Upgrading Pyrolysis Oil to Produce Liquid Transportation Fuels

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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 PYROLYSIS OIL TO PRODUCE LIQUID TRANSPORTATION FUELS

(Thesis format: Integrated Article)

by

Ehsan Reyhanitash

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 stabilizing fast pyrolysis oil via catalytic alcohol pretreatment on upgrading via hydrodeoxygenation or thermal treatment was studied by comparing the properties of upgraded-stabilized oils with those of upgraded-non-stabilized oils (benchmarks). The major expected effect was reduction in molar mass of upgraded oils, as stabilization was expected to reduce the reactivity of fast pyrolysis oil, thereby reducing polymerization. It was observed that molar mass reduction was induced by dilution effect of the alcohol rather than reactivity reduction due to stabilization. Also, the effects of different alcohols on stabilization and subsequent upgrading were examined at minimized dilution effect conditions. Stabilization did not significantly affect the molar mass distribution of upgraded oils. However, other properties (e.g. CO$_2$ production and H$_2$ consumption) were significantly affected by stabilization.

Keywords: fast pyrolysis oil, stabilization, hydrodeoxygenation, thermal treatment
Co-Authorship Statement

Chapters 3 and 4 are article manuscripts which will be submitted to peer reviewed journals. The contribution of each author is stated below.

Chapter 3:

Upgrading fast pyrolysis oil via hydrodeoxygenation and thermal treatment: effects of catalytic glycerol pretreatment

Authors: Ehsan Reyhanitash, Zhongshun Yuan, Katherine Albion, Guus van Rossum, Chunbao (Charles) Xu

Status: To be submitted to Energy & Fuels

Experimental work and data analysis were performed by Ehsan Reyhanitash. Chunbao (Charles) Xu, Guus van Rossum, Zhongshun Yuan and Katherine Albion provided consultation regarding experimental work and interpretation of results. The manuscript was written and revised by Ehsan Reyhanitash, and reviewed by Chunbao (Charles) Xu and Guus van Rossum.

Chapter 4:

The effects of stabilizing fast pyrolysis oil via catalytic alcohol pretreatment on hydrodeoxygenation: alcohol variation at minimized dilution

Authors: Ehsan Reyhanitash, Zhongshun Yuan, Katherine Albion, Guus van Rossum, Chunbao (Charles) Xu

Status: To be submitted to Energy & Fuels

Experimental work and data analysis were performed by Ehsan Reyhanitash. Chunbao (Charles) Xu, Guus van Rossum, Zhongshun Yuan and Katherine Albion provided consultation regarding experimental work and interpretation of results. The manuscript was written and revised by Ehsan Reyhanitash, and reviewed by Chunbao (Charles) Xu and Guus van Rossum.
Acknowledgements

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Preface

"Research is the process of going up alleys to see if they are blind" - Marston Bates

To my family
CHAPTER 1. INTRODUCTION

1.1. Thermochemical conversion of biomass

Due to extensive consumption of petroleum derived fuels across the world and concerns on depletion of petroleum resources over next decades, the importance of renewable energy is growing and it has been the focus of many researchers over recent years. In order to compensate energy needs of both developed and developing economies, biomass is considered a highly potential resource for renewable energy. Liquid, gaseous and solid fuels can only be produced via utilizing biomass. Wood, energy crops and agricultural wastes are some of available biomass resources. Fuels derived from these resources (biofuels) produce less greenhouse gas emissions than petroleum derived fuels do, contributing toward the objectives of the Kyoto Agreement at the same time. Biofuels are reported to be even greenhouse gas neutral, if their production methods are improved (Bridgwater, 2004; Huber et al., 2006). Table 1-1 provides information on the capacity of biomass production worldwide.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Production capacity (ton of dry biomass / year)</th>
<th>boe(^a) (barrels of oil energy equivalent)</th>
<th>Reported by</th>
</tr>
</thead>
<tbody>
<tr>
<td>U.S.</td>
<td>(1.3 \times 10^9)</td>
<td>(3.8 \times 10^9)</td>
<td>USDA &amp; Oak Ridge National Laboratory</td>
</tr>
<tr>
<td>Europe</td>
<td>(4.4 \times 10^8)</td>
<td>(1.4 \times 10^9)</td>
<td>EUBIA</td>
</tr>
<tr>
<td>Africa</td>
<td>(1.1 \times 10^9)</td>
<td>(3.5 \times 10^9)</td>
<td></td>
</tr>
<tr>
<td>Latin America</td>
<td>(1.0 \times 10^9)</td>
<td>(3.2 \times 10^9)</td>
<td></td>
</tr>
</tbody>
</table>

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

Combustion, gasification, liquefaction and pyrolysis are the major routes for thermochemical conversion of biomass (Bridgwater, 1994). The above routes will be further discussed, as the focus of this thesis is on a downstream process of pyrolysis.

1.1.1. Combustion

Combustion is a well-known route for generating heat from biomass. Generated heat can be directly used for heating, cooking etc. or converted to power. Although the technology
of combustion is commercialized, minimizing the risk of investment at the same time, reported overall efficiencies are typically as low as 15 % for small plants and up to 30 % for larger and newer plants. Furthermore, even for maximum possible power yields, emissions and ash handling are technical problems. Another drawback of combustion is the requirement for immediate use of generated energy (in the form of heat), as the storage of such an energy is not viable. Combustion is economically beneficial when the feed is the waste of other biomass utilizing industries such as pulp and paper and agriculture. There are several successful operational plants in North America and Europe which utilized wastes as the feed (Bridgwater, 2003).

