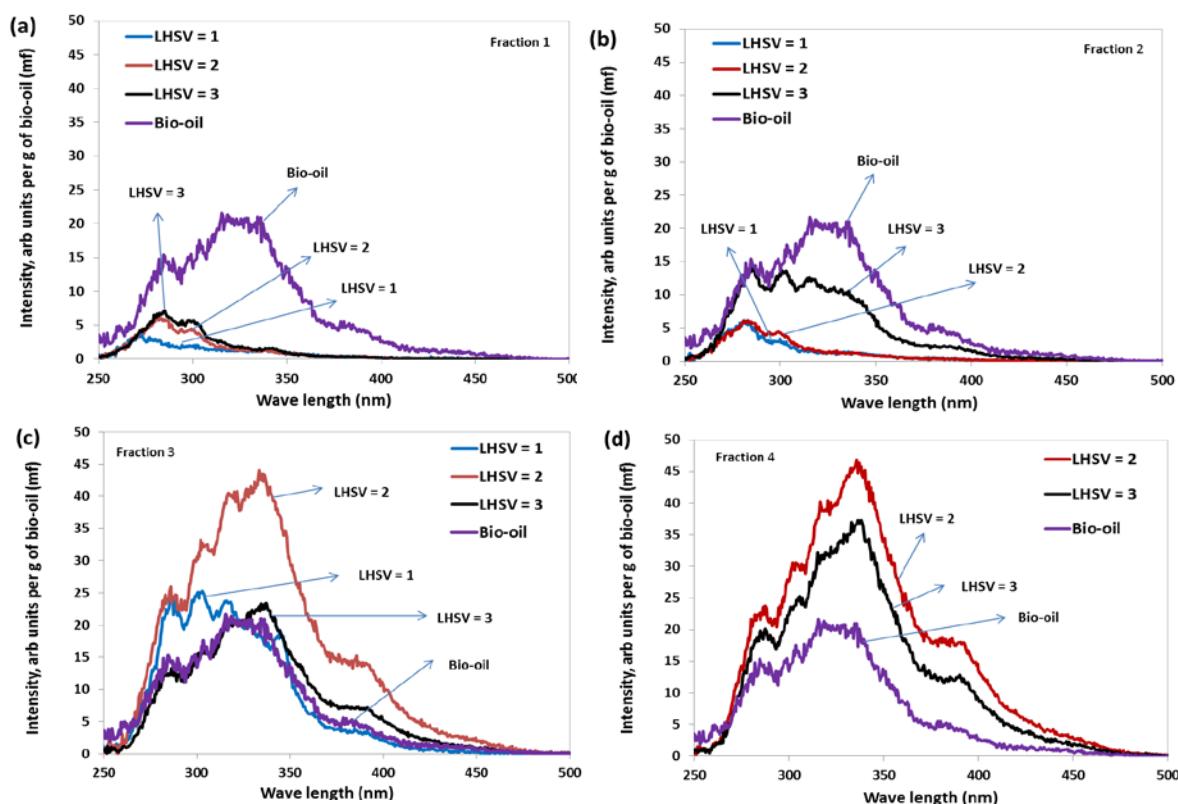


Figure 3-9. UV fluorescence synchronous spectra as a function of LHSV and catalyst time-on-stream (reflected by the amount of bio-oil fed into the reactor). Note: Fraction 1: 103–205 mL bio-oil fed in, Fraction 2: 205–307 mL bio-oil fed in, Fraction 3: 513–615 mL bio-oil fed in and Fraction 4: 715–820 mL bio-oil fed in.

The UV-fluorescence data in Figure 3-9 further support the discussion above in that the lighter species have behaved differently from the heavier species. The catalyst became increasing less effective in hydrogenating the aromatic structures.

3.4. Conclusions

The continuous hydrotreatment of bio-oil in a packed-bed catalytic reactor using a presulphided NiMo/ γ -Al₂O₃ catalyst was carried out under mild conditions (375°C, 70-80 bar). The aim was to investigate the hydrotreatment behaviour of the light and heavy components as a function of LHSV and catalyst time-on-stream. Our results indicate that the lighter and heavier components in the same bio-oil could behave very differently. The overall bio-oil liquid hourly space velocity can drastically affect the hydrotreatment process. While the residence time of the light species that evaporate instantly could be very short, the residence time of heavy species could be very long as they passed through the catalyst bed in the form of liquid. The initial contact of heavy bio-oil species with the pre-sulphided NiMo/Al₂O₃ catalyst could result in very significant exothermic peaks but did not create a thermal runaway situation, owing to the rapid deactivation of the hyperactive sites in the catalyst. The NiMo catalyst used was less active in hydrotreating the heavier bio-oil species than in hydrotreating the lighter bio-oil species. The potential coke yields of the hydrotreated bio-oils, even at very low extents of hydrotreatment, were drastically reduced.

Acknowledgements

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Chapter 4

Effects of temperature on the hydrotreatment behaviour of pyrolysis bio-oil and coke formation in a continuous hydrotreatment reactor

4.1. Introduction

Biomass is the only carbon-containing renewable resources that can be used directly to produce liquid transport fuels. The pyrolysis of biomass would produce a liquid bio-oil and a solid biochar together with a combustible gaseous product that would be burned in situ to meet the energy demand of pyrolysis itself. However, the crude bio-oil is not suitable to be used directly as a fuel in internal combustion engines due to its high oxygen content (20-50 wt %), low pH value (1.5-3.8) and thermal instability. Bio-oil requires further upgrading [1,2]. One of the bio-oil upgrading methods is the catalytic hydrotreatment, mainly HDO, under high hydrogen pressure and elevated temperature to convert bio-oil into a liquid fuel that can be used in the existing vehicles.

In early research papers, sulphided NiMo/ γ -Al₂O₃ and/or CoMo/ γ -Al₂O₃ were used as catalysts based on the experience from the hydrotreatment, especially the hydrodesulphurisation, of petroleum. The reactor temperature was varied between 200 and 450°C at pressures between 100 and 200 bar. The liquid hourly space velocity (LHSV) of bio-oil varied from 0.05 up to 2 h⁻¹ [3]. The most important finding of these earlier experiments was that bio-oil could not be processed in the same way as petroleum. The blockage of reactor due to coke formation has been the single biggest hurdle in upgrading bio-oil via hydrotreatment [4-7].

One approach to overcome this coke formation problem was to use a two-stage hydrotreatment process. In the first stage, the low-temperature (150-250°C) hydrotreatment was applied using a noble catalyst like Ru/C or Pd/C to “stabilise” the bio-oil by hydrotreating the most unstable components in bio-oil [4,8,9]. In the second stage, more severe conditions of higher temperatures (350-450°C) and high pressures (100-200 bar) was used for further deoxygenation. It was found that sulphided NiMo/Al₂O₃ and CoMo/Al₂O₃ catalysts became active especially at temperatures higher than 330°C [10-12]. Nevertheless, no success has been reported that this two-stage approach has resolved the notorious coke formation problem. Additional evidence for this problem will be reported in this work.

Much further fundamental knowledge is required in order to develop a technology/strategy to overcome the coke formation problem. This requires the detailed consideration of various types of reactions taking place during hydrotreatment. The breakage of weaker bonds is the first step of all hydrotreatment reactions. The radicals could then undergo many different types of reactions. For

example, the radicals could be further hydrogenated, (hydro)cracked or hydrodeoxygenated to form stable molecules. The radicals could also re-combine, i.e. to polymerise, into bigger molecules; polymerisation can continue and finally form coke. These different types of reactions occur simultaneously, in series and in parallel, in the vapour phase, in the liquid phase and on the catalyst surface to form a complicated reaction network during the hydrotreatment of bio-oil.

Obviously, the activation energies for different type of reactions in the reaction network will cover a wide range. Therefore, changing temperature would alter the relative reaction rates of different reactions and thus completely change the outcomes of the competitions among various reactions within the above-mentioned network. It is obvious that a balanced approach must be taken in choosing an operating temperature for a commercial process. For example, at higher temperatures, the deoxygenation rate is nearly 100% [9,13]. However, the hydrogenation of aromatics will also intensify to result in increases in hydrogen consumption. The effects of temperature are clearly important knowledge for the development of an effective hydrotreatment technology. Unfortunately, there are insufficient data reported in the literature, particularly on the continuous hydrotreatment.

Much has been done on the hydrotreatment of various model compounds [12], which are thought to represent the typical structures in bio-oil. These model compounds are normally simple compounds of low molecular masses. However, bio-oil is a lot more complicated than the model compounds. In particular, the knowledge about the behaviour of model compounds cannot possibly be used to predict the behaviour of heavy bio-oil molecules. Firstly, a big bio-oil molecule would have multiple reactive functional groups, each can be a centre or initial point of reaction, which cannot be easily predicted *a priori*, at least due to the complicated 3-D configuration of the molecule. Secondly, at best, only a small part of a big bio-oil molecule can be adsorbed on the catalyst surface whose behaviour would surely differ from that of a simple model compound. Unfortunately, very little is available in the literature about the mechanisms of coke formation during the hydrotreatment of a true bio-oil, as opposed to that of model compounds.

The purpose of this work is to investigate the effects of temperature on the hydrotreatment behaviour of bio-oil with a particular focus on coke formation. A better understanding about the effects of temperature on coke formation is gained by

simultaneously tracing the hydrotreatment product structure, including its aromatic structures that are likely the precursors for coke formation. The structural features of the coke formed in the catalyst were also characterised with FT-Raman spectroscopy.

4.2. Experimental

4.2.1. Bio-oil sample

The bio-oil for these experiments was produced in a grinding pyrolysis reactor at 450°C using mallee wood as feedstock [14]. 5 wt% palladium supported on activated carbon (Pd/C) and industrial pre-sulphided nickel-molybdenum supported on Al₂O₃ (NiMo/Al₂O₃) were purchased from Sigma Aldrich and Eurecat, respectively. The Pd/C catalyst was sieved to the 25-75 micron particle range. The NiMo/Al₂O₃ (hereafter termed simply as NiMo catalyst) was ground and sieved to the 600-800 micron particle size range.

4.2.2. Hydrotreatment

The details of the continuous catalytic hydrotreatment reactor can be found elsewhere [7,15]. Briefly, the hydrotreatment reactor (Figure 4-1) was made of ¾ inch stainless steel 316 tubing with a length of 40 cm, which was packed into two parts of 10 and 20 cm lengths with the Pd/C and NiMo catalysts, respectively, in the same reactor. The last 10 cm of the reactor at the outlet side was not used in the experiment as the outlet tubing was put at the end of NiMo catalyst bed (see Figure 4-1). The reactor was heated externally with a hot fluidised sand bath. The reactor part containing the Pd/C catalyst bed was not immersed in the sand bath while that containing the NiMo catalyst was immersed directly in the sand bath.

Two dual-syringe pumps were used to feed the bio-oil continuously into the reactor system. The hydrogen gas flow rate was constant at 4 L/min measured under ambient conditions. The bio-oil and hydrogen were pre-mixed before entering the reactor. The reaction products were continuously condensed and collected into one of two pressurised traps that were cooled with ice water. The traps were alternated

every 45 min to collect the hydrotreated liquid products into reaction-time-resolved fractions. The unreacted hydrogen and non-condensable gases exited the traps. A backpressure regulator downstream the traps was used to set the required operating pressure to 70 bar.

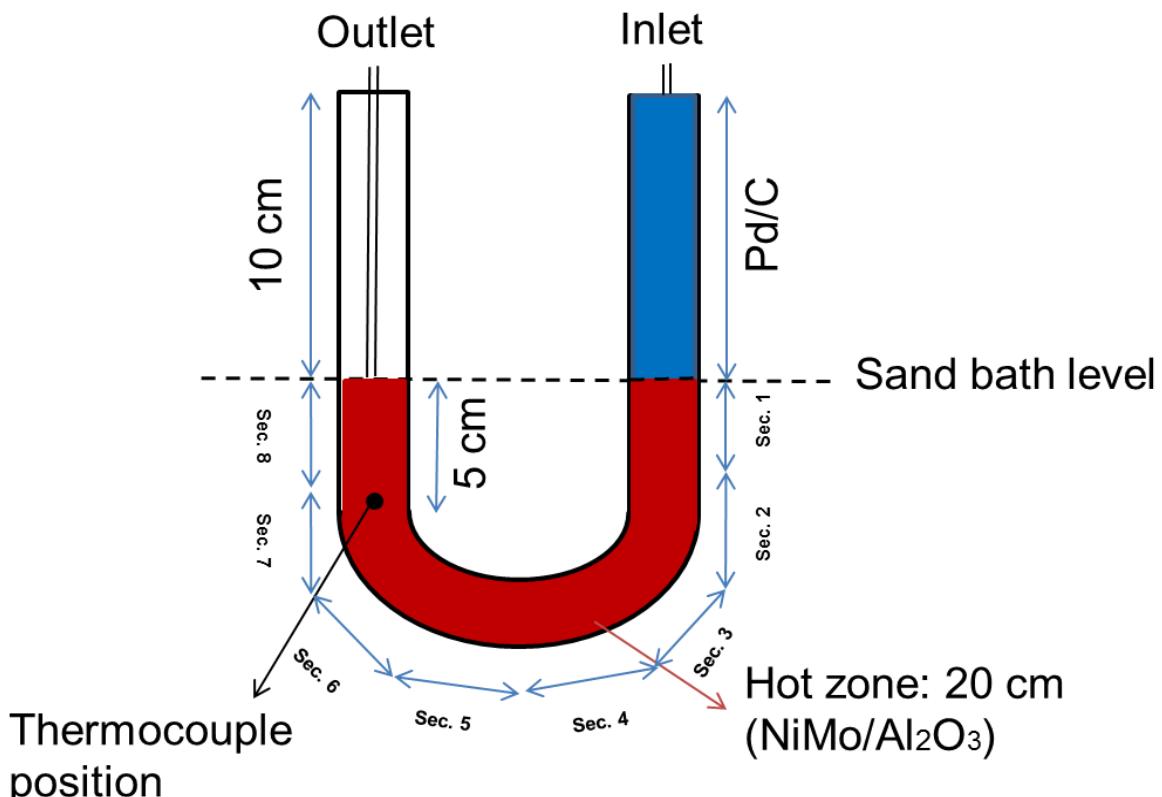


Figure 4-1. A schematic diagram of the reactor configuration.

The bio-oil was fed with a liquid hourly space velocity (LHSV) of 2 h^{-1} . The temperature of the catalyst bed (as shown in Figure 4-1) in the reactor was recorded. The steady state temperature in the end of the Pd/C bed was 215-230°C.

The reactor including the catalysts was weighed before and after the experiment. The weight difference was considered as the sum of formed coke and heavy residue. The weight of coke and heavy residue was distinguished by washing the reactor bed with tetrahydrofuran (THF), followed by drying with flowing nitrogen gas at 150°C for 2 hours.

The data reported in this work for the 375°C were from the same experiment as that reported previously [8] and are used here for comparison.

4.2.3. Product characterisation

UV-fluorescence spectroscopy. A Perkin-Elmer LS50B spectrometer was used for acquiring the UV-fluorescence spectra of bio-oil and hydrotreated oils [16].

GC-MS. For the analysis of light fractions of the bio-oil and liquid products, an Agilent 6890/5973 GC-MS with a capillary column (HP-INNOWax) (length, 30 m; internal diameter, 0.25 mm; film thickness, 0.25 µm) was used [17]. The yield of acetic acid was measured and will be reported as a function of reaction time on stream (measured as the amount of bio-oil fed into the reactor). Furthermore, the yields of phenol, 2-ethylphenol, 2,4,6-trimethylphenol, 2,4-xyleol, 4-(1-methylpropyl) phenol, 3,4,5-trimethylphenol were measured, which were summed together and will be reported as the yield of “phenolics”. The yield of “benzene compounds” reported in this work included the summed yields of ethylbenzene, 1,3-xylene, 1,2-xylene, 1,4-xylene, propylbenzene, 1-ethyl-2-toluene, 1,2,3-trimethylbenzene and (1-methylpropyl) benzene. Methylcyclopentane together with methylcyclohexane were also quantified and summed together.

Thermogravimetric analysis (TGA). A thermogravimetric analyser (TGA, TA Instruments Q5000) was used for measuring the coke forming propensity of the samples. The samples were heated from 25 to 500°C at a heating rate of 10°C min⁻¹ in nitrogen (flow rate 50 mL min⁻¹) [2,18]. The residue was termed as “potential coke yield” [7,18].

Elemental analysis was performed with a Thermo Flash 2000 CHNS-O analyser [19].

FT-Raman spectroscopy. The Raman spectra of the catalysts from different sections of the reactors were acquired using a Perkin–Elmer GX FT-IR/Raman spectrometer with a back-scattered configuration and equipped with a Nd:YAG laser at 1064 nm as its light source. For sample preparation, the catalyst was diluted with KBr (1 % of NiMo) to reduce the heating of sample by the laser [20]. The FT-Raman spectra in the range of 800–1800 cm⁻¹ were curve-fitted using 10 bands [20].

Carbon content analysis. The carbon content of the used NiMo/Al₂O₃ catalyst from different sections of the reactor (Figure 4-1) was measured by a combustion process in a quartz reactor. Briefly, 4-5 milligram (accurately weighed) of the sample grounded homogenously was loaded in the reactor and 15-20 mL/min ultra-high purity oxygen (purity = 99.999 v%) was used for the combustion. The combustion temperature was controlled at a pre-set temperature of 900°C to achieve the complete oxidation of the coke in the catalyst. The product gas exiting the reactor was collected in a gas bag and analysed with gas chromatography. The carbon content of the catalyst was calculated according to the CO₂ gas produced. The reproducibility of this method has been checked by measuring the carbon content of the catalyst from section 2 for the experiment at 375°C. The carbon content from these repeated analysis were 15.4, 14.5, 15.9 and 15.2 wt%.

4.3. Results and discussion

4.3.1. Reactor fouling due to coke formation

Initial trials were carried out using the NiMo catalyst only (i.e. without the Pd/C catalyst). The pressure drop across the reactor increased rapidly with time and the reactor was very soon blocked. A typical example is shown in Figure 4-2. Even at very low LHSV values (<0.5 h⁻¹), the experiment did not last for more than 90 min before the inlet pressure increased from 64 to 100 bar (pressure drop increased by more than 35 bar). Obviously, the formation of coke was the main reason for the blockage the reactor.

Based on the literature [10] and our previous work [15], it was decided that a Pd/C catalyst should be used to stabilise the bio-oil before the bio-oil came into contact with the NiMo catalyst. These two types of the catalysts were packed into the reactor, as is shown in Figure 4-1. While the reactor section containing the Pd/C catalyst was not immersed in the hot fluidised sand bath, the major portion of the Pd/C catalyst bed was still heated up with the temperature at the end of Pd/C bed to have reached around 215-230°C at which the Pd/C catalyst would be active to stabilise the bio-oil.

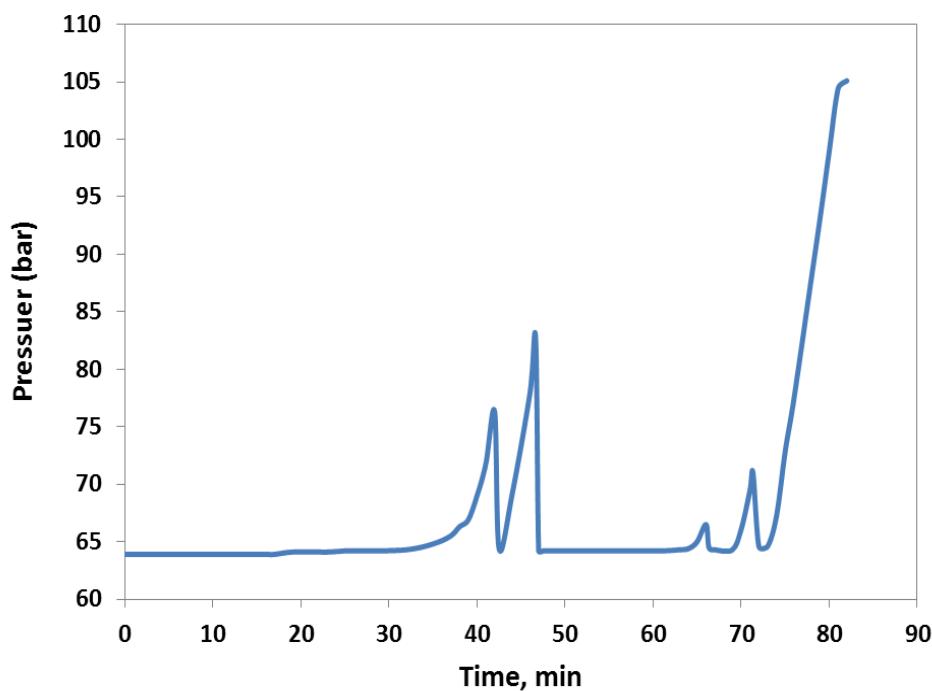


Figure 4-2. The pressure profile measured in the inlet of the reactor as a function of time.

