Upgrading of Fast Pyrolysis Oil via HDO Using Nano-Structured Catalysts

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Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree in Master of Engineering Science

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UPGRADING OF FAST PYROLYSIS OIL VIA HDO USING NANO-STRUCTURED CATALYSTS

(Thesis format: Integrated Article)

by

Shima Ahmadi

Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Engineering Science

The School of Graduate and Postdoctoral Studies
The University of Western Ontario
London, Ontario, Canada

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Abstract

The effects of type of solvents (hydro-treated or upgraded pyrolysis oil and ethanol) on hydro-de-oxygenation (HDO) of fast pyrolysis oil were studied. The presence and the type of solvent were found to be effective for prevention or reduction of self-polymerization during the bio-oil HDO process. Using ethanol as the solvent had superior performance in terms of the heating value, molecular weight and elemental composition of the upgraded oil products, compared to using hydro-treated oils as the solvent. Furthermore, novel CoMo catalysts supported on nano-structured materials including MCM-41 and SBA-15 were synthesized and tested on HDO of fast pyrolysis oil in supercritical ethanol, along with other commercial or in-house prepared CoMo catalysts supported on other materials (activated carbon and γ-alumina). Among all the supported CoMo catalysts, CoMo/MCM-41 produced the highest oil fraction yield, and the spent catalyst after regeneration produced the same oil yields as the fresh one. Furthermore, CoMo/SBA-15 and CoMo/MCM-41 catalysts showed better resistance to coke/carbon deposition in the HDO process, compared with the CoMo/HZSM-5 and CoMo/Al₂O₃ catalysts. Moreover, the study also demonstrated that the nano-structured catalysts can resist in the supercritical ethanol condition without collapsing of their crystalline structure.

Keywords: Bio-oil, Hydro-de-oxygenation, Upgrading, Supercritical ethanol, Mesoporous materials, Nano-structured catalysts, Molecular weight distribution, Carbon deposition.
Co-Authorship Statement

The following dissertation is presented in the integrated-article format. Chapters 3 and 4 are based on manuscripts that have been finalized for submission to peer reviewed journals. The contribution of each author is stated below.

Chapter 3:

**Hydro-de-oxygenation of fast pyrolysis oil using Ru/C catalyst- Effect of solvents**

Authors: Shima Ahmadi, Ehsan Reyhanitash, Zhongshun Yuan, Sohrab Rohani, Chunbao (Charles) Xu

Status: To be submitted to Energy & Fuels

Experimental work and data analysis were performed by Shima Ahmadi. Chunbao (Charles) Xu, Sohrab Rohani, Zhongshun Yuan, and Ehsan Reyhanitash, provided consultation regarding experimental work and interpretation of results. The manuscript was written and revised by Shima Ahmadi, and reviewed by Chunbao (Charles) Xu and Sohrab Rohani.

Chapter 4:

**Hydro-treatment of fast pyrolysis oil in supercritical ethanol using nano-structured catalysts**

Authors: Shima Ahmadi, Zhongshun Yuan, Sohrab Rohani, Chunbao (Charles) Xu

Status: To be submitted to Applied Energy

Experimental work and data analysis were performed by Shima Ahmadi. Chunbao (Charles) Xu, Sohrab Rohani, and Zhongshun Yuan, provided consultation regarding experimental work and interpretation of results. The manuscript was written and revised by Shima Ahmadi, and reviewed by Chunbao (Charles) Xu and Sohrab Rohani.
To my husband and my parents

for their endless love, encouragement and support.
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Chapter 1

1 Introduction

1.1 Biomass as an alternative energy source

With considerable consumption of petroleum derived fuels around the world and depleting of petroleum resources, the importance of producing fuels from renewable energy resources is rising and it has been the main concern of many researchers these days. Biomass, as one of the most promising renewable energy resources on earth, has drawn extensive attention recently (Bu et al., 2012a). It can be the only source of liquid, solid and gaseous fuels. There are many varieties of biomass feedstocks such as wood, vegetable oil, animal wastes and residues from agriculture and forestry (Lopes et al., 2013a). Fuels derived from biomass resources represent many advantages over fossil fuels. First, they considerably generate less emissions comparing to fossil fuels; virtually containing no sulfur emissions and NO\textsubscript{x} emissions are usually lower. Second, they are sustainable fuels. Third, biomass is carbon-neutral. It consumes carbon while the plants grow and returns it when the biomass is burned. So there is a close loop of carbon cycle without any increase in the atmospheric carbon dioxide level. Forth, it is distributed throughout several countries, so it has geopolitical advantages as well (Huber, Iborra, & Corma, 2006; Lopes et al., 2013; Xiu & Shahbazi, 2012). The global capacity of biomass production is shown in Table 1-1.

Different processes have been developed to convert biomass into various types of energy, depending on the feedstock characteristics and the form of desired energy. Therefore, an extensive range of conversion methods has been established. Among these conversion schemes, the thermochemical conversion of biomass appears to be a suitable way to produce liquid fuels (Xiu and Shahbazi, 2012). There are four major thermochemical methods for converting biomass: gasification, direct combustion, liquefaction and pyrolysis (Bridgwater, 1994). These methods will be discussed briefly since a downstream process of pyrolysis is the main focus of this research.
Table 1-1: Global capacity of biomass production (Huber et al., 2006)

<table>
<thead>
<tr>
<th>Continent</th>
<th>Production capacity (ton of dry biomass/year)</th>
<th>boe(^a) (barrels of oil energy equivalent)</th>
<th>Stated by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Africa</td>
<td>1.1×10^9</td>
<td>3.5×10^9</td>
<td>European Biomass Industry Association (EUBIA) (Huber et al., 2006)</td>
</tr>
<tr>
<td>Europe</td>
<td>4.4×10^8</td>
<td>1.4×10^9</td>
<td>The U.S. Department of Agriculture (USDA) &amp; Oak Ridge National Laboratory (Huber et al., 2006)</td>
</tr>
<tr>
<td>Latin America</td>
<td>1.0×10^9</td>
<td>3.2×10^9</td>
<td></td>
</tr>
<tr>
<td>U.S</td>
<td>1.3×10^9</td>
<td>3.8×10^9</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)each metric ton of dry biomass equals 3.15 boe.

1.1.1 Gasification

Among the different schemes for the thermochemical conversion of biomass into energy, gasification is one of the most suitable ways to produce gas. The aim of this process is to convert biomass into a gaseous fuel which can be burned in turbines to produce electricity. The produced gas has a low (~5 MJ/m\(^3\)) to medium (~10-20 MJ/m\(^3\)) heating value depending on modes of thermal gasification (Bridgwater, 2003). The gasification process consists of a specific sequence of steps to follow:

- Drying biomass to remove moisture
- Producing gas, tar and a solid char via pyrolysis
- Partial oxidation (in the presence of pure oxygen or air) of tar, char and gas to give CO, CO\(_2\) and H\(_2\) gases. By using steam reforming process, the main gas products are CO, CO\(_2\), H\(_2\) and CH\(_4\).

The operating temperatures in the presence of air and oxygen are 900 - 1100 °C and 1000 – 1400 °C, respectively. The composition of produced gas is affected by different parameters such as reaction temperature, moisture content and composition of feed, and the extent of oxidation of the pyrolysis products. In the char gasification process which is a combination of several gas-gas and solid-gas reactions, char is oxidised and produces CO and CO\(_2\). In this process, solid-gas reactions are the slowest ones. Therefore, the
overall reaction rate is limited by these kinds of reactions. Different kinds of alkali metal catalysts have been used in this process, but the problem has not yet been solved. The entire tar product via pyrolysis is not totally converted through gasification because of reaction or reactor restrictions. It also causes technical problems for consumers of gas such as turbines which require very high quality fuel gas. So removing tar is one of the most important aspects in implementing gasification technology which is usually achieved through thermal or catalytic cracking. Since the storage of the gas is very expensive, it has to be used instantly. Cold and hot gas efficiencies (energy in raw gas / energy in feed) of up to 85% and 97% are reported for close coupled turbines and boilers (Bridgwater, 2003, 1994; Castello and Fiori, 2011; Zhang et al., 2010).

1.1.2 Combustion

Combustion is a well-known technology which is used in most developing countries. It is extensively used to produce heat and power. Produced heat can be directly consumed for heating, cooking, etc. Although the technology is commercially available and the risk of investment is minimal, overall efficiencies are as low as 15% for small plants and up to 30% for larger ones. In addition, emissions and ash handling are technical problems. Another disadvantage of the combustion process is that the produced heat must be consumed immediately since the storage of this energy is not a feasible option. On the other hand, this process can be economically useful when waste of biomass utilizing industries is used as a feed such as paper, pulp and agricultural wastes. Some examples of these operational plants are in North America and Europe which use wastes as a feed (Bridgwater, 2003, 2012).

1.1.3 Liquefaction

Thermochemical conversion of biomass can also produce liquids and solids. There are different factors such as residence time, heating rate, and temperature that determine if thermochemical conversion of biomass process produces liquids, gases, and solids. Short residence times, fast heating rates, and lower temperatures lead to producing liquids. There are two main processes established to produce liquid products (known as bio-oil): pyrolysis and liquefaction. The first method needs biomass with a minimum moisture
content to achieve a liquid product of high quality but the second process can tolerate any moisture content of biomass to produce the high quality liquid. The latter process is suitable for a naturally wet biomass (Xiu and Shahbazi, 2012). It is usually performed at lower temperature (< 400 °C), higher residence time (0.2-1.0 h), and high pressure (5 - 20 MPa) comparing to the pyrolysis process. A number of different catalysts such as alkali and metals have been used for liquefaction process (Huber et al., 2006; Xiu and Shahbazi, 2012; Yang et al., 2009b). Water or organic material such as ethylene glycol and methanol can be used as a solvent in this process. In hydrothermal liquefaction, water or an aqueous media is used as a solvent. Water has some advantages over other solvents such as being cost effective and environmentally friendly (Zhang, 2010). It is reported that the bio-oil produced through liquefaction has a lower oxygen content, higher heating value, lower oil yield and higher capital cost due to the use of high pressure equipment, compared to the pyrolysis-derived liquid oil (Chumpoo and Prasassarakich, 2010; Xu and Etcheverry, 2008; Yang et al., 2009a; Zhang et al., 2011).

1.1.4 Pyrolysis

As mentioned before, one major way to produce liquid fuel is pyrolysis which has been used since the 1970s (Mohan et al., 2006). It entails the thermal decomposition of biomass in the absence of oxygen. The first step of gasification and combustion also is pyrolysis. Then, the first produced products undergo complete or partial oxidation respectively. To produce char, lower temperature and longer residence time are needed. Higher temperature and longer residence time lead to the production of gases. Liquid products are achieved at moderate temperatures and short vapor residence times (Bridgwater, 2003). Since the focus of this thesis is on upgrading of pyrolysis oil, the first section of next chapter “literature review” is dedicated to pyrolysis.

1.2 Thesis objective

The main objectives of this research are summarized as follows:

- Investigating the effects of solvents on upgrading of fast pyrolysis oil via hydro-de-oxygenation (HDO).
• Synthesizing some inexpensive CoMo-based catalysts supported on mesoporous materials such as SBA-15 and MCM-41 and, then studying their performance on HDO process in supercritical conditions.

1.3 Overview of the present work
Chapter 1 provides a brief discussion about the significant role of biomass in replacing fossil fuels. The capacity of producing biomass around the world is presented in a table. Then, available technologies for thermochemical conversion of biomass are briefly introduced. Pyrolysis process as one of the main processes to produce liquid fuel will be further discussed in Chapter 2.

A literature review of pyrolysis process is provided in Chapter 2. Afterward, different methods for upgrading of pyrolysis oil are introduced. Among the upgrading methods, hydro-de-oxygenation and supercritical fluids processes are discussed in detailed. The properties of the main feed for pyrolysis (lignocellulosic biomass) and pyrolysis oil are also described.

Chapter 3 and Chapter 4 contain a brief introduction of the properties of pyrolysis bio-oil and the importance of upgrading process. Chapter 3 centers on upgrading of fast pyrolysis bio-oil obtained from BTG Company (Netherlands) using hydro-de-oxygenation as the upgrading technique in a batch mode followed by studying the effect of two different solvents on the HDO process. Chapter 4 focuses on synthesizing and screening some new nano-structured catalysts and using them in upgrading process via supercritical fluids method in a batch mode.

Chapter 5 presents the overall conclusions of the thesis and recommendations for future studies.

1.4 References


Chapter 2

2 Literature Review

2.1 Pyrolysis

2.1.1 History of Pyrolysis

Pyrolysis is an old procedure. Thousands of years ago in the Amazon, native people used the pyrolysis process to produce bio char in order to enrich the rainforest soils. Bio char is a solid which looks like charcoal. The people who had the knowledge of making fire, started fire and when the fuel became hot, they covered it with soil to take oxygen away from fuel. Meanwhile, the high temperature led to the breakdown of the fuel in the absence of oxygen and bio char was formed (Magnum Group International Inc.).

During the two world wars, pyrolysis was used to produce transportation fuel from wood waste feedstock in the absence of fossil fuels. Gases which were obtained from biomass had an important role in transportation. By 1945 heavy vehicles such as trucks and buses and agricultural machines were driven by gasification. It is reported that around 9,000,000 vehicles were powered by bio-derived gases as fuel around the world (Magnum Group International Inc.).

2.1.2 Process of Pyrolysis

In the pyrolysis process, the product quality can be affected by different factors such as; feed material, catalyst, heating rate, feed water content, pressure, temperature, type of reactor, etc. (Bridgwater, 1994). This process is divided into three groups according to the process condition: slow pyrolysis, intermediate pyrolysis and fast pyrolysis which are shown in Table 2-1. Slow pyrolysis has a longer vapor residence time and operates at low temperature which leads to producing charcoal. Intermediate pyrolysis has a moderate temperature and a residence time of about 10-30 s. Fast or flash pyrolysis has a higher temperature and a short residence time which is ideal for producing liquids. Fast pyrolysis has been studied more since liquids can be carried or stored much easier and cheaper than solid biomass (reduced volumes) (Bridgwater, 2012, 2006).
Fast pyrolysis has a very short residence time. So, some phenomena such as mass and heat transfer and kinetics of the reaction become more significant. One of the most important tools in the pyrolysis process is the reactor which takes 10-15% of the total cost (Bridgwater, 2012). Different types of reactor such as bubbling fluid beds, cyclonic reactor and transport reactor have been used in the pyrolysis process to obtain high liquid yield of 70-80% based on the dry biomass (Oasmaa and Czernik, 1999). The other products which are obtained from the pyrolysis process are solid char and non-condensable gas with yields varying between 12 - 25% and 13 - 25%, respectively (Bridgwater, 2012). Practically, any type of biomass can be used in the pyrolysis process. Hundred types of biomass such as sorghum, straw, leather waster and nut shells have been used in the pyrolysis process. The most interesting type is wood due to its reliability repeatability between experiments (Mohan et al., 2006).

Effect of heating rate in pyrolysis process is investigated. In order to reduce the char formation and increase the liquid yield, applying high heating rates at temperatures of around 500 °C is appropriate. By raising the temperature higher than 500 °C, more gas will be produced (Bridgwater, 2012; Demirbas, 2009). It is reported that char is not produced under certain conditions. By applying fast heating rates and quenching of vapors, some transitional products are formed which condense instantly. Therefore, gaseous products are not formed (Demirbas, 2005). In contrast, at temperature above 700 °C and high reaction rates with short residence time, gas yield is maximized up to 80 wt % (Bridgwater, A.V. Cottam, 1992).

### Table 2-1: Different type of pyrolysis (Bridgwater, 2012, 2006)

<table>
<thead>
<tr>
<th>Type of pyrolysis</th>
<th>Temperature (°C)</th>
<th>Residence time</th>
<th>Yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow</td>
<td>400</td>
<td>Hours/days</td>
<td>30</td>
</tr>
<tr>
<td>intermediate</td>
<td>500</td>
<td>10-30 s</td>
<td>50</td>
</tr>
<tr>
<td>fast</td>
<td>500</td>
<td>~1 s</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Char</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>35</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>25</td>
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<td>12</td>
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<td></td>
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<td>gas</td>
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<td></td>
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<td>35</td>
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<td></td>
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<td>25</td>
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<td></td>
<td></td>
<td></td>
<td>13</td>
</tr>
</tbody>
</table>
2.1.3 Main components of pyrolysis oil

Since the initial requirement in generating biofuels is having an inexpensive and rich biomass feedstock, chemical composition of biomass and the rate of its growing are very important factors. Lignocellulose is the cheapest and accessible source of biomass (Huber et al., 2006). Lignocellulosic biomass consists of cellulose, hemicellulose and lignin which are the key blocks of biomass. Their weight percentage differs in each biomass source. Pyrolysis oil is obtained through depolymerisation and degradation of lignocellulosic biomass. It is a mixture of products which are obtained from pyrolysis of each block. Therefore, the elemental composition of bio-oil looks like biomass rather than fossil fuels (Czernik and Bridgwater, 2004; Huber et al., 2006; Mohan et al., 2006). The elemental composition of pyrolysis oil, their biomass resource, and heavy oil are compared in Table 2-2.

As shown in Table 2-2, the oxygen content of pyrolysis oil derived from pine and birch are 45.7 wt% and 44 wt%, respectively, while that used in heavy petroleum fuel oil is 0.1 wt%. So, bio-oil obtained from the pyrolysis process has a much higher oxygen content than fossil fuel oil which is the reason of lower heating value in pyrolysis bio-oil than heavy fuel oil (Huber et al., 2006; Zhang et al., 2013).

2.1.3.1 Cellulose

The structure of cellulose is shown in Figure 2-1. Cellulose is the basic structural framework of wood cell walls and comprises 40-50 wt% of dry wood. Cellulose, a crystalline material, is composed of glucose monomers which is a six-carbon ring sugar (Parham et al., 1984). By removing water from each glucose, glucose anhydride is obtained. Cellulose chains are obtained through polymerization of anhydride glucose and comprised of 5000-10000 glucose units (Huber et al., 2006; Mohan et al., 2006).
Table 2-2: Elemental compositions of pyrolysis oil, their biomass resource, and heavy oil (Cai et al., 1999; Fagernäs et al., 2012; Mohan et al., 2006; Oasmaa and Czernik, 1999; Sannigrahi and Ragauskas, 2010; Zhang et al., 2013).