1.1.2. Gasification

Gasification aims to convert biomass into fuel gas with a low (~ 5 MJ/m³) to medium heating value (up to 20 MJ/m³). The process simply called “gasification” is comprised of three major steps: moisture removal from biomass via drying; char, tar and gas production via pyrolysis; partial oxidation of the char, tar and gas in presence of oxygen (in the form of pure oxygen or air) below stoichiometric amount which results in a gas rich in CO, CO₂ and H₂. Supplying steam with oxygen increases H₂ and CH₄ contents of the gas via steam reforming reaction. Operating temperatures of 900 - 1100 ºC with air and 1000 - 1400 ºC with oxygen were achieved. The gas composition is dependent on the composition and water content of feed, reaction temperature, and the extent of oxidation of pyrolysis products. The tar produced via pyrolysis is not completely converted during gasification due to either reactor or reaction limitations causing technical problems for downstream consumers of the gas like turbines. Therefore, further refining of the produced gas is needed which is usually performed via catalytic or thermal cracking of tar. The gas has to be consumed immediately due to the high cost of storage. Hot gas efficiencies (energy content of raw gas / energy content of feed) of up to 97 % was reported for close coupled turbines and boilers (Bridgwater, 2003; Castello and Fiori, 2011; Bridgwater, 1994).
1.1.3. Liquefaction

Biomass can be directly liquefied without undergoing pyrolysis. Although biomass moisture must be minimized for pyrolysis to obtain a liquid product of high quality, liquefaction can achieve a high quality liquid product utilizing biomass with any moisture content. The operating conditions for liquefaction are high pressures (5 - 20 MPa) and relatively low temperatures (< 400 °C). A suitable solvent (water or organic solvents) with/without a catalyst must also be employed (Yang et al., 2009; Xiu and Shahbazi, 2012). Hydrothermal liquefaction uses water as the solvent, while water also acts as a reactant (Toor et al., 2011). Water can be advantageous over other solvents, as it has low cost being environmentally benign at the same time (Zhang, 2010). It is reported that higher liquid yields with lower oxygen content can be achieved by supplying a reducing environment (H₂). H₂ stabilizes the reactive intermediate fragments formed from degradation of biomass reducing polymerization and char formation consequently (Yang et al., 2009; Chumpoo and Prasassarakich, 2010; Xu and Etcheverry, 2008; Zhang et al., 2011).

1.1.4. Pyrolysis

Pyrolysis always precedes combustion and gasification providing intermediate fragments for further conversion of biomass via combustion or gasification where they undergo complete or partial oxidation respectively. Biomass can be converted to gaseous product at higher temperature and longer vapor residence times. However, lower temperatures and longer residence times of vapors increase char yield. Liquid product known as “pyrolysis oil” is obtained at moderate temperatures and short vapor residence times (Bridgwater, 2003). The first part of chapter two “Literature Review” is dedicated to pyrolysis, as this thesis has focused on upgrading pyrolysis oil to produce transportation fuels.

1.2. Thesis objectives

The overall objective of the research conducted for this thesis was to investigate the effect of stabilizing fast pyrolysis oil on upgrading. The quality of upgraded oils as the
potential co-feeds for co-refining was the basis of assessment instead of tracking specific compounds. Initially, stabilization of fast pyrolysis oil was performed in presence of glycerol named “catalytic glycerol pretreatment” followed by upgrading via hydrodeoxygenation and thermal treatment. Since, it was observed that the dilution effect of glycerol as a solvent (due to the relatively high concentration utilized) had the major positive effect on upgrading, for the second part of the research, the concentration of used alcohol was minimized to clarify the possible positive effects of stabilization (here called catalytic alcohol pretreatment) on upgrading. Also various alcohols were tested for catalytic alcohol pretreatment. The whole research is summarized in two manuscripts presented in chapters 3 and 4.

1.3. Thesis overview

Chapter 1 provides a short discussion about the important role of biomass in energy security. The capacity of biomass production worldwide is summarized in a table. Afterwards, a short introduction of available routes for thermochemical conversion of biomass is provided. Pyrolysis as the only industrial technology so far to convert biomass into a liquid will be further described in chapter 2.

Chapter 2 provides a literature review of pyrolysis followed by introducing utilized methods for upgrading pyrolysis oil. A detailed discussion is provided for hydrodeoxygenation, as it has been the most successful upgrading method. The properties of lignocellulosic biomass (the major feed for pyrolysis) and pyrolysis oil are also described.

Chapters 3 and 4 also include a short introduction on the properties of pyrolysis oil while focusing on necessity of upgrading. Chapter 3 focuses on stabilization of fast pyrolysis oil in presence of glycerol named “catalytic glycerol pretreatment” followed by upgrading via hydrodeoxygenation (in batch mode of hydrogen) and thermal treatment. The focus of chapter 4 is on minimizing alcohol consumption while screening methanol, ethanol and glycerol as the potential alcohols for “catalytic alcohol pretreatment” followed by upgrading via hydrodeoxygenation (in semi-batch mode of hydrogen). A new setup was developed for the research of chapter 4 to improve hydrodeoxygenation
conditions via continuous injection of hydrogen while maintaining the pressure of the autoclave at a desired level. The new setup was able to accurately measure the amount of consumed hydrogen.

Chapter 5 provides an overall conclusion for the thesis research.
1.4. References


CHAPTER 2. LITERATURE REVIEW

2.1. Pyrolysis

2.1.1. History

Pyrolysis is a very old process. It was initially employed not to produce any liquid, but to produce biochar, a solid very similar to charcoal. Thousands of years ago in Amazon rainforest, indigenous peoples who already had the knowledge of creating and controlling fire came to the realization that with the aid of fire, they can produce a material which is able to enrich the nutrient poor rainforest soils. They started fire and when the fuel seemed to be hot enough, they covered it by earth to prevent oxygen from reaching the fuel. The achieved high temperature in the absence of oxygen led to decomposition of fuel and consequently production of biochar (Magnum Group International Inc.).

The two world wars were the periods over which due to lack of fossil fuels, pyrolysis of wood waste feedstock was employed to produce alternative fuels for vehicles. Biomass derived gases also played an important role in transportation. Heavy vehicles and agricultural machines were the dominant targets of producing biomass derived gases by 1956 and approximately 9,000,000 vehicles in many places around the world were using biomass derived gases as fuel (Magnum Group International Inc.).

2.1.2. Process

Effective operating conditions on pyrolysis are temperature, heating rate and vapor residence time (Bridgwater, 1994). Depending on operating conditions, pyrolysis can be either slow (or conventional) or fast (or flash) (Maschio et al., 1992). However, the names do not specify any precise range of the above parameters. Vapor residence time seems to be the most useful parameter to distinguish between pyrolysis processes.