With the use of Pd/C and NiMo catalysts in series, the reactor could be run for much longer time. Figure 4-3 shows the changes in the reactor inlet pressure as a function of temperature with a constant LHSV of 2 h^{-1} . The catalyst temperature in the reactor was not uniform with the initial sections of the NiMo catalyst being at a lower temperature where the colder bio-oil was still being heated up. The temperatures labelled in Figure 4-3 refer to those of the fluidised sand bath that had a relatively uniform temperature.

The experiments at 400, 425 and 450°C (all sand temperatures) had to be stopped when the inlet pressure of the reactor increased rapidly due to the reactor fouling by coke formation, as is shown in Figure 4-3. The experiment at 375°C continued for 13.7 h and was then stopped as planned. The ability to operate the reactor at 375°C for longer time was further confirmed by carrying out another experiment under reduced hydrogen flow rate (2000 mL/min) that still ensured that hydrogen was supplied in great excess, as is shown in Figure 4-4. The experiment continued with the LHSV being varied from 1 to 5 h^{-1} .

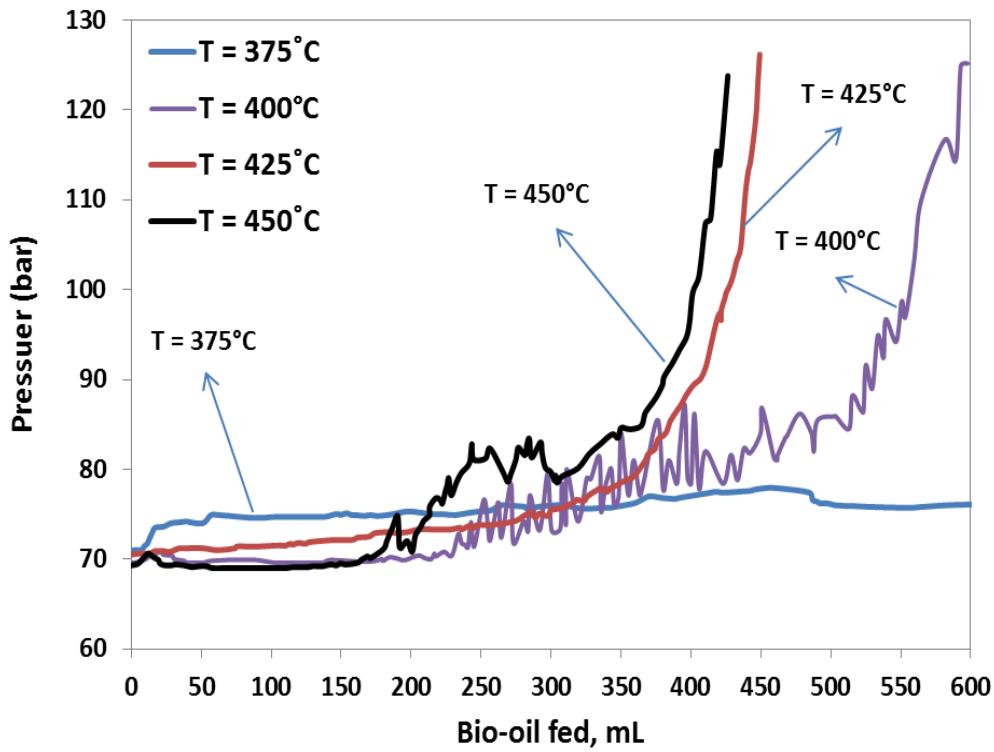


Figure 4-3. The pressure profiles measured in the inlet of the reactors as a function of temperature. The data reported in this work for the 375°C were from the same experiment as that reported previously [7] and are used here for comparison.

The data in Figures 4-2 to 4-4 show that the Pd/C catalyst could indeed help to reduce coke formation in the catalyst bed and prolong the experiment. However, this stabilising effect was still rather limited. Even when a lot more Pd/C catalyst was used by packing Pd/C into a whole reactor as the first stage followed by another reactor of NiMo catalyst, the reactor blockage still could not be avoided. It seems that the higher the temperature, the quicker the reactor fouling took place. This can be explained by more intensive polymerisation at higher temperatures [9]. Within the complicated reaction network as outlined in the Introduction section, increasing temperature would tend to result in the intensified breakage of (weaker) bonds within a short period of time. Unless active hydrogen was supplied to stabilise the radicals, the radicals could rapidly polymerise. The continued bond breakage and polymerisation would result in coke formation. Obviously, the catalyst was not active enough to supply abundant active hydrogen. Alternatively, the (large) bio-oil molecules with abundant oxygen-containing functional groups were more

preferentially adsorbed on the catalyst surface than hydrogen, relatively limiting the generation of active hydrogen. Even for the experiments at 375°C, the significant coke did form, as will be discussed below. After some prolonged operation, the Pd/C catalyst bed itself could also block, in agreement with the literature [10,15].

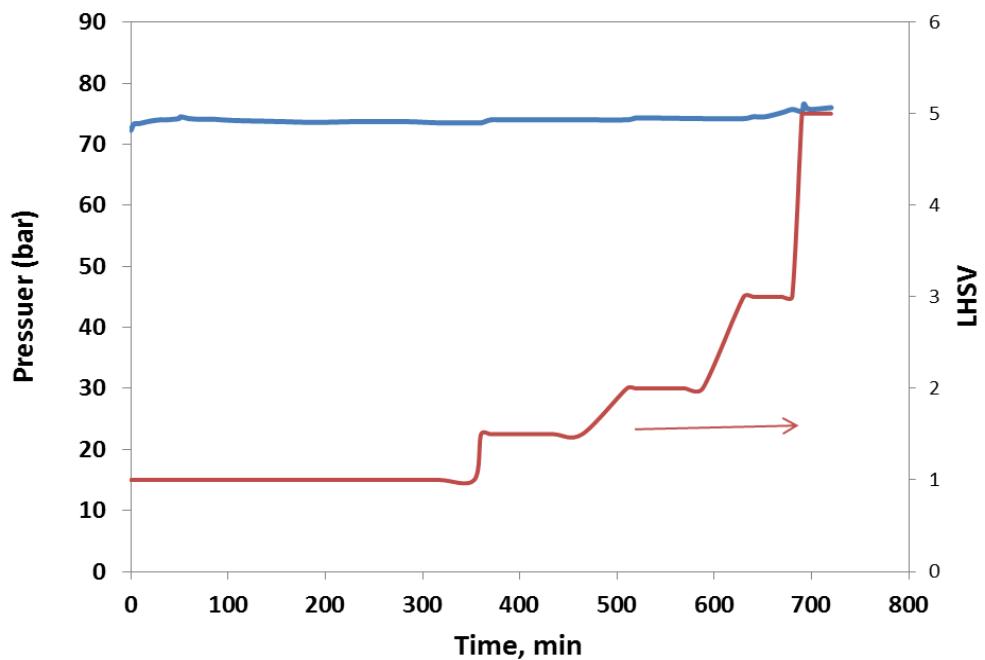


Figure 4-4. The pressure profiles measured in the inlet of the reactors as a function of time and LHSV.

4.3.2. Some dynamic behaviour - exothermic peaks

As is shown in Figure 4-1, a thermocouple was inserted into the NiMo catalyst bed, which is at the position of 15 cm into the NiMo catalyst bed in the direction of fluid flow. Figure 4-5 shows the temperature increase at this position for different sand bath temperatures. In our previous work [7,15], it was concluded that the light and heavy bio-oil species had different speeds travelling through the reactor. The heavier species being in the liquid phase were more responsible for the exothermic wave front (peak) moving through the reactor. An interesting observation in Figure 4-5 is the exothermic peaks at 375 and 400°C while no such clear peak was observed at 425 and 450°C. Instead, a gradual increase in reactor temperature can be seen

for the experiments at the two higher temperatures of 425 and 450°C. Increasing temperature from 375 to 400°C made the exothermic peak to appear at a later time.

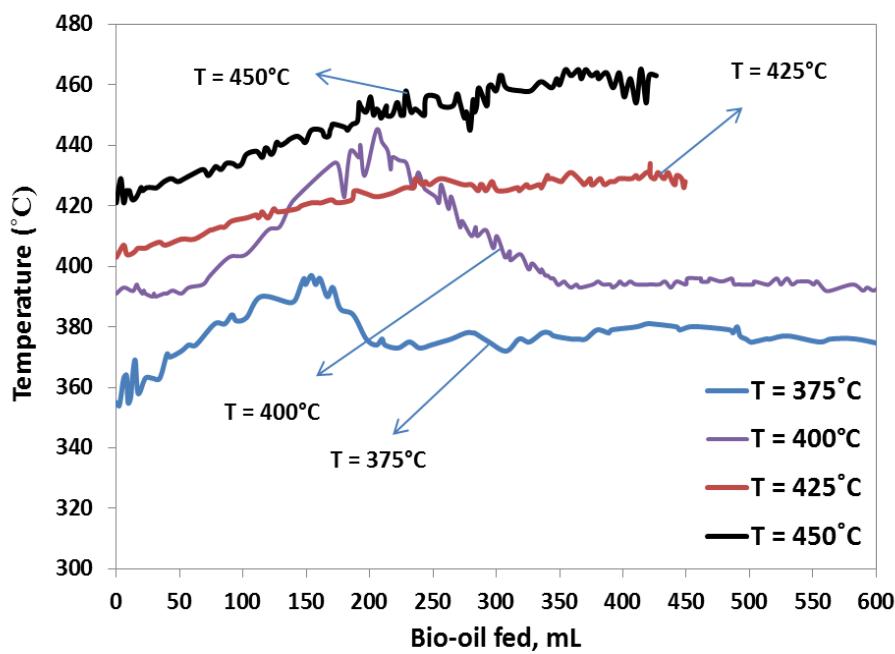


Figure 4-5. The temperature profiles measured at 15 cm into the NiMo/Al₂O₃ catalyst bed as a function of temperature. The data reported in this work for the 375°C were from the same experiment as that reported previously [7] and are used here for comparison.

One plausible explanation for the effects of temperature on the observed peaks could be that, at 425 and 450°C, before the heavy fraction that was in the liquid phase started to reach the location of the thermocouple, the reactor blockage had happened. It is worthwhile to mention that the amount of heavy species inside the reactor would have decreased with increasing temperature. Firstly, increasing temperature would cause more cracking to reduce the amount of heavier species. Secondly, increasing temperature would transfer some liquid-phase species into the gas/vapour phase as a result of equilibrium shift. The net result is that longer time would be required to fill the intra-particle pores and the inter-particle voids, requiring longer time for the liquid to pass through the reactor and to reach the location of thermocouple than in the case of lower temperature. At 425 and 450°C, it is suspected that the heavy liquid phase did not reach the position for the inserted thermocouple. This can be caused by the observed blockage of the reactor before the thermocouple. Visual observation of the catalyst bed after the experiments

indicated that the catalyst bed formed hard lumps in the mid-way of the reactor (around 10 cm into the NiMo catalyst bed). The steady and gradual increases in temperature were then caused by the vapour phase passing by catalyst bed where the thermocouple tip was positioned.

Another possible explanation for the effects of temperature on the observed exothermic peaks was the changes in relative reactivities of the active sites on the catalyst surface. The occurrence of a peak itself means that some hyperactive sites on the catalyst were deactivated [7]. With increasing temperature, the reactivity of all sites would increase so that the difference among the various reactive sites were no longer significant. In other words, the hyperactive sites that are the cause of the exothermic peaks no longer existed at high temperatures in the relative sense.

4.3.3. Product yield and properties

4.3.3.1. Yields of hydrotreated oil

The hydrotreated bio-oils always separated into two phases: one rich in organics (hereafter called “oil phase”) and another one rich in water (hereafter call “aqueous phase”). The effect of temperature on the yields of organics in oil phases (on moisture free) are shown in Figure 4-6. In all experiments, the organic phase of produced hydrotreated sample was on top while the aqueous phase was at the bottom. Two different regions could be observed.

In the first region (up to 250 mL bio-oil feeding), filling of reactor happened and the produced oil contained light components which produced from light molecules in the bio-oil or from cracking of the large molecules. In this region, the yields of organics for all temperatures were increasing.

In the second region (> 250 mL bio-oil feeding), at 375 and 400°C the yields of organics in oil phases increased because the heavy compounds which were most likely in the liquid phase were flowing out. These heavy compounds spent longer time in the reactor compared to the light compounds [15]. At 425 and 450°C, the yields in the second region were constant. This could be because of higher cracking rate which resulted in less volume of the heavy fraction in the reactor and longer time

of reactor to fill up and/or coke formation from heavy species resulted in flowing less heavy compounds from the reactor.

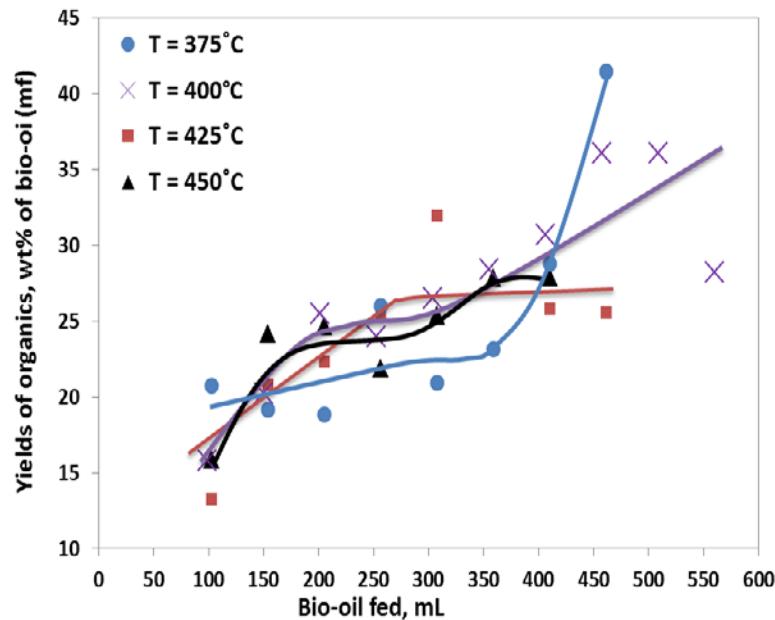


Figure 4-6. The yields of organics in organic phases from the hydrotreatment of bio-oil as a function of the volume of bio-oil fed into the reactor and temperature. The data reported in this work for the 375°C were from the same experiment as that reported previously [7] and are used here for comparison.

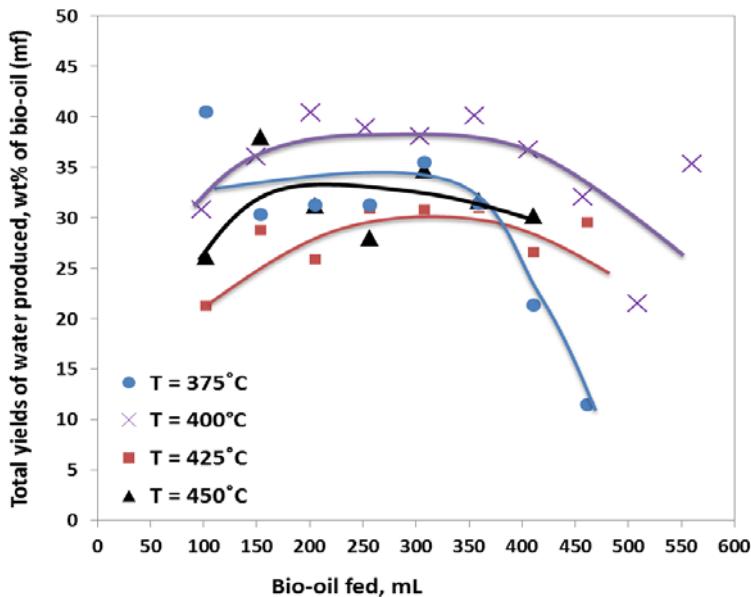


Figure 4-7. The yields of total water formation as a function of the amount of bio-oil fed into the reactor and temperature. The data reported in this work for the 375°C were from the same experiment as that reported previously [7] and are used here for comparison.

The yields of water formation calculated from both phases are shown in Figure 4-7. In the first region (up to 250 mL bio-oil feeding) at 375°C the water yield had a slight increase while in the second region (> 250 mL bio-oil feeding), the yield decreased to 10 wt%. This decrease is because of incomplete hydrotreatment of heavy components flowing out of the reactor or catalyst deactivation which resulted in lower water production. At 425 and 450°C, the water yield increased in the first region while after that it decreased. Moreover, in the first region higher temperature resulted in lower yields of water which was possibly due to sooner catalyst deactivation [7,13]. At 450°C, in the first region the yields of water formation increased from 26 to 35 wt% while in the second region it decreased to 30 wt%.

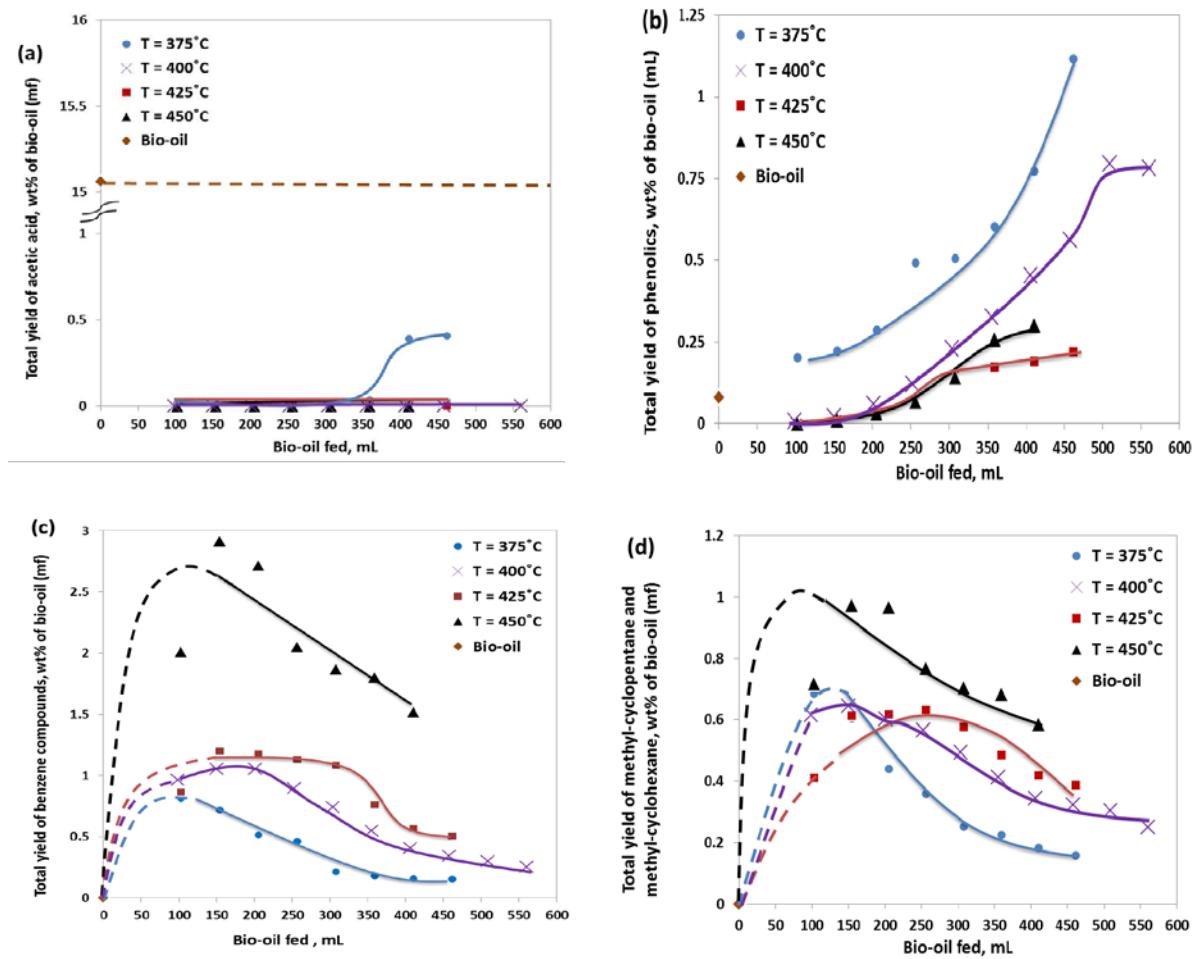


Figure 4-8. The yields of lighter species from the hydrotreatment of bio-oil as a function of the amount of bio-oil fed into the reactor and temperature. The data reported in this work for the 375°C were from the same experiment as that reported previously [7] and are used here for comparison.