<table>
<thead>
<tr>
<th>Elemental composition</th>
<th>Pyrolysis oil</th>
<th>Biomass resources</th>
<th>Heavy petroleum fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feedstocks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C (wt %)</td>
<td>Pine: 45.7</td>
<td>Birch: 44.0</td>
<td>Pine: 49.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Birch: 49.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>85</td>
</tr>
<tr>
<td>H (wt %)</td>
<td>Pine: 7.0</td>
<td>Birch: 6.9</td>
<td>Pine: 5.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Birch: 6.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>O (wt %)</td>
<td>Pine: 47</td>
<td>Birch: 49.0</td>
<td>Pine: 44.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Birch: 44.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>S (wt %)</td>
<td>Pine: 0.02</td>
<td>Birch: 0.00</td>
<td>Pine: 0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Birch: 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>N (wt %)</td>
<td>Pine: &lt;0.1</td>
<td>Birch: &lt;0.1</td>
<td>Pine: 0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Birch: 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3</td>
</tr>
</tbody>
</table>

Figure 2-1: Cellulose structure.

Long chains of cellulose are joined together through hydrogen bonds which are shown in Figure 2-2. These hydrogen bonds aid the cellulose chain to be preserved. Hydrogen bonds can be made through the sides of the cellulose chain which are hydrophilic. By applying incomplete hydrolysis, cellulose is converted to three components: cellobiose, cellotriose, and cellotetrose, while glucose is obtained through complete acid hydrolysis (Huber et al., 2006). The degradation temperature of cellulose is in the range of 240 to 350 °C (Mohan et al., 2006).
2.1.3.2 Hemicellulose

After cellulose, hemicellulose is the main wood component which is also called polyose. It comprises 25 – 35 wt% of dry wood; 28 wt% of softwoods and 35 wt% of hardwoods. Despite cellulose which is a polymer of one sugar, glucose; hemicellulose is a polymer of different monosaccharides; galactose, glucose, mannose, xylose, arabinose, 4-O-methyl glucuronic acid and galacturonic acid residues which are shown in Figure 2-3. Xylan, xylose polymer, is the main sugar in hardwood hemicellulose structure. Comparing to cellulose which has a crystalline structure, hemicellulose has an amorphous structure due to its branched nature. It can be easily hydrolyzed and broken down to its monomer rather than cellulose. The molecular weight of hemicellulose is lower than cellulose since it comprises around 150 monomer units. Temperature of decomposition of hemicellulose is in the range of 200 to 260 °C which is lower than that of cellulose. It is reported that hemicellulose can be decomposed during the pyrolysis process in few seconds by applying a fast heating rate. During the decomposition of hemicellulose compared to cellulose, more volatiles, and less char and tar are produced. By de-acetylation of hemicellulose during the pyrolysis process, acetic acid is released from wood (Huber et al., 2006; Mohan et al., 2006).
2.1.3.3 Lignin

The word lignin is obtained from lignum, Latin word, which means wood (Jr. et al., 2001). The third main constituent of wood is lignin which comprises of 23 - 33 wt% of softwood and 16 - 25 wt% of hardwood. Lignin is a highly branched, amorphous, and polyphenolic material which is located at the cell walls. It is accompanied by hemicellulose and cellulose to form lignocellulose composites. The skeletal units of lignin are shown in Figure 2-4. Softwood lignin contains coniferyl alcohol and, hardwood lignin comprises coniferyl and sinapyl alcohols (Huber et al., 2006; Mohan et al., 2006). The decomposition temperature for lignin is in the range of 280 to 500 °C. During the pyrolysis process, phenol compounds are made through cleavage of carbon-carbon bonds and ether. It is more difficult to remove water from lignin than from cellulose or hemicellulose. During the pyrolysis process of lignin compared to cellulose, more char is formed (Mohan et al., 2006).

The amount of cellulose, hemicellulose and lignin vary in different biomass species. The weight percents of each constituent for different biomass species are compared in Table 2-3.
2.1.4 Pyrolysis oil chemistry

Bio-oil is a dark brown, highly viscous liquid which has a smoky odor. Various numbers of reactions such as hydrolysis, dehydrogenation, aromatization, condensation and coking happen during the pyrolysis process. Different factors such as feedstock, rate of heat and mass transfer, temperature, pressure and time of pyrolysis have significant effects on bio-oil composition which defines the physical properties of bio-oils (Huber et al., 2006; Jacobson et al., 2013a; Xiu and Shahbazi, 2012). The physical properties of bio-oil represent that water, oxygen and ash contents of bio-oil is higher than fossil fuel, and on the other hand, the heating value of bio-oil is also lower than fossil fuels (Bu et al., 2012a).

The chemical composition of bio-oil is shown in Figure 2-5. Bio-oil contains more than 400 organic compounds. From Figure 2-5 it can be seen that bio-oil comprises ester, acids, alcohols, ketones, aldehydes, phenols, sugars, etc. Some of these compounds are

<table>
<thead>
<tr>
<th>component</th>
<th>corn stover</th>
<th>pine</th>
<th>sugarcane</th>
<th>switchgrass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose (wt %)</td>
<td>36</td>
<td>46-50</td>
<td>22</td>
<td>40-45</td>
</tr>
<tr>
<td>Hemicellulose (wt %)</td>
<td>23</td>
<td>19-22</td>
<td>15</td>
<td>31-35</td>
</tr>
<tr>
<td>Lignin (wt %)</td>
<td>17</td>
<td>21-29</td>
<td>11</td>
<td>6-12</td>
</tr>
</tbody>
</table>
the source of detrimental properties of bio-oil such as high oxygen content, high water content, high viscosity, low heating value, low pH value, poor ignition properties, chemical and thermal instability, and high acidity and corrosiveness (Huber et al., 2006; Zhang et al., 2013).

![Figure 2-5: chemical composition of bio-oil; reprinted (adapted) with permission from (Huber et al., 2006). Copyright (2014) American Chemical Society.](image)

Bio-oil is rich in water which is obtained from the initial moisture of the feedstock and dehydration reactions which occur during the pyrolysis process. The range of water in bio-oil is about 15 – 35 wt% which is influenced by the biomass species and reaction conditions. There are some hydrophilic compounds such as ketones, alcohols, hydroxyaldehydes, and acids in bio-oil which are formed through decomposition of carbohydrates that improve miscibility of water with the oligomeric lignin-derived components. Although water has some undesirable effects on bio-oil properties such as reducing heating value, decreasing combustion rate and delaying ignition, but it has some positive effects such as enhancing bio-oil flow characteristics, and lower NO\textsubscript{x} emissions (Bridgwater, 2004a; Czernik and Bridgwater, 2004).
Bio-oil contains oxygen in the range of 45 to 50 wt% which exists in more than 300 compounds in bio-oil such as hydroxyketones, hydroxyaldehyde, carboxylic acid, phenolics, suger, and dehydrosuger. The oxygen content of bio-oil is dependent on its water content. A chemical formula of \( \text{CH}_{1.9}\text{O}_{0.7} \) is defined for bio-oil which is a representative of 46 wt% oxygen in bio-oil. The oxygen content of wood is reported as 42 wt%. This difference is due to the oxygen content of gases and of water in bio-oil (Mohan et al., 2006). Distribution of these compounds rely on the biomass species and process condition such as heating rate, temperature and residence time. By increasing the temperature, more gaseous products are obtained, but the liquids products have lower oxygen content as well (Bridgwater, 2004a).

The high oxygen content of bio-oil is the main reason for some undesirable properties of bio-oil such as: thermal instability, low energy density, corrosiveness and less miscibility which will be discussed below.

Pyrolysis bio-oils have reactive organic compounds such as aldehydes and phenols, so they are chemically unstable over time. These compounds would react with each other and make macromolecules through polymerization. This process can be promoted in acidic conditions. So, physical properties of bio-oil such as the flow characteristic are changed; viscosity of bio-oil and its molecular weight are increased. Since this process occurs with time, it is called “aging”. The main reactions which occur during aging are polymerization, etherification, esterification, and condensation which produce water (Diebold and Czernik, 1997; Zhang et al., 2013). Among these reactions, polymerization has to be inhibited due to reactor plugging and coke formation (Elliott and Neuenschwander, 1996).

The high acidity of bio-oil leads to corrosion of equipment which are used in the pyrolysis process (Zhang et al., 2013). Bio-oil contains some organic acids such as formic and acetic acid which lead to a pH in the range of 2 – 3. Although their presence in bio-oil can lead to corrosion of carbon steel and aluminum, they will not have any effect on stainless steels. Corrosiveness of bio-oil can be promoted at high temperatures and water contents (Oasmaa and Czernik, 1999).
Bio-oil is immiscible with conventional hydrocarbons due to its high polarity and hydrophilic compounds. There is a considerable amount of polar compounds in bio-oil. Non-bonded electrons of functional groups which have oxygen result in the polarity of these compounds (Mortensen et al., 2011a).

Although bio-oils have various detrimental properties which were discussed above, they also have some promising characteristics such as low toxicity, producing less pollution (NOx pollution is half of that from fossil fuel), forming negligible amounts of SOx, being CO2 neutral, and easier for handling and transportation. It is also used in boilers, has turbines and engines to produce heat and electricity under particular conditions (He and Wang, 2012; Tanneru and Steele, 2014; Zhang et al., 2013). Therefore, pyrolysis oil should go through specific process named upgrading to gain physical and chemical characteristics similar to petroleum derived fuels.

2.1.5 Upgrading of bio-oil

Carbon and hydrogen are the main components of conventional hydrocarbons which lead to its low oxygen content; O/C molar ratio of petroleum is less than 0.06, while it is higher than 0.3 in wood (Wang et al., 2007). So, pyrolysis bio-oils have to be upgraded if they are to be used as a replacement for petroleum derived fuels due to its detrimental properties (mentioned above). In Figure 2-6, H/C and O/C molar ratios of different components are compared with each other. As presented in Figure 2-6, the O/C and H/C molar ratios of pyrolysis oil are 0.6 and 1.7, respectively. In order to produce fuel for the transportation sector, bio-oil has to go through an upgrading process to remove oxygen and meet the O/C and H/C molar ratios of conventional hydrocarbons; 0 and 1.5 – 2, respectively. One way to introduce bio-oil in the transportation sector is to co-process it with petroleum refineries. Several studies have been conducted on processing bio-oil in fluid catalytic cracking (FCC). However, low yields and char formation in FCC units are unavoidable. So, an intermediate process to upgrade bio-oil before co-processing it with petroleum refineries is essential (Mercader et al., 2010).
There are two main methods for upgrading pyrolysis oil; catalytic cracking, and hydrode-oxygenation. Catalytic cracking intends to directly convert pyrolysis bio-oil to transportation fuel while hydro-de-oxygenation (HDO) process aims to decrease the oxygen content of pyrolysis oil and yield intermediate oil which can go through more upgrading. Recently, a new method, supercritical fluids (SFCs) has been used widely in upgrading. The following is a brief discussion on catalytic cracking since it is not the main focus of this research. Then, hydro-de-oxygenation and supercritical fluids will be discussed in more detail since the former is used in chapter three and the latter one is used in chapter four for upgrading.

2.1.5.1 Atmospheric pressure upgrading (catalytic cracking)

Catalytic cracking of bio-oil is performed at atmospheric pressure and high temperature of 350 – 500 °C. This high temperature leads to cleave bonds in macromolecules and also helps the de-oxygenation of bio-oil compounds (Jacobson et al., 2013b). Different kinds of catalysts such as zeolites and aluminosilicates are used in this process. The products
are hydrocarbons, water soluble organic compounds, water, oil soluble organic compounds, gases, and coke. The oxygen is removed in the form of water and carbon dioxide. This process has drawn attention due to low operating pressure, no need for hydrogen, and low operating cost. However, low hydrocarbon yield, catalyst deactivation, and extreme coke formation limit its usage as an upgrading process. So, continuous regenerating of catalyst is required (Bulushev and Ross, 2011; Huber et al., 2006).

2.1.5.2 Hydro-de-oxygenation

The other upgrading process is called hydro-de-oxygenation (HDO). In this process hydrogen is used to remove oxygen in the form of water from pyrolysis oil by saturating the carbon-carbon bonds and aromatic rings at moderate temperature (300 - 600 °C) (Bu et al., 2012a; He and Wang, 2012; Huber et al., 2006). Carbon dioxide and negligible amounts of carbon monoxide are also formed. In this process the type of catalyst, temperature and residence time have a significant effect on the HDO process which is discussed below.

The HDO process is very similar to hydro-de-nitrogenation (HDN) and hydro-de-sulfurization (HDS) processes which proceeds at the same time with HDN and HDS during hydro-processing. So many researchers have focused on using conventional catalysts such as CoMo/Al₂O₃ and NiMo/Al₂O₃ in HDO process which have been used to eliminate nitrogen and sulfur in HDN and HDS processes (Furimsky, 2000a).

Mortensen et al. (2011a) and Wildschut et al. (2009a) summarized the reactions that may occur during the HDO process: separation of water, condensation and polymerization which lead to dehydration reaction, decarboxylation reaction which leads to water formation, hydrogenation which saturates unsaturated components, breaking carbon-oxygen bonds which are called hydrogenolysis and, breaking macromolecules into smaller ones which is called cracking.

Elliott and Neuenschwander (1996) employed a two-stage packed bed down flow reactor for a HDO process at 21 MPa in Pacific Northwest National Laboratory (PNNL). The
same catalyst, sulfided NiMo/Al₂O₃ or CoMo/spinel, was used in both stages. The objective of the first stage was to stabilize the pyrolysis oil through HDO at 150 °C. The main HDO was performed at a higher temperature (300 - 400 °C) in the second stage. Although an oxygen removal of up to 99% was attained, but catalyst deactivation and plugging of the reactor lines were detected due to tar and coke formation during the process, which were the main obstacles.

Baldauf et al. (1994) proposed a continuous bench scale reactor with the option of using up or down flow for HDO of pyrolysis oil. Catalysts which were used in this process were sulfided CoMo/Al₂O₃ and NiMo/Al₂O₃. The reaction conditions were 350 - 370 °C and up to 300 bar pressure. Although the yield of de-oxygenation was high about 88 – 99.9 wt%, but the yields of oil products was 30 – 35 wt%. Plugging of catalyst bed and lines and catalyst deactivation happened quickly due to forming gum-like materials, so the reactor could not operate continuously for a long time.

Samolada et al. (1998) studied HDO of fast pyrolysis oil in a packed bed reactor with up and down flow. They used CoMo and NiMo as catalysts and gained an oxygen removal of 88 – 99.9 wt%. The operating conditions were temperature of up to 500 °C and pressure of up to 325 bar. They reported the yield of oils between 30 and 55 wt%.

The other catalysts which have been used in HDO of fast pyrolysis oil are noble metals such as Pd, Pt, Ru, Rh or bimetallic catalysts. These catalysts have drawn more attention due to the resulting higher yield of oil and lower yield of solid (He and Wang, 2012).

Wildschut et al. (2009a) studied some catalysts such as Pt/C, Pd/C, Ru/TiO₂, Ru/Al₂O₃, and Ru/C in HDO process and compared their activities with conventional catalysts, sulfided CoMo/Al₂O₃ and NiMo/Al₂O₃, at two different temperatures and pressures in a batch reactor. It was conducted that Ru/C catalyst worked best in terms of oil yield and oxygen removal compared to the conventional catalysts. The highest oxygen removal, 55 wt%, was attained by Ru/C catalyst at 350 °C, 200 bar and, 4 h. By using sulfided CoMo/Al₂O₃ and NiMo/Al₂O₃, the oxygen content was reported around 8 wt% and 11 wt% and the oil yield did not go above 30 wt%. By comparing two different temperatures which were used, it was conducted that Ru/C catalyst at 350 °C was more effective than
at 250 °C. It was reported that the yield of oil products and the degree of de-oxygenation were enhanced at higher temperature.

Elliot et al. (2012) used Ru/C as catalyst in a fixed bed down flow reactor consisting of two portions to hydrogenate pyrolysis oil at 170 °C and 2000 psig. The first portion of bed was filled with Ru/C and the second one was filled with sulfided CoMo catalyst. The aim of the first portion was to do a partial upgrading. The temperature of the second portion was 400 °C and its pressure was the same as first portion. The oxygen content of pyrolysis oil was reduced from 50 wt% to less than 3 wt %.

Another study on HDO process was performed by Venderbosch et al. (2010a) using Ru/C as a catalyst in a fixed bed reactor. They studied different reactions such as polymerization of oil during high pressure thermal treatment, hydrogenation of oil at temperatures up to 250 °C, HDO at higher temperature (up to 400 °C), and hydrocracking process. They found that parallel reactions such as re-polymerization, decarboxylation and hydrotreating happened at temperatures up to 250 °C, and the former reaction took place faster than hydrotreating reactions (Venderbosch et al., 2010a).

Ru/C was used in a batch reactor as a catalyst in a HDO of pyrolysis oil by de Miguel Mercader et al. (2011). In order to keep the pressure of the reactor constant, hydrogen was added to the reactor continuously. Various temperatures (220, 270, and 310 °C) and a retention time of 4h were applied for HDO process. It was reported that oxygen removal was promoted by increasing the temperature from 220 °C to 310 °C. In addition, coke formation and molar mass of oil fraction were reduced by rising temperature.

Wildschut et al. (2010) studied the stability of Ru/C catalyst in HDO process at 350 °C and 200 bar in a batch reactor. A significant reduction of 55 - 30 wt% in liquid yield and H/C ratio (1.24 – 1.08) and an increase of solid yields from 3 wt% to 20 wt% were detected after a number of catalyst recycles. In addition, the amount of methane in gas products was declined. Moreover, the effect of ruthenium precursor (RuCl₃, Ru(NO)(NO₃)₃ and Ru(acac)₃) and its loading on HDO of pyrolysis oil and phenol as feeds were investigated. Among these catalysts, Ru/C which was prepared by using RuCl₃ as precursor and loading of 5 wt% performed best.
2.1.5.3 Supercritical fluids

When a fluid’s temperature and pressure go above the critical point, it is called supercritical. Supercritical fluids (SCFs) have specific transport characteristics; effusing through solid similar to gas (low viscosity and diffusivity) and dissolving ingredient similar to a liquid (high density comparable to liquids). They also can dissolve materials that are not usually soluble in a liquid or a gas phase of a solvent reactions (Xiu and Shahbazi, 2012; Xu and Etcheverry, 2008). This technique has the benefits of unique and great properties of supercritical reaction media such as faster mass and heat transfer rates, better dissolving, and gas-like viscosity and diffusivity (Zhang et al., 2007). Supercritical fluids have been employed to produce oils and for upgrading oils. It has a great potential to produce bio-oils with lower viscosity (Xiu and Shahbazi, 2012). SCFs have been used lately to enhance the oil quality and yield. It is established that SCFs have an abundant potential to generate bio-oils with higher quality and lower viscosity (Zhang et al., 2013).