Slow pyrolysis has a longer residence time of vapor ranging from 0.5 to 5 minutes which involves low heating rates to reach a temperature of ~ 500 °C (Bridgwater, 1994; Mohan et al., 2006). Therefore, vapors can undergo subsequent reactions to form biochar or liquids (Mohan et al., 2006).
Fast pyrolysis is performed at a higher heating rate of 1000 °C/s, or even 10000 °C/s and much lower vapor residence times of a few seconds or less (Demirbas, 2005; Bridgwater, 2003). The reactor provides heat for pyrolysis while maximizing heat transfer rate between media (solid and/or gas) and biomass particles (solid). Various reactor configurations (bubbling fluid beds, transport reactors and cyclonic reactors) achieved high liquid oil yields of 70 - 80 % on dry biomass weight basis (Oasmaa and Czernik, 1999). Solid char is the other product formed with a yield of 12 - 25 wt% and non-condensable gas formation reaches a yield of 13 - 25 wt% (on dry biomass weight basis) (Bridgwater, 2012). Since oil and char are collected as the value added products and gases are recycled to be combusted and provide heat for pyrolysis, no waste is produced (Mohan et al., 2006). Over the past twenty years, fast pyrolysis of different biomass feedstock has been widely studied to increase the yields of liquid and gaseous products to obtain valuable chemicals and fuels (Bridgwater et al., 2001).

High heating rates are effective to minimize char yield and maximize liquid yield at temperatures of ~ 500. Further increase in temperature will increase gas yield (Demirbas, 2009; Bridgwater, 2012). No char was observed under some conditions (Demirbas, 2005). High heating rate and rapid quenching of vapors lead to formation of intermediate liquid products which immediately condense into liquid oil, thereby preventing them from being decomposed to gaseous products (Demirbas, 2009). At high temperatures of above 700 °C and short residence times, very high gaseous product yields up to 80 wt% were observed (Bridgwater, 1992).

Intermediate products formed during pyrolysis are estimated to exceed 200 species (Emmons and Atreya, 1982). Model compound studies are conducted on cellulose as a dominant constituent of wood to obtain more insight into the mechanisms of decomposition during pyrolysis, as it decomposes over almost the entire range of pyrolysis temperatures (Bridgwater and Peacocke, 2000; Meier and Faix, 1997).

### 2.1.3. Pyrolysis oil constituents

Fast pyrolysis oil is derived from depolymerization and degradation of lignocellulosic biomass. Since lignocellulosic biomass is comprised of cellulose, hemicellulose and
lignin as the three main structural blocks, fast pyrolysis oil is a complex mixture of fragments originating from the above blocks. Therefore, it has such an elemental composition that represents its origin rather than crude oil (Czernik and Bridgwater, 2004). In Table 2-1, the elemental composition of two fast pyrolysis oil samples is compared with that of biomass resources from which they are derived and heavy fuel oil.

Table 2-1: Approximate elemental composition of two fast pyrolysis oil samples in comparison to that of their resources and heavy fuel oil (Oasmaa and Czernik, 1999; Mohan et al., 2006; Fagernäs et al., 2012; Sannigrahi et al., 2010)

<table>
<thead>
<tr>
<th></th>
<th>biomass resource</th>
<th>pyrolysis oil</th>
<th>heavy fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>birch</td>
<td>pine</td>
<td>birch</td>
</tr>
<tr>
<td>C (wt%)</td>
<td>50.0</td>
<td>49.0</td>
<td>44.0</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>6.0</td>
<td>6.0</td>
<td>6.9</td>
</tr>
<tr>
<td>N (wt%)</td>
<td>0.1</td>
<td>0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>S (wt%)</td>
<td>0.01</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>O (wt%)</td>
<td>43.0</td>
<td>44.0</td>
<td>49.0</td>
</tr>
</tbody>
</table>

Cellulose is the basic skeletal constituent of wood cell walls which comprises ~ 40 - 45 wt% of dry wood (Parham and Gray, 1984). Glucose anhydride is formed via removal of one mole of water from one mole of glucose. Each unit of cellulose (called cellobiose) is formed via the reaction of anhydride group of one glucose anhydride with the hydroxyl group of another glucose anhydride on the opposite side of molecule. 5000 - 10000 glucose anhydride units exceeding molecular weights of $10^6$ and more polymerize to form cellulose chains (Mohan et al., 2006).

Figure 2-1: Cellobiose and cellulose

Hydrogen bonds create long chains of cellulose as shown in Figure 2-2. They also cause cellulose to form crystals and consequently be completely insoluble in normal aqueous solutions. During pyrolysis over the range of 240 - 350 °C, cellulose degrades while producing anhydrocellulose and levoglucosan (Mohan et al. 2006).
Hemicellulose (also known as polyose) comprises 25 - 35 wt% of dry wood as the second major constituent; 28 wt% of softwoods and 35 wt% of hardwoods. The units polymerizing to form hemicellulose are various monosaccharides such as glucose, mannose, galactose, xylose, arabinose, 4-\textit{O}-methyl glucuronic acid and galacturonic acid residues (Mohan et al., 2006).

Despite cellulose whose only constituent is glucose, hemicellulose is composed of various saccharides creating a non-uniform polymer which sometimes contains side chains along the main polymeric chain. Hemicellulose is formed of \sim{} 150 units (despite 5000 - 1000 units of cellulose) which lead to lower molecular weights than cellulose (Mohan et al., 2006).
The temperature range over which decomposition of hemicelluloses occurs during pyrolysis is lower than cellulose ranging from 200 °C to 260 °C which results in rapid disappearance of hemicellulose in high hating rates. However, there is no sufficient information to describe this phenomenon. Hemicellulose produces more volatiles, less tars and less chars than cellulose during decomposition. The acetic acid originating from wood is majorly formed via deacetylation of hemicelluloses (Mohan et al., 2006).

Lignin is the third major constituent of wood. 24 - 33 wt% of softwoods and 19 - 28 wt% of temperature-zone hardwoods are comprised of lignin. It is a highly branched polyphenolic substrate with a high concentration at the boundary of middle lamella and primary cell walls. It provides mechanical strength and resistance to biological degradation for plants. Despite cellulose, lignin lacks an ordered repeating unit (Lebo et al., 2001). \( p \)-coumaryl, coniferyl, and sinapyl structures are the general “hydroxy-” and “methoxy-” substituted phenylpropane units that form lignin (Mohan et al. 2006).