Figure 4-8 shows the total yields of acetic acid, phenolics, benzene compounds and the sum of methyl-cyclopentane and methyl-cyclohexane. Their contents in the bio-oil are shown as the yields when “0 mL” of bio-oil was fed into the reactor for comparison purpose. The deoxygenation of acetic acid and phenolics is often considered to be difficult [21] and therefore the effects of temperature on their yields were studied. During the initial periods of experiments (e.g. < 250 mL bio-oil fed in), the yield of acetic acid (Figure 4-8a) was very low (< 0.1 wt%) for all temperatures. However, the acetic acid yield increased at the later periods of experiment (> 250 mL bio-oil feeding) at 375°C. This is in a good agreement with the explanation given above that the catalyst was increasingly occupied by the heavier species (and even deactivated) and then became less reactive for the destruction of acetic acid. It then

follows that even at the time when the reactor was blocked during the experiments at >400°C (sand temperature), there were still significant amounts of the active sites in the catalyst that could catalyse the destruction of acetic acid. In other words, the blockage of the reactor took place mainly in some part of the reactor and did not take place uniformly everywhere in the catalyst bed, as was confirmed by the above-mentioned visual observation of agglomerated catalyst lumps at about 10 cm into the NiMo catalyst bed.

The term “phenolics” in this work included phenol and substituted phenols, all are light species that could pass through the GC column. The observed phenolics is the net result of formation (e.g. from the breakdown of large lignin-derived molecules) and consumption (e.g. being hydrogenated to benzene compounds). Figure 4-8b shows that the yield of phenolics tended to increases for all temperatures investigated in this study, which were accompanied by the decreases in the yields of benzene compounds (Figure 4-8c). These trends are clearly due to the gradual deactivation of the NiMo catalyst, confirming that the hydrogenation of phenol structure is a slow process with the NiMo catalyst [12]. This conclusion of catalyst deactivation is further supported by the decreasing yields of methyl-cyclopentane and methyl-cyclohexane, which are the fully hydrogenated products.

4.3.3.2. The properties of hydrotreated oil

Elemental analysis. The elemental compositions of the organic products in the oil phases are shown in Table 4-1. The data clearly show that, at higher temperatures, hydrotreated oils with lower oxygen contents were produced. In the initial stages (up to 250 mL bio-oil fed into the reactor), the oxygen content varied between < 0.2 and 2.2 wt%. As the products were mainly from the lighter species, these results indicate that the HDO of light molecules was relatively easy. After the reactor was filled with heavier species in the later stages (> 250 mL bio-oil feeding), at 375°C the oxygen content increased fast and reached 8.7 wt%. On the contrary, at > 400°C, the oxygen content stayed below 2 wt%. The increases in the oxygen content could be due to catalyst deactivation and/or due to the contribution of less hydrodeoxigenated heavy molecules in the product. The increases in the oxygen content were mainly due to the corresponding deceases in the carbon content. The

data show that a higher temperature leads to deeper deoxygenation. These results are in broad agreement with the literature [10,11].

Table 4-1. The elemental composition (wt%,mf) of the organics in the oil phase as function of the bio-oil fed into the reactor and temperature. The data reported in this work for the 375°C were from the same experiment as that reported previously [7] and are used here for comparison

	Temperature	375°C	400°C	425°C	450°C
	Bio-oil fed (mL)				
51 - 103	Oxygen	2.1			
	Hydrogen	12.2			
	Carbon	84.9			
154 - 205	Oxygen	2.2	<0.2	<0.2	
	Hydrogen	11.8	11.9	11.7	
	Carbon	85.3	87.2	88.1	
303 - 359	Oxygen	3.3	<0.2	0.2	1.4
	Hydrogen	11.1	10.9	11.6	10.9
	Carbon	84.7	88.4	87.5	86.9
410 - 457	Oxygen	8.7	0.9	1.6	1.4
	Hydrogen	10.3	10.9	11.1	10.8
	Carbon	80.2	87.4	86.3	87.0

Volatility. Thermogravimetric analysis was used for quantifying the volatility and coke forming propensity of hydrotreated oil products based on their evaporation characteristics [22]. Figure 4-9 shows the yield of residue, termed as the potential coke representing the coke that could form when the hydrotreated oil is heated to 500°C, as a function of hydrotreatment temperature and time on stream (measured as the amount of bio-oil fed into the reactor). To facilitate comparison, the data are expressed on the basis of moisture-free bio-oil. Within the experimental conditions shown in the figure, the potential coke yield was all low, indicating that the majority of heavy species in the raw bio-oil that could potentially give coke upon heating was either broken down or polymerised into coke during hydrotreatment. The potential coke yield from the oil samples hydrotreated at 375°C tended to increase with time, signalling that increasingly more materials of high molecular mass had come out of the reactor with the progress of experiment.

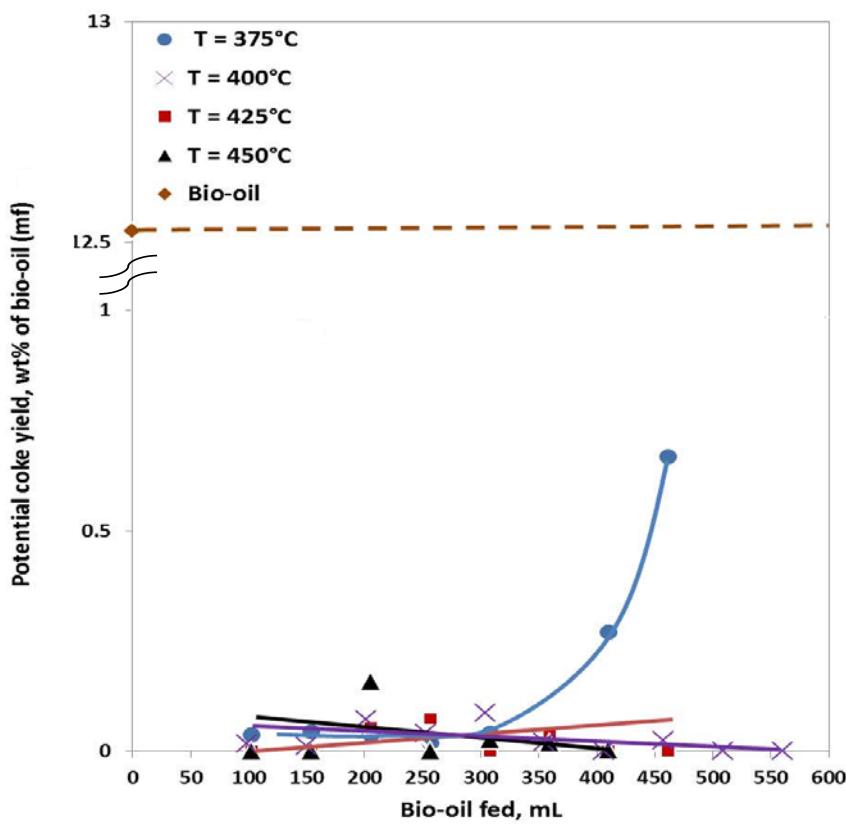


Figure 4-9. The potential coke yields of the hydrotreated bio-oils (oil phases) measured by TGA as a function of the catalyst time-on-stream (reflected by the amount of bio-oil fed into the reactor) and temperature. The data reported in this work for the 375°C were from the same experiment as that reported previously [7] and are used here for comparison.

Aromatic structures. UV-fluorescence spectroscopy was used to characterise the aromatic structural features of the hydrotreated oils in comparison with that of the raw bio-oil. Figure 4-10 shows the synchronous spectra. At the early stage of experiments (Fraction 4-1, Figure 4-10a), the aromatics in the hydrotreated oil were

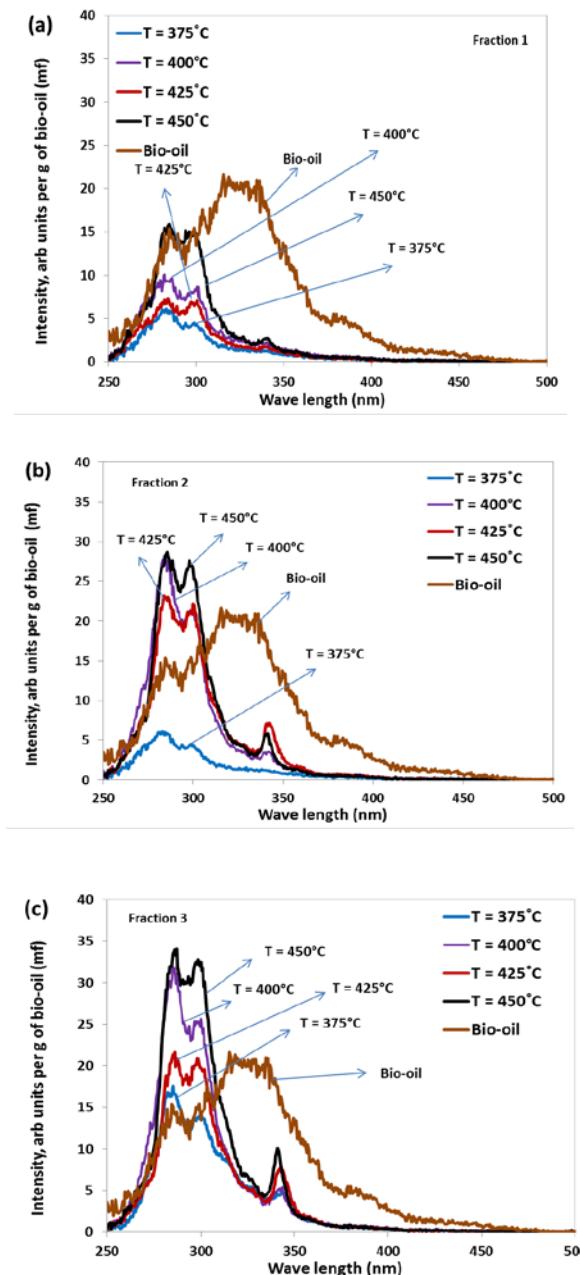


Figure 4-10. UV fluorescence synchronous spectra as a function of temperature and catalyst time-on-stream (reflected by the amount of bio-oil fed into the reactor). Note: Fraction 1: 103–205 mL bio-oil fed in, Fraction 2: 205–307 mL bio-oil fed in, Fraction 3: 359–410 mL bio-oil fed in. The data reported in this work for the 375°C were from the same experiment as that reported previously [7] and are used here for comparison.

mostly small aromatic ring systems with wavelengths < 310 nm. The large aromatic ring systems in the bio-oil had been hydrogenated, yet still retained in the reactor or

turned into coke. However, the amounts of larger aromatic ring structures (> 310 nm) started to appear with the prolonged reaction time (Fractions 2 and 3, Figures 4-10b and 4-10c). Increasing temperature appeared to have increased the formation of small and large aromatic ring systems. Obviously, the catalyst became less reactive for the hydrogenation reactions, possibly due to the occupation of the active sites by heavier species and/or due to the deactivation of the catalyst. It should be noted that the fluorescence data in Figure 4-10 are in good agreement with the GC-MS data in Figure 4-8, showing the decreased activity for hydrogenation as the experiment progressed.

4.3.4. Further insights into the mechanisms of coke formation during hydrotreatment

The raw bio-oil itself is a complicated mixture of light and heavy species ranging in size from simple molecules such as acetic acid to cellulose- and lignin-derived oligomers, representing the fragments from the partial thermal breakdown of biomass macromolecular structures during pyrolysis. It can be easily imagined that the molecules existing in the reactor at any moment would range in size from small molecules to heavy liquid and to solid coke. There is a continuous transition in dual/opposite directions along the whole spectrum of the molecular sizes. Further insights were gained into the mechanisms of coke formation during hydrotreatment by examining the heavy liquids and solid coke retained in the reactor.

The heavy residue remaining in the reactor after an experiment at 425°C (see conditions given in the caption of Figure 4-11) was washed out with tetrahydrofuran (THF). After evaporating the solvent, the remaining was a viscous and dark brown liquid.

Figure 4-11 shows the DTG curves of the raw bio-oil, the hydrotreated oil produced nearly at the end of the experiment at 425°C and the heavy residue staying inside the reactor after the experiment at the same temperature. The data indicate that mainly hydrotreated oil evaporated before 300°C in TGA (this is not necessarily the boiling point). However, a very significant portion of the hydrotreated oil only evaporated after 300°C. The data in Figure 4-11 clearly show that the heavy residue left in the reactor was even a lot heavier than the raw bio-oil, also giving a

potential coke yield of 25.7%. These data clearly provide the direct evidence that the polymerisation reactions, even if under the hydrotreatment/hydrocracking conditions, could result in the formation of very significant amounts of materials heavier (less volatile) than the raw bio-oil. These data highlight the difficulties in minimising the polymerisation reactions.

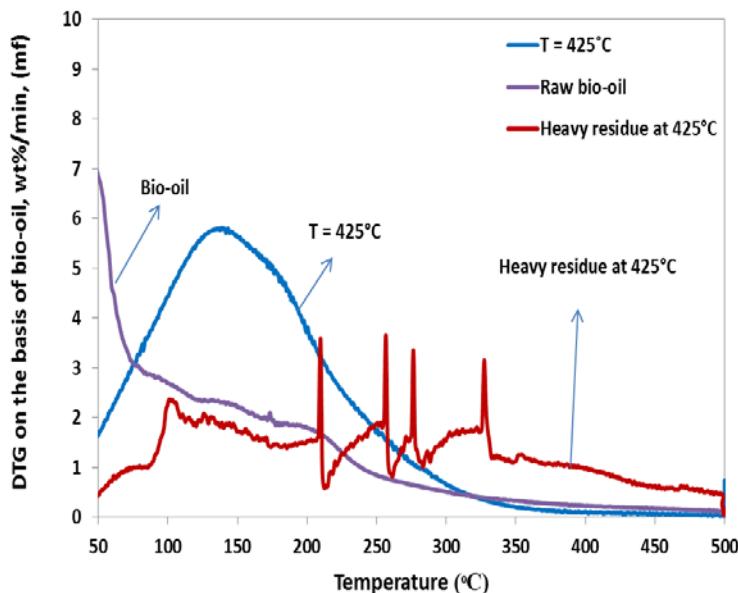


Figure 4-11. DTG curves of hydrotreated oil at 425°C after (1080–1315) mL bio-oil fed into the reactor, bio-oil and heavy residue stayed inside the reactor after the experiment. The noise in DTG curve of heavy residue is due to the shaking of the TGA cup. The data is from the experiment which had the temperature of 425°C at the end of the experiment. For that experiment LHSV changed between 1–3 and the time length of the experiment was 9 hours and 13 min. Note: All the data are expressed on wet basis.

Figure 4-12 shows the UV-fluorescence spectra of the heavy residue washed out from the reactor in comparison with those of the raw bio-oil and the hydrotreated oil collected after 1080-1315 mL of pyrolysis oil had been fed into the reactor. The heavy residue clearly shows much stronger intensity in the synchronous spectra than the raw bio-oil, implying the presence of abundant large aromatic ring structures in the residue. These data provide direct evidence for the ring condensation reaction (i.e. ring growth) to form large aromatic ring systems even under the hydrotreatment/hydrogenation conditions. The hydrotreated oil products (i.e. what

came out of the reactor) tended to have smaller rings than the residue remaining in the reactor. This type of ring growth is obviously responsible for the formation of highly aromatic coke in the reactor. Furthermore, these data suggest that at least some extent of aromatic ring growth, an essential aspect of coke formation, did not have to take place on the catalyst surface in order for coke to form. It may be imagined that at most a few sites of the polymeric macromolecules could be adsorbed on the catalyst sites. A significant portion of the macromolecule would just be “dangled” near the catalyst sites to undergo dehydrogenation and possibly cross-linking, which in turn make the molecule even more difficult to crack. The direct deposition of highly aromatic polymers may be an important route of coke formation.

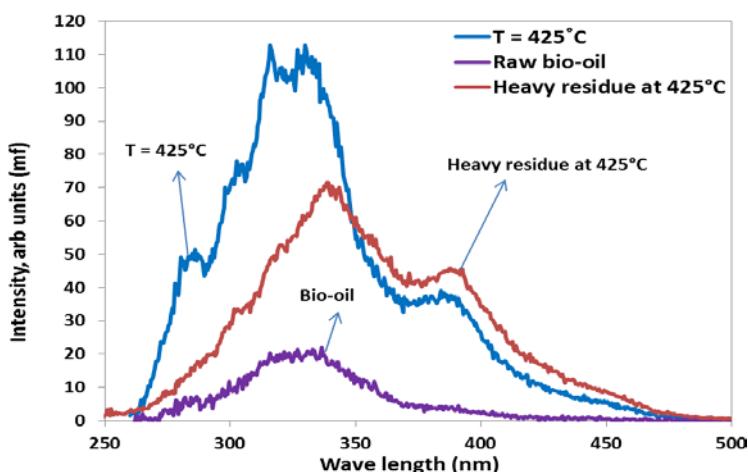


Figure 4-12. UV fluorescence synchronous spectra of the biofuel produced at 425°C after feeding of (1080–1315) mL bio-oil, bio-oil and heavy residue stayed in the reactor after the experiment. For that experiment LHSV changed between 1–3 and the time length of the experiment was 9 hours and 13 min. Note: All the data are expressed on wet basis.

As is shown in Figure 4-1, after washing the reactor with THF, the spent catalyst was taken out from the reactor and collected into 8 fractions according to their positions in the reactor with Section 1 being the one next to the Pd/C catalyst. The carbon contents of the spent catalyst from different sections of the reactor are shown in Table 4-2. The data for Section 1 may be less reliable than others due to the possible contamination by the Pd/C catalyst. For the experiment at 375°C (sand temperature), the coke in the reactor appeared to be rather uniform except from that at the beginning of the NiMo catalyst bed. With increasing temperature, the earlier

sections (in the fluid direction) showed high carbon contents than the later sections. There were a sudden/step change in carbon content between Sections 4 and 5 for 425°C and between Sections 5 and 6 for 450°C. These could well indicate the rough position where the heavy liquid has reached during the experiment. It is fair to conclude that the increasing temperature has particularly intensified the coke formation from the heavy liquid. As was discussed above, these large molecules could have had great difficulties to reach the active sites within the (micro) pores. Even if they reached and were adsorbed onto the active sites, many structural units within the big molecules were little affected by the catalyst. In the absence of abundant active hydrogen supply, they would undergo dehydrogenation and polymerisation to form coke.