SFCs can improve gasification or liquefaction reactions (Xiu and Shahbazi, 2012; Xu and Etcheverry, 2008). Water as a solvent for liquefaction process has been used as a supercritical fluid as it is cheap, but it has some drawbacks such as resulting in high viscous oil with high oxygen content, and low yield of oil products which are not soluble in water phase. In order to increase the oil yields and its quality, organic solvents such as ethanol (Street, 2010), methanol (Yang et al., 2009b), n-hexane (Street, 2010), acetone (Heitz et al., 1994; Liu and Zhang, 2008), 1, 4-dioxane (Cemek and Ku, 2001; Mazaheri et al., 2010) have been employed. It is reported that these solvents have significant effect on bio-oil yields and qualities.

Some of the above solvents such as ethanol (Peng et al., 2009a, 2008; Tang et al., 2010, 2009; Zhang et al., 2012), water (Duan and Savage, 2011), methanol (Cui et al., 2011; Li et al., 2011a, 2011b) and CO₂ (Cui et al., 2010) were applied in many upgrading researches.

The main difference between simply adding a solvent and adding it in a supercritical state is excessive conversion of unwanted compounds to desirable ones which results in improving the bio-oil properties (Butler et al., 2011). Conversion can be improved by
esterification in supercritical ethanol (Peng et al., 2009a; Tang et al., 2009). Another advantage of catalyzed esterification is that the reaction conditions are milder than hydro-processing and catalytic cracking. Tang et al. studied upgrading of lignin-derived oligomers in supercritical ethanol and reported that the quality of oil such as heating value, pH and viscosity were improved. The amount of ketones and aldehydes were decreased to produce stable compounds. Most of the acids were converted to esters. Since aldehydes and compounds which have unsaturated carbon bonds promote polymerization and condensation reactions and lead to increase viscosity and phase separation, preventing these reactions can avoid the tar or coke formation (Tang et al., 2009).

Yang et al. (2009a) investigated the hydro-de-oxygenation of phenol as a model compound in supercritical hexane at 300 - 450 °C under hydrogen atmosphere over CoMo/MgO and CoMoP/MgO catalysts. Both catalysts were effective for upgrading phenol in supercritical hexane at temperatures above 350 °C and they had an excellent resistance to the coke formation.

Dang et al. (2012) investigated the effect of hydrogen pressure using Pt/\text{SO}_4^{2-}/\text{ZrO}_2/$\text{SBA}$-15 as a catalyst in supercritical ethanol and reported that higher initial pressure (2.0 MPa) could prevent coke formation. By increasing mass ratio of solvent to bio-oil, heating value and desired products can be improved. Although by increasing the temperature, the heating value is enhanced, but the amount of desired products decreased and coke formation became more serious.

Chen et al. (2014) studied the upgrading of guaiacol as a model compound in supercritical ethanol using different supports such as SBA-15, ZrO$_2$/SBA-15 and SO$_4^{2-}$/ZrO$_2$/SBA-15. It was concluded that the temperature has no specific effect on guaiacol conversion and yields of desired products while initial pressure lower than 4.0 MPa could considerably reduce the guaiacol conversion.

Peng et al. (2009a) investigated the upgrading process of bio-oil obtained from rice husk in sub- and supercritical ethanol over HZSM-5 catalysts with different Si/Al ratio. The results confirmed that supercritical conditions worked better than subcritical and HZSM-
5 with lower Si/Al ratio can crack heavy components more efficiently. It was concluded that acids were converted to esters (no more corrosion) through esterification.

Cui et al. (2011) examined the esterification upgrading of some acids such as acetic acid and acrylic acid in supercritical methanol under atmospheric pressure. The results show that supercritical esterification performed better than normal esterification in terms of acid removal.

Upgrading of low-boiling fraction of bio-oil in supercritical methanol over Pt/Al$_2$(SiO3)$_3$, Pt/C and Pt/MgO was studied by Li et al. (2011b). It was found that esterification was simplified in supercritical conditions. He also studied the upgrading process of high-boiling fractions of bio-oil in supercritical methanol using different catalysts and found out that PtNi/MgO had a good performance. In this process, cracking and esterification are the main reactions (Li et al., 2011a).

Zhang et al. (2012) studied upgrading of the fast pyrolysis of Pinus sylvestris L. over SO$_4^{2-}$/ZrO$_2$/SBA-15 and HZSM-5 supported catalysts in supercritical ethanol and methanol and concluded that the former catalysts performed better in upgrading process. They also concluded that using ethanol as a supercritical fluid was more effective than methanol in the upgrading process. In addition, ethanol is a renewable solvent which can be obtained from lignocellulosic biomass such as corn grain and sugarcane (Chen et al., 2013; Peng et al., 2009a). Furthermore, it can be used as gasoline additive and its critical points are lower than methanol and water (Chen et al., 2013).

Generally, using supercritical fluids is environmentally friendly and also can be performed in lower temperatures. The only drawback of using SCFs is their costs (Zhang et al., 2013), but by using ethanol as a renewable solvent it would be economically feasible.

2.2 Summary

Considering the continuously rising world requirement for energy, it seems necessary to find a substitute for fossil fuels. Pyrolysis oil which is obtained from biomass resources can be a potential source for fuels. Though pyrolysis oil has to go through some
upgrading processes to gain the physical and chemical characteristics of fossil fuels, but it is one of the resources that can produce liquid fuels. The liquefaction process as another way to produce bio-oil should undergo more improvement to meet the present state of pyrolysis process. The upgrading process of pyrolysis oil should be integrated into the petroleum refinery to reduce the capital cost.

The pyrolysis oil has oxygen content in the range of 45 to 50 wt% which is present in more than 300 compounds in bio-oil and is responsible for the reactive nature of bio-oil. The polymerization reaction occurs during the storage and processing due to bio-oil reactive nature. So during storage the viscosity of bio-oil is increased and phase separation occurs, while during processing coke and char formation, deactivation of catalyst and plugging of the reactor are detected. The upgrading process can improve the pyrolysis bio-oil quality by reducing the oxygen content to make the bio oil more stable.

This thesis has centered on studying the upgrading processes; hydro-de-oxygenation and supercritical fluids in order to decrease the oxygen content of pyrolysis bio-oil. In chapter three, upgrading of fast pyrolysis oil purchased from BTG Company (Netherlands) using hydro-de-oxygenation process was investigated. In chapter four, supercritical fluids were used as upgrading process using the same feedstock.

2.3 References


Chapter 3

3 Hydro-de-oxygenation of fast pyrolysis oil using Ru/C catalyst- Effect of solvents

3.1 Introduction

Recently, growing population, the decreasing of fossil fuels and severe environmental issues have resulted in searching for renewable and environmentally friendly resources for energy and chemicals (Dang et al., 2013; Hong et al., 2014; Kanaujia et al., 2014). Biomass is a renewable, clean, carbon neutral, immense and readily available resource, so it has attracted increasing attentions worldwide (Huber, Iborra, & Corma, 2006; Lopes et al., 2013; Xiu & Shahbazi, 2012).

Different technologies have been established to convert biomass into a variety of energy and chemical products, depending to the feedstock’s characteristics and the form of desired energy/chemicals. Therefore, a wide range of conversion processes have been developed. Among these conversion processes, thermochemical conversion of biomass is believed to be an viable route to produce liquid fuels and chemical feedstock (Xiu and Shahbazi, 2012).

Among all thermochemical processes for converting biomass, fast pyrolysis is by far the only industrially realized technology for conversion of lignocellulosic biomass and waste materials into liquid oils (i.e., fast pyrolysis oils, PO). Fast pyrolysis oils have a great potential to be a renewable energy source for the production of bio-energy, bio-fuels and bio-based chemicals. However, upgrading of fast pyrolysis oil is needed due to the many detrimental properties of pyrolysis oils such as a high water content, high viscosity, large molecular weight, low stability, and high oxygen content etc. The high oxygen content of the PO leads to low stability and a lower caloric value of PO whose lower heating value (LHV) is 15-20 MJ/kg, approximately half of the conventional hydrocarbon fuels (Bu et al., 2012; Jacobson et al., 2013; Mortensen et al., 2011).
The large molecular weight and high oxygen contents of pyrolysis oils also makes them immiscible with conventional hydrocarbon fuels, and unstable caused by self-polymerization during storage and processing due to the presence of some reactive oxygen-containing functional groups (such as hydroxyaldehydes, hydroxyketones, carboxylic acids, sugars and phenolic). Thus, reducing molecular weight and removing oxygen from a PO are necessary to enhance its thermal stability, miscibility with fossil fuel and heating value (Bridgwater, 2004b; Joshi and Lawal, 2012). On the other hand, reducing molecular weight and removing oxygen are also needed in order to prevent from self-polymerization of pyrolysis oil during processing and hence avoid reactor plugging and catalyst deactivation.

Fast pyrolysis oils can be effectively upgraded by catalytic cracking (Gandarias and Arias, 2013; Vitolo et al., 1999), steam reforming (Basagiannis and Verykios, 2007; Rioche et al., 2005), emulsification (Ikura et al., 2003), esterification (Zhang et al., 2006), and hydro-de-oxygenation (HDO) (Furimsky, 2000b). Among these routes, HDO could be a promising way for upgrading of bio-oils because HDO could lead to high quality oil products containing less oxygen with lower molecular weights. For example, very recently the author’s group (Reyhanitash et al., 2014) has published a research work investigating the effects of stabilizing fast pyrolysis oil (PO) with glycerol via catalytic glycerol pretreatment on upgrading via HDO using Ru/C catalyst or thermal treatment (TT). It was found that HDO decreases the molecular weight of PO. The major beneficial effect of stabilization with glycerol was reduction in molecular weight of upgraded oils. After HDO, the oil fractions of both stabilized and non-stabilized PO exhibited similar molar H/C and O/C ratios, suggesting that oxygen removal from the oil fractions was not significantly affected by stabilization.

Over the past 20 years, there have been extensive efforts reported in the literature on the HDO of biomass-derived oils using high pressure hydrogen and/or in the presence of hydrogen donor solvents such as tetralin, and conventional petroleum hydro-treating catalysts, i.e., sulfided CoMo and NiMo supported on γ-alumina (Adjaye, Katikaneni, & Bakhshi, 1996; Elliott, 2007). Xu and his group were successful in developing a novel series of sulfided CoMo catalysts supported on MgO with phosphorus as a catalyst
promoter for HDO of bio crude using phenol as a model compound in supercritical hexane at temperatures of 300 - 450°C and cold pressure of hydrogen 5.0 MPa. It was reported that both MgO-supported catalysts can significantly increase the yield of benzene and cyclohexyl-aromatics when the temperature goes higher than 350 °C. CoMoP/MgO catalyst at 450 °C led to a product consisting of 65 wt.% benzene and more than 10 wt.% cyclohexyl-compounds (Yang et al., 2009a). Supercritical fluids as bio-oil HDO solvents have drawn increasing attention due to the unique properties of supercritical fluids such as faster rates of mass and heat transfer, liquid-like density and dissolving power, gas-like diffusivity and viscosity (Baiker, 1999). Recently, sub- and super-critical ethanol (240 - 300°C) was used for HDO of pyrolysis bio-oil using HZSM-5 as a catalyst (Chen et al., 2013; Peng et al., 2009b), and a bi-functional catalyst 5%Pt/SO$_4^{2-}$/ZrO$_2$/SBA-15 catalyst (Dang et al., 2013). It was found that acidic catalysts (HZSM-5) helps esterification in supercritical ethanol to convert carboxylic acids contained in crude bio-oil into different types of esters. The results showed that higher initial hydrogen pressure could inhibit coke formation effectively. Increasing mass ratio of ethanol to bio-oil increased desired products formation and heating value and reduced coke yield.

It is thus clear that the type and composition of solvent (and the amount of solvent used in relation to the bio-oil in the HDO treatment) played an important role in the performance of the catalyst in the HDO tests. Hydrogen donor solvents such as tetralin are expensive. In this work, for the first time, hydro-treated or upgraded pyrolysis oil was used as a solvent for HDO of wood-derived pyrolysis oil in a batch reactor using a commercially obtained Ru/C catalyst. For comparison, supercritical ethanol was also tested for HDO of the same pyrolysis oil. The present research aims to examining the effects of type of solvents (hydro-treated or upgraded pyrolysis oil and anhydrous ethanol) on HDO process. The quality of upgraded oils as the possible co-feeds for co-refining is an important factor which should be considered. So, preventing or reducing of self-polymerization through upgrading process is preferred.
3.2 Material and Methods

3.2.1 Materials

Fast pyrolysis oil (PO) used for this research was obtained from Biomass Technology Group (BTG) in the Netherlands. It had a higher heating value (HHV) of 21.48 MJ/kg and a water content of 27.92 wt%. In the fast pyrolysis process, hardwood sawdust was used as the feed which was quickly heated up to 450-600 °C in the absence of air. A commercial catalyst, Ru/C, was obtained from Sigma/Aldrich. The catalyst has a Ru loading of 5 wt%, BET surface area of 780.91 m²/g, Langmuir surface area of 1042.44 m²/g, pore diameter of 33.92 Å, and was used without any pre-treatment. Pure (anhydrous) ethanol was obtained from Commercial Alcohols (density 0.7885 g/mL, and water content < 0.1 wt%). Acetone used was ACS reagent grade solvent, obtained from Sigma/Aldrich and used as received.

3.2.2 Apparatus and Experimental Procedure

For the HDO process for PO upgrading, a Parr Instrument stirred autoclave with a nominal reactor volume of 500 mL was used. This setup can be run in batch or semi-batch mode of hydrogen. The reactor was operated in batch mode in this work. Figure 3-1 presents the schematic diagram of the setup.

The experimental conditions are shown in Figure 3-1. In the first 3 replicate runs, UO1, typically 150 g PO was loaded to the reactor and Ru/C was added as the catalyst at 3.3 wt% of the feed (on wet liquid basis). These replicate runs were performed to obtain sufficient amount of upgraded oil which were then used as a solvent for next runs.
Figure 3-1: Schematic diagram of the experimental setup

Table 3-1: Experimental conditions

<table>
<thead>
<tr>
<th>No.</th>
<th>Feed (g)</th>
<th>Ru/C (g)</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO1</td>
<td>150 PO</td>
<td>5</td>
<td>300</td>
</tr>
<tr>
<td>UO1</td>
<td>150 PO</td>
<td>5</td>
<td>300</td>
</tr>
<tr>
<td>UO1</td>
<td>150 PO</td>
<td>5</td>
<td>300</td>
</tr>
<tr>
<td>UO2</td>
<td>120 HDO₁ + 30 PO</td>
<td>1</td>
<td>300</td>
</tr>
<tr>
<td>UO3</td>
<td>100 HDO₂ + 50 PO</td>
<td>1.67</td>
<td>300</td>
</tr>
<tr>
<td>UO4</td>
<td>100 HDO₃ + 50 PO</td>
<td>1.67</td>
<td>300</td>
</tr>
<tr>
<td>UO5</td>
<td>100 HDO₄ + 50 PO</td>
<td>1.67</td>
<td>300</td>
</tr>
<tr>
<td>UO6</td>
<td>100 HDO₅ + 50 PO</td>
<td>1.67</td>
<td>300</td>
</tr>
<tr>
<td>UO7</td>
<td>100 ethanol + 50 PO</td>
<td>1.67</td>
<td>300</td>
</tr>
<tr>
<td>UO8</td>
<td>50 ethanol + 100 PO</td>
<td>3.33</td>
<td>300</td>
</tr>
<tr>
<td>UO9</td>
<td>150 PO</td>
<td>5</td>
<td>350</td>
</tr>
</tbody>
</table>

HDO₁: The oil fraction (OF) obtained from the test UO1; HDO₂: The OF obtained from the test UO2; HDO₃: The OF obtained from the test UO3; HDO₄: The OF obtained from the test UO4; HDO₅: The OF obtained from the test UO5.
In UO2, 120 g upgraded oil (as a solvent), HDO1, obtained from UO1, and 30 g PO were loaded to the reactor and, Ru/C at 3.3 wt% of the PO feed (on wet liquid basis) was added to the liquid mixture. From UO3 to UO6, the amount of solvent obtained from the previous run was decreased to 100 g and amount of PO was increased to 50 g to make 150 g total feed. In UO7 and UO8, 100g ethanol+ 50g PO and 50g ethanol+ 100g PO were charged into the reactor, respectively. Experimental condition of UO9 was the same as UO1 except the temperature of UO9 was 350°C, higher than that of UO1 (300°C).

Then, the reactor was sealed and a leak test was carried out at 150 barg of hydrogen for 30 min. If no leak was detected, the hydrogen was released while displacing a part of the residual air from the inside of reactor. By using a vacuum pump the residual air was entirely removed from hydrogen supply vessel, reactor lines and reactor vessel. Then, the reactor was pressurized with hydrogen to 100 barg as the initial pressure. From run UO1 to UO8, the temperature was set at 300 °C with a ramp of approx. 10 °C/min, while for run UO9 the set temperature was 350 °C. The speed of stirrer was set at 360 rpm. The retention time of the feed, solvent and catalyst inside the reactor was 3 h including the heating time. After 3 h, the heater was turned off and the reactor was cooled to the room temperature using an ice-water bath. During the cooling process, the stirrer speed was hold on at 360 rpm. For the duration of collecting the produced gas, the stirrer was on at 180 rpm to help release any dissoluble gas from the liquid products. The gas was collected in a gas bag at room temperature for further analyzing. Then, the reactor was opened to collect the liquid product. To separate the catalyst, the liquid products were poured in centrifuge vials subject to centrifugation for 30 min at a speed of 4500 rpm. The coke products along with the used catalysts were then separated using vacuum filtration. They were washed several times with acetone until no acetone-soluble products were remained. After filtration, the filters were dried and weighted. The amount of coke formed during HDO process was obtained by subtracting the initial weight of catalyst from total solids weight, assuming no catalyst loss. For runs UO1 to UO6 and UO9, two phases were achieved after centrifugation: an organic phase (known as oil fraction; OF) and an aqueous phase (known as aqueous fraction; AF). The OF and AF phases were separated for further analysis. For runs UO7 and UO8 the aqueous and oil fractions were
unable to be separated since they were soluble in ethanol. So, OF was separated using rotary evaporator to evaporate all the solvent and water (or maybe the low boiling points components derived from HDO of PO). The amount of AF was calculated by mass balance. In all tests, the amount of coke formation was very minimal or negligible.