Over the range of 280 - 500 °C, lignin decomposes while producing phenols via breaking ether and carbon-carbon bonds. It shows higher char yields than cellulose during pyrolysis (Mohan et al., 2006).
Table 2-2: Approximate lignocellulosic content of two biomass resources (Mohan et al., 2006; Huber et al., 2006)

<table>
<thead>
<tr>
<th></th>
<th>birch</th>
<th>pine</th>
</tr>
</thead>
<tbody>
<tr>
<td>cellulose (wt%)</td>
<td>40</td>
<td>46 - 50</td>
</tr>
<tr>
<td>hemicelluloses (wt%)</td>
<td>26</td>
<td>19 - 22</td>
</tr>
<tr>
<td>lignin (wt%)</td>
<td>16</td>
<td>21 - 29</td>
</tr>
</tbody>
</table>

2.1.4. Pyrolysis oil properties

Pyrolysis oil has a high oxygen content (usually 45 - 50 wt%) in the form of water and functional groups which contain oxygen (majorly hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics).

![Simplest hydroxyaldehyde and hydroxyketone](image)

Around 300 compounds are identified in pyrolysis oil in the most of which oxygen is present. Pyrolysis operating conditions (discussed above) and biomass type are the most effective parameters on distribution of these compounds. High temperature pyrolysis on one hand results in high gaseous products yield (as the already formed vapors undergo further cracking to form gas) and on the other hand increases the yield of liquid products with less oxygen content (Bridgwater 2004).

The water content (15 - 30 wt%) originates either from the initial moisture of biomass or dehydration reactions which occur during pyrolysis. Due to solubilizing effect of hydrophilic compounds of pyrolysis oil (low molar mass acids, alcohols, hydroxyaldehydes and ketones) which are mostly the products of decomposition of carbohydrates, water is miscible with oligomeric lignin-derived components. This phenomenon results in formation of one phase in pyrolysis oil. However, adding extra water to pyrolysis oil leads to phase separation due to decreasing the concentration of
above compounds and increasing polarity. The bottom phase (pyrolytic lignin) contains oligomeric lignin-derived compounds (hydrophobic) and the top phase majorly contains sugar constituents (hydrophilic). The main beneficial effect of water on pyrolysis oil is improving its flow characteristics (Czernik and Bridgwater, 2004; de Miguel Mercader et al., 2011).

The high oxygen (and water) content is the main reason for several critical differences between hydrocarbon fuels and pyrolysis oil as discussed below:

Low energy density (caused by high oxygen and water content): pyrolysis oil has an energy density of around that of biomass and half that of hydrocarbon fuels (14 - 18 MJ/kg compared to 40 MJ/kg). Pyrolysis oil has a volumetric energy density of 60% of that of diesel fuel due to its higher density (1150 - 1250 kg/m³ compared to 850 - 100 kg/m³) (Wildschut et al., 2009; Oasmaa and Czernik, 1999).

Low stability (caused by functional groups which contain oxygen): despite hydrocarbon fuels, pyrolysis oil is not chemically stable over time. The functional groups (some of them are mentioned above) are reactive even at room temperature. The lack of chemical stability during storage appears in the form of polymerization which leads to increase in molar mass of pyrolysis oil and consequently changes in its physical properties (Diebold and Czernik, 1997). Polymerization of double-bonds, etherification and esterification between hydroxyl, carbonyl, and carboxyl groups with production of water as a byproduct are the major chemical reactions observed (Oasmaa and Czernik, 1999). Polymerization must be highly prevented during processing, as it can lead to reactor plugging and coke formation (Elliot and Neuenschwander, 1996).

Corrosiveness (caused by organic acids): the high acidity (pH = 2 - 3; acid number = 50 - 100 mg KOH/g) and subsequent corrosiveness of pyrolysis oil is due to a considerable concentration of organic acids mostly formic and acetic acid. Therefore, it is corrosive to common construction materials such as carbon steel and aluminum, but not to stainless steels. Higher temperatures and water contents increase the acidity of pyrolysis oil (Oasmaa and Czernik, 1999).
Less miscibility with hydrocarbon fuels (caused by high oxygen content): there is a significant concentration of polar compounds in pyrolysis oil. The polarity of these compounds is mainly associated with non-bonding electrons of functional groups which contain oxygen. These compounds make pyrolysis oil almost immiscible with conventional hydrocarbon fuels.

Although pyrolysis oil has several drawbacks (mentioned above) making it less suitable to be utilized as a standard fuel (in comparison to hydrocarbon fuels), under specific operating circumstances, it is burnt to generate heat and electricity in boilers, engines and gas turbines (Bridgwater and Peacocke, 2000). However, in order to utilize pyrolysis oil as a transportation fuels, the above drawbacks must be addressed beforehand. Even direct co-refining of pyrolysis oil in petroleum refineries seems to be highly problematic due to extensive coking. Another potential application is to produce value-added chemicals from pyrolysis oil.

Pyrolysis oil should undergo further processing called “upgrading” to obtain chemical and physical properties similar to those of hydrocarbon fuels.

2.2. Upgrading pyrolysis oil to produce transportation fuels

Pyrolysis oil has high oxygen content in the form of water and bonded oxygen. The high oxygen content results in a very different elemental composition from that of petroleum. Carbon and hydrogen are the major constituent elements of petroleum leading to a low oxygen content of less than 0.06 (Wang et al., 2007). In contrast, oxygen accounts for almost half the mass of pyrolysis oil. Figure 2-6 compares molar H/C and O/C of pyrolysis oil with various compounds.
As shown in Figure 2-6, pyrolysis oil has to undergo a significant oxygen removal to meet the elemental composition of petroleum derived transportation fuels (e.g. gasoline). An interesting approach to produce transportation fuels from pyrolysis oil is to co-process upgraded pyrolysis oil with a petroleum fraction (e.g. vacuum gas oil) using petroleum refinery processes (e.g. via fluid catalytic cracking). A recent study shows that complete oxygen removal of upgraded pyrolysis oil may not be necessary for subsequent coprocessing with petroleum fractions (de Miguel Mercader et al., 2011).

Currently, three major routes are proposed for upgrading pyrolysis oil to produce transportation fuels. These are catalytic cracking (direct utilization of pyrolysis oil in petroleum refinery), high pressure thermal treatment and hydrodeoxygenation. Catalytic cracking aims to directly convert pyrolysis oil to transportation fuels. However, high pressure thermal treatment and hydrodeoxygenation reduce the oxygen content of pyrolysis oil to produce intermediate oil which can undergo further processing (e.g. corefining). The following is a short discussion on catalytic cracking and high pressure
thermal treatment, as they are not the focus of the experimental work of this thesis. Hydrodeoxygenation will be widely discussed.