Table 4-2. The carbon content (wt%) of the used catalyst from different parts of the reactor at different temperatures

Section no.	T = 375°C	T = 400°C	T = 425°C	T = 450°C
1	23	24	22	19
2	15	21	22	16
3	10	16	17	19
4	10	15	23	18
5	10	13	8	22
6	10	11	6	9
7	9	9	6	7
8	10	6	5	7

The above spent catalyst samples were also characterised with FT-Raman spectroscopy to understand their carbon skeleton structural features. Figure 4-13 shows the changes in the total Raman peak area between 800 and 1800 cm⁻¹ and the ratio of $I_{(Gr+Vl+Vr)}/I_D$. The ratio reflects the ratio of small (with < 6 fused benzene rings) to large aromatic ring systems [20]. For the experiments at 425 and 450°C, both the total peak area and the $I_{(Gr+Vl+Vr)}/I_D$ ratio showed step changes around

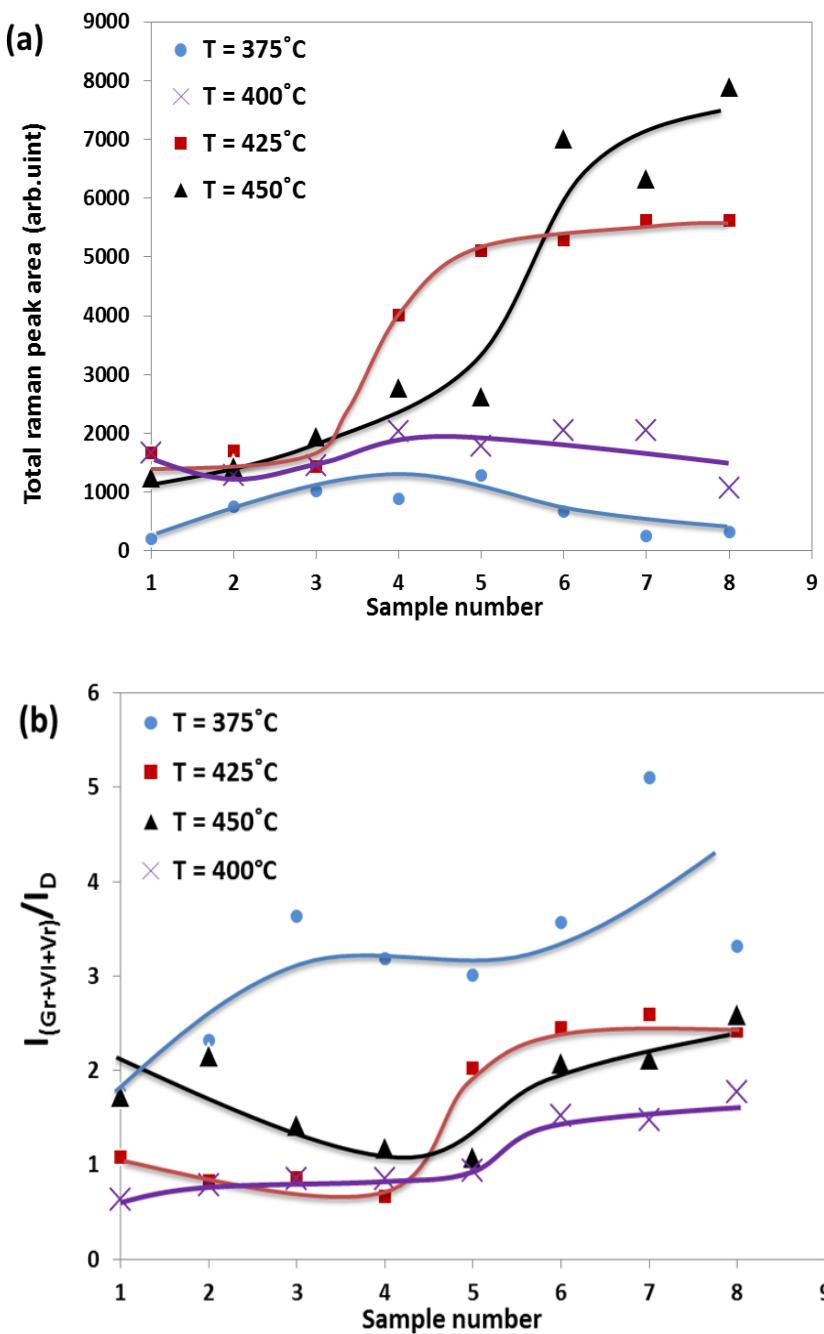


Figure 4-13. Raman spectra change for NiMo/Al₂O₃ catalyst taken out from every 2.5 cm of the length of reactor after experiment at different temperature.

Sections 4 to 6 where the carbon content also showed step changes. The 400°C samples also show some step changes but to a much less extent. These data appear to indicate that the coke formed from the heavy liquid was richer in large aromatic ring systems (lower $I_{(Gr+VI+Vr)}/I_D$ ratio) and well deoxygenated (lower Raman peak area) than the coke formed from light liquid or vapour in the downstream. At a low temperature of 375°C, the coke appeared to have quite high $I_{(Gr+VI+Vr)}/I_D$ (small to

large rings) ratios. With the catalyst still active and prolonged holding, the coke appeared to have been well de-oxygenated to give low peak area.

4.4. Conclusions

Catalytic hydrotreatment of bio-oil has been investigated in a continuous-flow packed-bed reactor system at different temperature with a constant LHSV 2 h⁻¹ at low pressure (70-80 bar). The aim was to study the effect of temperature on the behaviour bio-oil during the hydrotreatment and coke formation inside the reactor. Our results show that Pd/C catalyst in upstream of the reactor can have some effects on stabilising of bio-oil. However, in long-term operation its effect is not sufficient to prevent coke formation. Aromatic ring growth and polymerisation could take place continuously even under the overall dominating hydrotreatment/hydrocracking conditions. It was observed that quality of produced biofuels and coke formation depend on temperature and high temperature (e.g. 450°C) produces more coke inside the reactor. The heavy species remained inside the reactor at 425 and 450°C and made coke before reaching to the thermocouple. In addition, the coke from heavy liquid was very different from the coke formed from light species.

Acknowledgements

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Chapter 5

The importance of hydrogen and bio-oil inlet temperature during the hydrotreatment of bio-oil

5.1. Introduction

Biomass is an attractive option for the production of renewable liquid fuels. Pyrolysis converts biomass into bio-oil. Because of high oxygen content and high concentrations of heavy components, bio-oil needs to be upgraded. It is also very unstable and acidic [1-3]. The catalytic hydrotreatment of bio-oil under mild conditions (150-450°C and pressure > 50 bar) is one of the main routes to upgrade the bio-oil. A lot of reactions can occur during hydrotreatment, including hydrogenation, HDO, cracking and polymerisation. Coke formation and blockage of the reactor are the main challenges in the hydrotreatment of bio-oil [4,5].

Different catalysts including noble metal catalysts and cheaper catalysts such as the NiMo/Al₂O₃ catalyst have been trialed for the hydrotreatment of bio-oil. The use of noble metal catalyst (like Pd/C) is not cost effective, especially when the catalyst cannot be easily regenerated (carbon supported catalyst). The main industrial catalysts trialed in the hydrotreatment of bio-oil were the hydrodesulphurisation catalysts from petroleum refineries [4,5]. The initial tests demonstrated that the common hydrotreatment processes in the refineries with NiMo/Al₂O₃ or CoMo/Al₂O₃ were inappropriate for bio-oil as it resulted in quick severe coke formation and reactor blocking [5]. Commonly, fixed-bed reactors are used for the hydrotreatment of bio-oil [4,5]. In conventional fixed-bed reactors, temperature gradient cannot be avoided, especially at the feeding point where cold bio-oil and hydrogen are introduced to the reactor.

To overcome coke formation, a two-stage process was developed and used for the hydrotreatment of bio-oil. However, the coke formation and consequently reactor blockage was still reported [5].

Further fundamental studies are required to overcome the coke formation problem in the hydrotreatment of bio-oil. Various parameters including catalyst activity and availability of hot active hydrogen to stabilise radicals produced from the bond breakage of big molecules in bio-oil should be studied in details. Unfortunately, almost no data have been reported in literature on this matter.

It is believed that the possible reason of coke formation could be at least partly due to the slow heating up of the bio-oil where the bond breakage was not matched by the supply of insufficient active hydrogen produced from the relatively cold catalyst [6]. In other words, the bonds in bio-oil can break at a low temperature level

at which the catalyst is not sufficiently active to produce the active hydrogen required to stabilise the broken bonds (free radicals). Different types of reactions including hydrogenation, hydrocracking, HDO and recombination can take place between radicals [6]. All these reactions could occur simultaneously. The provision of active hydrogen could reduce the coke formation. One way to do this is heating up the hydrogen and injecting the hot hydrogen. Therefore, this paper is focused on the effects of the injection of hot hydrogen to the upper section of the reactor, where bio-oil is injected, on the stabilisation of the radicals and consequently the coke formation in the hydrotreatment of bio-oil.

5.2. Experimental

5.2.1. Bio-oil sample

The bio-oil used in this study was obtained from the pyrolysis of mallee wood (*Eucalyptus loxophleba*, ssp *lissophloia*) at fast heating rates in a grinding pyrolysis reactor at 450°C [7]. The bio-oil was filtered after production using 0.2 micron filter paper to remove all possible char particles. Commercial pre-sulphided NiMo/Al₂O₃ catalyst (hereafter referred as NiMo catalyst) supplied by Eurecat was used for the hydrotreatment. The catalyst was ground and sieved to obtain the particles in the size range of 600-800 microns for the hydrotreatment process. Other chemicals were purchased from Sigma Aldrich.

5.2.2. Hydrotreatment

For hydrotreating the mallee wood bio-oil, a bench scale apparatus was designed and used. More details on the system have been reported elsewhere [8]. The principles of reactor design have been explained in detail elsewhere [6]. The reactors were made from 1 inch stainless steel 316 straight tubing (0.125" wall thickness) with a length of 30 cm (as shown in Figure 5-1). During the experiment the reactor was immersed inside the hot sand and the temperature of sand was kept at 390°C. The bio-oil sample was fed into the reactor at a specified liquid hourly space velocity (on the basis of organic in the inlet bio-oil), LHSV, of 1 h⁻¹.

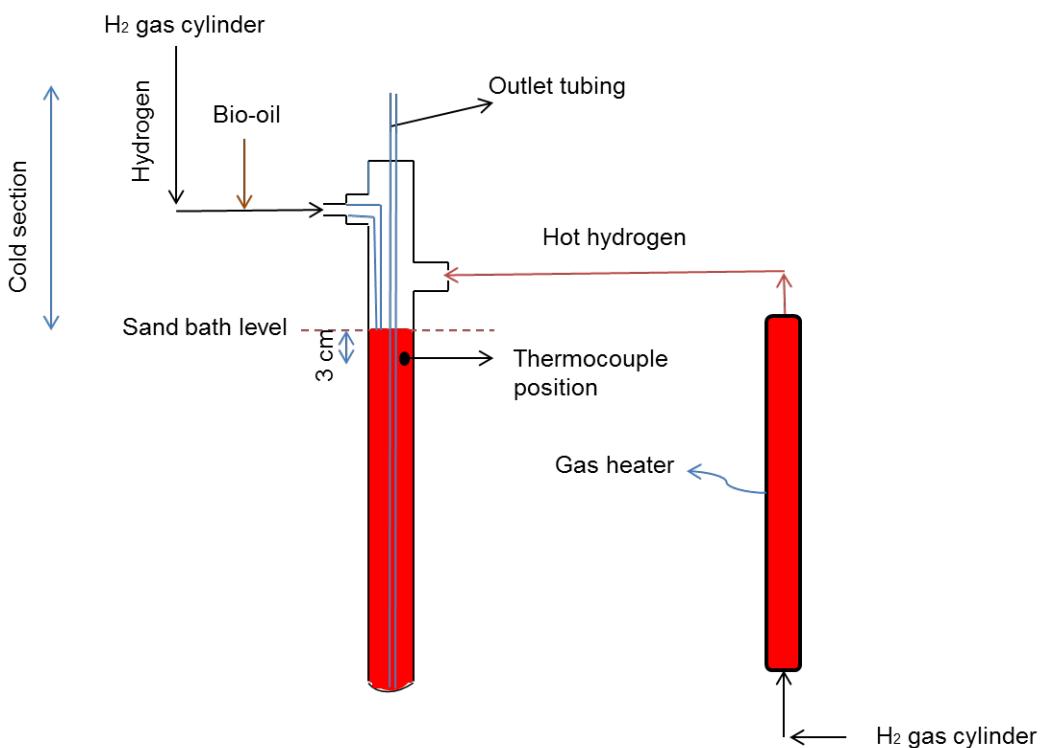


Figure 5-1. A schematic diagram showing the reactor configuration and the heating system.

A simple way to heat up the bio-oil feed rapidly was to feed the bio-oil directly into the hot catalytic bed in the reactor. The bio-oil to be hydrotreated was mixed with 2 L/min hydrogen gas before it was fed into the reactor. In other words, the liquid bio-oil was entrained with hydrogen before it was carried through a thin tube (1/8 inch) into the hot catalyst bed in the reactor (at the sand bath level – Figure 5-1). The entrainment of liquid bio-oil by the hydrogen gas ensured that the bio-oil would spend a very short period of time (around 0.6 ms) in the thin tube before it met the hot catalyst particles, during which the bio-oil would not have been heated up appreciably. The linear velocity of the bio-oil/hydrogen in the feeding line at room temperature is 8.1 m/s. This can prevent the coke formation inside the feeding tube.

To prevent coke formation, the upper section of the reactor is required to be kept hot to make the catalyst active enough to stabilise the radicals from the bond breakage of the molecules present in bio-oil. One way to keep the upper section of the reactor hot is to bring the heat from an external source. In these experiments, to keep the upper section of the reactors hot, 4 L/min hydrogen was pre-heated (to

various temperatures – see below) and fed from the top of the hot zone (Figure 5-1). The heater was made of 1 inch tubing filled with NiMo catalyst 600-800 micron particle size and immersed in a separate hot sand bath. The hydrotreated bio-oil product was mixed with hydrogen and other gases such as steam and hydrotreating gaseous products (CO, CO₂, CH₄ etc). Similarly, this product stream would exit the reactor via a thin tube (1/4 inch) positioned in the center of the reactor with an inlet at the bottom of the reactor. This minimised the time the hydrotreated bio-oil would spend at high temperature without being in contact with the catalyst. Moreover, it transferred some heat back to the upper section of the reactor from the bottom.

A number of sets of experimental conditions were tried in this study. Table 5-1 lists the key variables of each set of the reaction conditions.

The products were collected into time-resolved product fractions (samples) at an interval of 1 hour for product yield quantification and analysis. The heavy residue in the reactors was measured by weighing the reactors before and after the experiments. The weight difference was considered as the sum of formed coke and heavy residue.

Table 5-1. Key variables of the reaction conditions in the experiments

Condition Number	T _{sand bath} (°C)	LHSV (h ⁻¹)	Outlet pressure (bar)	Bio-oil and H ₂ mixture Injection point	Injection tubing size (inch)	Hot hydrogen (L/min)
1	390	1	70	Upper section of hot zone	1/8	Not used
2	390	1	70	Upper section of hot zone	1/8	2
3	390	1	70	Upper section of hot zone	1/8	2
4	390	1	70	Upper section of hot zone	1/8	2
5	390	1	70	Upper section of hot zone	1/4	2

5.2.3. Product characterisation

UV-fluorescence spectroscopy. The UV-fluorescence spectra of bio-oil and its hydrotreated products were acquired with a Perkin-Elmer LS50B spectrometer. The samples were diluted with methanol [Uvasol for spectroscopy; purity (GC): ≥ 99.9%] to 4 ppm by weight (wet basis). The synchronous fluorescence 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 [9].

GC-MS. The light components of the products and bio-oil were quantified by using an Agilent 6890/5973 GC-MS with a capillary column (HP-INNOWax) (length, 30 m; internal diameter, 0.25 mm; film thickness, 0.25 µm of crosslinked polyethylene glycol) [7,10]. The yields of formic acid, acetic acid, propionic acid, butanoic acid, pentanoic acid, hexanoic acid and heptanoic acid were calculated, added together and the total amount was considered as “acid yield”. The compounds including phenol, 2,6-xylenol, 3,4-xylenol, 4-(1-methylpropyl)phenol, 2,4,6-trimethylphenol, 2,4-xylenol and 3-methylphenol were summed as phenolics. In benzene compounds the following components were considered and summed: ethylbenzene, 1,2-dimethylbenzene, 1,4-dimethylbenzene, propylbenzene, 1-ethyl-2-toluene, 1,2,3-trimethylbenzene, (1-methylpropyl)benzene.

Thermogravimetric analysis (TGA). The samples were heated up in a thermogravimetric analyser (TGA, TA Instruments Q600) from 25 to 500°C at a heating rate of 10°C min⁻¹ in nitrogen (flow rate 50 mL min⁻¹) to determine the coke formation tendency of the bio-oil and the hydrotreated bio-oils [11-14].

5.3. Results and discussion

5.3.1. The importance of feeding hot hydrogen into the upper section of reactor

Initial trial (Condition #1) was carried out without using hot hydrogen. For this aim, an 1 inch straight tube was used as the reactor. The reactor was filled with the NiMo catalyst with 600-800 micron particle size. Bio-oil was pre-mixed with hydrogen and injected directly into the hot zone of the reactor. In this experiment, the pressure across the reactor rapidly increased from 70 to 120 bar and the experiment was stopped within 52 min (105 mL bio-oil fed into the reactor), as is shown in Figure 5-2. The visual inspection of the internal of the reactor after the experiment indicated that the coke formation in the upper section of the reactor hot zone was the main reason for the pressure increase.

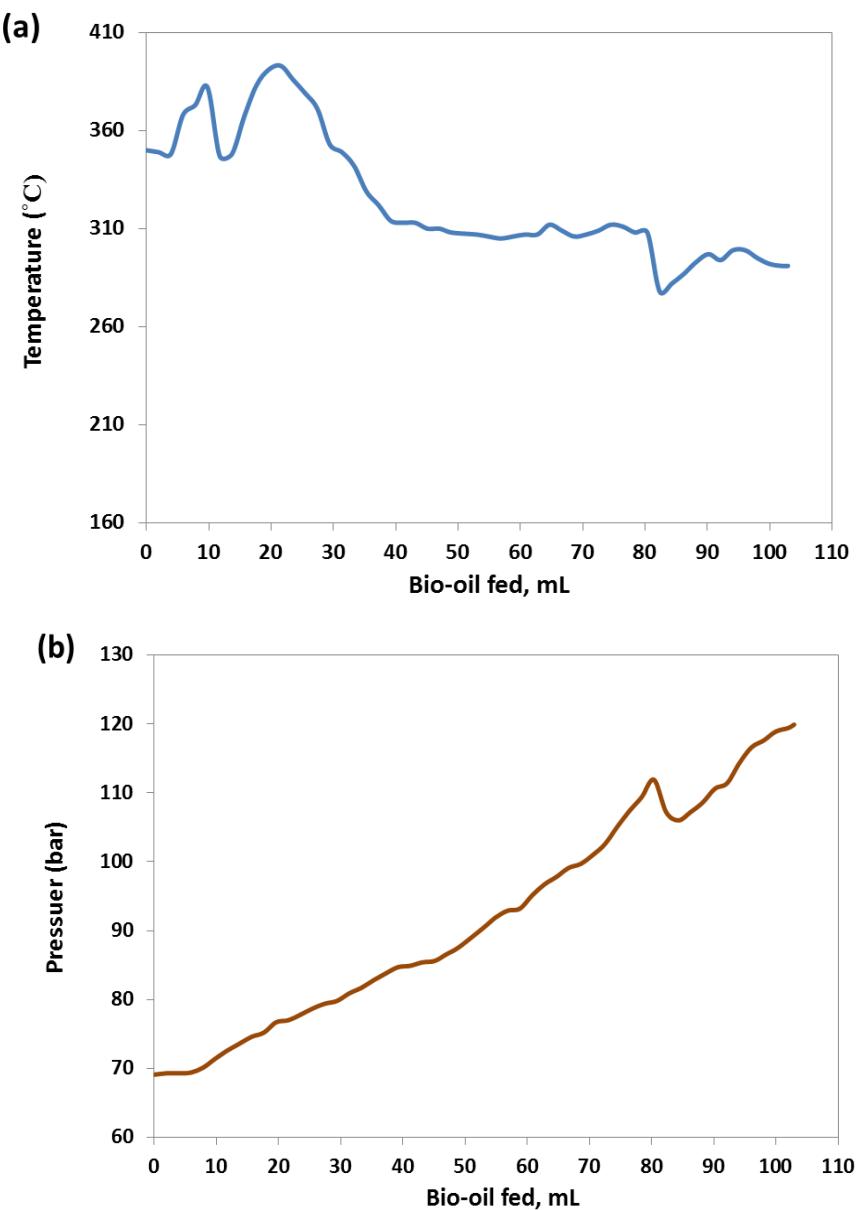


Figure 5-2. The profiles of (a) temperature at 3 cm from upper section of the hot zone and (b) pressure as a function of time under Condition #1 ($LHSV = 1 \text{ h}^{-1}$, $T_{\text{sand bath}} = 390^\circ\text{C}$ and reactor outlet pressure = 70 bar).

Other experiments with using hot hydrogen injection into the upper section of the hot zone of the reactor were carried out (Condition #2, Condition #3 and Condition #4) for comparison with the experiment without using hot hydrogen injection. Hydrogen was heated at different temperatures in the heater to have different temperatures in the upper section of the hot zone. In these experiments, the temperature at 3 cm inside the hot zone of the reactor (see Figure 5-1) was

recorded. Figure 5-3 shows the profiles of temperature and pressure at the injection point during the hydrotreatment of bio-oil.