3.2.3 Product Characterization

Elemental composition and water content of the OF and AF were measured on a CHNS-O analyzer (Thermo Electron Corporation Flash-EA-1112 series) and a volumetric Karl-Fischer titrator (Mettler Toledo V20), respectively. Molecular weights and distribution were analyzed with a GPC (Waters 1525 HPLC/GPC pumps, Waters 2414 RI-detector, Waters 2487 UV-detector, THF eluent phase). GPC is calibrated by using polystyrene standard. The calibration curve is presented in Figure 3-2.

![Calibration curve of GPC using polystyrene standard](image)

Figure 3-2: Calibration curve of GPC using polystyrene standard.

Composition of the produced gas was analyzed by GC-TCD (Agilent Micro-GC 3000). The degree of de-oxygenation (DOD) is calculated from the following equation:

\[
DOD = \left(1 - \frac{wt\% \text{ of oxygen in product}}{wt\% \text{ of oxygen in feed}}\right) \times 100\% \tag{3.1}
\]
3.3 Results and Discussion

Elemental composition and water content of the feeds are shown in Table 3-2. Obviously the elemental compositions of UO1 and UO9 are the same as the same feed (i.e., PO) was used in both experiments. Elemental composition of the feeds for UO7 and UO8 on water free basis must be similar to that of UO1 and UO9 (i.e., PO). For the feeds in UO2-UO6, they have a higher content of carbon and hydrogen and a lower content of oxygen than that of PO, as upgraded oil from the previous run was used as a solvent in these experiments. However, by comparing elemental composition of UO2-UO6 feeds with each other, it is obvious that they almost the same and not changed, indicating that using the upgrade oil as a solvent has no significant effect on the elemental composition of the feeds.

Table 3-3 shows properties of the oil fractions (OFs) produced via HDO of UO1 to UO9 at 300 °C (or 350 °C for UO9) under 100 bar of H₂ for 3 h. The initial alcohol in feed and residual alcohol after the HDO tests in UO7 and UO8 are also shown in Table 3-3. The HDO oil fractions are relatively dry, containing 3-6 wt% water. UO1 shows the elemental composition of the OF produced via HDO of PO without using any solvent. Comparing with the original PO feed (53.11 wt% C, 6.24 wt% H and 40.65 wt% O, water free basis) the HDO treatment produced an OF product (74.25 wt% C, 8.24 wt% H and 17.52 wt% O, water free basis) with significantly increased C and H contents and lower O content. It can be seen that by using upgrade bio-oil from the previous test as solvent (UO2-UO6), the elemental composition of produced OF was changed although not significantly. However, comparing with the OF from UO1, the OFs (74-76 wt% C, 8.2-9.3 wt% H and 15.5-17.4 wt% O, water free basis) from these tests UO2-UO6 have improved qualities, e.g., higher C and H contents and lower O content, suggesting positive effects of using upgrade bio-oil from the previous test as the HDO solvent.
### Table 3-2: Properties of feeds in each experimental run

<table>
<thead>
<tr>
<th>PO, UO1, UO9</th>
<th>UO2</th>
<th>UO3</th>
<th>UO4</th>
<th>UO5</th>
<th>UO6</th>
<th>UO7</th>
<th>UO8</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Elemental composition and water content</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C (wt%)</td>
<td>38.28</td>
<td>64.60</td>
<td>61.61</td>
<td>61.84</td>
<td>60.51</td>
<td>61.16</td>
<td>47.50</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>7.60</td>
<td>8.2</td>
<td>8.10</td>
<td>8.07</td>
<td>8.33</td>
<td>8.57</td>
<td>11.22</td>
</tr>
<tr>
<td>O (wt%)</td>
<td>54.12</td>
<td>27.2</td>
<td>30.29</td>
<td>30.09</td>
<td>31.16</td>
<td>30.27</td>
<td>41.29</td>
</tr>
<tr>
<td>C (water free wt%)</td>
<td>53.11</td>
<td>70.82</td>
<td>69.79</td>
<td>69.83</td>
<td>68.31</td>
<td>69.36</td>
<td>53.12</td>
</tr>
<tr>
<td>H (water free wt%)</td>
<td>6.24</td>
<td>7.92</td>
<td>7.70</td>
<td>7.68</td>
<td>7.97</td>
<td>8.23</td>
<td>6.24</td>
</tr>
<tr>
<td>O (water free wt%)</td>
<td>40.65</td>
<td>21.26</td>
<td>22.51</td>
<td>22.49</td>
<td>23.72</td>
<td>22.41</td>
<td>40.65</td>
</tr>
<tr>
<td>H/C (water free wt%)</td>
<td>1.41</td>
<td>1.34</td>
<td>1.32</td>
<td>1.32</td>
<td>1.40</td>
<td>1.42</td>
<td>1.41</td>
</tr>
<tr>
<td>O/C (water free wt%)</td>
<td>0.57</td>
<td>0.23</td>
<td>0.24</td>
<td>0.24</td>
<td>0.26</td>
<td>0.24</td>
<td>0.57</td>
</tr>
<tr>
<td>H/C\text{eff} (water free)</td>
<td>0.26</td>
<td>0.89</td>
<td>0.84</td>
<td>0.84</td>
<td>0.88</td>
<td>0.94</td>
<td>0.26</td>
</tr>
<tr>
<td>Water (wt%)</td>
<td>27.92</td>
<td>8.78</td>
<td>11.72</td>
<td>11.44</td>
<td>11.41</td>
<td>11.82</td>
<td>9.31</td>
</tr>
</tbody>
</table>

### Alcohol content

| Initial alcohol (g/150g of feed) | - | - | - | - | - | 100.1 | 50.02 |

\( ^a \) calculated by difference

\( ^b \) \( \text{H/C}_{\text{eff}} = \text{molar H/C} - 2 \times \text{molar O/C} \). \( \text{H/C}_{\text{eff}} \) is the molar H/C of a compound after removing its whole oxygen content in the form of water. The value gives an estimate for the chemical structure of a compound. \( \text{H/C}_{\text{eff}} \) (sugars) = 0, \( \text{H/C}_{\text{eff}} \) (aromatics) = 1, \( \text{H/C}_{\text{eff}} \) (alkanes) = 2.

Very interesting, using ethanol (UO7 and UO8) as the HDO solvent has considerable effects on the elemental composition of the produced OFs (81.5-82.9 wt% C, 8.8-9.3 wt% H and 8.4-9.2 wt% O, water free basis): the carbon/hydrogen were remarkably increased and oxygen contents was greatly reduced. Similar results were reported in literature using tetraline, decalin, diesel and diesel/isopropanol as a solvent (Xu et al., 2013a). By comparing UO9 (350°C) with UO1 (300°C), it can be concluded that a higher temperature has a very positive effect on HDO process for increasing carbon and hydrogen contents and decreasing oxygen content. By comparing the OFs from UO9 (350°C, no solvent) with UO8 (300°C, ethanol solvent), it can be seen that HDO in ethanol solvent at a lower temperature achieved even better performance than the HDO without solvent at a higher temperature, in terms of oil quality and HDO efficiency. From
the Table 3-3, it is also seen that hydro-treatment tests in supercritical ethanol (UO7 – UO8) produced OFs of a much lower O/C value (0.08), compared with the OFs from other tests (with O/C molar ratio of 0.18 for UO1, 0.15-0.18 for UO2-UO6, and 0.11 for UO9). The calculated values of degree of deoxygenation are also shown in Table 3-3. Clearly, using ethanol as the HDO solvent remarkably increased DOD (77-79% for UO7 and UO8), compared with DOD values in other tests without solvent (56.9% for UO1 and 70.7% for UO9) or with upgraded oil solvent (57-62% for UO2-UO6). The obtained DOD values in this study are in the similar range as reported in the literature. Venderbosch et al. (2010) studied mild HDO using Ru/C catalyst at different temperatures (175–400 °C) and reported the degree of deoxygenation of 54 wt%. Clearly, one of the advantages of adding solvent in HDO treatment of bio-oils is to reduce the oxygen content of the bio-oils at a higher degree of deoxygenation efficiency (Venderbosch, Ardiyanti, Wildschut, Oasmaa, & Heeres, 2010; X. Xu et al., 2013). As shown by initial and residual alcohol, a negligibly small part of ethanol were consumed or lost during HDO of UO7 and UO8, which might be explained by the ethanol gasification in the process, as confirmed by the increased CH₄ production in UO7 and UO8 (shown in Figure 3-4).

Figure 3-3 is Van Krevelen Plots of the feeds and oil fractions (OFs) for all HDO experiments (UO1 ~ UO9) as listed in Table 3-1. The Figure 3-3 shows that although there is significant difference between the feeds for UO1/UO7-UO9 and UO2-UO6 in terms of elemental compositions and O/C ratio, the O/C ratios in the OFs from all tests are significantly lower than those of the corresponding feeds, but in a very narrow range of 0.08-0.18. As shown in the Figure, HDO of PO in UO4, UO5, and UO6 resulted in oil fractions with decreased O/C ratio and increased H/C ratio, which is highly desirable for bio-fuels production. In contrast, treatment of UO1-UO3 and UO7-UO9 resulted in OFs of a lower H/C. However, the reduced H/C in the OFs does not mean that the HDO treatment in these experiments were not effective. As given in Table 3-2, the effective H/C, i.e., H/Cₑff defined by (H/Cₑff = molar H/C – 2 × molar O/C) was used in this work to correct the molar ratio of H/C for a compound after removing its whole oxygen content in the form of water. The H/Cₑff value gives an estimate for the chemical structure of a compound, e.g., H/Cₑff (sugars) ≈ 0, H/Cₑff (aromatics) ≈ 1, H/Cₑff (alkanes) ≈ 2. As
such, $H/C_{\text{eff}}$ ratio is superior to $H/C$ ratio to evaluate the effectiveness of an HDO process. Compared with $H/C_{\text{eff}} = 0.26$ for the original PO, all experiments produced an OF with a greatly improved $H/C_{\text{eff}}$ value in the narrow range of 1.0 ~ 1.2, suggesting the PO of sugar-like structure were effectively upgraded to OFs of aromatic structure.

Hydro-treatment tests in supercritical ethanol (UO7, UO8) showed a better HDO effect than other tests resulting in a lower $O/C$ value ($O/C = 0.08$) in the resulted OFs, although these tests with ethanol solvent also produced OFs with significantly decreased $H/C$ (Figure 3-3) but increased $H/C_{\text{eff}}$, implying the occurring of de-hydration reactions in these tests (removing $H_2O$ from the bio-oil will decrease $O/C$ significantly, decrease $H/C$ but increase $H/C_{\text{eff}}$). Very interestingly, the hydro-treatment tests with hydro-treated oil as the solvent produced OFs with a slightly decrease in $O/C$ ratio and a marked increase in $H/C$ ratio. This result suggests that hydro-treatment of pyrolysis oil in the hydro-treated oil solvent is effective for both HDO (to reduce oxygen) and hydro-treating (to add hydrogen) of the pyrolysis oils. HDO efficiency was significantly improved at a higher temperature (UO9), decreasing $O/C$ and $H/C$ at the same time. Decreasing oxygen content is expected due to higher anticipated deoxygenation activity at higher temperature. However, lower $H/C$ is not expected since higher hydrogenation activity is also predicted at higher temperature. There are two probable reasons; changing the distribution of the organics between the water and oil fractions and forming repolymerized products with low $H/C$ ratios at a higher temperature (Wildschut et al., 2009a).

Figure 3-4 displays $H_2$ consumption and production of $CO_2$ and $CH_4$ in various experiments (UO1 - UO9). Generally, HDO tests with upgraded oil as the solvent (UO2-UO6) consumed more $H_2$, when compared with the HDO tests without solvent (UO1 and 9) or with ethanol solvent (UO7 and UO8). HDO experiments without solvent (UO1 and UO9) produced more $CO_2$ in particular at a higher temperature. The $CO_2$ production was negligibly small in the HDO tests with either upgraded oil solvent or ethanol solvent.
Table 3-3: Properties of HDO oil fractions (OFs) obtained from the experiments

<table>
<thead>
<tr>
<th></th>
<th>UO1</th>
<th>UO2</th>
<th>UO3</th>
<th>UO4</th>
<th>UO5</th>
<th>UO6</th>
<th>UO7</th>
<th>UO8</th>
<th>UO9</th>
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<tbody>
<tr>
<td><strong>Elemental composition and water content</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C (wt%)</td>
<td>71.18 ± 0.3</td>
<td>73.27</td>
<td>73.62</td>
<td>71.63</td>
<td>72.60</td>
<td>72.16</td>
<td>77.55</td>
<td>76.31</td>
<td>76.31</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>8.35 ± 0.3</td>
<td>8.35</td>
<td>8.31</td>
<td>8.69</td>
<td>9.06</td>
<td>9.38</td>
<td>8.91</td>
<td>9.40</td>
<td>9.21</td>
</tr>
<tr>
<td>O (wt%)</td>
<td>20.47±0.2</td>
<td>18.38</td>
<td>18.07</td>
<td>19.68</td>
<td>18.34</td>
<td>18.46</td>
<td>13.54</td>
<td>14.29</td>
<td>14.48</td>
</tr>
<tr>
<td>C (water free wt%)</td>
<td>74.25</td>
<td>76.02</td>
<td>76.05</td>
<td>73.97</td>
<td>75.44</td>
<td>75.15</td>
<td>82.85</td>
<td>81.53</td>
<td>78.94</td>
</tr>
<tr>
<td>H (water free wt%)</td>
<td>8.24</td>
<td>8.25</td>
<td>8.22</td>
<td>8.61</td>
<td>8.98</td>
<td>9.31</td>
<td>8.76</td>
<td>9.29</td>
<td>9.15</td>
</tr>
<tr>
<td>O (water free wt%)</td>
<td>17.52</td>
<td>15.73</td>
<td>15.74</td>
<td>17.42</td>
<td>15.58</td>
<td>15.54</td>
<td>8.38</td>
<td>9.19</td>
<td>11.91</td>
</tr>
<tr>
<td>Degree of deoxygenation (wt%)</td>
<td>56.9</td>
<td>61.30</td>
<td>61.28</td>
<td>57.15</td>
<td>61.67</td>
<td>61.77</td>
<td>79.38</td>
<td>77.39</td>
<td>70.70</td>
</tr>
<tr>
<td>H/C (water free wt%)</td>
<td>1.33</td>
<td>1.30</td>
<td>1.30</td>
<td>1.40</td>
<td>1.43</td>
<td>1.49</td>
<td>1.27</td>
<td>1.37</td>
<td>1.39</td>
</tr>
<tr>
<td>O/C (water free wt%)</td>
<td>0.18</td>
<td>0.16</td>
<td>0.16</td>
<td>0.18</td>
<td>0.15</td>
<td>0.16</td>
<td>0.08</td>
<td>0.08</td>
<td>0.11</td>
</tr>
<tr>
<td>H/C$_{eff}$ (water free)$^b$</td>
<td>0.98</td>
<td>0.99</td>
<td>0.99</td>
<td>1.04</td>
<td>1.12</td>
<td>1.18</td>
<td>1.12</td>
<td>1.20</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Residual alcohol in oil factions

<table>
<thead>
<tr>
<th></th>
<th>UO1</th>
<th>UO2</th>
<th>UO3</th>
<th>UO4</th>
<th>UO5</th>
<th>UO6</th>
<th>UO7</th>
<th>UO8</th>
<th>UO9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial alcohol in feed (g/150g of feed)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100.1</td>
<td>50.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Residual alcohol (g/150g of feed)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>96.0</td>
<td>45.58</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ calculated by difference

$^b$ $H/C_{eff} = \text{molar } H/C - 2 \times \text{molar } O/C$

The production of CO$_2$ in HDO of PO is likely due to thermal decomposition of carboxylic acids in pyrolysis oils (Venderbosch et al., 2010b; Wang et al., 2012). The content of carboxylic acid in pyrolysis oils normally varies between 1.9 to 10 wt% (Wildschut et al., 2009a). CH$_4$ was observed in all HDO tests. A reaction route to produce methane could be demethylation of phenolic derivatives (Bykova et al., 2012). Compared with other HDO conditions, HDO of PO in supercritical ethanol (UO7 and UO8) solvent produced more CH$_4$, which might be due to the decomposition of ethanol forming CH$_4$, CO and H$_2$ ($C_2H_5OH \rightarrow CH_4 + CO + H_2$) catalyzed by the Ru/C catalyst during the HDO process, evidenced by some loss of ethanol during the tests (Table 3-2).
Figure 3-3: Van Krevelan plot of feeds and HDO oil fractions from all HDO tests

Figure 3-4: H\textsubscript{2} consumption and production of CO\textsubscript{2} and CH\textsubscript{4} in all HDO experiments

Figure 3-5 shows the higher heating value (HHV) of feeds and OFs from all the tests, where HHV was calculated from Dulong’s formula using elemental composition of the feed or OF presented in : HHV=0.3383C+1.442×(H−O/8) MJ/kg. Although the heating values of the feeds varies substantially from 21 to 31 MJ/kg, the OF products from all tests have an HHV in a narrow range of 35-40 MJ/kg. Such high HHVs of upgraded pyrolysis oil were also reported by Capunitan and Capareda (2014) using Ru/C as a catalyst in HDO of pyrolysis oil at 300°C. The OFs from UO7/UO8 have the highest HHV due to their highest C and lowest O contents. It can be seen that HDO of PO using hydro-treated bio-oil as the solvent could not significantly increase the heating value of
the oil, while HDO using ethanol as the solvent remarkably increased the heating value of the oil. Therefore, using ethanol as the solvent for HDO of pyrolysis oil is a promising choice in terms of improving heating value (Xu et al., 2013b).

Figure 3-5: HHVs of the feeds and the HDO oil fractions from all HDO tests

Figure 3-6 shows the yields of OF, AF, and GF in all runs. Clearly, from Figure 3-6, the oil yields from all the HDO treatment tests ranges from 60-90 wt%, depending on the solvent used and temperature. Comparing the products yields from runs UO2 – UO6 (using hydro-treated bio-oil as the solvent in the HDO test) with those from the UO1 (without any solvent), using hydro-treated bio-oil as the solvent increased the OF yield, accompanied by decreased yields of AF and GF. When comparing the product yields results of UO7/UO8 with those of UO1, the use of supercritical ethanol solvent (300°C) in the HDO tests promoted the OF yield, but it also remarkably increased the gas yield. At the same conditions (300°C and 3 h), HDO tests with hydro-treated bio-oil as the solvent produced more OF yields and reduced GF yields than those with supercritical ethanol solvent. If comparing the results from UO9 (at 350°C without solvent) with the other experiments at 300°C with or without solvent, an increase in HDO temperature resulted in a decrease in the OF yield, but an marked increase in the GF yield, as expected due to the enhanced hydro-cracking/gasification of the reaction materials at a high temperature. An increase in HDO temperature led to a reduced OF yield has also been widely reported in the literature (Boocock, 1992; Capunitan and Capareda, 2014a;
Gagnon and Kaliaguine, 1988; Samolada et al., 1998; Venderbosch et al., 2010b; Wildschut et al., 2009a).