2.2.1. Upgrading via catalytic cracking

Catalytic cracking of pyrolysis oil is inspired by catalytic cracking of petroleum fractions in petroleum refinery. It is performed at atmospheric pressure without the requirement of added hydrogen. Various catalysts such as zeolite, silica-alumina and molecular sieves have been tested. This route has attracted the interest of many studies due to low operating pressure and no need of added hydrogen (Adjave and Bakhshi, 1995; Katikaneni et al., 1995; Adjave et al., 1996). However, its critical drawback is excessive char formation and consequently low gasoline yields (de Miguel Mercader et al., 2010). Therefore, to prevent catalyst deactivation due to char formation, continuous regenerating of used catalysts must be highly considered.

2.2.2. Upgrading via high pressure thermal treatment

In contrast to catalytic cracking and hydrodeoxygenation, high pressure thermal treatment does not employ any catalyst. Also, despite hydrodeoxygenation (defined below), hydrogen is not used for upgrading and pressurizing is achieved with nitrogen. This appears to be an advantage over hydrodeoxygenation which may improve the economics of upgrading. Recently, an interesting study on upgrading fast pyrolysis oil via high pressure thermal treatment was published (de Miguel Mercader et al., 2010). In this study, a tubular reactor was designed to determine the effect of temperature and residence time on quality and yield of produced oils from fast pyrolysis oil at 200 bar. High pressure is needed to keep water in liquid state, as evaporation of water leads to extensive char formation. Temperatures between 200 and 350 °C and residence times between 1.5 - 3.5 min were examined. Molar mass increase of oil fractions and sugar content decrease of aqueous fractions were observed at the same time by increasing temperature. However, residence time did not have a strong effect as temperature indicating that polymerization reactions were very fast. It might be concluded that polymerization of sugars (and disappearing from aqueous fraction at the same time) (partly) accounted for molar mass
increase of oil fractions. Molar mass increase of produce oils via high pressure thermal treatment is the major drawback of this upgrading route.

2.2.3. Upgrading via hydrodeoxygenation

Hydrodeoxygenation seems to be a promising route for upgrading pyrolysis oil. Despite catalytic cracking, hydrodeoxygenation employs hydrogen to remove oxygen from pyrolysis oil in the form of water. Hydrogen also saturates C=C bonds (Huber et al., 2006). CO$_2$ and CO (usually not a considerable amount) are also formed during hydrodeoxygenation. Hydrogen is supplied in the form of pressurized gas in the presence of heterogeneous catalysts at moderate temperatures (300 - 600 °C) (Huber et al., 2006). The effect of catalyst, temperature, residence time will be discussed below.

2.2.3.1. Catalyst effect

Many studies on hydrodeoxygenation of pyrolysis oil have focused on conventional hydrotreating catalysts used to remove sulfur, nitrogen and oxygen from petroleum fractions in petroleum refineries (e.g. CoMo/Al$_2$O$_3$ and NiMo/Al$_2$O$_3$).

A two-stage packed bed downflow reactor was employed for hydrodeoxygenation of fast pyrolysis oil at Pacific Northwest National Laboratory (PNNL). Sulfided NiMo/Al$_2$O$_3$ or CoMo/spinel catalysts were used for both of the stages. The aim of the first stage was to stabilize fast pyrolysis oil fragments via hydrodeoxygenation at 150 °C. The second stage was performing deep hydrodeoxygenation at a higher temperature (∼ 350 °C for NiMo/Al$_2$O$_3$ and ∼ 400 °C for CoMo/spinel). A high oxygen removal of up to 99 wt% was achieved. However, catalyst deactivation due to coke buildup and plugging of the lines due to tar buildup in the reactors and effluent lines (which resulted in obligatory experiment termination) were observed to be the major challenges (Elliott and Neuenschwander, 1996).

A packed bed up and downflow reactor was developed by Baldauf et al. (1994). Sulfided CoMo/Al$_2$O$_3$ and NiMo/Al$_2$O$_3$ catalysts were used for both of the flow directions. A high deoxygenation yield of 88 - 99.9 wt% was observed at a temperature of 350 - 370 °C and pressure of up to 300 bar. However, the yield of obtained oils was only 30 - 35 wt%.
Rapid catalyst deactivation occurred preventing the setup from operating at steady state for a long time. Lines and valves are also plugged by gum-like deposits formed due to instability of fast pyrolysis oil.

A bench scale continuous flow reactor was used by Elliot and Baker (1984) for hydrodeoxygenation of pyrolysis oil at a temperature of 350 °C to 450 °C and a pressure of 138 bar. CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts achieved an oxygen removal of 90 - 95 wt% and an oil yield of 80 wt% (Wildschut et al., 2009).

Another study conducted on hydrodeoxygenation of fast pyrolysis oil using a packed bed up and downflow reactor developed by Samolada et al. (1998). They achieved a high oxygen removal of 88 - 99.9 wt% with CoMo and NiMo catalysts at a temperature of up to 500 °C and a pressure of up to 325 bar. The yield of produced oils was between 30 to 55 wt%.

Other studies also reported on utilizing sulfided CoMo and NiMo catalysts for hydrodeoxygenation of pyrolysis oil in a batch slurry reactor and a two-stage packed bed upflow reactor respectively (Su-Ping, 2003; Conti et al., 1995).

The other common catalysts for hydrodeoxygenation are noble metals such as Ru, Pd, Rh and Pt on various supports. These catalysts attracted much interest, as they are found to be capable of achieving more oil yields and reducing solid yields.

A study was conducted on screening noble catalysts by Wildschut et al. (2009). Ru/C, Ru/TiO₂, Ru/Al₂O₃, Pt/C and Pd/C catalysts were examined and compared with classical hydrodeoxygenation catalysts (sulfided CoMo/Al₂O₃ and NiMo/Al₂O₃) at temperatures of 250 and 350 °C and pressures of 100 and 200 bar in a batch reactor. It was reported that Ru/C was superior to classical hydrodeoxygenation catalysts in terms of oil yield (up to 60 wt%) and oxygen removal (up to 90 wt%). At 350 °C and 200 bar and a retention time of 4 h, Ru/C achieved the highest oxygen removal among the screened catalysts (oxygen content of less than 6 wt%). The oil yield was around 55 wt% at the same time. However, at the same conditions, the oil yields of sulfided CoMo/Al₂O₃ and NiMo/Al₂O₃ did not exceed 30 wt% and the oxygen content was around 8 wt% and 11 wt% respectively.
Ru/C was used for another study by Elliot et al. (2012) to hydrogenate fast pyrolysis oil at mild conditions (170 °C and 2000 psig). The experimental setup was a fixed bed downflow reactor comprised of two portions. The first portion was packed with Ru/C to hydrogenate fast pyrolysis oil providing a partial upgrading at the same time. The second portion was packed with sulfided CoMo to perform hydroprocessing at 400 °C and 2000 psig. The oxygen content of fast pyrolysis oil was decreased from around 50 wt% to less than 3 wt%.