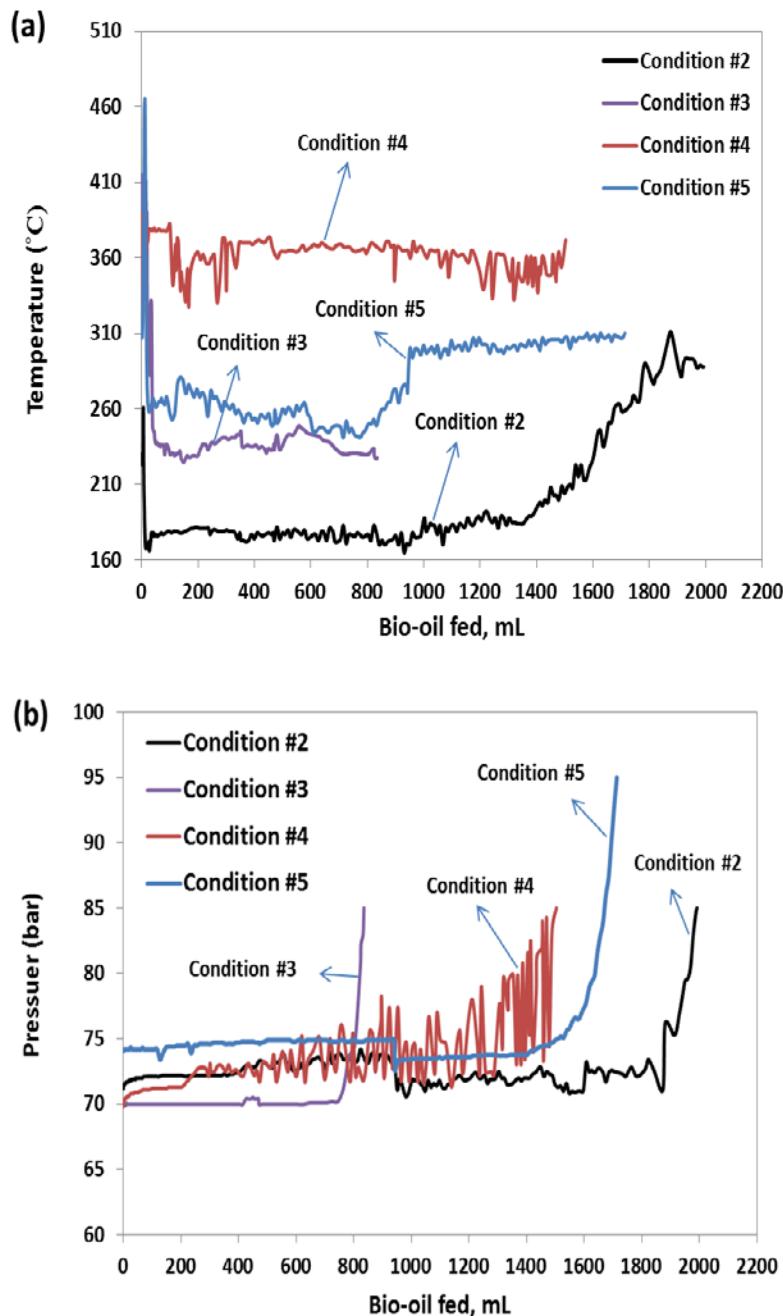


Figure 5-3. The profiles of (a) temperature at 3 cm from upper section of the hot zone and (b) pressure as a function of time.

As can be seen in Figure 5-3, the experiments could continue for longer time; 17.5 (1980 mL), 7.6 (825 mL) and 13.4 (1470 mL) hours for Condition #2, Condition

#3 and Condition #4, respectively. These experiments had to be stopped when the reactor inlet pressure increased rapidly due to coke formation. The data in Figures 5-2 and 5-3 indeed show that the presence of hot hydrogen could reduce the coke formation and extend the experiment time length. This could be due to the stabilisation of the radicals produced from the breakage of the bonds by the active hot hydrogen. Another possible reason for polymerisation in the absence of hot active hydrogen is that the large bio-oil molecules with abundant oxygen-containing functional groups could be adsorbed on the surface of catalyst and limit the generation of active hydrogen. In short, the presence of hot active hydrogen could enhance the cracking and minimise the polymerisation of bio-oil molecules. As a result, the catalyst remained active (for longer time).

An exothermic peak was observed for these experiments (Conditions #2-4) during the early stage of the experiment, which are to be in agreement with previous findings [15,16].

As can be seen in Figure 5-3a, the temperature at the injection point for Condition #2 was stable at around 185°C up to 1200 mL of bio-oil fed into the reactor before it was significantly increased to 300°C. The increase in temperature could be because of heat transfer from the bottom to the upper section of the reactor by outlet tubing when the exothermic reactions take place in the bottom of the reactor. The pressure remained relatively constant under Condition #2 before it rapidly increased when the volume of the bio-oil fed into the reactor reached 1900 mL. On the other hand, under Condition #4 where the temperature of the injection point was maintained at around 360°C, the pressure was fluctuating before it was completely blocked when the volume of bio-oil fed into the reactor reached 1400 mL. More importantly, we could only hydrotreated 800 mL of bio-oil when the temperature of the injection point was maintained at 235°C (Condition #3).

From the weight difference (before and after experiment) for each experiment, the yields of the coke and heavy residue left inside the reactor were determined. The yields were 1.9 wt% (44.2 g), 2.6 wt% (25.1 g) and 2.3 wt% (39.6 g) under Condition #2, Condition #3 and Condition #4, respectively. In order to have a better understanding of where the coke/blockage formed, the reactors were opened and inspected carefully. It was found that under Condition #2, the blockage occurred for the whole hot catalyst bed area of the reactor and the feeding line too. However,

blockages were only found in the feeding line (in the injection point) under Condition #3 and Condition #4 due to higher temperature in the injection point. It is believed that hotter hydrogen (e.g 360°C) could crack the formed coke inside the feeding line and therefore experiment could continue longer than Condition #3. Under Condition #4, mainly the residue left inside the reactor was heavy compounds, which were soluble in the acetone. In addition, the pressure fluctuation started after 300 mL bio-oil fed into the reactor under Condition #4. This could be because of sooner and more coke formation in the feeding tube under Condition #4 than Conditions #2 and 3 due to higher temperature inside the injection tubing in the absence of catalyst [17]. It is believed that the fluctuation of pressure observed under Condition #4 was due to the formation of heavy polymer (as coke precursor) in the feeding line followed by the cracking of the heavy component at high temperature. In short, the less coke formation under Condition #4 indicated that the use of hot active hydrogen in the upper section of the reactor could improve cracking of heavy species and reduce coke formation inside the reactor.

Further experiment (Condition #5) was carried out to investigate the effect of feeding tubing size on pressure fluctuation in the inlet of the reactor. Under Condition #5, the feeding line size was changed from 1/8 to 1/4 inch. The temperature of the reactor in 3 cm of hot zone from the top of reactor under Condition #5 is shown Figure 5-3a. As it can be seen from Figure 5-3b, in this experiment almost no pressure fluctuation was seen and also it could continue longer than Condition #3 and Condition #4. The reason for this was the bigger diameter of injection tubing that took longer time to block. The temperature under Condition #5 increased after feeding of 800 mL bio-oil due to the heat transfer from the bottom of the reactor to the upper section by the reactor outlet tubing. The inspection of the reactor after the experiment showed that the coke formed mainly in the upper section of the reactor. It seems that under Condition #5, the increase of feeding line diameter reduced the availability of hot active hydrogen to stabilise the radicals. This is because of the decrease of hot hydrogen speed due to the increase of feeding line diameter resulted in ineffective spray of hot active hydrogen and consequently less accessibility of active hydrogen to the catalyst. The measured residue (heavy species and coke) under Condition #5 was 2.1 wt% (40.7 g). In short, the increase of the injection tubing diameter could decrease the pressure fluctuation. However, the

reactor blockage in the upper section of the reactor and inside the feeding line happened due to insufficient presence of hot active hydrogen.

5.3.2. Product yields

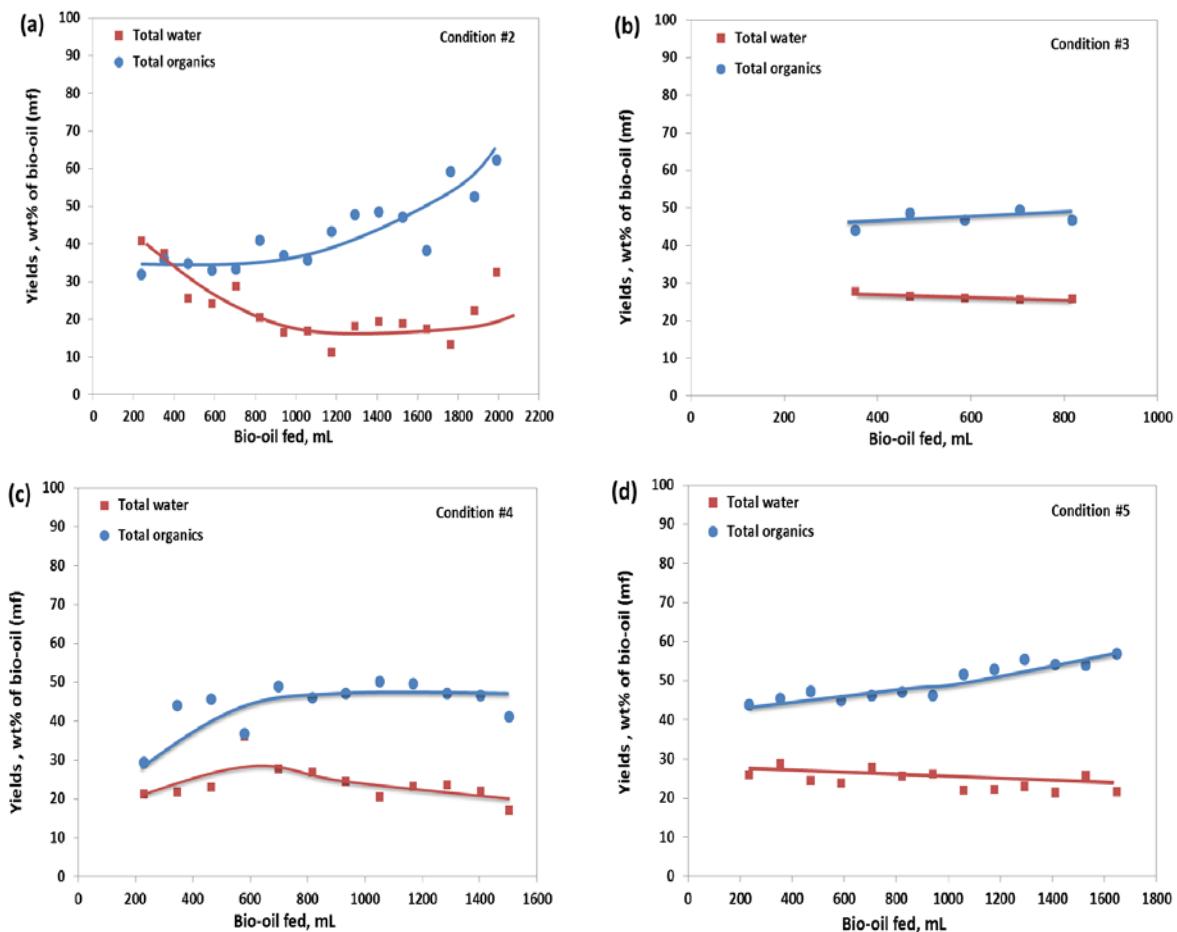


Figure 5-4. The yields of organics and total water formation as a function of bio-oil fed into the reactor under (a) Condition #2, (b) Condition #3, (c) Condition #4 and (d) Condition #5.

The total yields of organic products and water formation are shown in Figure 5-4. The first sample point is not included in the data because of possible contamination from the sample collecting system. All the conditions (# 2-5) resulted in two liquid phases; i.e. an oil phase on the top and an aqueous phase in the bottom. For calculating the yields, the oil and aqueous phases were separated by decanting. Later the water contents of phases were measured for calculating organic product yields. Difficulties in collecting the samples from the system outlet at high

pressure and accuracy in the phase separation affected to the data scatterings in the Figure 5-4. The data are expressed on moisture free basis.

Total yields of water under the Conditions #3-5, showed a slight decrease. This is because of partial catalyst deactivation and/or covering the catalyst active sites with the heavy species preventing all components inside the bio-oil to have an effective contact with the catalyst [15,16]. The total yields of water formation under Conditions #3-5 were ~23 wt% (moisture free basis) after 800 mL bio-oil fed into the reactor. On the other hand, the total yields of organic products were increasing from initial stages under Condition #2 and reached from 32 to 62 wt%. It is interesting to observe the change of water yields under Condition #2. As shown in Figure 5-4a, the total yields of organics under Condition #2 were showing opposite change trend to total water formation yields. The main reason could be the low deoxygenation amount of heavy species while the reactor is flooded with heavy species. The total yields of organics Under Conditions #3-5 showed a slight increase. The data show that total yields of organics increased and reached 48, 45 and 56 wt% under Conditions #3-5, respectively. This could be because of partially catalyst deactivation and/or flowing the heavy species out of the reactor, which were difficult to be hydrodeoxygenated [15,16]. In short, the presence of hot active hydrogen in the upper section of reactor enhanced cracking and HDO reactions and partially could prevent coke formation.

5.3.3. Product properties

Aromatic structure. The UV-fluorescence analysis results for the bio-oil and hydrotreated bio-oils are shown in Figure 5-5. The observed fluorescence intensities have been multiplied by the yields of organics in oil phase to be comparable. The bio-oil clearly shows one peak at 300-370 nm. This implies the presence of large aromatics in the bio-oil which are normally originated from lignin-derived oligomers [18]. As it can be seen from Figure 5-5a and b, in the initial samples (< 588 mL bio-oil fed into the reactor) the intensity of aromatics was low and was mainly in the range of 250-330 nm. This range indicates the presence of aromatics with less than 2 fused benzene rings. In our previous study, it was concluded that the early samples are produced from the hydrotreatment of light species in vapour phase. It

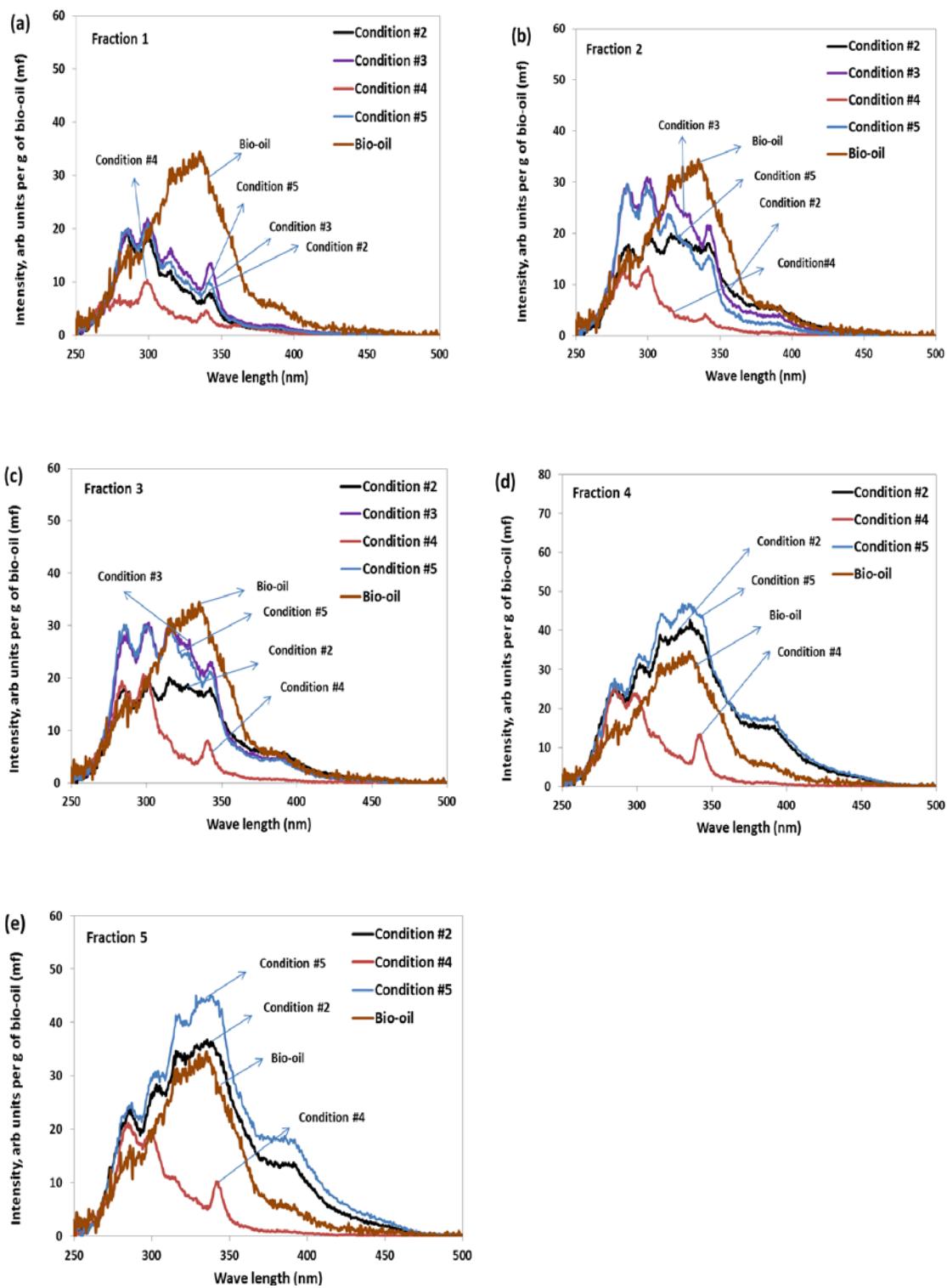


Figure 5-5. UV fluorescence synchronous spectra as a function of temperature in the upper section of reactor and catalyst time-on-stream (reflected by the amount of bio-oil fed into the reactor). Note: Fraction 1: 238–352 mL bio-oil fed, Fraction 2: 470–588 mL bio-oil fed, Fraction 3: 588–705 mL bio-oil fed, Fraction 4: 1175–1293 mL bio-oil fed, Fraction 5: 1411–1528 mL bio-oil fed.

was also shown that the light species were well hydrotreated [16]. Therefore, the large aromatic ring systems in the bio-oil were mainly hydrogenated and/or polymerised into coke and retained inside the reactor [15,16]. However, with time-on-stream the intensity of larger aromatics increased in all the conditions. This could be due to the presence of large molecules in liquid phase that were difficult to be well hydrotreated [15]. Under Conditions #3 and 4, for the whole samples, the aromatics synchronous spectra stayed mainly below 350 nm. However, in particular under Condition #2 and Condition #5, after 1175 mL bio-oil fed into the reactor, the aromatic ring size and amount increased drastically and stayed more and larger than original feed bio-oil (Figure 5-5d and e). As discussed in our previous study, the larger intensity of aromatics in the hydrotreated bio-oil than bio-oil could be because intra-molecular energy transfer resulted in large aromatic ring systems in the bio-oil not well shown [15,16]. In addition, the peaks of aromatics presented in the hydrotreated bio-oils under Condition #4 were different from the ones under conditions #2, 3 and 5. Clearly the hydrotreated bio-oils under Condition #4 showed three broad peaks centered at 270-290 nm, 290-310 nm and 340-350 nm. However, the data under Conditions #2, 3 and 5 showed five peaks centered at 270-290 nm, 290-310 nm, 310-340 nm, 340-370 nm and 370-420 nm. Clearly the wave lengths at 310-420 nm are due to the presence of aromatics with more than 2 (equivalent) fused benzene rings. These spectra indicate that with increasing temperature in the upper section of the reactor, the peaks after 340 nm significantly decreased. This confirms the better cracking of heavier species that in turn restricted the formal of aromatic rings when hotter active hydrogen (e.g. 360°C) was used to achieve the better activity of catalyst [18-21].

Results from TGA. The hydrotreated bio-oils and bio-oil (< 10 mg) were heated to 500°C at a heating rate of 10°C/min in TGA with the nitrogen gas flowing at 50 mL/min. The residue left after 500°C in the TGA pan was considered as potential coke. The results shown in Figure 5-6 are on moisture free basis. To facilitate comparision, the data have been multiplied by the yields of organics in oil phase. As expected, the hydrotreated bio-oils produced under Condition #4 had the least potential coke yield (< 0.5 wt%) because of better cracking and hydrotreatment due to the high temperature in the upper section of the reactor. Under Condition #2, the coke yields were low (< 2.0 wt%) up to 800 mL of bio-oil fed into the reactor.