Figure 3-6: Yields of OF, AF and GF in all HDO tests

Figure 3-7 shows the molar mass distribution of the PO feed, hydro-treated oil from PO without any solvent and the oil fractions after HDO of the PO using hydro-treated bio-oil as a solvent at 300 °C. Clearly, the molar masses of all HDO oil fractions are lower than the PO feed after hydro-treatment at 300 °C. Generally, HDO of the PO using hydro-treated bio-oil as a solvent reduced the molecular weight of the resulted OF, while the differences in molar masses are not significant between the oil products from the UO2-UO6 runs. Thus, using hydro-treated bio-oil as the solvent for HDO of a bio-oil is not very effective for reducing the molecular weight of the bio-oil.

Molar mass distribution of the PO feed and the oil fractions from HDO of the PO using supercritical ethanol as solvent at 300 °C (UO7 and UO8) are shown in Figure 3-8. It can be seen that the molar mass of the oil was remarkably reduced by the hydro-treatment in supercritical ethanol solvent, suggesting that ethanol can be an effective solvent for reducing the molecular weight of a bio-oil by HDO. Figure 3-9 further compares the molar mass distribution of the PO feed and the oil products from HDO of the PO using hydro-treated bio-oil and ethanol as the solvent, respectively at 300 °C. The comparison clearly shows that ethanol is more effective as a solvent for HDO of bio-oils for molecular weight reduction.
Figure 3-7: Molar mass distribution of the PO feed, hydro-treated oil from PO without any solvent, and the oil fractions after HDO of the PO using hydro-treated bio-oil as solvent at 300 °C.

Figure 3-10 compares the molar mass distribution of the PO feed and the oil products from HDO of the PO without any solvent at 300 and 350 °C, respectively, and from the HDO in supercritical ethanol solvent. It can be seen that a higher temperature (350 °C) remarkably reduced molecular weight of the bio-oil via HDO, even without any solvent. By comparing the results of UO7/UO8 and UO9, it can be concluded that using ethanol as an HDO solvent in bio-oil upgrading and applying a higher HDO temperature have similar effects on reducing molar mass of the bio-oil.

Figure 3-8: Molar mass distribution of the PO feed and the oil fractions from HDO of the PO using supercritical ethanol as solvent at 300 °C.
Figure 3-9: Molar mass distribution of the PO feed and the oil products from HDO of the PO using hydro-treated bio-oil and ethanol as the solvent, respectively at 300 °C.

Figure 3-10: Comparing Molar mass distribution of the PO feed and the oil products from HDO of the PO without any solvent at 300 and 350 °C, respectively and from the HDO in supercritical ethanol solvent.
3.4 Conclusions

Catalytic hydro-treatment of pyrolysis oil was performed using Ru/C as a catalyst. The effects of different type of solvents, i.e., upgraded pyrolysis oil obtained from repetitive HDO runs and ethanol, and temperature (300 and 350°C) on pyrolysis oil upgrading were studied. Some key conclusions drawn from this study are summarized as follows:

(1) The oil yields from all the HDO treatment tests ranges from 60-90 wt%, depending on the solvent used and temperature. HDO of pyrolysis oil using hydro-treated bio-oil as the solvent increased the OF yield, accompanied by decreased yields of AF and GF. The use of supercritical ethanol solvent (300°C) in the HDO tests also promoted the OF yield, but it also remarkably increased the gas yield. At the same conditions (300°C and 3 h), HDO tests with hydro-treated bio-oil as the solvent produced more OF yields and reduced GF yields than those with supercritical ethanol solvent. An increase in HDO temperature resulted in a decrease in the OF yield, but a marked increase in the GF yield.

(2) Comparing with the original PO feed, the HDO treatment produced an OF product with significantly increased C and H contents and lower O content, although using upgrade bio-oil from the previous test as the HDO solvent, the elemental composition of produced OF was not changed significantly. Very interesting, using ethanol as the HDO solvent has considerable effects on the elemental composition of the produced OFs: the carbon/hydrogen was remarkably increased and oxygen content was greatly reduced. HDO of the pyrolysis oil in ethanol solvent at a lower temperature achieved even better performance than the HDO without solvent at a higher temperature, in terms of oil quality and HDO efficiency. Hydro-treatment tests in supercritical ethanol showed a better HDO effect than other tests resulting in a lower O/C value (O/C = 0.08) in the resulted OFs.

(3) HDO tests with upgraded oil as the solvent consumed more H₂, when compared with the HDO tests without solvent or with ethanol solvent. HDO
experiments without solvent produced more CO$_2$ in particular at a higher temperature. HDO of PO in supercritical ethanol solvent produced more CH$_4$, which might be due to the decomposition of ethanol catalyzed by the Ru/C catalyst during the HDO process, evidenced by some loss of ethanol during the tests.

(4) Although the heating values of the PO feeds varies substantially from 21 to 31 MJ/kg, the OF products from all tests have an HHV in a narrow range of 35-40 MJ/kg. HDO of PO using hydro-treated bio-oil as the solvent could not significantly increase the heating value of the oil, while HDO using ethanol as the solvent remarkably increased the heating value of the oil. Therefore, using ethanol as the solvent for HDO of pyrolysis oil is a promising choice in terms of improving heating value of the bio-oil.

(5) The molar mass of the bio-oil could be remarkably reduced by the hydro-treatment in supercritical ethanol solvent, suggesting that supercritical ethanol can be an effective solvent for reducing the molecular weight of a bio-oil by HDO, more effective than using hydro-treated bio-oil as an HDO solvent.

3.5 Acknowledgements
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3.6 References
Adjaye, J.D., Katikaneni, S.P.R., Bakhshi, N.N., 1996. Catalytic conversion of a biofuel to hydrocarbons: effect of mixtures of HZSM-5 and silica-alumina catalysts on


Chapter 4

4  Hydro-treatment of fast pyrolysis oil in supercritical ethanol using nano-structured catalysts

4.1 Introduction

Biomass has drawn considerable attention as it has a great potential to be a sustainable, renewable and clean replacement for fossil fuels for the production of energy, fuels and chemicals (Alonso et al., 2010; Bertero et al., 2012). Lignocellulosic biomass such as forestry/agricultural biomass and residues can be converted to solid, liquid and gaseous biofuel or chemicals through different technologies using biological, thermal or thermo-chemical methods (Bridgwater, 2012).

Pyrolysis oil (PO) is also called bio-oil usually obtained from fast pyrolysis of biomass – a thermochemical conversion process by rapid heating of biomass in oxygen-depleted atmosphere at 400-600°C to thermally crack the cellulose/hemi-cellulose and lignin components into vapor. Condensation of the vapor forms a viscous and water containing liquid – fast pyrolysis oil. It is a complex mixture of various organic compounds such as ketones, aldehydes, alcohols, carboxylic acids, phenols, sugar, etc. (Zhang et al., 2007). The composition of bio-oil depends on different factors such as the production condition and raw materials (Dang et al., 2012). Carboxylic acids such as acetic acid in bio-oil lead to corrosion of the vessels and lower stability (Tang et al., 2009). Aldehydes and phenols in bio-oil with unsaturated carbon bond are prone for condensation and polymerization reactions; so large molecules would form especially in presence of acids. Therefore, these reactions lead to rising of viscosity, instability, and difficulty in transportation and phase separation of bio-oil (Diebold, 2000). Thus, pyrolysis oils have many undesirable characteristics such as high viscosity, poor stability, high acidity and corrosiveness, due to their high molecular weights and high oxygen content it cannot be used directly as the engine fuel (Czernik and Bridgwater, 2004). High oxygen content of bio-oil also results in a low heating value (LHV), being only half of the fossil fuels (Oasmaa and Czernik, 1999; Wildschut et al., 2009a). In addition, bio-oil is immiscible and difficult for being co-processed with fossil fuels (Baldauf, W., Baldauf, U., Rupp, 1994; Joshi and Lawal,
Moreover, lignin-derived compounds with molecular weight between 650 and 1000 g/mol have considerable effect on bio-oil properties such as low stability, high reactivity and viscosity. They can easily react with other compounds in bio-oil such as aldehydes and ketones (Jiang and Ellis, 2010; Tang et al., 2010). Therefore, bio-oil upgrading processes are needed to overcome the undesirable properties in order to utilize the oil for fuels or chemicals.

Due to the complexity of the reactions in bio-oil upgrading processes, model compounds are usually applied for investigating the mechanisms of the process (Elliott and Hart, 2009; Mahfud et al., 2007). Several methods such as thermal/catalytic cracking (Vitolo et al., 1999), esterification (Zhang et al., 2006), steam reforming (Basagiannis and Verykios, 2007; Rioche et al., 2005), emulsification (Ikura et al., 2003) and hydro-de-oxygenation (called HDO) (Furimsky, 2000c) have been used to upgrade bio-oil. In a catalytic cracking process, it operates at atmospheric pressure and it does not need hydrogen. However, severe coke/char deposition and fast catalyst deactivation are the main problems. In a steam reforming process, bio-oil is reacted with steam over a metallic catalyst to produce hydrogen rich syngas, but coke formation and catalyst deactivation is also the major problem here. HDO is a widely used process aiming to exclude oxygen from a bio-oil at moderate temperatures and high hydrogen pressure using heterogeneous catalysts. Some conventional petroleum-refining catalysts (NiMo or CoMo) have been used for bio-oil HDO. Nevertheless, since this process requires significant amounts of hydrogen, the capital cost would be higher (Wildschut et al., 2009a).

Almost in all bio-oil upgrading methods, finding suitable catalysts is essential, as bio-oil has macromolecular compounds which can block the pores of catalysts and make them quickly deactivate (Antonakou et al., 2006a; Tang et al., 2009). Mesoporous materials such as SBA-15(Adam et al., 2006) and MCM-41(Adam et al., 2006, 2005; Antonakou et al., 2006b; Iliopoulou et al., 2007; Nilsen et al., 2007) are promising catalysts or support materials for various bio-oil upgrading processes, as these catalysts could considerably improve the composition of bio-oil, reducing the contents of oxygenated carbonyl and acid compounds, and maintain a longer catalyst lifetime (Abu Bakar and Titiloye, 2013).
SBA-15, a mesoporous silica support, has distinguished characteristics such as proper thermal stability, adaptable pore size, and an easy preparing method (Sundaramurthy et al., 2008). It has been used in bio-oil upgrading process recently. Another mesoporous silica material is MCM-41 which was initially found in 1992. It has a very high surface area (~ 1000 m²/g) and well-defined pore size (Beck et al., 1992). By incorporating of metals of Mo and Co into the mesoporous materials, the mesoporous material-supported catalysts proved to be very effective for HDO of bio-oils (Antonakou et al., 2006a). The large pore size with the strong acidity of SBA-15 or MCM-41 would lead to making promising catalysts for bio-oil upgrading to prevent the pore blocking by macromolecules (Tang et al., 2010). As such, in this study, SBA-15 and MCM-41 mesoporous materials were chosen as the support for preparation of CoMo catalysts for pyrolysis oil HDO.

Recently, supercritical fluids have been demonstrated to be effective solvents for HDO upgrading of bio-oil (Dang et al., 2013). By using supercritical fluids as reaction media for bio-oil HDO, mass and heat transfer, diffusivity and viscosity of the reaction system can be improved (Baiker, 1999; Wen et al., 2009), converting the detrimental oxygenated compounds into stable and noncorrosive ones. Peng et al. (2008, 2009a) studied upgrading of bio-oil in subcritical and supercritical ethanol using Al₂(SiO₃)₃ or HZSM-5 catalyst. It was reported that supercritical condition improved the oil quality more effectively than subcritical condition. It also found that stronger acidic HZSM-5 (Si/Al=22) catalyst can significantly improve cracking of heavy components of crude bio-oil in supercritical upgrading process. Al₂(SiO₃)₃ catalyst also can facilitate esterification reaction in supercritical condition and promote the acids conversion into different kinds of esters. Li et al. (2011a and 2011b) investigated on upgrading of low boiling fraction of bio-oil over Pt/Al₂(SiO₃)₃, Pt/C and Pt/MgO catalysts and high boiling fraction over a series of supported mono and bimetallic catalysts in supercritical methanol. Tang et al. (2009, 2010b) studied the bio-oil upgrading process in supercritical ethanol under hydrogen atmosphere using Pd/SO₄²⁻/ZrO₂/SBA-15 catalyst and also hydro-cracking of pyrolytic lignin derived from rice husk at 260 °C over Ru/ZrO₂/SBA-15 or Ru/SO₄²⁻/ZrO₂/SBA-15 catalyst in supercritical ethanol under hydrogen atmosphere. Zhang et al. (2012) studied upgrading of bio-oil over Pt/SO₄²⁻/ZrO₂/SBA-15
in supercritical methanol/ethanol under a hydrogen atmosphere, showing that supercritical ethanol performed better than supercritical methanol in the upgrading process since it had a longer alkyl chain that can dissolve higher molecular weight products and led to less coke formation. In addition, ethanol is a renewable solvent which can be easily produced from biomass via fermentation, which also can be used as a gasoline additive (Chen et al., 2013). The critical pressure and temperature of ethanol are 6.148 MPa and 240.75 °C, which are lower than those of water and methanol. From the author’s own research work as described in the previous chapter, supercritical ethanol demonstrated to be very effective for HDO upgrading of pyrolysis in terms of HDO efficiency. As such, supercritical ethanol was used as the HDO solvent in this study for pyrolysis oil upgrading.

In this research supercritical ethanol under hydrogen atmosphere was used for HDO upgrading of fast pyrolysis bio-oil into advanced drop-in bio-fuels over some nano-structured catalyst at two different temperatures, 300 and 350 °C. The commercial Ru/C catalyst proved to be highly effective in bio-oil HDO though, it is extremely expensive and difficult for regeneration, so it is not a viable catalyst for bio-oil upgrading on a large scale. The main goals of this research was to explore inexpensive CoMo-based catalysts supported on nano-structured supports materials, i.e., SBA-15 and MCM-41, and then investigate their performance in the HDO upgrading process. To compare the effectiveness of those new supports, conventional supports such as Al₂O₃, activated carbon (pellet and powder form) and HZSM-5 were also studied. Ru/C, a commercial catalyst, was tested as a bench mark in this work since it is known to be active in hydrogenation and HDO process (Elliott et al., 2004; Gagnon and Kaliaguine, 1988). All the CoMo-based catalysts were prepared using successive wetness impregnation method. The produced catalysts were characterized by means of various instrumental techniques such as the Brunauer–Emmett–Teller (BET) surface area measuring technique, X-ray diffraction (XRD), and field emission scanning electron microscopy (FESEM). Coke deposition was characterized by thermogravimetric analysis (TGA). The upgraded oil products obtained were analyzed for elemental composition, water content and molecular weight distribution.
4.2 Experimental

4.2.1 Materials
Cobalt (II) nitrate hexahydrate, ammonium molybdate tetra-hydrate, Tetraethyl orthosilicate (TEOS), ruthenium on carbon (Ru/C; Ru loading: 5 wt% Ru loading, BET surface area of 780.91 m$^2$/g, pore diameter of 33.92 Å), hexadecyltrimethylammonium bromide (CTAB), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEG-PPG-PEG; Pluronic® (P-123) with an average molecular weight of ~5800), were all purchased from Sigma–Aldrich Inc, USA. Activated carbon (0.8 mm pellets) and powder were purchased from Alfa Aesar, USA. HZSM-5 (SiO$_2$/Al$_2$O$_3$=38) was purchased from China. γ-Al$_2$O$_3$ was purchased from Inframat Advance Material, USA. Hardwood sawdust fast pyrolysis oil (PO; water content of 20.99 wt%, oxygen content of 36.40 wt%, and a heating value of 24.56 MJ/kg (on dry basis)) was obtained from Biomass Technology Group (BTG), Netherlands. All of the chemicals were used as received without further purification. Pure (anhydrous) ethanol was obtained from Commercial Alcohols (density 0.7885 g/mL, and water content < 0.1 wt%). Acetone used was ACS reagent grade solvent, obtained from Sigma/Aldrich and used as received.

4.2.2 Preparation of mesoporous materials as supports and supported catalysts
The common method of synthesizing SBA-15 as described below was adopted (Kazemian et al., 2012; Zhao et al., 1998). A solution of 3g pluronic surfactant (P123) and 200 mL of 2 M HCl was first prepared. This solution was stirred and heated for 3 h till the surfactant was dissolved in the solution and a homogenous solution was obtained. In the meantime, a solution of 22.5 mL of distilled water and 7.75 g of TEOS was made and added dropwise to the former solution and stirring was kept for about 2 h. Then, the final solution was transferred into a Teflon reactor and aged at 35 °C for 24 h. Afterward, the temperature was raised to 100°C for 24 hours to promote crystallization. Finally, the resulting product was filtered, washed with distilled water, dried and followed by calcination at 500 °C for 5 h.
A synthetic procedure of MCM-41 was as follows: first a solution of NH$_4$OH 25 wt% and deionized water was made; then specific amount of CTAB was added to the solution. The solution was stirred and heated until it turned into homogenous. Afterward, TEOS was added dropwise to the final solution. It was stirred and heated at 40 °C for more 2 h. Finally, the solid product was filtered, washed with sufficient deionized water, dried at room temperature and calcined at 550 °C for 4 h (Cai et al., 1999).