Ru/C was used by Venderbosch et al. (2010) for hydro(deoxy)genation in a comprehensive study on upgrading fast pyrolysis oil using a fixed bed flow reactor. Their research focused on examining polymerization of fast pyrolysis oil during high pressure thermal treatment, hydrogenation of fast pyrolysis oil at low temperatures (up to 250 °C), hydrodeoxygenation of fast pyrolysis oil at elevated temperatures (up to 400 °C) and hydrocracking of hydrodeoxygenation oil.

de Miguel Mercader et al. (2011) performed a study on hydrodeoxygenation of fast pyrolysis oil fractions in a batch reactor. The experimental setup was capable of injecting hydrogen into the reactor continuously (achieving a semi-batch mode) to maintain the pressure of the reactor at 190 bar and measure hydrogen consumption. Ru/C was used for hydrodeoxygenation of all fast pyrolysis oil derived fractions at different temperatures (220, 270 and 310 °C) and a retention time of 4 h.

Commercial Ru/C was used by Wildschut et al. (2010) to investigate catalyst stability for hydrodeoxygenation of fast pyrolysis oil in a batch reactor at 350 °C and 200 bar. After a number of catalyst recycles, a reduction of 55 - 30 wt% was observed in liquid yield; solid yield increased (3 - 20 wt%) and liquid H/C ratio decreased (1.24 - 1.08). Also, methane content of gas reduced. Furthermore, hydrodeoxygenation of fast pyrolysis oil and phenol over in-house prepared Ru/Cs using three different Ruthenium precursors (RuCl₃, Ru(NO)(NO₃)₂ and Ru(acac)₃) and three different Ruthenium loadings (1, 3 or 5 wt%) was studied. The Ru/C prepared using RuCl₃ with the loading of 5 wt% was found to be the most active catalyst among the nine resulted Ru/Cs.
In another research by Wildschut et al. (2010), hydro(deoxy)genation of fast pyrolysis oil over Ru/C at 350 °C and 200 bar in a batch reactor was studied to better understand the effect of retention time on oil yield and elemental composition of produced fractions. The results will be discussed later in the "retention time effect" section.

### 2.2.3.2. Temperature effect

Temperature is another dominating parameter during hydrodeoxygenation of pyrolysis oil. The effect of temperature is discussed below according to formerly described studies by Wildschut et al. (2009) and de Miguel Mercader et al. (2011) which utilized Ru/C for hydrodeoxygenation of fast pyrolysis oil in a batch reactor.

According to the study on screening noble catalysts by Wildschut et al. (2009), Ru/C was successful at 350 °C rather than 250 °C. Its oxygen removal and oil yield significantly improved with increasing temperature from 250 °C to 350 °C; the oxygen content of oil decreased from ~ 23 wt% to ~ 6 wt% and its yield increased from ~ 25 wt% to ~ 55 wt% (summation of top and bottom oil).

Temperature effect was well studied by de Miguel Mercader et al. (2011) on hydrodeoxygenation of fast pyrolysis oil fractions. Fast pyrolysis oil underwent induced phase separation by adding water and two fractions were obtained; aqueous fraction and oil fraction (pyrolytic lignin). Then, these two fractions and whole fast pyrolysis oil were hydrodeoxygenated at 220 °C, 270 °C and 310 °C. Oxygen removal improved with temperature for all of the feeds (except for aqueous fraction, it remained constant from 220 °C to 270 °C). The oil yield of aqueous fraction increased with temperature from 220 °C to 270 °C and remained constant from 270 °C to 310 °C. In contrast, the oil yield of oil fraction decreased within the whole temperature range due to increase in the amount of produced water. However for the whole oil, it remained almost constant due to increase in water production and decrease in aqueous phase yield obtained after hydrodeoxygenation. Although the oil yield of whole oil was remained almost constant with temperature, its quality improved. Coke formation tendency (determined by micro carbon residue test; MCRT) decreased and molar mass distribution shifted to a lower molar mass range.
2.2.3.3. Retention time effect

Retention time is another important parameter for hydrodeoxygenation of pyrolysis oil. Batch reactor seems to be the most suitable experimental setup to study the effect of retention time on hydrodeoxygenation product quality.

Wildschut et al. (2010) explored the effect of retention time on oil yield and elemental composition of produced fractions via hydro(deoxy)genation of fast pyrolysis oil. The experimental setup was a batch reactor with the capability of continuous hydrogen injection during hydro(deoxy)genation runs. The experiments were done at 350 °C, 200 bar and retention times of 1, 2, 4 and 6 h. Oil yield increased from 1 to 4 h and decreased from 4 to 6 h by about 10 %. From 4 to 6 h, the amount of produced gas increased showing that hydrocracking of the oil is increasing. The methane content of gas remained almost constant indicating that retention time does not likely play an important role in its production. Therefore, catalyst and temperature may be the major affecting parameters. CO₂ production increased from 13 to 19 mol%. It seems that the initial rapid CO₂ production via decarboxylation reactions becomes slower with time. The higher alkanes content of gas also increased with time which could be due to hydrocracking of oil. Solid yield is also appears to decrease with increasing temperature which is likely due to conversion of solid components to liquid and/or gas components. Hydrogen consumption remained almost constant after 4 h suggesting that catalyst deactivation occurred. However, the amount and composition of produced fractions changed at the same time. It can be concluded that the ongoing reactions after 4 h are either thermal or hydrogen inert. Molar H/C of the oils increased (from 1.05 to 1.32) due to further interaction with hydrogen throughout the course of reaction. On the other hand, their molar O/C increased (from 0.02 to 0.07) which is likely because of transferring fragments with low O/C from oil to gas (induced by hydrocracking). It can also be explained by transferring high molar O/C fragments of aqueous fraction to oil.