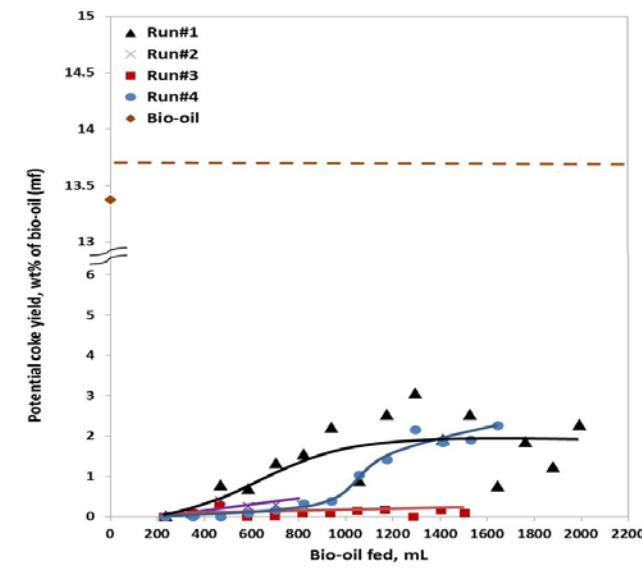
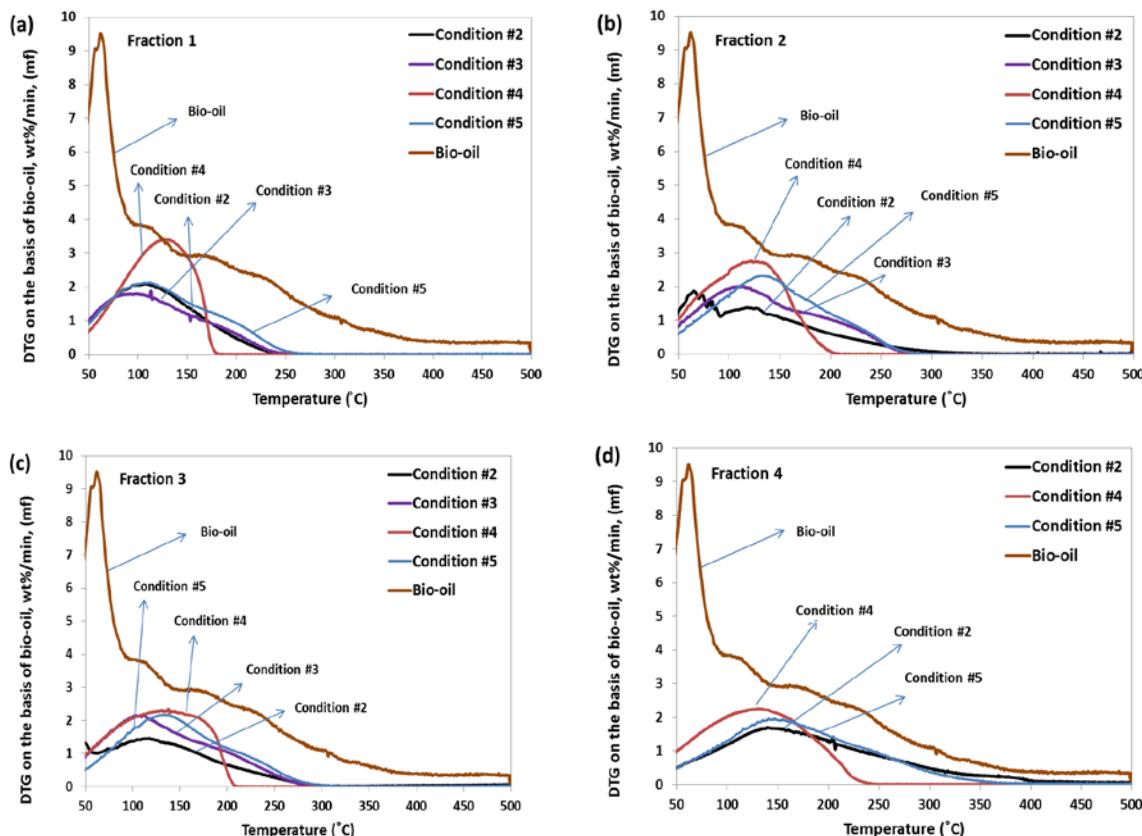


Figure 5-6. The potential coke yields of the hydrotreated bio-oils (oil phase) measured by TGA as a function of the catalyst time-on-stream (reflected by the amount of bio-oil fed into the reactor) and temperature in the upper section of reactor.



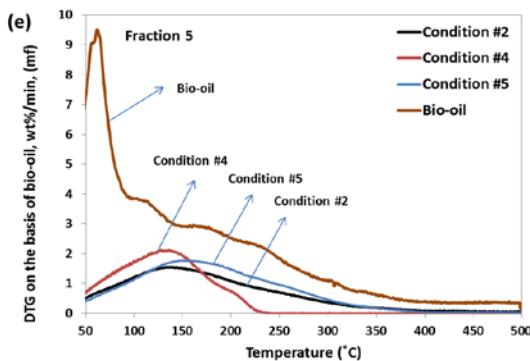


Figure 5-7. DTG curves of the hydrotreated bio-oils (oil phases) produced with having different temperatures at the upper section of reactor as a function of the catalyst time-on-stream(reflected by the amount of bio-oil fed into the reactor under Conditions #2-5. Note: Fraction 1: 238–352 mL bio-oil fed, Fraction 2: 470–588 mL bio-oil fed, Fraction 3: 588–705 mL bio-oil fed, Fraction 4: 1175–1293 mL bio-oil fed, Fraction 5: 1411–1528 mL bio-oil fed.

However, after 800 mL bio-oil fed in, it increased gradually and later by the end of experiment it stayed nearly to 2.0 wt%. Under Condition #5, the potential coke slightly increased from the beginning and reached to 2.2 wt% after 1650 mL bio-oil fed into the reactor. This indicates that more materials with high molecular mass came out of the reactor with prolonged time due to partially catalyst deactivation and/or covering of active sites of the catalyst by heavy species resulted in less hydrotreatment of them [16]. Note that the coke amount (on moisture free basis) for pyrolysis oil was 13.4 wt%.

The comparison of differential thermogravimetric (DTG) curves for the hydrotreated bio-oils produced at different volumes of bio-oil fed into the reactor is depicted in Figure 5-7. Figures 5-7a and b show that the initial samples (< 588 mL bio-oil fed into the reactor) contained mainly light volatile molecules evaporated at < 300°C with almost no residue left in TGA pan after increasing the temperature to 500°C. In this region, the hydrotreated bio-oils under Condition #4 were lighter than the samples under Conditions #2, 3 and 5. As the experiments progressed, the hydrotreated bio-oils became heavier and higher temperature was required for their evaporation. Under Condition #2 and Condition #5 the hydrotreated bio-oils evaporated at almost 400°C in TGA and heavy residue rapidly increased thereafter. However, the potential coke of bio-oil still was higher than that of the hydrotreated

bio-oils. This was because of high reactivity and instability of bio-oil, which polymerised once it was heated. Therefore, it could be concluded that even at later stages of the hydrotreatment, the catalyst still was partially active to stabilise the instable compounds in the bio-oil. The data in Figure 5-7 clearly indicate that under Condition #4, the lightest hydrotreated bio-oils were produced. The reason for this was at least due to the enhanced cracking of bio-oil fragments when hotter hydrogen (e.g. 360°C) was injected into the upper section of reactor [16]. However, under other conditions the lack of active hot hydrogen limited the hydrogenation and cracking reactions, favouring the flowing of the heavy species out of the reactor [15,16].

Light compounds detectable by GC-MS. The total yields of carboxylic acids, phenolics and benzene compounds are presented in Figure 5-8. For comparison purpose, their contents in the bio-oil are shown as the yields when “0 mL” of bio-oil was fed into the reactor. The data are calculated by the ratio of the mass flow rate of the components in the system outlet to their flow rate in the bio-oil and are presented as “yield”.

Carboxylic acids have a high content in the bio-oil. Their presence makes the bio-oil very acidic. Therefore, their destruction during the hydrotreatment process was studied here. Under Conditions #3 and 4, the yields of acids were almost zero for the whole experiments. This shows the better activities of the catalyst when hot active hydrogen was used. Under Conditions #2 and 5, initially the yields of acids were zero. However, after 900 mL bio-oil fed into the reactor, their amount increased gradually and reached 0.6 and 1.6 wt%, respectively. This means that in early stage of the experiments when the light species were the main occupants of the reactor, the acids were completely removed. However, when the active sites of the catalyst were covered by heavy species, it did not destroy the acids completely [16]. Therefore it can be concluded that the higher temperature of hydrogen in the upper section of the reactor could keep the catalyst more active and improved the acid conversion [17].

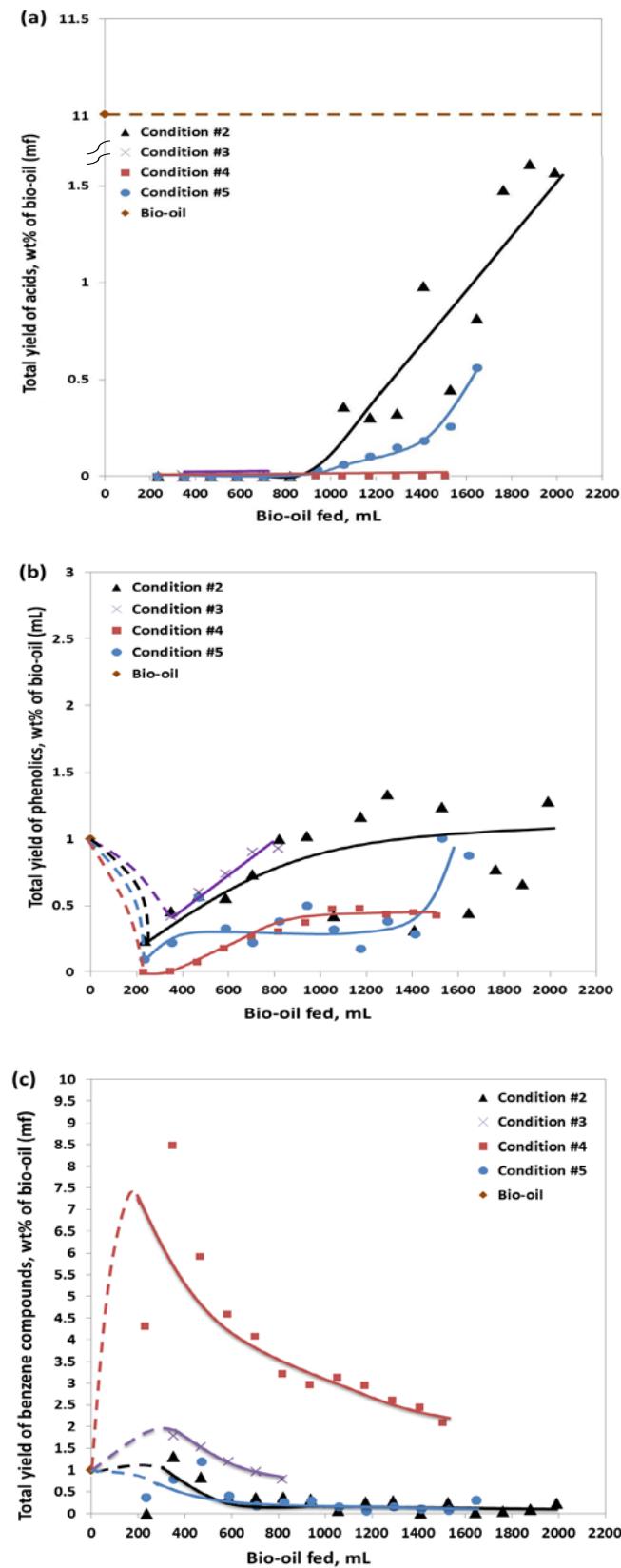


Figure 5-8. The yields of lighter species from the hydrotreatment of bio-oil as a function of the amount of bio-oil fed into the reactor and temperature in the upper section of reactor.

The yields of phenolics and benzene compounds were presented in Figure 5-8. The phenolic compounds in this work include phenol and the light phenol substituted species that could pass the GC column. Under Condition #4, their concentrations increased from zero to 0.4 wt% while Under Conditions #2, 3 and 5 they increased from < 0.5 up to < 1.5 wt%. This shows that the catalyst was active in the early stage of the experiments. However, at later periods of experiments, the conversion was less effective due to the covering of the active sites of the catalyst by heavy liquid species [15,16]. In addition, less production of phenolics under Condition #4 is because of the better conversion of phenolics with hotter active hydrogen in the upper section of the reactor. This means that using hot active hydrogen can promote catalyst activity in hydrotreatment.

On the other hand, in all experiments, the yields of benzene compounds had higher yields in the early samples whereas they decreased gradually by prolonged time. This was because of higher activity of catalyst for converting light phenols to benzene compounds in the early stage of experiment and/or high active site accessibility of the catalyst for hydrotreatment [15,16]. The highest yield of benzene compounds was observed under Condition #4 as shown in Figure 5-8c, confirming their production favoured by using hot active hydrogen.

5.4. Conclusions

This study has investigated the effects of hydrogen and bio-oil inlet temperature on coke formation in a continuous-flow packed-bed reactor system with commercial NiMo/Al₂O₃ catalyst at 390°C and pressure of 70 bar. The results showed that the presence of enough hot hydrogen in the upper section of the reactor can reduce the coke formation. The presence of hot active hydrogen in the upper section of the reactor enhanced the cracking of heavy species in the bio-oil and minimised their polymerisation. TGA, UV-fluorescence and GC-MS analyses indicated that, when the injection point of bio-oil was hotter (e.g. 360°C), the hydrotreated bio-oils contained less acids, phenolics and higher yield of benzene compounds. In short, the analysis of the products was showing better activity of catalyst for the hydrotreatment when hot (e.g. 360°C) hydrogen was fed into the upper section of the

reactor. More importantly, it was found that the slow heating up of the bio-oil is partially the reason for coke formation and the bond breakage should matched by the supply of active hydrogen from the catalyst to prevent coke formation.

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Chapter 6

**A new hydrotreatment reactor configuration for
reduced coke formation and improved energy
efficiency during bio-oil hydrotreatment**

6.1. Introduction

Bio-oil is a crude liquid from the pyrolysis of biomass. However, the high oxygen content and the high proportion of heavy components in bio-oil lower the heating value of bio-oil and create many undesirable properties [1]. The catalytic hydrotreatment of bio-oil at high hydrogen pressure (> 50 bar) is a promising route for upgrading bio-oil to reduce its oxygen content and break down its heavy components [2].

A class of promising catalysts for the hydrotreatment of bio-oil were sulphided catalysts ($\text{NiMo}/\text{Al}_2\text{O}_3$ or $\text{CoMo}/\text{Al}_2\text{O}_3$) [2,3]. However, serious coke formation during the hydrotreatment of bio-oil always leads to the rapid deactivation of catalysts [2].

To address the coking issue, Baker and Elliot reported that the reactor inlet temperature must be kept below 280°C to avoid coke formation [3]. For this aim, two or more stages in series were proposed. In the first stage, the temperature was kept from 250 to 280°C while in the second stage the temperature from 370 to 400°C was chosen.

A two-stage set-up with noble metal catalyst (Pd/C) in the first stage for low temperature hydrotreatment followed by the second stage with sulphided conventional catalysts was used [4]. In this experiment, 98 to 99 wt% of removal of oxygen with the stream-on-time of 102 hours were achieved at low LHSV in the range of $0.15\text{--}0.25 \text{ h}^{-1}$. However, coke formation was still found to be the major issue [4].

Venderbosch used the two-stage hydrotreatment process as well using Ru/C as a catalyst. The temperature ranges from 175 to 225°C for the first stage and from 350 to 400°C for the second stage were chosen. They could achieve the oxygen contents down to 14 wt% in the product. However, their experiments had the problem of the considerable coke formation in the first stage [5].

French et al. investigated the hydrotreatment of bio-oil using a semi-batch reactor. They proposed both one-stage and two-stage systems using the $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst. In the first stage the temperature was 150°C while in the second stage the temperature was kept between 340 and 400°C . The authors reported some issues including unsteady operation and long-time heating-up of the reactor. Furthermore, substantial coke formation and catalyst deactivation were the major issues [6].

The above trials clearly identify the challenge of serious coke formation in the bio-oil hydrotreatment using one- or multiple-stage processes. Coke formation

deactivates the hydrotreating catalyst and leads to the blockage of reactor, making hydrotreatment of bio-oil difficult.

In addition to the coke formation, the significant amount of water in bio-oil (20-40 wt%) imposes another challenge as a large amount of energy needs to be consumed to evaporate the water when bio-oil is heated up. This is not energy efficient and this issue has to be addressed.

In this study, we tried to address the above challenges by developing a new configuration of reactor for bio-oil hydrotreatment. The coke formation during the heating up of bio-oil in the initial stage can be significantly reduced and the energy efficiency is remarkably improved.

6.2. Experimental

6.2.1. Bio-oil sample

The bio-oil used in this study was obtained from the pyrolysis of mallee tree (whole tree or only wood) (*Eucalyptus loxophleba, ssplissophloia*) at fast heating rates in the grinding pyrolysis reactor at 450-465°C [7]. The bio-oil from the pyrolysis of only wood was made of one phase while the bio-oil from the pyrolysis of the whole (mixed) mallee biomass settled into two phases: a lighter phase and a heavier phase. Filter paper (0.2 micron) was used to remove char particles. A commercial pre-sulphided NiMo/Al₂O₃ catalyst (hereafter referred as NiMo catalyst) supplied by Eurecat was used for hydrotreatment. The catalyst was ground and the particle size ranges of 250-600 or 600-800 microns were used. 5 % palladium supported on activated carbon (Pd/C, Bioscientific) with a particle size range of 25-125 microns was also used as the catalyst in the cold zone of the reactor in some runs for comparison. Other chemicals were also obtained commercially.

6.2.2. Hydrotreatment

A bench scale apparatus was designed and used for the hydrotreatment. The details of the system can be found elsewhere [8]. The reactors were made of stainless steel 316 straight tubing. Further details will be given below.

6.2.3. Product characterisation

UV-fluorescence spectroscopy. A Perkin-Elmer LS50B spectrometer was used to acquire the UV-fluorescence spectra of the bio-oil and the hydrotreated bio-oils. Methanol [Uvasol for spectroscopy; purity (GC): $\geq 99.9\%$] was used to dilute the samples to 4 ppm (wet basis). At a constant energy difference of -2800 cm^{-1} , the synchronous fluorescence spectra were recorded. The slit widths of 2.5 nm and the scan speed of 200 nm/min were used [9]. The data were multiplied to the yields of organics in oil phases to be comparable.

GC-MS. An Agilent 6890/5973 GC-MS with a capillary column (HP-INNOWax) (length, 30 m; internal diameter, 0.25 mm; film thickness, 0.25 μm) was used for analysing the light components of the bio-oil and hydrotreated bio-oils [10,11]. For being able to compare the data, they were multiplied to the yields of organics in oil phase.

Thermogravimetric analysis (TGA). The samples were analysed in a thermogravimetric analyser (TGA, TA Instruments Q600 or Q5000) from 25 to 500°C at a heating rate of $10^\circ\text{C min}^{-1}$ in nitrogen (flow rate 50 mL min^{-1}) to determine the potential coke formation in the bio-oil and hydrotreated bio-oils [12,13].

6.3. Results and discussion

6.3.1. Coke formation and reactor fouling with a conventional fixed-bed reactor

An experiment (Condition #1) was performed to explore the possibility to eliminate the need for the expensive noble metal Pd/C catalyst and the use of the NiMo catalyst alone to carry out the hydrotreatment of bio-oil. For this aim, initially a two-stage process was carried out. The reactors were made of 40 cm U-shape tubing filled with the NiMo catalyst with a 250-600 micron particle size range. Initially, 18 cm of the each reactor was immersed in the hot sand bath with the remaining length outside the sand bath and considered as the cold zone of the reactors.

As expected, the hydrotreated products were separated into two phases with an oil phase floating on top of an aqueous phase. Figure 6-1 show the hydrotreated bio-oil samples produced together with the key reaction conditions.

Samples	1	2	3	4	5	6	7
Reaction time (min)	60	180	300	360	430	470	493
First stage sand bath temperature (°C)	400	375-400	400	400	400	415	425
Second stage sand bath temperature (°C)	400	400	400	400	400	415	425
LHSV (h⁻¹)	1-2	1.1-2	1.1-1.5	2	0.5-3	3	3

Figure 6-1. Hydrotreated bio-oil samples produced from the two-stage hydrotreatment (Condition #1) using the NiMo/Al₂O₃ catalyst of a bio-oil sample produced from the grinding pyrolysis of mallee wood at around 455°C.

The GC-MS analysis showed the hydrotreated bio-oils produced at low LHSVs containing negligible amounts of water while the corresponding aqueous phases containing negligible amounts of organics. Little phenolic compounds were found in the oil phase. However, at later stages with higher LHSVs, the amounts of phenolic compounds together with water started to increase. Similarly, the organics in the aqueous phases started to increase as well.