CoMo/SBA-15 (Nava et al., 2009a), CoMo/MCM-41 (Turaga and Song, 2003), CoMo/γ-Al$_2$O$_3$ (Pérez-martínez et al., 2010), CoMo/HZSM-5 (Botas et al., 2012), CoMo/C-Pellet, and CoMo/C-Powder (de la Puente et al., 1998; Ferrari et al., 2002) were prepared by successive impregnation method using aqueous solutions of ammonium molybdate tetra-hydrate ((NH$_4$)$_6$Mo$_7$O$_24$), followed by drying, calcining, and loading of the second metal – Co (using cobalt nitrate hexa-hydrate (CoN$_2$O$_6$.6H$_2$O) as the Co precursor). In each catalyst, the metal loading was fixed at Co 5 wt% and Mo 10 wt% of the catalyst support. A typical impregnation method is described here: The calcined supports were impregnated using aqueous solution of the metal precursor. The mixture was stirred overnight to allow the salt precursor transport into the pores of the supports. Then, water was removed using a rotary evaporator. The metals loaded CoMo/SBA-15, CoMo/MCM-41, CoMo/γ-Al$_2$O$_3$, and CoMo/HZSM-5 are dried at 110°C, 60°C, 120°C and 110°C, respectively, and calcined in air at 500°C for 3h, 500°C for 4h, 500°C for 4h, and 550°C for 4 h, respectively. The metals loaded CoMo/C-Pellet and CoMo/C-Powder were dried at 130°C for 12 h and calcined in nitrogen stream at 400°C for 3h.

In this study, the spent CoMo/MCM-41 catalyst after 300°C HDO test was also regenerated at 600 °C in air for 2h (to burn out the deposited coke). The regenerated CoMo/MCM-41 catalyst is designated as CoMo/MCM-41-reg to distinguish it from the fresh catalyst of CoMo/MCM-41.

4.2.3 Characterization of catalysts and products

Small angle x-ray diffraction analysis was applied to identify the crystalline phase formation and crystalline size of MCM-41 and SBA-15 supports on a D8 Advance diffractometer of the Bruker Company, equipped with copper X-Ray tube coupled with a
Göbel mirror, according to the step-scanning procedure (step size of 0.01 deg and a time/step of 5 s) and using Cu Kα (λ = 1.5418 Å) over the 2θ range of 0.5° to 8°. X-ray powder diffraction (powder XRD) was used to define the phase formation and determination of crystalline size for the CoMo-based catalysts supported on SBA-15, MCM-41, γ-Al₂O₃, HZSM-5, C-Pellet, C-Powder, and Ru/C. The powder XRD was conducted on an X-ray powder diffractometer (Rigaku-MiniFlex; Woodlands, USA) using Cu Kα over the 2θ range of 5° to 80° with a step of 0.02°. Field emission scanning electron microscope (FE-SEM; Hitachi S-4500) equipped with a Quartz XOne EDX system and transmission electron microscope (Philips CM 10) were used to investigate the morphology, structure, size distribution, and particle size for the as-synthesized catalysts. Using a BET surface analyzer (Micrometrics ASAP 2010), the surface area and porosity of the catalyst supports and catalyst samples were measured using N₂ isothermal adsorption at 77 K. In a typical run, a specific amount of the sample (approx. 50–100 mg) was placed into the BET sample tube and then degassed under vacuum (10–5 Torr) at 125 °C. The BET model was carried out to calculate the specific surface area of the samples. The carbon/coke/solid residue deposition on the spent supported CoMo-based catalysts was measured by thermogravimetric analysis (TGA) on a TGA instrument (TGA 1000i, Instrument Specialists Inc, USA), where the sample was heated from 40 to 800 °C at a heating rate of 10 °C/min under 20.0 ml/min air flow.

The original PO feed and the oil/aqueous fractions from the HDO experiments were analyzed for their elemental composition, water contents and Molecular weight distribution, on a CHNS-O analyzer (Thermo Electron Corporation Flash-EA-1112 series), a volumetric Karl-Fischer titrator (Mettler Toledo V20), and a GPC equipment (Waters 1525 HPLC/GPC pumps, Waters 2414 RI-detector, Waters 2487 UV-detector), respectively. GPC is calibrated by using polystyrene standard. The calibration curve is presented in Figure 4-1.
Gas composition analysis was performed with GC-TCD (Agilent Micro-GC 3000). The GC system used in this work enabled analysis of gas species up to C₃, including O₂, N₂, H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₈, C₃H₆.

4.2.4 Bio-oil HDO experimental procedure
The bio-oil HDO experiments were carried out in a stirred autoclave reactor (Parr Instrument Company) with a nominal internal volume of 500 mL. The reactor system is illustrated in Figure 4-2. The experimental conditions (catalyst, feed composition and temperature) are shown in Table 4-1. In each run, typically 50 g PO and 100 g anhydrous ethanol as the solvent were charged to the reactor and, a catalyst was loaded (3.3 wt% of the wet liquid bio-oil feed). The reactor was sealed and a leak test was performed at 10 MPa of hydrogen for 30 min. If no leak was detected, the hydrogen was vented while taking out a part of remaining air from the inside of reactor.

Then, by using a vacuum pump the residual air was completely removed from lines, supply vessel, and inside of the reactor. Afterward, the reactor was pressurized with hydrogen at 5 MPa as the initial pressure. The reactor was then heated up to the specified temperature (300 °C or 350 °C) with a ramp of 11 °C/min under continuous at 360 rpm stirring. All catalysts were tested at 300°C, and a selected set of catalysts including CoMo/MCM-41, CoMo/γ-Al₂O₃, CoMo/C-Powder, and Ru/C were also tested at a higher temperature (350°C). The retention time of the feed, solvent and catalyst inside the
reactor was fixed at 3 h including the heating time for all tests. After 3 h, the heating process was terminated and the reactor was cooled down to room temperature using an ice-water bath. During the cooling process, the stirring speed was remained at 360 rpm. To allow any dissolved gas release from the liquid products after reaction, the stirrer speed was kept on 180 rpm during the produced gas collection. The produced gas was collected in a gas bag at room temperature for GC-TCD analysis.

After collecting the produced gas products, the reactor was opened. The liquid products along with catalyst/coke were transferred in centrifuge vials and went through centrifugation for 30 min at a speed of 4500 rpm to separate the catalyst particles with deposited coke. With all catalysts except Ru/C, two types of oil phase were obtained: an ethanol/water soluble oil phase (known as light oil, LO) and an ethanol insoluble but acetone soluble oil phase (known as heavy oil, HO). LO and HO were obtained by rotary evaporation of ethanol/water and acetone, respectively. With Ru/C catalyst, only one oil phase, LO, was obtained. The amount of aqueous products (i.e., aqueous fraction, AF) was calculated by mass balance. The solid products (coke) along with the spent catalysts were separated using vacuum filtration. They were washed several times with acetone until no acetone-soluble products were remained. After filtration, the filters were dried and weighted. The amount of coke formed during HDO process was obtained by subtracting the initial weight of catalyst from total solids weight, assuming no catalyst loss.
4.3 Results and Discussion

4.3.1 Characterization of catalyst supports

The fresh SBA-15 and MCM-41 supports were characterized extensively for their phase formation and crystalline size, morphology, structure, size distribution, particle size and textual properties (i.e., BET surface area, pore volume, pore diameter), since these properties are believed to be critical for defining the catalytic activities.

The phase formations of SBA-15 and MCM-41 supports were studied by the low angle XRD technique. Typical small angle XRD patterns of the synthesized samples are shown in Figure 4-3, which confirm successful synthesis of these supports. The small angle XRD patterns of SBA-15 supports (Figure 4-3(A)) represents three well-resolved typical diffraction peaks which are associated with a well-known bi-dimensional p6mm hexagonal symmetry of SBA-15 materials: one high-intensity peak at about $2\theta = 1.0^\circ$ and two low-intensity peaks at about $2\theta = 1.7^\circ$ and $2.0^\circ$ corresponding to $(1 1 0)$ and $(2 0 0)$ reflections, respectively. Figure 4-3(B) presents well-resolved hexagonal XRD patterns of MCM-41. There is a strong peak at $2.55^\circ$ and two weak peaks at $4.41^\circ$ and
5.09° which are corresponded to (100), (110), and (200), respectively (Cai et al., 2001; Huirache-Acuña et al., 2009; Loricera et al., 2011; Peña et al., 2014a; Zhao et al., 1998).

Table 4-1: Experimental conditions

<table>
<thead>
<tr>
<th>No.</th>
<th>Catalyst</th>
<th>Feed (g)</th>
<th>Temp (°C)</th>
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<tbody>
<tr>
<td>1</td>
<td>CoMo/SBA-15</td>
<td>100 ethanol + 50 PO</td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td>CoMo/MCM-41</td>
<td>100 ethanol + 50 PO</td>
<td>300</td>
</tr>
<tr>
<td>3</td>
<td>CoMo/γ-Al₂O₃</td>
<td>100 ethanol + 50 PO</td>
<td>300</td>
</tr>
<tr>
<td>4</td>
<td>CoMo/HZSM-5</td>
<td>100 ethanol + 50 PO</td>
<td>300</td>
</tr>
<tr>
<td>5</td>
<td>CoMo/C-Pellet</td>
<td>100 ethanol + 50 PO</td>
<td>300</td>
</tr>
<tr>
<td>6</td>
<td>CoMo/C-Powder</td>
<td>100 ethanol + 50 PO</td>
<td>300</td>
</tr>
<tr>
<td>7</td>
<td>Ru/C</td>
<td>100 ethanol + 50 PO</td>
<td>300</td>
</tr>
<tr>
<td>8</td>
<td>CoMo/MCM-41</td>
<td>100 ethanol + 50 PO</td>
<td>350</td>
</tr>
<tr>
<td>9</td>
<td>CoMo/γ-Al₂O₃</td>
<td>100 ethanol + 50 PO</td>
<td>350</td>
</tr>
<tr>
<td>10</td>
<td>CoMo/C-Powder</td>
<td>100 ethanol + 50 PO</td>
<td>350</td>
</tr>
<tr>
<td>11</td>
<td>Ru/C</td>
<td>100 ethanol + 50 PO</td>
<td>350</td>
</tr>
</tbody>
</table>

The FESEM images of the calcined SBA-15 are illustrated in Figure 4-4(A). These micrographs show the surface microstructures with different magnifications. Figure 4-4(A) reveals that the synthesized SBA-15 sample consists of many rope-like domains with relatively uniform sizes, which are aggregated into wheat-like macrostructures. The morphology of synthesized SBA-15 is in a good agreement with the literature (Almeida and Airoldi, 2008; Kazemian et al., 2012; Lestari et al., 2009). Figure 4-4(B) shows the representative FESEM images of the single crystal of MCM-41. Perfect hexagonal single crystal of MCM-41 without any intergrowth and twinned aggregation can be seen. It can be clearly seen that the nanoparticles stack compactly. The morphological features of the synthesized mesoporous MCM-41 materials in our study are similar to that reported in the literature (Cai et al., 2001; Yu et al., 2009).
comparing the FESEM images of MCM-41 with SBA-15, it can be concluded that MCM-41 has a smaller size.

![Figure 4-3: Low angle XRD pattern of SBA-15(A) and MCM-41 (B) powders calcined in air at 500 °C and 550 °C at 5 °C/minute, respectively.](image)

The results of the textural properties of the in-house prepared supported catalysts (and 5wt%Co10wt%Mo, or simply CoMo) and the respective support materials are presented in Table 4-2. Compared with the supported metal oxide(s) catalysts, each support has the highest surface area and pore volume. After impregnation of cobalt and molybdenum metal oxides into a support, both its surface area and pore volume were greatly reduced due to plugging of some pores by the metal compound(s), particularly the micro-pores. However, pore sizes of SBA-15, MCM-41, and HZSM-5 supports were found to increase after the impregnation process while the pore size of γ-Al₂O₃ support was reduced after metal impregnation. However, pore size of carbon-based catalysts is almost the same as the support after metal impregnation. Among all the supported metal oxide catalysts, CoMo/C-Powder has the highest surface area (397 m²/g) with a small pore size of 20 Å, and CoMo/γ-Al₂O₃ has the least surface area (62 m²/g) with a very large pore size of 109 Å. Ru/C has a much higher surface area (781 m²/g) than all other supported metal oxide catalysts as prepared in this study. All the support materials and the supported metal oxide catalysts have an average pore size in the range of 20-500 Å, thus they are all mesoporous materials.
4.3.2 Products yields

Figure 4-5 shows the yields of the produced LO, HO, AF, GF, and solid residue (or coke) from HDO of the PO with different catalysts mostly at 300°C (or at 350 °C for several experiments as specified in the Figure 4-5). The highest oil yield obtained was with Ru/C catalyst at both temperatures (66.6 wt% at 300 °C and 61.0 wt% at 350 °C) with the lowest and negligible coke formation (<1 wt%). Different from the performance of other catalysts that produced approx. 8-20 wt% HO in the process, as shown in the Figure 4-5, the Ru/C catalyst generated no HO fraction at both temperatures. However, the use of all catalysts produced almost similar yields of total oil products (HO+LO) as the Ru/C catalyst did. The total oil yield in all tests (although with different catalysts and temperatures) varies in a narrow range of 55-65 wt%. Such range of oil yield is in a good agreement with that reported in the literature (Capunitan and Capareda, 2014b; Chen et al., 2013; Dang et al., 2012; Elkasabi et al., 2014; Wildschut et al., 2009b). Among all the in-house prepared catalysts (other than the commercial Ru/C catalyst), CoMo/MCM-41 produced the highest oil fraction OF (= LO + HO) yield at both temperatures (61.9 wt% at 300 °C and 57.8wt% at 350 °C), better than CoMo/SBA-15 and other catalysts such as CoMo/γ-Al₂O₃, CoMo/HZSM-5, CoMo/C-Pellet and CoMo/C-Powder. As clearly shown in the Figure 4-5, at 300 °C CoMo/γ-Al₂O₃ and CoMo/HZSM-5 produced the highest HO (~ 20 wt%) and coke (~ 10 wt%) yields, respectively. The high coke yield from the test with CoMo/HZSM-5 catalyst is likely due to the strong acidity of the catalyst support that catalyze the condensation/polymerization reactions responsible for the coke formation in bio-oil HDO process (Nava et al., 2009a). As shown in the Figure 4-5, a higher hydro-treatment temperature (350 °C) remarkably increased the gas, coke and LO yields, accompanied by reducing the HO and AF yields, suggesting that a higher temperature promotes the gasification/hydro-cracking reactions (leading to more gas formation) and conversion of HO into LO and coke.
Figure 4-4: FESEM micrographs of calcined SBA-15 (A) and MCM-41 (B) in three different magnifications.
Table 4-2: Textural properties of synthesized catalysts

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample Name</th>
<th>BET Surface Area (m²/g)</th>
<th>Micropore volume (cm³/g)</th>
<th>Pore Diameter Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MCM-41</td>
<td>1176</td>
<td>0.402</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td>5%Co10%Mo/MCM-41</td>
<td>140</td>
<td>0.005</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>SBA-15</td>
<td>839</td>
<td>0.054</td>
<td>49</td>
</tr>
<tr>
<td>4</td>
<td>5%Co10%Mo/SBA-15</td>
<td>178</td>
<td>0.01</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>HZSM-5 a</td>
<td>373</td>
<td>0.126</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>5%Co10%Mo/HZSM-5</td>
<td>100</td>
<td>0.041</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>γ-Al₂O₃ b</td>
<td>169</td>
<td>0.006</td>
<td>127</td>
</tr>
<tr>
<td>8</td>
<td>5%Co10%Mo/γ-Al₂O₃</td>
<td>62</td>
<td>0.0004</td>
<td>109</td>
</tr>
<tr>
<td>9</td>
<td>Activated Carbon-Pellet c</td>
<td>1342</td>
<td>0.358</td>
<td>19</td>
</tr>
<tr>
<td>10</td>
<td>5%Co10%Mo/C-Pellet</td>
<td>397</td>
<td>0.101</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>Activated Carbon-Powder c</td>
<td>1448</td>
<td>0.393</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>5%Co10%Mo/C-Powder</td>
<td>397</td>
<td>0.101</td>
<td>20</td>
</tr>
<tr>
<td>13</td>
<td>Ru/C d</td>
<td>781</td>
<td>0.211</td>
<td>34</td>
</tr>
</tbody>
</table>

 a From China, b Supplied by Inframat Advance Material, c Supplied by Alfa Aesar, d Supplied by sigma-Aldrich.

Although the commercial Ru/C catalyst was also demonstrated to be highly effective in bio-oil HDO, it is extremely expensive and difficult for regeneration, not viable for large scale operation. Thus, the main goals of this research were to explore inexpensive CoMo-based catalysts supported on nano-structured supports materials, i.e., SBA-15 and MCM-41. The above results demonstrated that the CoMo/MCM-41 catalyst produced high oil fraction OF (= LO + HO) yield at both temperatures comparable to those of Ru/C. It shall be noted that when comparing fresh and regenerated CoMo/MCM-41, it is obvious that the oil yields from both tests are nearly the same and the performance of the regenerated CoMo/MCM-41 catalyst is as good as the fresh one. Therefore, the CoMo/MCM-41
catalyst was chosen as the catalyst of the most interest in this work, and more investigation and characterization work were carried out on this catalyst.

![Figure 4-5: Yields of LO, HO, AF, GF and coke.](image)

4.3.3 Elemental composition of the upgraded oil products

It is noticeable that MCM-41 and SBA-15 were tested at 300 °C, 50 bar for 3h in the HDO process and just heavy oil was obtained. It is shown that using support is not effective and using cobalt and molybdenum as metal are necessary. Properties of LO and HO oil fractions from the 300 °C experiments (elemental composition, water content, heating value) are shown in Table 4-3. By comparing elemental composition of PO feed (56.2 wt% C; 7.4 wt% H and 36.4 wt% O, water-free basis) with obtained LO’s (70-73 wt% C; 7.4-8.4 wt% H and 20-22 wt% O, water-free basis), it can be seen that the HDO treatment produced LO products of increased carbon and hydrogen contents and decreased oxygen content. However, by comparing elemental composition of obtained LO from different catalysts, it is obvious that they almost the same and there is no significant difference between them, in particular C and O contents. Elemental compositions of LO using fresh and regenerated CoMo/MCM-41 catalyst are also in Table 4-3. Performance of fresh and regenerated catalyst was almost the same, although it appears that the fresh catalyst reduced the oxygen content slightly more than the
regenerated one. Table 4-3 shows that heating value of the LO was improved to 31-33 MJ/kg from approx. 25 MJ/kg (for the PO) during the HDO upgrading. Zhang et al. (2012) studied the upgrading of bio-oil from fast pyrolysis of Pinus sylvestris L. over Pt/\(\text{SO}_4^2/\text{ZrO}_2/\text{SBA}-15\) under hydrogen atmosphere in supercritical ethanol and reported that the heating value of upgraded oil was increased from 20.8 to 29.2 MJ/kg. As such, the performance of all catalysts in this work is better than the above literature result.