2.3. Stabilizing pyrolysis oil prior to upgrading

Pyrolysis oil can be stabilized before upgrading via removing or reducing the concentration of its reactive components. The aim of stabilization is to decrease/inhibit
polymerization during upgrading to achieve less/no coking and molar mass reduction of upgraded oil. Carboxylic acids are amongst the reactive components of pyrolysis oil. Esterification is a route to stabilize pyrolysis oil through neutralizing carboxylic acids with alcohols (Zhang et al., 2006). Carbohydrates are the other reactive constituents of pyrolysis oil being (partly) responsible for molar mass increase (polymerization) of pyrolysis oil during hydrolysis, hydrotreating, steam reforming or high pressure thermal treatment (Hu et al., 2011; Megawati et al., 2011; Li et al., 2011; Wildschut et al., 2009; Marquevich et al., 1999; de Miguel Mercader et al., 2010).

2.4. Summary and conclusion

Pyrolysis oil is a potential resource for fuels and chemicals which are derived from petroleum currently. Considering the decline in petroleum resources on one hand and the rise in demand by emerging economies on the other hand, it seems imperative to find a replacement for petroleum. Although pyrolysis oil must undergo a treatment to meet the chemical and physical properties of petroleum in order to enter petroleum refinery network, it is the only commercialized lignocellulosic biomass derivative from which liquid fuels can be produced. Liquefaction technologies need further development to reach an equivalent status to current status of pyrolysis. In order to decrease the capital cost of producing liquid fuels from pyrolysis oil, the treatment process can be incorporated in petroleum refinery connected to its established network.

Pyrolysis oil has a reactive nature originating from its high oxygen content. The reactive nature leads to polymerization (molar mass increase) of pyrolysis oil during storage and processing. During storage, polymerization results in viscosity increase and phase separation of pyrolysis oil. During processing, it results in coke and char formation deactivating the catalyst and plugging the reactor. A mild pretreatment (stabilization) can make pyrolysis oil more resistant to polymerization during storage and processing. Stabilization seems to be more effective while dealing with a pyrolysis oil sample which is less stable due to production equipment limitation and/or less suitable type of biomass.

This thesis has focused on examining the effects of stabilization with an alcohol (predominantly via esterification) on processing which is done via upgrading. Two
different pyrolysis oil samples were used for this study. The sample used for chapter 3 had a high water content likely containing more carboxylic acids and sugars which are the main compounds responsible for instability of pyrolysis oil. It was product of ICFAR (Canada). The other sample used for chapter 4 was more stable and product of BTG (The Netherlands).
2.5. References


CHAPTER 3. UPGRADING FAST PYROLYSIS OIL VIA HYDRODEOXYGENATION AND THERMAL TREATMENT: EFFECTS OF CATALYTIC GLYCEROL PRETREATMENT

3.1. Introduction

Since mankind’s energy demand is increasing rapidly due to a growing population and high economic development, lignocellulosic biomass can contribute to energy security (Czernik & Bridgwater, 2004; Huber et al., 2006; Wang et al., 2007). Furthermore, it can be a resource to produce chemicals which are derived from crude oil (Ibáñez et al., 2012). However, due to low volumetric energy density, lignocellulosic biomass should undergo an initial energy condensation process. Pyrolysis while performing energy condensation provides feasibility for further processing (Venderbosch et al., 2010), as processing a biomass derived liquid is more viable than processing solid biomass. Therefore, to minimize transportation cost, pyrolysis plants can be built at the nearest point to the origin of biomass and pyrolysis oil can be transported to processing facilities.

Pyrolysis oil has high oxygen content in the form of water and functional groups that results in a similar elemental composition to that of biomass from which it has been derived rather than crude oil (Mohan et al., 2006; Vitolo et al., 1999). The oxygen content leads to a lower heating value (LHV) of around that of biomass and half that of hydrocarbon fuels (Oasmaa & Czernik, 1999; Wildschut et al., 2009). It also makes pyrolysis oil immiscible with conventional hydrocarbon fuels (Joshi & Lawal, 2012; Baldauf et al., 1994). The functional groups (majorly hydroxyaldehydes, hydroxyketones, carboxylic acids, sugars and phenolics) cause pyrolysis oil to be chemically unstable (Bridgwater, 2004; Fisk et al., 2009). The high acidity and subsequent corrosiveness of pyrolysis oil is due to its considerable carboxylic acid and phenolics content. The lack of chemical stability mainly appears in the form of self-polymerization during storage and processing (Hu et al., 2012; Diebold & Czernik, 1997). Self-polymerization of pyrolysis oil must be highly prevented during processing, as it can lead to reactor plugging and

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1 A version of this chapter will be submitted to Energy & Fuels.
coke formation (Elliott & Neuenschwander, 1996). The above drawbacks prevent pyrolysis oil from being suitable for direct use as a transportation fuel, thereby emphasizing the necessity of upgrading.

The process of producing transportation fuels from pyrolysis oil can be integrated with the existing infrastructure via incorporating a stabilization process in pyrolysis plant and an upgrading process in standard petroleum refinery. Pyrolysis oil can be stabilized after production at pyrolysis plant. Then, stabilized pyrolysis oil is transported to the standard petroleum refinery in which the upgrading process is incorporated. The upgrading process which is performed via hydrodeoxygenation (HDO) reduces the oxygen content of stabilized pyrolysis oil, thereby improving miscibility with crude oil fractions (Elliott, 2007). Upgraded oil is blended with conventional crude oil fractions (e.g. vacuum gas oil) and undergoes co-refining (e.g. FCC) to produce transportation fuels. To summarize, the overall process is comprised of three steps: stabilization, upgrading and co-refining.

The advantages of this process are as follows:

1) Increasing the stability of pyrolysis oil to reduce self-polymerization during storage and processing.

2) Decreasing the capital cost of producing transportation fuels from pyrolysis oil due to using the existing infrastructure for stabilization and upgrading.

3) Reduction in hydrogen gas consumption during upgrading, as for co-refining upgraded pyrolysis oil with a crude oil fraction, complete oxygen removal of pyrolysis oil is not necessary (de Miguel Mercader et al., 2011).

In literature, stabilization with an alcohol (esterification) is raised as a promising route to reduce the reactivity of fast pyrolysis oil (Zhang et al., 2006; Lohitharn and Shanks, 2009; Hilten et al., 2010).