Under Condition #1, significant increases in the inlet pressure of the first-stage reactor were experienced, as is shown in Figure 6-2. However, when the cold section of the reactor outside the sand bath was immersed into the sand bath, the pressure decreased. It was suspected that the pressure increase was mainly due to the formation of coke, or the accumulation of the heavy components which could be the precursors for coke, on surface of the catalyst or in between the void of the catalyst particles. The heavy components (coke) on the relatively cold catalyst must

have been removed via hydrogenation or cracking as the cold catalysts previous outside the hot sand bath was heated up by immersing them into the hot sand bath.

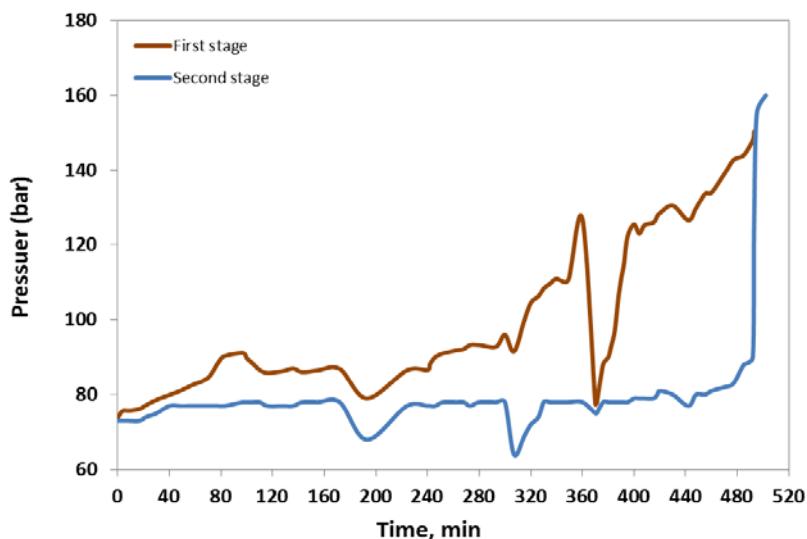


Figure 6-2. The reactor inlet pressure profiles in the first and second stages as a function of time under Condition #1. Note: the pressure drop at 370 min is because of reducing LHSV to 0.3 h^{-1} to prevent coke formation.

At lower LHSVs, the pressure in the inlet of the second reactor remained constant. At a higher LHSV of 3.0 h^{-1} , the heavy components or reactive components that might not have been well hydrotreated in the first reactor flew into the second reactor. Similarly, these heavy/reactive components started to accumulate at the cold inlet/initial section of the second reactor. At the later stage, the coke formation results in the complete blockage of the reactor: A sudden increase of pressure at ca. 500 min of time-on-stream (Figure 6-2).

Figure 6-3 shows the yields of organic products at different LHSV. The time between the first and the second sample appears to be the time for the bio-oil feedstock to “wet” the catalyst bed (to “fill” the pores and voids in the catalyst bed). The high yields of organics in the second and third samples must have contributions from the organics held in the catalyst bed previously. It is also possible that some residual exist in the sampling system, causing some hydrotreated bio-oil samples not to be completely recovered.

The above-mentioned trials clearly indicate that the NiMo catalyst can catalyse the hydrotreatment of bio-oil to produce hydrotreated bio-oils. LHSV values up to 3.0 h^{-1} can be used while still maintain reasonable hydrotreated bio-oil quality. The

hydrotreating conditions (around 375 to 425°C and well below 100 bars) are no severer than those used in the exiting petroleum refinery. Therefore, the NiMo catalyst, which could be more than one magnitude cheaper than the noble metal catalysts, has great potential to replace the noble metal catalysts in hydrotreatment of bio-oil, especially for commercial applications. The above results also gave us the clues to the design of a new configuration of the hydrotreating reactor to overcome the coke formation problem, which will be discussed below. The work to be reported below was focused on the development of new reactor configurations with the aim to minimise the coke formation during the hydrotreating of bio-oil.

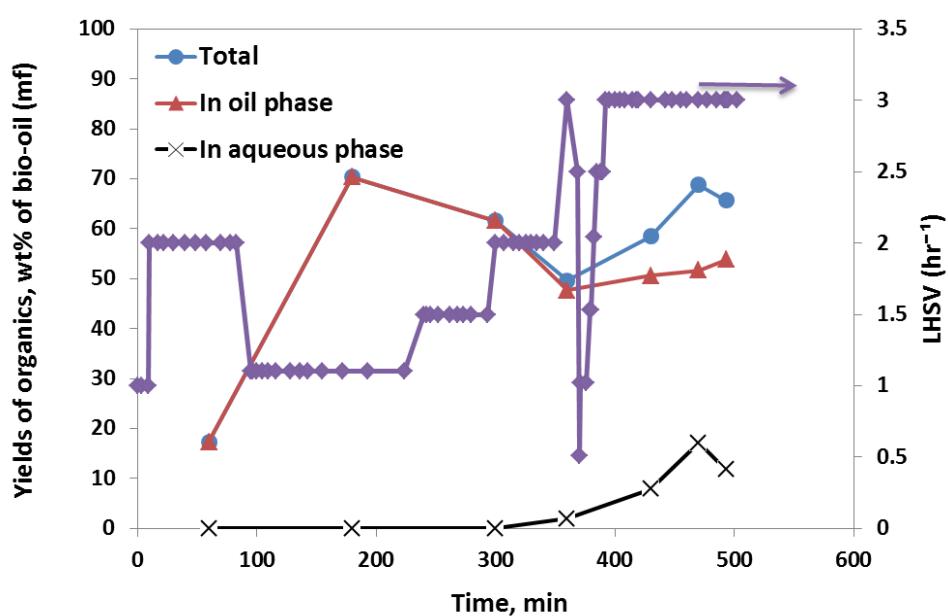


Figure 6-3. The yields of organics from the hydrotreatment of bio-oil using a conventional fixed-bed configuration (Condition #1).

6.3.2. Hydrotreatment of bio-oil in a reactor with new configuration

The data in Figure 6-2 indicate that the possible reason of coke formation was at least partly due to the slow heating up of the bio-oil. There is not enough activated hydrogen formed over the cold catalyst to effectively hydrogenate the bio-oil. The radicals formed from the breakage of weaker bonds in the bio-oil were required to be stabilised by hot active hydrogen. However, the lack of active hydrogen resulted in the re-combination of the radicals and polymerisation of them to bigger compounds

and finally coke [14-17]. To minimise the coke formation and to activate hydrogen, the rapid heating up of bio-oil and the temperature which is enough to activate the catalyst are the prerequisite [17].

The most straightforward way to achieve a high heating rate of bio-oil is to feed it directly into the hot zone of the catalytic reactor, as is schematically shown in Figure 6-4. The bio-oil to be hydrotreated was mixed with hydrogen gas before it was fed into the reactor. In other words, the liquid bio-oil was entrained with hydrogen before it was carried through a thin tube (e.g. a $\frac{1}{4}$ inch tubing in the experiments to be reported below) into the hot zone of the reactor. The entrainment of liquid bio-oil by the hydrogen gas ensured that the bio-oil would spend a very short period of time (around 0.4 ms) in the feeding tube before it encounters the catalyst particles in the high-temperature zone during which the bio-oil would not be heated up remarkably.

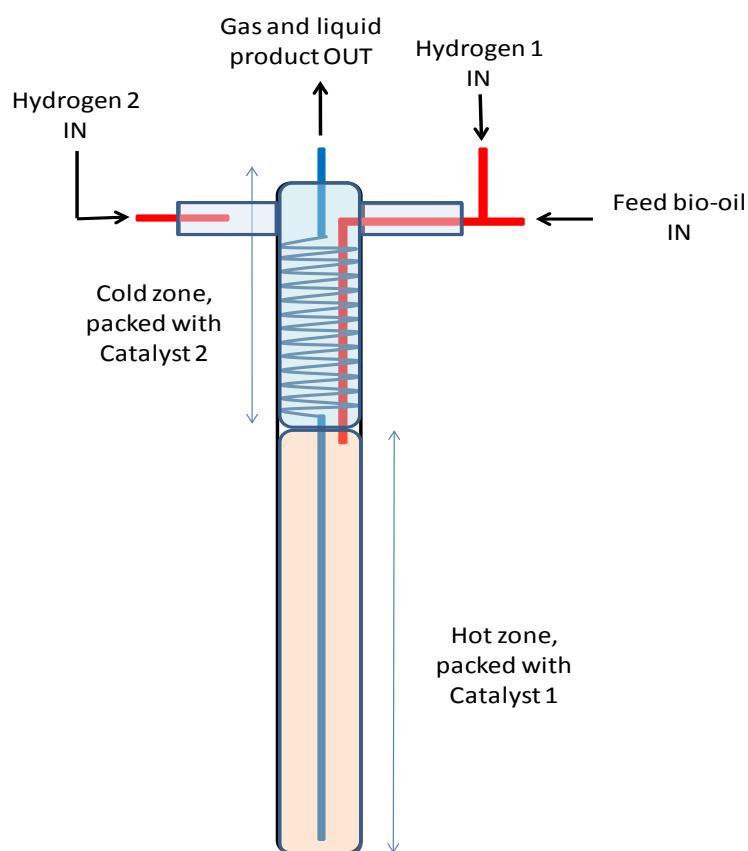


Figure 6-4. Configuration of the novel reactor design for the hydrotreatment of bio-oil [14].

The (partially) hydrotreated bio-oil product in the new reactor would exit mostly as vapour and liquid together with hydrogen and other gases such as steam and hydrotreating gaseous products (like CO, CO₂, CH₄) via a thin tube (e.g. a ¼ inch OD in the experiments to be reported below) positioned in the centre of the reactor. This minimised the contact time of the (partially) hydrotreated bio-oil with the catalyst, which minimised the potential thermal cracking of the (partially) hydrotreated bio-oil product. The product would either be rapidly fed into the hot zone of another reactor or be quenched. Another benefit is the heat which the products carry can be transferred/recovered in the cold zone of the catalyst bed to the reactants (bio-oil and hydrogen), which improves the energy efficiency.

The ability to minimise coke formation by increasing the bio-oil heating rate on entering the reactor and increasing the hydrotreated bio-oil quenching rate on exiting the reactor was proved by using the reactor design shown in Figure 6-4 in two steps, as will be detailed below.

6.3.2.1. Minimising the coke formation in the reactor

The first step is to prove the design in minimising the coke formation due to the polymerisation of radicals in the absence of hot active hydrogen. A 1-inch OD reactor using the design shown in Figure 6-4 was used in this trial (Condition #2). Catalyst 1 was the NiMo catalyst with 600–800 micron particle size range packed in the main body of the reactor (that was immersed in the sand bath). Catalyst 2 was the Pd/C catalyst with 25–125 micron particle size range packed in the initial section of the reactor. The bio-oil and hydrogen, after being mixed at the entrance of the reactor, would flow downwards from the cold zone (initial section) of the reactor along the reactor length for the bio-oil to be hydrotreated (direct injection to hot zone of the reactor was not used yet and bio-oil was fed into the reactor from the upper section of Pd/C catalyst bed). The hydrotreated product stream would change flow direction at the bottom of the reactor and be taken out via a thin tube before it is quenched. Only one stream of hydrogen was used and the heat exchange coil was not yet installed in this trial.

In this experiment, the bio-oil from mixed biomass was used. Two different fractions of bio-oil, “light” and “heavy”, were used in this trial to test if the hydrotreating properties of the lighter and heavier fractions would differ greatly.

Figure 6-5 shows the changes in the inlet pressure of the reactor with prolonged time. For the light fraction, the inlet pressure increased with increasing flow rates of bio-oil, as was expected. The sudden pressure drops at the reactor outlet was due to the partial depressurisation of the system when the product stream was switched from one product trap to another. It was surprising that the reactor was not blocked until reaching a LHSV of 9.0 h^{-1} , indicating insignificant coke formation.

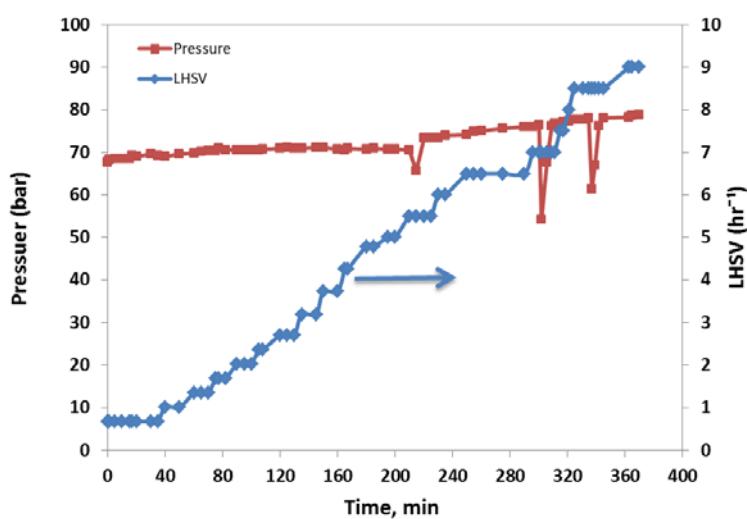


Figure 6-5. The reactor inlet pressure and LHSV profiles as a function of time under Condition #2 (a 1-inch straight reactor with Pd/C catalyst in the cold zone and NiMo catalyst in the hot zone was used. The injection point is located in the upper section of cold zone and coil was not used). The hydrotreatment reactor was immersed in a fluidised sand bath set at 385°C . Light fraction of bio-oil was fed into the reactor.

At LHSV of 9 h^{-1} , the liquid products settled into two phases with a clear organic phase floating on top of an emulsified aqueous phase containing some organics (oil). Figure 6-6 shows the yields of organic products. The hydrotreated bio-oils (oil phase) contained < 5 wt% of water with the water content increasing with increasing LHSV value.

Following the hydrotreatment of the light fraction, the heavy fraction was fed into the same reactor. Figure 6-7 shows the changes in the inlet pressure as a function of time and LHSV. No clear sign of reactor blockage due to coke formation

was observed until a LHSV of 6.5 h^{-1} . In fact, the same reactor was cooled down and reheated for the hydrotreatment of heavy fraction of bio-oil as mentioned above, clearly indicating the absence of any significant formation of coke even when the

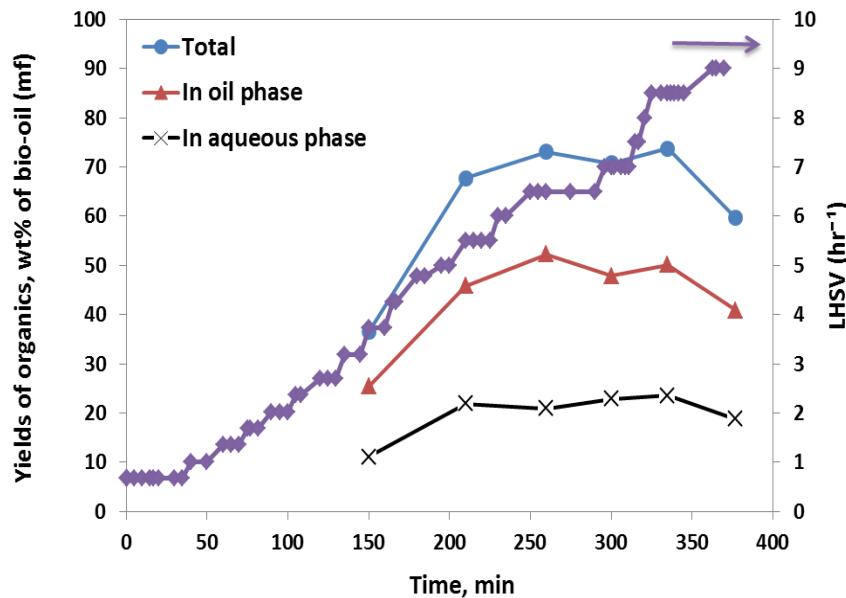


Figure 6-6. The yields of organics from the hydrotreatment of bio-oil at different LHSV under Condition #2 (a 1-inch straight reactor with Pd/C catalyst in the cold zone and NiMo catalyst in the hot zone was used. The injection point is located in the upper section of cold zone and coil was not used). Light fraction of bio-oil was fed into the reactor.

heavy fraction was hydrotreated under the experiment conditions with the time frame. The slight pressure increase (see Figure 6-7) was due to the effect of increasing bio-oil flow rate.

The hydrotreated bio-oils produced from the hydrotreatment of the heavy fraction contained around 2-3 wt% of water. It is also noted that the heavy fraction can produce a lot higher yields of hydrotreated bio-oils than the light fraction.

In a subsequent experiment (Condition #3), the Pd/C catalyst was omitted and the whole reactor was filled with the NiMo catalyst. The pressure increased continuously. The examination of the reactor after experiment revealed that the substantial coke had formed at the reactor entrance where bio-oil was being heated

up. This problem was overcome by heating up the bio-oil feed rapidly as will be detailed in below.

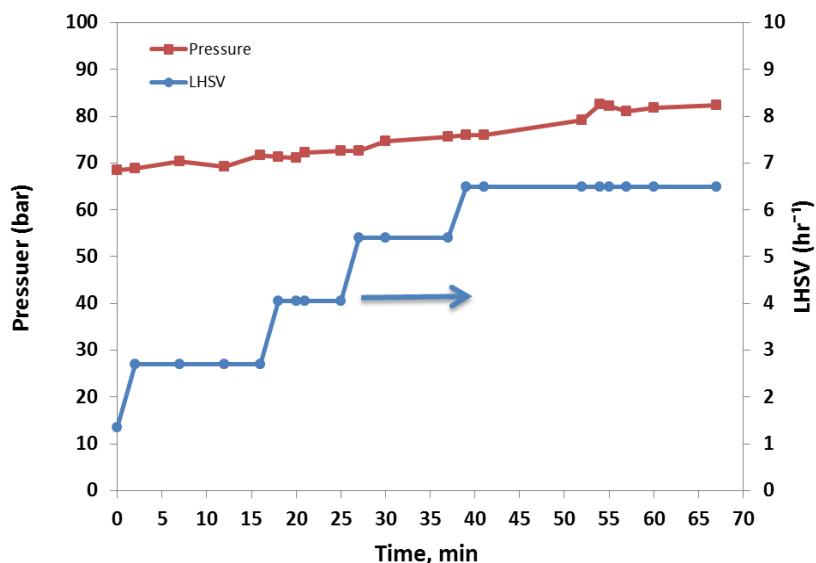


Figure 6-7. The reactor inlet pressure and LHSV profiles as a function of time under Condition #2 (a 1-inch straight reactor with Pd/C catalyst in the cold zone and NiMo catalyst in the hot zone was used. The injection point is located in the upper section of cold zone and coil was not used). Heavy fraction of bio-oil was fed into the reactor.

To minimise the coke formation when bio-oil was heated up, subsequent trials used an inlet tube (Figure 6-4) that transfer the bio-oil and hydrogen mixture directly into the hot zone of the catalyst bed. This minimised the heat up of bio-oil before it was in contact with the catalyst and ensured that the heat up and breakdown of bio-oil would only take place in the presence of activated hydrogen provided by the catalyst at sufficiently high temperatures. The particle size range of the NiMo catalyst in this trial (Condition #4) was 600–800 microns.

Figure 6-8 shows the inlet pressure profile of the reactor as a function of reaction time during the run (Condition #4). The heat exchange coil (Figure 6-4) was still not yet installed and only one stream of hydrogen was used. Even at the highest LHSV of 12.0 h^{-1} , no significant increases in the pressure drop were observed when the mixture of light and heavy fractions was fed into the reactor together.

To gain more understanding of the importance of the bond breakage in the presence of active catalyst, another experiment was carried out (Condition #5). In Condition #5, 4 L/min of H_2 was pre-mixed with bio-oil and directly fed on the upper

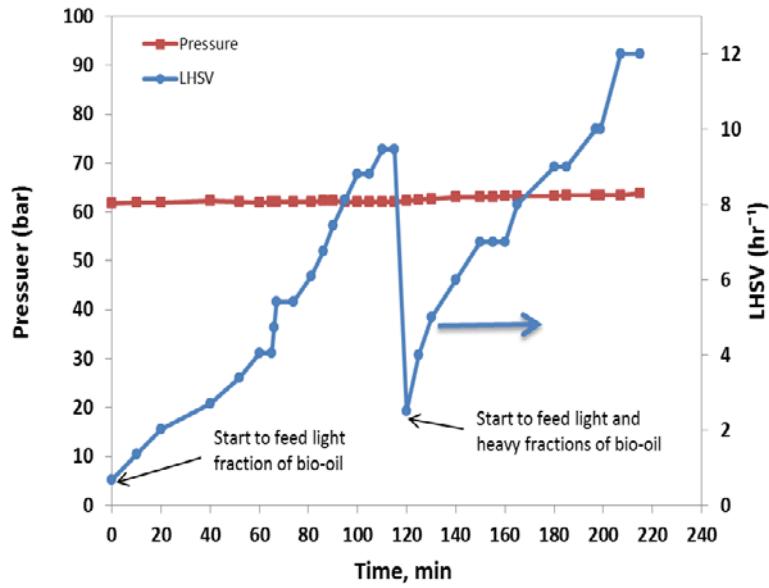


Figure 6-8. The reactor inlet pressure and LHSV profiles as a function of time under Condition #4 (a 1-inch straight reactor with NiMo catalyst in the hot zone was used. Direct injection of mixture of bio-oil and hydrogen into the upper section of the hot zone was used. Coil was not installed yet).