Elemental composition, water content and heating value of HO from the HDO experiments at 300 °C and 5 MPa H\(_2\) are also shown in Table 4-3. Similarly as those of LO discussed above, the carbon content and heating value of the HO were greatly increased while markedly reduced its oxygen content, compared with those of the PO feed. All the catalysts performed very similarly, except the CoMo/MCM-41-reg which resulted in an HO of a much lower H/C (0.81) and smaller HHV (29.9 MJ/kg), compared with H/C of ~ 1.1 and HHV of ~ 32-36 MJ/kg for the HOs with the fresh CoMo/MCM-41 and other catalysts.

Table 4-4 shows the elemental composition of LO and HO at 350 °C. Compared with the 300°C LO’s as presented in previous Table 4-3 (70-73 wt% C; 7.4-8.4 wt% H and 20-22 wt% O, water-free basis), it can be seen that the HDO treatment at a higher temperature (350°C) produced LO products of further increased carbon and hydrogen contents and further decreased oxygen content (73-75 wt% C; 8.6-9.1 wt% H and 16-18 wt% O, water-free basis). It is thus concluded that a higher temperature has a positive effect on the HDO process, as commonly reported in literature (Wildschut et al., 2009b). Hydro-treatment at a higher temperature in supercritical ethanol also led to LO products of increased H/C ratio (1.4-1.5) and reduced O/C ratio (0.16-0.19) at 350°C, compared with those an H/C of 1.3-1.4 and a O/C of 0.21-0.24 for the LO from the 300°C tests. A higher process temperature has a positive effect on heating value HHV, increased from 31-33 MJ/kg (300°C) to 34-35 MJ/kg (350°C). These results are in line with those reported in literature (Capunitan and Capareda, 2014b). Similarly as observed at 300°C (Table 4-3), the performance of the in-house prepared catalysts tested at 350°C (CoMo/C-Powder, CoMo/MCM-41 and CoMo/\(\gamma\)-Al\(_2\)O\(_3\)) is very similar to that of the commercial Ru/C catalyst at the same temperature.
Table 4-3: Properties of LO and HO oil fractions from the 300 °C experiments

<table>
<thead>
<tr>
<th></th>
<th>PO</th>
<th>CoMo/ SBA-15</th>
<th>CoMo/ γ-Al2O3</th>
<th>CoMo/ MCM-41</th>
<th>CoMo/ MCM-41-reg</th>
<th>CoMo/ HZSM-5</th>
<th>CoMo/C- Pellet</th>
<th>CoMo/C- Powder</th>
<th>Ru/C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Light oil (LO)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C (wt%)</td>
<td>44.41</td>
<td>70.61</td>
<td>71.01</td>
<td>68.74</td>
<td>66.23</td>
<td>69.68</td>
<td>70.14</td>
<td>70.16</td>
<td>64.48</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>8.17</td>
<td>7.49</td>
<td>8.09</td>
<td>8.15</td>
<td>7.58</td>
<td>8.02</td>
<td>7.56</td>
<td>7.91</td>
<td>6.62</td>
</tr>
<tr>
<td>O (wt%)</td>
<td>47.42</td>
<td>21.45</td>
<td>20.89</td>
<td>23.11</td>
<td>26.19</td>
<td>22.30</td>
<td>22.21</td>
<td>21.93</td>
<td>26.89</td>
</tr>
<tr>
<td>C (water free wt%)</td>
<td>56.21</td>
<td>71.40</td>
<td>71.40</td>
<td>70.40</td>
<td>70.40</td>
<td>70.40</td>
<td>70.40</td>
<td>70.40</td>
<td></td>
</tr>
<tr>
<td>H (water free wt%)</td>
<td>7.38</td>
<td>7.90</td>
<td>8.08</td>
<td>8.08</td>
<td>7.37</td>
<td>7.99</td>
<td>7.54</td>
<td>7.90</td>
<td></td>
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<tr>
<td>O (water free wt%)</td>
<td>36.40</td>
<td>20.70</td>
<td>20.56</td>
<td>21.52</td>
<td>22.49</td>
<td>21.71</td>
<td>20.07</td>
<td>21.53</td>
<td></td>
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<tr>
<td>H/C (water free wt%)</td>
<td>1.58</td>
<td>1.33</td>
<td>1.26</td>
<td>1.38</td>
<td>1.26</td>
<td>1.36</td>
<td>1.25</td>
<td>1.34</td>
<td>1.41</td>
</tr>
<tr>
<td>O/C (water free wt%)</td>
<td>0.49</td>
<td>0.22</td>
<td>0.22</td>
<td>0.23</td>
<td>0.24</td>
<td>0.23</td>
<td>0.21</td>
<td>0.23</td>
<td>0.22</td>
</tr>
<tr>
<td>H/C eff (water free)</td>
<td>0.61</td>
<td>0.89</td>
<td>0.93</td>
<td>0.92</td>
<td>0.78</td>
<td>0.9</td>
<td>0.83</td>
<td>0.88</td>
<td>0.98</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>24.56</td>
<td>32.31</td>
<td>32.56</td>
<td>32.10</td>
<td>30.97</td>
<td>31.93</td>
<td>32.24</td>
<td>31.92</td>
<td>32.85</td>
</tr>
<tr>
<td>Water (wt%)</td>
<td>20.99</td>
<td>1.11</td>
<td>0.54</td>
<td>2.35</td>
<td>5.58</td>
<td>0.87</td>
<td>3.11</td>
<td>0.59</td>
<td>9.28</td>
</tr>
</tbody>
</table>

|               |            |              |               |              |                |              |               |                |      |
| **Heavy oil (HO)** |           |              |               |              |                |              |               |                |      |
| C (wt%)       | 44.41      | 75.51        | 77.41         | 73.52        | 65.02          | 81.15        | 73.93         | 75.37          |      |
| H (wt%)       | 8.17       | 7.22         | 7.36          | 7.28         | 5.86           | 7.30         | 6.66          | 6.98           |      |
| O (wt%)       | 47.42      | 17.27        | 15.22         | 19.20        | 29.12          | 11.56        | 19.40         | 17.65          |      |
| C (water free wt%) | 56.21      | 75.93        | 78.28         | 74.20        | 74.20          | 82.09        | 74.28         | 75.77          |      |
| H (water free wt%) | 7.38       | 7.19         | 7.32          | 7.24         | 5.06           | 7.25         | 6.64          | 6.96           |      |
| O (water free wt%) | 36.40      | 16.88        | 14.40         | 18.56        | 19.99          | 10.66        | 19.08         | 17.27          |      |
| H/C (water free wt%) | 1.58       | 1.14         | 1.12          | 1.17         | 0.81           | 1.06         | 1.07          | 1.10           |      |
| O/C (water free wt%) | 0.49       | 0.17         | 0.14          | 0.19         | 0.2            | 0.1          | 0.19          | 0.17           |      |
| H/C eff (water free) | 0.61       | 0.80         | 0.85          | 0.80         | 0.41           | 0.87         | 0.69          | 0.76           |      |
| HHV (MJ/kg)   | 24.56      | 33.38        | 34.65         | 32.65        | 29.89          | 36.30        | 31.82         | 32.96          |      |
| Water (wt%)   | 20.99      | 0.55         | 1.11          | 0.91         | 13.25          | 1.15         | 0.46          | 0.53           |      |

*a* calculated by difference

*b* H/C eff = molar H/C – 2 × molar O/C

*c* HHV was calculated from Dulong’s formula using elemental composition of the feed or oil:

\[
HHV = 0.3383C + 1.442\times(\text{H-O}/8) \text{ MJ/kg}
\]

Table 4-4 also presents the elemental composition, water content and heating value of HO fractions from HDO tests at 350 °C and 5 MPa H\(_2\). Similarly as those of LO discussed above, the carbon content and heating value of the HO from the 350 °C tests were greatly increased while its oxygen content was markedly reduced, compared with those of the PO feed. All the catalysts performed similarly. HOs with very low O/C ratio <0.1 and very high HHV (36-37 MJ/kg) were obtained by HDO treatment of the pyrolysis oil at 350 °C and 5 MPa H\(_2\).
Table 4-4: Properties of LO and HO oil fractions from the 350 °C experiments

<table>
<thead>
<tr>
<th></th>
<th>Light oil (LO)</th>
<th>Heavy oil (HO)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CoMo/</td>
<td>CoMo/</td>
</tr>
<tr>
<td></td>
<td>C-Powder</td>
<td>MCM-41</td>
</tr>
<tr>
<td>C (wt%)</td>
<td>44.41</td>
<td>73.15</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>8.17</td>
<td>8.61</td>
</tr>
<tr>
<td>O (wt%)</td>
<td>47.42</td>
<td>18.24</td>
</tr>
<tr>
<td>C (water free wt%)</td>
<td>56.21</td>
<td>73.23</td>
</tr>
<tr>
<td>H (water free wt%)</td>
<td>7.38</td>
<td>8.65</td>
</tr>
<tr>
<td>O (water free wt%)</td>
<td>36.40</td>
<td>18.16</td>
</tr>
<tr>
<td>C/H (water free wt%)</td>
<td>1.58</td>
<td>1.41</td>
</tr>
<tr>
<td>O/C (water free wt%)</td>
<td>0.49</td>
<td>0.19</td>
</tr>
<tr>
<td>H/C eff (water free)</td>
<td>0.61</td>
<td>1.04</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>24.56</td>
<td>34.17</td>
</tr>
<tr>
<td>Water (wt%)</td>
<td>20.99</td>
<td>1.11</td>
</tr>
</tbody>
</table>

- a calculated by difference
- b $H/C_{eff} = \text{molar } H/C - 2 \times \text{molar } O/C$
- c HHV was calculated from Dulong’s formula using elemental composition of the feed or oil: HHV=0.3383C+1.442×(H-O/8) MJ/kg

Figure 4-6 shows the Van Krevelen plot of the PO feed, LO and HO fractions obtained from HDO of the PO at 300 °C and 5MPa H₂. Generally, the LOs have a significantly higher H/C ratio than the HOs, suggesting a higher aliphatic character. The O/C ratio for the LOs is slightly higher than that for the HOs, indicating that LOs have more oxygenates compounds than HOs (Wildschut et al., 2010, 2009a). As clearly shown, LO obtained with Ru/C has the highest H/C ratio, but similar O/C ratio as those with other catalysts. No HO fraction is obtained for Ru/C. It can be seen that all LOs have a much higher H/C ratio but nearly similar O/C ratio than those of HOs. The oil products (HO and LO) from the pyrolysis oil HDO process with all catalysts have a remarkably reduced O/C ratio, suggesting good HDO efficiencies for all catalysts. Among all the catalysts in-house prepared, the CoMo/MCM-41 catalyst produced HO and LO of the highest H/C, although of a similar O/C ratio. By comparing fresh and regenerated CoMo/MCM-41, it is clear that LO and HO obtained with the regenerated one have almost the same O/C ratios but lower H/C ratios. A higher H/C ratio may be related to a higher hydrogenation activity for the catalyst. Hence, the hydrogenation activity of the catalyst is decreased after catalyst regeneration (Wildschut et al., 2010).
Figure 4-6: Van Krevelen plot of the feed, LO and HO fractions from HDO of the pyrolysis oil at 300 °C.

Figure 4-7 compares the O/C and H/C ratio of the PO feed, LO and HO fractions from HDO of the PO at 300 °C and 350 °C using various catalysts, including CoMo/MCM-41, CoMo/γ-Al₂O₃, CoMo/C-Powder and Ru/C. As clearly shown, the O/C and H/C ratios for either LO or HO fraction are strongly dependent on the reaction temperature: a higher temperature resulted in oil products (LO and HO) of a lower O/C ratio, and an LO product of increased H/C ratio. However, for either LO or HO fraction the O/C ratio obtained with different catalysts is very similar. All LOs or HOs have a decreased H/C ratio compared with the un-treated PO feed, suggesting the occurrence of de-hydration and re-polymerization reactions during the HDO process responsible for the decrease in H/C ratio. For LO - the main upgraded oil fraction, the highest H/C ratio is obtained with Ru/C, followed by CoMo/MCM-41, CoMo/γ-Al₂O₃ and CoMo/C-Powder. Interestingly, it can be clearly observed from Figure 4-7 that an increase in reaction temperature led to a decrease in H/C ratio for HOs, but an increase in H/C ratio for LOs. Some possible explanations are discussed here: (1) a higher temperature might alter the distribution of organic compounds between oil and water phase, allowing more high H/C compounds transfer from water phase into the LO phase; (2) a higher temperature may promote the hydrogenation reactions of LO compounds; (3) a higher temperature might enhance re-
polymerization of the HO compounds to form condensed aromatics with a low H/C ratio. (Wildschut et al., 2009a).

![Van Krevelen plot](image)

**Figure 4-7:** Van Krevelen plot the PO feed, LO and HO fractions from HDO of the PO using CoMo/MCM-41, CoMo/\(\gamma\)-Al\(_2\)O\(_3\), CoMo/C-Powder and Ru/C catalysts at 300 °C and 350 °C.

4.3.4 Molecular weight distribution of the upgraded oil products

Molar mass distribution of the PO feed and LO products from HDO of the PO at 300 °C and 350 °C is illustrated in Figure 4-8. From Figure 4-8(A), apparently HDO with Ru/C at 300 °C significantly reduced the molar mass distribution of the PO. However, the Figure 4-8(A) shows that feed and the LO products produced with other catalysts have similar molar mass distribution, suggesting that HDO of the PO at 300 °C with all catalysts except Ru/C could not effectively reduce the molecular weight distribution of the bio-oil. Figure 4-8(B) shows that at a higher temperature, 350 °C, all catalysts including Ru/C, CoMo/MCM-41, CoMo/\(\gamma\)-Al\(_2\)O\(_3\), and CoMo/C-Powder were effective for reducing the molecular weight of the pyrolysis oil by HDO treatment.
Figure 4-8: Molar mass distribution of the PO feed and the produced LO oil fractions with CoMo/MCM-41, CoMo/γ-Al2O3, CoMo/C-Powder and Ru/C catalysts at 300°C (A) and 350°C (B).

Figure 4-9 presents the molar mass distribution of the PO feed and HO fractions from HDO of the PO at 300 °C and 350 °C, respectively. Figure 4-9(A) indicates that at 300 °C all produced HO fractions, irrespective of the catalyst used, have much greatly increased molar mass when compared with the PO feed, indicating that self-polymerization took place during the HDO process. The difference between the molar mass distributions of all HO fractions obtained with different catalysts at 300 °C is minimal, suggesting similar performance of all catalysts at a lower reaction temperature in affecting the HO molecular weight distribution. When increasing temperature from 300 °C to 350 °C, it can be seen from Figure 4-9(B) that the extent of the self-polymerization reaction was reduced, although the molecular weights of the HO products are still larger than the PO
feed. Again, the difference between the molar mass distributions of all HO fractions obtained with different catalysts at 350 °C is also minimal.

4.3.5 Gas yield and H₂ consumption

CO₂ and CH₄ yield and H₂ consumption during HDO of the PO at 300°C and 350°C are shown in Figure 4-10. Among all catalysts tested, Ru/C catalyst produced the highest CH₄ and CO₂ yields, and consumed the largest amount of H₂ at both temperatures, suggesting the highest activity of Ru/C for bio-oil HDO, as similarly reported by Jelle Wildschut et al. (2009a). Generally, catalysts with higher hydrogen consumption have a better hydro-treatment effect (Capunitan and Capareda, 2014b; Venderbosch et al., 2010a; Wildschut et al., 2010, 2009a). This may be evidenced by our own results presented in Figure 4-10 and Figure 4-7. When increasing the HDO temperature from 300 °C to 350 °C, the O/C ratios for both LO and HO decreased (Figure 4-7), accompanied by increased hydrogen consumption for all catalysts tested (Figure 4-10). It can also be noticed that the H₂ consumption for all in-house prepared catalysts is similar, which might explain their similar performance in HDO of the PO according to the O/C ratios (Table 4-3 and Table 4-4, Figure 4-6 and Figure 4-7).

In all HDO experiments, CH₄ and CO₂ are the major gas products. As shown in Figure 4-10, at 300 °C, CO₂ is the main gas product with negligible formation of CH₄, but formation of both CH₄ and CO₂ increased while increasing temperature from 300 °C to 350 °C. CO₂ can form through thermal decarboxylation of organic acids (Venderbosch et al., 2010a; Wang et al., 2012). CH₄ may form via methanation of CO₂ and H₂, favorable at a higher temperature (Brooks et al., 2007; Weatherbee and Bartholomew, 1982; Ru et al., 1979; Winslow and Bell, 1985).
Figure 4-9: Molar mass distribution of the PO feed and produced HO oil fractions from HDO of the PO with CoMo/MCM-41, CoMo/γ-Al₂O₃ and CoMo/C-Powder at 300°C (A) and 350°C (B).

\[
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}
\]

(4-1)
As mentioned previously, the PO used in this study is a softwood derived bio-oil containing coniferyl alcohol. During the HDO of the bio-oil, the following HDO reaction involving hydro-conversion of coniferyl alcohol may also explain the formation of CH₄ at a higher temperature.

![Graph showing CO₂ and CH₄ yields and H₂ consumption during HDO of the PO at 300°C and 350°C.](image)

**Figure 4-10:** CO₂ and CH₄ yields and H₂ consumption during HDO of the PO at 300°C and 350°C.

4.3.6 Coke deposition on the supported catalysts

In order to study the extent of coke deposition during the hydro-treatment of bio-oil in supercritical ethanol under H₂ atmosphere with CoMo-based catalysts, TGA measurement (from 40 to 800 °C at a heating rate of 10 °C/min under 20.0 ml/min air flow) was employed for the spent catalysts. Figure 4-11(A) illustrates the TGA profiles of various spent CoMo-based catalysts at 300°C and 350°C. As shown in the TGA profiles, the mass loss starts at 300-350°C and ends at 550-600°C. The mass loss in this temperature range could be attributed to the combustion of the high molecular weight materials derived from bio-oils via condensation or re-polymerization reactions during the HDO process, or the carbon/coke deposition. In this study, the mass loss was collectively called coke for simplification.
Figure 4-11(A) clearly shows that the amount of coke deposits significantly depend on the type of support. Based on the mass loss in the temperature range from 300-350°C to 800°C, the % coke deposits in the spent catalysts from 300 °C HDO reaction decrease in the following order: CoMo/HZSM-5 (81.1 wt%) > CoMo/γ-Al2O3 (62.9 wt%) > CoMo/MCM-41 (56.5 wt%) > CoMo/SBA-15 (53.3 wt%). This result suggest that two catalysts supported on mesoporous support (SBA and MCM-41) produced less coke in the bio-oil HDO process, compared with the catalysts supported on HZSM-5 and Al2O3, likely because that the latter have stronger acidity (Nava et al., 2009a; Zhang et al., 2012). As also shown in the Figure 4-11(A), the spent catalysts contain more coke deposits after HDO at a higher temperature: e.g., the % coke deposits in the spent catalysts of CoMo/γ-Al2O3 and CoMo/MCM-41 from 350 °C HDO tests increased to 70.2 wt% and 65.2 wt%, respectively.