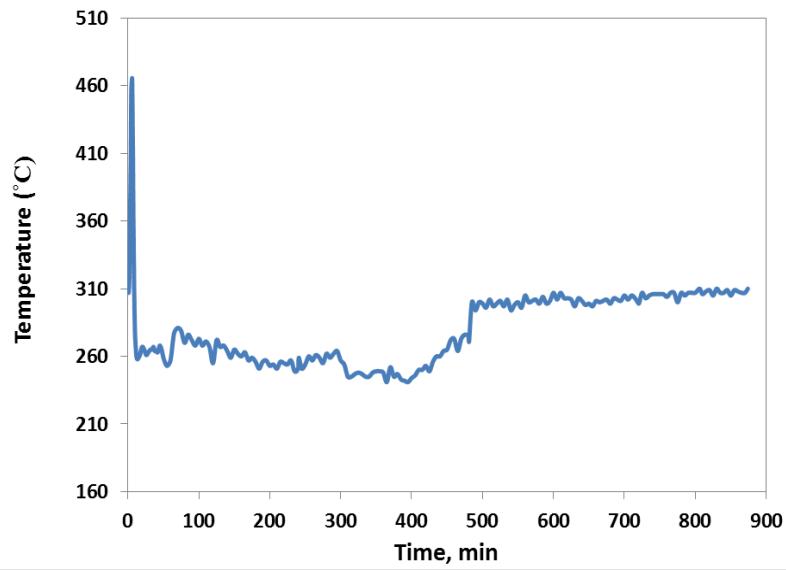


Figure 6-9. The temperature profile measured at the location 3 cm into the hot zone of reactor as function of the volume of bio-oil fed into the reactor under Condition #5. The data reported under Condition #5 are the same as that reported previously [17] and used here for comparison.

section of the hot zone of the reactor through 1/4 inch feeding line. The length of 30 cm for reactor, LHSV of 1 h^{-1} (on organic base) and 390°C for sand bath were chosen in this experiment. More details under Condition #5 are reported elsewhere [17]. The data reported under Condition #5 are the same as that reported previously [17] and used here for comparison. The temperature of the reactor in 3 cm of hot zone from the top of reactor is shown Figure 6-9.

Condition #5 could continue for 14.5 hours and after that pressure increase due to coke formation resulted in the termination of the experiment. The residue amount remaining in the reactor was measured 40.68 g. The reactor after the experiment was opened to study the coke formation area. Mainly upper section of the reactor under Condition #5 including feeding line was blocked due to coke formation. The yields of organic products are shown in Figure 6-10.

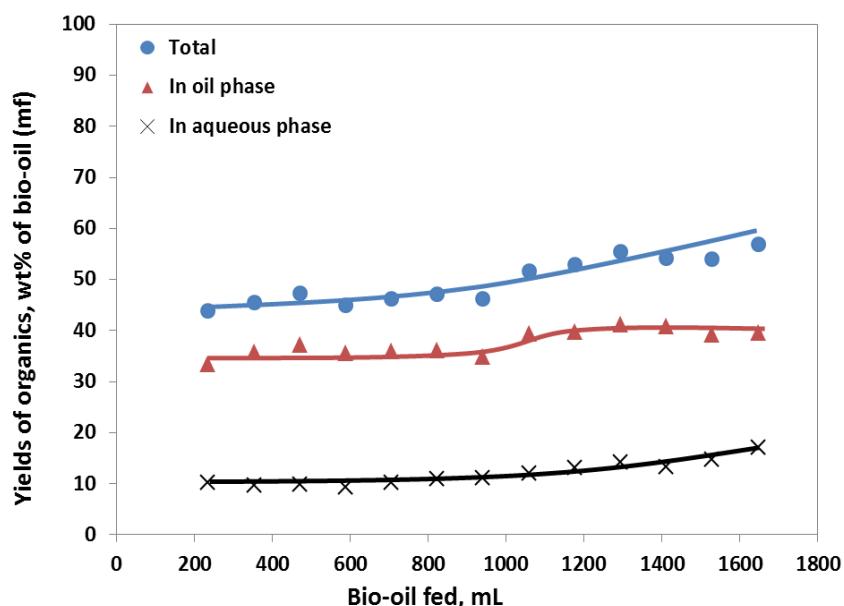


Figure 6-10. The yields of organics from the hydrotreatment of bio-oil as a function of the volume of bio-oil fed into the reactor under Condition #5. The data reported under Condition #5 are the same as that reported previously [17] and used here for comparison.

The yields of organics in oil phase slightly increased from 34 wt% to 37 wt% and stayed constant at 37 wt% until after ~ 1000 mL of bio-oil had been fed into the reactor. On the other hand, the total yields of organic products had a slight increase

from the start of the experiment, going from 44 to 54 wt%. This also indicates that the system could not reach a steady state before blocking.

Taken together, the results under Condition #5 showed longer run time than Condition #1. However, still the reactor design needed improvement. This indicates the importance of keeping the injection point hot during the bond breakage of the bio-oil to stabilise the radicals that are responsible for coke formation.

6.3.2.2. Use of coil to enhance the heat transfer

The above trials clearly indicate that the rapid heating of bio-oil and immediate availability of active hydrogen are essential to avoid excessive coke formation on the catalyst surface. It then became clear that heat supply to heat up the bio-oil feed could become a rate-limiting step.

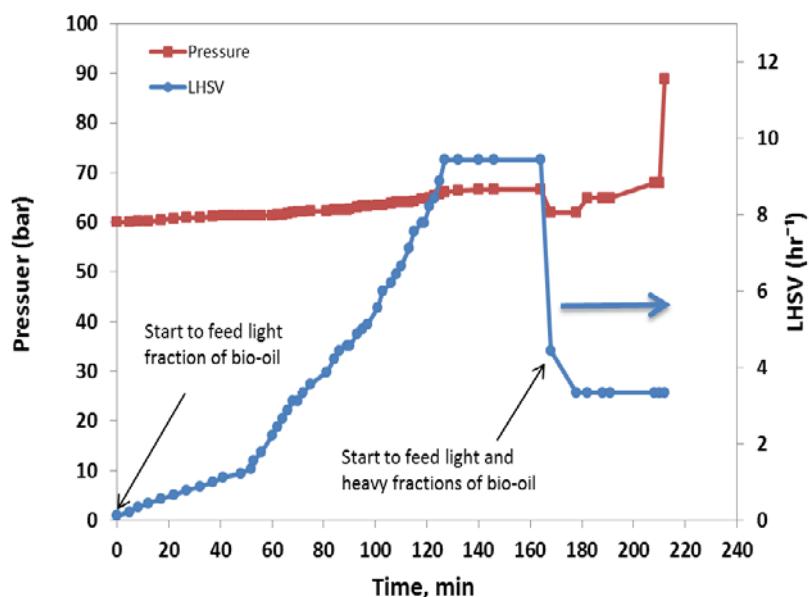


Figure 6-11. The reactor inlet pressure and LHSV profiles as a function of time under Condition #6 (a 2-inch reactor with direct injection of bio-oil and hydrogen to the hot zone of the reactor was used. Coil was installed and hydrogen 2 (Figure 4) was also used).

Under Condition #6, the heat exchange coil shown in Figure 6-4 was designed to bring the heat released from the cooling down of the product stream to heat up the feed stream. As the product stream flowing inside the tubing made up the coil is

cooled down, substantial amounts of heat would be released from the condensation of water and organic vapour as well as the temperature difference of the whole stream. The heat released is then transferred by hydrogen (“Hydrogen 2” in Figure 6-4) to the catalyst bed where bio-oil meets the catalyst.

Under Condition #6, a 2-inch reactor packed fully with NiMo catalyst with the particle size range of 600-800 microns (“Catalyst 1” in Figure 6-4). The average ratio of “Hydrogen 1” and “Hydrogen 2” was around 1:4.

Figure 6-11 shows the changes in the inlet pressure and LHSV when the light fraction and the mixture of light and heavy fractions were fed into the reactor. For the light fraction, no significant pressure increases were observed even when the bio-oil feed rate was 5 L h^{-1} . The product stream was effectively cooled down as it flew out of the reactor and the product outlet tubing was below 50°C . These observations demonstrated the effectiveness of novel design.

When the heavy fraction was blended into the feed at the ratio of 30:70 (heavy:light) as they existed in the bio-oil after pyrolysis, the pressure started to increase at a total flow rate of 1.8 L h^{-1} ($\text{LHSV} = 3.3 \text{ h}^{-1}$). This is due to the high coking propensity of the heavy fraction. From the TGA, the potential coke yields of the hydrotreated bio-oils obtained from the light fraction ($\text{LHSV} = 9.5 \text{ h}^{-1}$) and the heavy fraction ($\text{LHSV} = 3.3 \text{ h}^{-1}$) were 2.15 and 3.67 wt%, respectively. These data indicate that the hydrotreatment at such high LHSV can still effectively reduce the components that are prone to form coke upon heating.

Another experiment (Condition #7) was performed to monitor the effect of coil in the upper section of reactor (Figure 6-4). For this aim, a 2-inch (diameter) reactor with the length of 33 cm in hot zone was chosen and packed with NiMo catalyst with the particle size range of 600-800 microns. Bio-oil and hydrogen were pre-mixed and directly injected through a 1/8 inch tubing to the hot zone of reactor. A coil was made from 1/8 inch tubing was installed inside the reactor. In addition, inside the reactor, two thermocouples with 3 and 18 cm below injection point of hydrogen and bio-oil mixture were installed. Hydrogen flow rate was 12 L/min (hydrogen 1 was 2 and hydrogen 2 was 10 L/min – Figure 6-4). The bio-oil flow rate was gradually increased from 0.5 up to 9 mL/min. The recorded temperature in the installed thermocouples was shown in Figure 6-12a.

As Figure 6-12a shows, an exothermic peak was seen in the top thermocouple position. According to our previous work [15], the exothermic transfers from the top

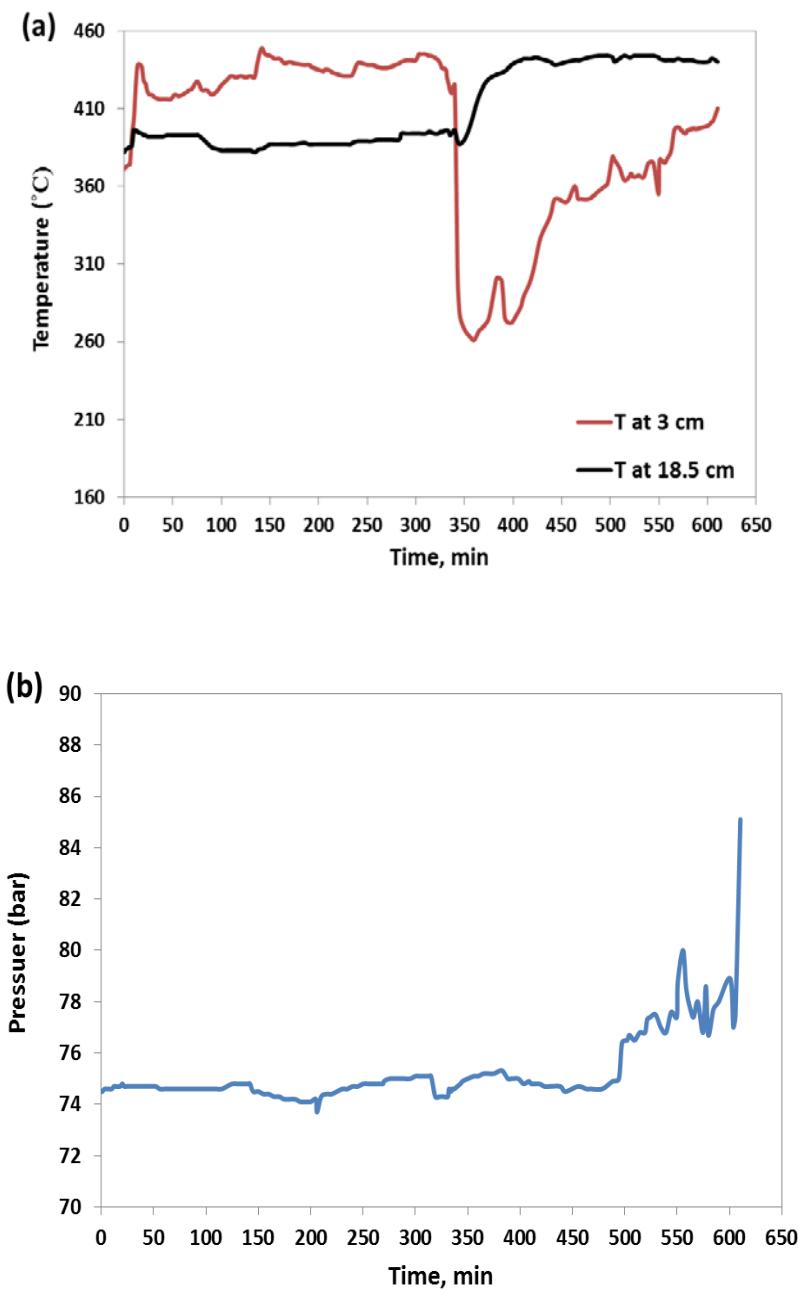


Figure 6-12. (a) Temperature profiles in 3 and 18.5 cm from the start of hot zone inside the reactor. (b) Inlet pressure profile in the feeding line of mixture of bio-oil and hydrogen under Condition #7 (a 2-inch reactor with direct injection of bio-oil and hydrogen to the hot zone of the reactor was used. Coil was installed and hydrogen 2 (Figure 4) was also used).

of reactor to the bottom with a time delay as it takes time for heavy components to travel. Under Condition #7, when the exothermic reactions finished in the top of reactor, the heavy components could reach to the second thermocouple position

resulting in the temperature increase in that position. As it is clear from Figure 6-12a, while the exothermic reactions started to happen in the position of the second thermocouple, the temperature at the top of reactor started to increase. This is due to the heat transfer by installed coil from the lower part of reactor to the top part which brings the heat from the bottom to the top of reactor. Condition #7 could continue for 10.1 hours until the pressure increased in the feeding line (Figure 6-12b). To monitor the coke formation area, the reactor was opened and visually inspected. The feeding line was completely blocked. However, the catalyst inside the reactor was not completely coked up and some catalyst lumps were only found in the top part of reactor.

6.4. Conclusions

In this study, a reactor with a new configuration was developed to manage the coke formation and to improve the energy efficiency in the hydrotreatment of bio-oil. The results clearly indicated that by feeding bio-oil directly into a catalyst bed at a temperature which could activate both, coke formation could be effectively reduced. The fast heating rate of bio-oil minimised the chance for the polymerisation of bio-oil to form coke and maximised the chance for the involvement of the bio-oil in the hydrogenation reactions. Another key feature of the novel reactor design was the improvement of energy efficiency. There was a coiled tubing extended from the bottom to the upper section of the reactor where the reactants were fed into the reactor. This unique design minimised the prolonged contact of the products with catalyst, preventing their further polymerisation or cracking to coke on catalyst surface. Moreover, the heat that products carried could efficiently be transferred to the incoming bio-oil and hydrogen when the products travel from the coiled tubing to the upper section of the reactor where the reactants and the catalyst contacted with the coiled tubing. This significantly promoted the heating rate of bio-oil and improved the overall energy efficiency.

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Chapter 7

Conclusions and recommendations

7.1. Introduction

The purpose of this study is to gain the fundamental understanding on the effects of process conditions on the hydrotreatment of bio-oil using NiMo/ γ -Al₂O₃ catalyst. The coke and heavy residue were quantified. The bio-oil and its hydrotreated bio-oils produced under different process conditions were analysed. The hydrotreatment of light and heavy species in the bio-oil were discussed to explain the reactor blockage and product quality. The product yields including the yields of organics and water were plotted and compared to investigate the effects of different parameters on them. The characterisation of fresh and used catalysts was discussed to determine the effects of different parameters on coke formation. In addition, the importance of hydrogen and bio-oil inlet temperature on coke formation was discussed. A new design of reactor to reduce the coke formation and enhance energy recovery was also studied. The main conclusions from the present study are written below.

7.2 Conclusions

7.2.1. Differences in the reaction behaviour of light and heavy species during the hydrotreatment of pyrolysis bio-oil in a continuous pack-bed reactor

- Lighter and heavier components in the same bio-oil could behave very differently.
- The overall bio-oil liquid hourly space velocity can drastically affect the hydrotreatment process.
- The residence time of the light species that evaporate instantly could be very short, while the residence time of heavy species could be very long.
- The initial contact of heavy bio-oil species with the pre-sulphided NiMo/Al₂O₃ catalyst could result in very significant exothermic peaks and the rapid deactivation of the hyperactive sites in the catalyst.
- NiMo catalyst used was less active in hydrotreating the heavier bio-oil species than in hydrotreating the lighter bio-oil species.

7.2.2. Effects of temperature on the hydrotreatment behaviour of pyrolysis bio-oil and coke formation in a continuous hydrotreatment reactor

- Pd/C catalyst in upstream of the reactor can have some effects on stabilising of bio-oil.
- Aromatic ring growth and polymerisation could take place continuously even under the overall dominating hydrotreatment/hydrocracking conditions.
- Quality of produced biofuels and coke formation depend on temperature and high temperature (e.g. 450°C) produces more coke inside the reactor.
- The coke from heavy liquid was very different from the coke formed from light species.

7.2.3. The importance of hydrogen and bio-oil inlet temperature during the hydrotreatment of bio-oil

- The presence of enough hot hydrogen in the upper section of the reactor can reduce the coke formation.
- The hot hydrogen enhanced the cracking of heavy species in the bio-oil.
- The hydrotreated bio-oils contained less acids, phenolics and higher yield of benzene compounds.
- Slow heating up of the bio-oil is partially the reason for coke formation and the bond breakage should be matched by the supply of active hydrogen from the catalyst to prevent coke formation.

7.2.4. A new hydrotreatment reactor configuration for reduced coke formation and improved energy efficiency during bio-oil hydrotreatment

- A reactor with a new configuration was developed to manage the coke formation and to improve the energy efficiency in the hydrotreatment of bio-oil.
- By feeding bio-oil directly into a catalyst bed at a temperature which could activate both bio-oil and hydrogen, coke formation could be effectively reduced.
- The fast heating rate of bio-oil minimised the chance for the polymerisation of bio-

oil to form coke and maximised the chance for the involvement of the bio-oil in the hydrogenation reactions.

- The unique design of the reactor minimised the prolonged contact of the products with catalyst, preventing their further polymerisation or cracking to coke on catalyst surface.
- The heat that products carried could efficiently be transferred to the incoming bio-oil and hydrogen in the new reactor which improved the overall energy efficiency.

7.3. Recommendations

This study mainly focused on the effects of LHSV, temperature of reaction and pre-heating of hydrogen on the product quality, cracking and deoxygenation of heavy and light species of the bio-oil, coke formation and reactor blockage using commercial NiMo/ γ -Al₂O₃ catalyst. New reactor design was developed in this study to reduce the coke formation. However, based on the results from this study, further work can be done to further minimise the coke formation during the hydrotreating of bio-oil. The high tendency of bio-oil towards coke formation is the intrinsic reason for the coking problem during bio-oil hydrotreatment. Thus, to tackle this coke problem, the very first question to be answered is how the coke forms in both heating up of bio-oil and the steady-state operation in the hydrotreatment. Bio-oil is a mixture of hundreds of chemicals but these chemicals can be roughly grouped as sugars, sugar-derivatives and phenolics. What are the contributions of these groups of chemicals towards coke formation need to be clarified. In addition, how bio-oil interacts with the catalyst and how this interaction affects the coking tendency of bio-oil will also need to be clarified. Moreover, how the process parameters affect coke formation from bio-oil will also need to be investigated. This study has demonstrated that some parameters such as pre-heating of hydrogen can significantly affect coke formation during the bio-oil hydrotreatment. However, the effects of other parameters such as pre-treatment of bio-oil via modification the composition of bio-oil or pre-heating of bio-oil on coke formation will also need to be investigated. Furthermore, the activity of other catalysts should be screened for HDO process. Model compounds study could be useful to investigate the mechanism for the bio-oil upgrading.