Figure 4-11(B) indicates the TGA profiles for the fresh and spent Ru/C catalysts from the 300°C and 350°C HDO tests. The weight loss of the fresh Ru/C catalyst up to 100 °C and 300-350°C is approximately 8.7 wt% and 15 wt%, respectively, likely due to the evaporation moisture in the catalyst before 100 °C and the thermal decomposition of the Ru-compound used in preparation of the Ru/C catalyst. The mass loss in the temperature range from 300-350°C to 800°C for the fresh Ru/C catalyst is approx. 75 wt% due to the combustion of C support material. The mass loss of both spent Ru/C catalysts (from the 300°C and 350°C tests) in the same temperature range is approx. 85 wt%. If subtracting the mass loss attributed to the C-support, the coke deposits in both spent Ru/C catalysts are approx. 10 wt%, which is much less significant when compared with the HZSM-5, Al2O3, SBA-15 and MCM-41 supported CoMo catalysts. The TGA results are consistent with the results as shown in Figure 4-5, which indicate that the coke yield on the Ru/C catalyst is minimum after the HDO reaction at both temperatures, as also reported in the literature (Xu et al., 2014). The above results strongly suggest that the Ru/C catalyst has superb resistance to coking.
Figure 4-11: Weight losses determined by TGA analysis of the spent catalysts after hydro-treatment of bio-oil in supercritical ethanol under 5 MPa H₂ for 3h at 300°C and 350°C: (A) spent CoMo-based catalysts and (B) fresh and spent Ru/C catalysts.

4.3.7 Spent catalysts characterization

All fresh and spent catalysts obtained from the 300 °C and 350 °C HDO tests were characterized for their crystalline structure by powder XRD measurement. Figure 4-12 illustrated XRD patterns for three representative catalysts (CoMo/MCM-41, CoMo/γ-Al₂O₃ and Ru/C) before and after the bio-oil hydro-treatment tests at 300 °C and 350 °C.

Figure 4-12(A) and Figure 4-12(B) are the XRD patterns of fresh/regenerated/spent CoMo/MCM-41 and fresh/spent CoMo/γ-Al₂O₃, respectively. For each fresh/regenerated CoMo catalyst there are characteristic peaks detected which correspond to cobalt and
molybdenum oxides, as labeled in the Figure 4-12(A). For instance, the XRD peaks at 2θ of 12.5° (0 2 0), 23.5° (1 1 0), 26.7° (0 4 0), 33.7° (1 1 1) and 39.0 (0 6 0) can be attributed to the diffraction of the MoO₃ phase (Ali et al., 2012; Cauzzi et al., 1999; Mora et al., 2014; Nava et al., 2009a; Peña et al., 2014a, 2014b; Salerno, 2004; Thanabodeekij et al., 2007; Valencia and Klimova, 2011; Wang et al., 2001; Zepeda, 2008). The diffraction at 2θ of 23.3°, 26.8° and 27.5° may also related to β-CoMoO₄ phase (Nava et al., 2009b; Zepeda et al., 2006, 2005). From Figure 4-12(A), in the regenerated CoMo/MCM-41 catalyst, the MoO₃ peaks are detected in much stronger signals than its fresh catalyst. The sharper and stronger XRD signals imply sintering of the species during the regeneration process, which would lead to the growth of the crystalline sizes, increased crystallinity and poor dispersion of the MoO₃ species in the support. This poor catalyst dispersion for the regenerated CoMo/MCM-41 catalyst is evidenced by its significantly reduced BET surface area (39 m²/g) compared with that of the fresh CoMo/MCM-41 (140 m²/g), as shown in Table 4-5. In the spent catalysts of both CoMo/MCM-41 and CoMo/γ-Al₂O₃, two broad diffraction peaks at 25.4° and 43.5° were detected, which are corresponding to the (002) and (100) diffraction of carbon which are indication of the carbon/coke deposits on the spent catalysts (Poh et al., 2012; Tsubouchi et al., 2003). From the obtained XRD patterns for all spent catalysts, it can be seen that the diffraction lines of the Co and Mo oxides peaks are remarkably weakened or disappear, which could be covered and masked by the carbon/coke deposition during the upgrading process, which could deactivate the catalyst in the process. The severe carbon/coke deposition on the spent catalysts of both CoMo/MCM-41 and CoMo/γ-Al₂O₃ is evidenced previously by TGA analysis (Figure 4-11(A)).

Figure 4-12(C) displays the XRD patterns of the fresh and spent Ru/C catalysts. In all XRD plots, two broad and strong diffraction carbon peaks at 2θ of 25.4° (002) and 43.5° (100) were detected, which come from the diffraction of carbon support materials. In both the fresh and spent Ru/C catalysts, a strong XRD peak at 2θ of 28° and a weak XRD peak at 2θ of 59° were detected, ascribing to the diffraction of RuO₂ (Hyun et al., 2010; Okal, 2009). It is also observed that the XRD patterns of the fresh and spent Ru/C catalysts are very similar, and the diffraction lines of RuO₂ species are still detectable in
the spent catalysts, implying that the coke deposits in the spent Ru/C catalysts (300°C and 350°C) are not severe, which can be evidenced by the TGA results discussed previously in Figure 4-11(B).

Figure 4-13 shows FESEM micrographs of fresh and regenerated CoMo/MCM-41 in three different magnifications. By comparing fresh CoMo/MCM-41 catalyst (Figure 4-13(A)) with regenerated CoMo/MCM-41 images (Figure 4-13(B)), it is clear that the size and shape of MCM-41 crystal are almost of no change. The similar morphology of regenerated catalyst as that the fresh one, suggesting that the crystalline structure of catalyst was retained after the bio-oil HDO process at 300°C in supercritical ethanol followed by regeneration, or the MCM-41 catalyst support can resist in supercritical ethanol condition. Figure 4-14 represents FESEM micrographs of fresh and spent CoMo/SBA-15 catalysts in three different magnifications. In the spent CoMo/SBA-15 catalyst as illustrated in Figure 4-14(B) the surfaces of the SBA-15 crystals are more rough and some spherical particles can be observed, which may represent carbon/coke deposits formed during the bio-oil HDO process (Hu et al., 2011; Wang et al., 2012). Comparing the FESEM images of fresh and spent CoMo/SBA-15 catalysts, the morphology of crystals is very similar, suggesting that the crystalline structure of CoMo/SBA-15 was retained after the bio-oil HDO process at 300°C in supercritical ethanol. Thus, the mesoporous catalyst support materials SBA-15 or MCM-41 (as per Figure 4-13) can resist in supercritical ethanol condition at 300 or 350°C without collapsing of their crystalline structure.

Comparing the FESEM images of the calcined mesoporous catalyst support materials MCM-41 and SBA-15 (Figure 4-4) and the FESEM images of the CoMo loaded fresh/regenerated/spent catalysts (Figure 4-13 and Figure 4-14), the particle sizes of the metal loaded fresh/regenerated/spent catalysts are generally bigger than those of the calcined support materials. This suggests that the metal loading, calcination, and HDO tests could increase the particle sizes of the MCM-41 and SBA-15 crystals, as expected.
Figure 4-12: Powder XRD patterns of fresh and spent catalysts: (a) CoMo/MCM-41, (b) CoMo/γ-Al₂O₃ and (c) Ru/C.
### Table 4-5: Textural properties of fresh and regenerated CoMo/MCM-41

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<th>Langmuir surface area (m²/g)</th>
<th>Micropore volume (cm³/g)</th>
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**Figure 4-13:** FESEM micrographs of fresh CoMo/MCM-41 (A) and regenerated CoMo/MCM-41 (B) in three different magnifications.
4.4 Conclusions

A catalyst screening study for the hydro-de-oxygenation of fast pyrolysis oil in supercritical ethanol solvent was accomplished using CoMo-supported on mesoporous materials (SBA-15, MCM-41), commercial materials (HZSM-5, γ-Al₂O₃ and activated carbon) as catalysts in comparison with a commercial catalyst of Ru/C. The HDO of the
pyrolysis oil (PO) with the mesoporous materials-supported CoMo catalysts at 300 and 350°C effectively converted the PO into light oil (LO) fraction and a heavy oil (HO) fraction. The following conclusions were obtained.

(1) The highest oil yield obtained was with Ru/C catalyst at both temperatures (66.6 wt% at 300 °C and 61.0 wt% at 350 °C) with the lowest and negligible coke formation (<1 wt%). Different from the performance of other catalysts that produced approx. 8-20 wt% HO in the process, Ru/C catalyst generated no HO fraction at both temperatures.

(2) The use of all mesoporous materials-supported CoMo catalysts produced almost similar yields of total oil products (HO+LO) as the Ru/C catalyst did. The total oil yield in all tests (although with different catalysts and temperatures) varies in a very narrow range of 55-65 wt%.

(3) Among all the supported CoMo catalysts, CoMo/MCM-41 produced the highest oil fraction OF (= LO + HO) yield at both temperatures (61.9 wt% at 300 °C and 57.8wt% at 350 °C). The spent CoMo/MCM-41 can be regenerated and the regenerated CoMo/MCM-41, produced similar oil yields as the fresh catalyst. Furthermore, the CoMo/MCM-41 catalyst produced HO and LO of the highest H/C, although of a similar O/C ratio.

(4) A higher hydro-treatment temperature (350 °C) remarkably increased the gas, coke and LO yields, accompanied by reducing the HO and AF yields, suggesting that a higher temperature promotes the gasification/hydro-cracking reactions (leading to more gas formation) and conversion of HO into LO and coke. With any catalyst, hydro-treatment at a higher temperature in supercritical ethanol although reduced the oil yields, but it led to LO products of increased H/C ratio and reduced O/C ratio and increased heating value HHV

(5) Compared with the elemental composition of PO feed, the HDO treatment produced LO and HO products of increased carbon and hydrogen contents
and decreased oxygen content. The HHV of the LO and HOs was improved to 31-33 MJ/kg and 36-37 MJ/kg, respectively, compared with ~25 MJ/kg for the PO. The HO has a very low O/C ratio <0.1.

(6) HDO of the PO at 300 °C with all catalysts except Ru/C could not effectively reduce the molecular weight distribution of the bio-oil. However, at a higher temperature, 350 °C, all catalysts were effective for reducing the molecular weight of the pyrolysis oil by HDO treatment.

(7) Among all catalysts tested, Ru/C catalyst produced the highest CH₄ and CO₂ yields, and consumed the largest amount of H₂ at both temperatures, suggesting the highest activity of Ru/C for bio-oil HDO. The H₂ consumption for all in-house prepared catalysts is similar, which might explain their similar performance in HDO of the PO according to the O/C ratios.

(8) The Ru/C catalyst has superb resistance to coking. However, for all CoMo-based catalysts, the amount of coke deposits during the HDO tests was significant, depending on the type of support. Two catalysts supported on mesoporous support (SBA and MCM-41) produced less coke in the bio-oil HDO process, compared with the catalysts supported on HZSM-5 and Al₂O₃. Moreover, the mesoporous catalyst support materials SBA-15 or MCM-41 and can resist in supercritical ethanol condition at 300 or 350°C without collapsing of their crystalline structure.

4.5 References


Chapter 5

5 Conclusions and Recommendations

5.1 Overall conclusions

Fast pyrolysis oils have a great potential as a renewable energy source for fuels. However, they have many detrimental properties such as a high water content, high viscosity, large molecular weight, low stability, and high oxygen content. The high oxygen content of pyrolysis oil leads to self-polymerization reaction during storage and processing which should be reduced or inhibited to prevent coke formation, catalysts deactivation and reactor plugging. Since the high oxygen content also leads to other undesirable properties, it must be minimized to obtain comparable properties to fossil derived fuels. Upgrading of fast pyrolysis oil is essential to reduce oxygen content of pyrolysis oil, thereby decreasing self-polymerization. In the literature, upgrading of fast pyrolysis oil via hydro-de-oxygenation (HDO) process is reported as a promising technique to reduce oxygen content of pyrolysis oil. In the first part of this research, the effects of solvent (hydro-treated or upgraded pyrolysis oil and ethanol) on HDO process using Ru/C catalyst were investigated. Since Ru/C catalyst is very expensive and its regeneration is difficult, it is not a feasible catalyst for upgrading process in a large scale. So, in the second part of this research, inexpensive CoMo-based catalysts supported on nano-structured supports materials, such as SBA-15 and MCM-41 were explored and their performance in HDO process, using supercritical ethanol as a solvent, was studied.

From the first part of the thesis, it was conducted that the oil fraction yields were in the range of 60-90 wt%, depending on the type of the solvent and the applied temperature. Using hydro-treated bio-oil as the solvent produced more OF yield and decreased GF yield compared to the supercritical ethanol solvent process. Increasing the temperature from 300 °C to 350 °C, resulted in a decrease in the OF yield, but a noticeable increase in the GF yield. In terms of elemental composition, the HDO treatment produced oil fractions with considerably increased C and H contents and lower O content, compared with the initial oil. Using ethanol as solvent had remarkable effects on elemental composition, molecular weight, and heating value of oil products, compared with the
hydro-treated solvent. It significantly reduced oxygen content, increased the heating value, and reduced the molecular weight of oil products. Furthermore, in terms of oil quality and HDO efficiency, using ethanol as a solvent at a lower temperature resulted in even better performance than the HDO without solvent at a higher temperature. Therefore, ethanol as solvent is a promising choice in terms of improving heating value, reducing oxygen content and molecular weight of bio-oil. Hydrogen consumption was higher by using hydro-treated oil as a solvent, compared to the HDO tests without solvent or with ethanol solvent. More CO₂ was produced during HDO experiments without solvent, in particular at a higher temperature. During HDO of pyrolysis oil in supercritical ethanol process, more CH₄ was produced, which might be due to the decomposition of ethanol catalyzed by the Ru/C catalyst during the HDO process, evidenced by some loss of ethanol during the tests.

In the second part of this research, a catalyst screening study using CoMo-supported on mesoporous materials (SBA-15, MCM-41), commercial materials (HZSM-5, γ-Al₂O₃ and activated carbon) as catalysts in comparison with a commercial catalyst of Ru/C in HDO for fast pyrolysis oil in supercritical ethanol solvent was conducted. The PO was converted into light oil (LO) fraction and heavy oil (HO) fraction during HDO process with the CoMo-based catalysts. Ru/C catalyst led to the highest oil yield at both temperatures (66.6 wt% at 300 °C and 61.0 wt% at 350 °C) with the lowest and negligible coke formation (<1 wt%). Although, other catalysts produced approx. 8-20 wt% HO in the process, Ru/C catalyst created no HO fraction at both temperatures. Almost similar yields of total oil products (HO+LO) were produced by using all mesoporous materials-supported CoMo catalysts, compared to the Ru/C catalyst. The total yields were in the range of 55-65 wt%, depending on the catalysts and temperatures. Among all the CoMo-based catalysts, CoMo/MCM-41 generated the highest oil fraction OF (= LO + HO) yield at both temperatures (61.9 wt% at 300 °C and 57.8 wt% at 350 °C). After regeneration, CoMo/MCM-41 produced similar oil yields as the fresh catalyst. Moreover, it produced HO and LO of the highest H/C and a similar O/C ratio. For all CoMo-based catalysts, the amount of coke deposits during the HDO tests was considerable, depending on the type of support. CoMo/SBA-15 and CoMo/MCM-41
catalysts produced less coke in the bio-oil HDO process, compared with the catalysts supported on HZSM-5 and Al2O3. Furthermore, CoMo/SBA-15 and CoMo/MCM-41 can resist in supercritical ethanol condition without collapsing of their crystalline structure. In contrast, Ru/C catalyst showed excellent resistance to coking. It generated the highest CH4 and CO2 yields and, consumed the largest amount of H2 at both temperatures, indicating its highest activity in HDO process. All in-house prepared catalysts showed similar hydrogen consumption, which might clarify their similar performance in HDO of the PO according to the O/C ratios. Although all catalysts were effective for decreasing the molecular weight of the pyrolysis oil by HDO treatment at a higher temperature, 350 ºC, HDO of the PO at 300 ºC with all catalysts except Ru/C could not effectively reduce the molecular weight distribution of the bio-oil. The HDO process produced LO and HO products of increased carbon and hydrogen contents and decreased oxygen content, compared to the original oil. The heating value of the LO and HOs was enhanced to 31-33 MJ/kg and 36-37 MJ/kg, respectively, compared with ~ 25 MJ/kg for the PO. A higher temperature significantly increased the gas, coke, and LO yields, accompanied by decreasing the HO and AF yields, proposing that a higher temperature improves the gasification/hydro-cracking reactions (leading to more gas formation) and conversion of HO into LO and coke. Although hydro-treatment at a higher temperature in supercritical ethanol with any catalyst decreased the oil yields, but it led to LO products of increased H/C ratio, reduced O/C ratio and increased heating value.

With current results obtained, using inexpensive mesoporous catalysts in supercritical solvent, is recommended since they show significant effects on the upgrading process. As such, seeking other bimetallic catalysts and solvents would be a focus of the future work.

5.2 Recommendations for future work

To carry on the pathway of this research, it is recommended to improve the activity of CoMo/MCM-41 catalyst by modifying its structure due to its significant performance in HDO process. Furthermore, the effects of different copolymers on synthesizing of nano-structured catalyst can be studied. Other bimetallic catalysts such as NiMo-based catalysts on HDO process can be examined to investigate the effect of the type of metals.
Studying the effects of other solvents in supercritical conditions on reducing polymerization reaction during upgrading process, needs more investigation. In this study, the type of solvents, solvent to bio-oil ratio, amount of catalysts, and metal dispersion over supports were not studied which should be performed in future work. Moreover, a continuous flow setup can be developed to replace the batch setup and promote feasibility of scaling up process.
Appendices

Appendix A

Appendix A: Copyright releases

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Publications (Conferences):

S. Ahmadi, C. Xu, S. Rohani, Hydro-treatment of fast pyrolysis oil in supercritical ethanol using nano-structured catalysts, Advanced Biofuels Symposium Program, Ottawa, Canada.


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