This research focuses on examining the effects of stabilization with an alcohol (namely catalytic alcohol pretreatment) on subsequent upgrading. The quality of upgraded oils as the potential co-feeds for co-refining is the basis of assessment instead of tracking specific compounds. Therefore, inhibition or reduction of self-polymerization during
upgrading is desired. Thermal treatment (TT) is selected as a parallel upgrading route with HDO to obtain more insight into the effects of catalytic alcohol pretreatment on self-polymerization during upgrading. To produce stabilized fast pyrolysis oil (GPO) via catalytic alcohol pretreatment, glycerol (a byproduct of biodiesel industry) was used. However, other alcohols can also be effective to different extents. Then, GPO was upgraded via HDO or TT and the processed oils were compared with those obtained via HDO or TT of non-stabilized fast pyrolysis oil.

3.2. Material and Methods

Fast pyrolysis oil (PO) was produced using a mechanically fluidized reactor (MFR) designed at Institute for Chemicals and Fuels from Alternative Resources (ICFAR). Biochar was the other product of the MFR. PO had a water content of 52 wt% and a heating value of 14.6 MJ/kg. This unit was operated in continuous mode with a feed rate of 30 kg/h. Hardwood sawdust was used as the feed with an average particle size of 2 mm at a pyrolysis temperature of 500 ºC and a vapor residence time of a few seconds.

Stabilized fast pyrolysis oil (GPO) was produced in a stirred autoclave supplied by Parr Instrument Company with a nominal internal volume of 500 mL. In each GPO production run, approximately 150 g of PO and 75 g of glycerol was loaded into the autoclave and 3 wt% (on wet liquid feed basis) dry Amberlyst 35 (Rohm and Haas) was added to the liquid. Then, the autoclave was sealed and a leak test was performed at 30 barg of nitrogen for 20 min. If no leak was observed, the nitrogen was vented while removing the remaining air from the inside of autoclave. The autoclave was flushed twice by nitrogen at 30 barg to remove any residual air and filled with nitrogen at 2 barg as the initial pressure. The stirrer speed was set at 360 rpm and heating started at an approximate rate of 2 ºC/min and the temperature was maintained at 120 ºC. The retention time of the liquid inside the autoclave was 2 h including the heating time. After 2 h, heating was stopped and a cooling water bath was used to quench the vessel to room temperature. The gas was collected in a gas bag for analysis and the autoclave was opened to collect the liquid product. Since the amount of produced gas was negligible, its composition is not included here. The stirrer was kept on at 180 rpm until the whole gas was collected to
remove any dissolved gas from the liquid. No phase separation of the liquid was observed. The liquid product was collected and the spent catalyst was separated by centrifuge.

HDO experiments were performed using the same setup previously used to produce GPO. The setup had the ability of being operated in batch or semi-batch mode of hydrogen. It was operated in batch mode for all of the HDO experiments performed for this article. The schematic view of the setup is shown in Figure 3-1.

![Figure 3-1: Schematic view of experimental setup](image)

In each HDO run, approximately 150 g of the feed (PO or GPO) was loaded into the autoclave and 3.33 wt% (on wet feed basis) Ru/C (Sigma/Aldrich; Ru loading: 5 wt%; used without any pretreatment) as the catalyst was added to the liquid. The autoclave was sealed and a leak test was performed at 1500 psig (103 barg) of hydrogen for 20 min. If no leak was detected, the gas was vented and the air which was inside the autoclave from the beginning was removed by the hydrogen. Afterwards, the autoclave was purged twice with 20 bar of hydrogen to remove any remaining air from the inside and filled with hydrogen at 1000 psig (69 barg) as the initial pressure. The stirrer speed was set at 360 rpm and heating started at an approximate rate of 11 ºC/min and the temperature was
maintained at 300 °C. The retention time of the liquid and the catalyst inside the autoclave was 3 h including the heating time. After 3 h, heating was stopped and the cooling loop which was inside the autoclave was used to quench the content of the autoclave with ice cooled water for 30 min. During internal cooling, the stirrer was kept on at 360 rpm. After 30 min, the temperature of autoclave reached ~ 75 °C and for further cooling to room temperature, the cooling loop was switched to an ice cooled water bath to continue cooling from outside. Also, the stirrer speed was reduced to 180 rpm and the stirrer was kept on until the whole gas was collected to remove any dissolved gas from the liquid. The gas was collected at room temperature in a gas bag for analysis. The autoclave was opened to collect the liquid product. Phase separation was observed in the liquid product. To improve phase separation, the liquid product was poured in centrifuge vials and underwent centrifugation for 30 min at a speed of 4500 rpm. Afterwards, two phases were obtained; an organic phase (namely oil fraction; OF) which contained oxygen lean (semi-hydrophobic; AF) fragments and the spent catalyst and an aqueous phase (namely aqueous fraction) which contained water and hydrophilic fragments. The obtained fractions were separated for analysis.

For TT experiments, the procedure was similar to HDO experiments. No catalyst was added to the feed. To perform the leak test and flushing the autoclave, nitrogen was used at the same pressures of hydrogen and the autoclave was filled with nitrogen at 1000 psig (69 barg) as the initial pressure. The heating rate, temperature set point and residence time were identical. The quenching procedure was also the same. After quenching the autoclave to room temperature, the gas was collected. Since a clear phase separation was observed, only decantation was used to separate the two phases. The obtained oil fractions were visually very different from that obtained from HDO. The oil fractions were very viscous and contained char to some extent. A higher amount of char was observed in oil fraction of PO.

3.3. Results and Discussion

Table 3-1 compares the properties of PO and GPO with those of glycerol and dehydrated glycerol.
**Table 3-1: Properties of PO, GPO, glycerol and dehydrated glycerol**

<table>
<thead>
<tr>
<th></th>
<th>PO</th>
<th>GPO</th>
<th>glycerol</th>
<th>dehydrated glycerol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Elemental composition and water content</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C (wt%)</td>
<td>23.1</td>
<td>29.7</td>
<td>39.1</td>
<td>48.6</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>9.0</td>
<td>8.9</td>
<td>8.7</td>
<td>8.1</td>
</tr>
<tr>
<td>O (wt%)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>67.9</td>
<td>61.4</td>
<td>52.2</td>
<td>43.2</td>
</tr>
<tr>
<td>C (glycerol and water free wt%)</td>
<td>47.9</td>
<td>48.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H (glycerol and water free wt%)</td>
<td>6.7</td>
<td>7.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O (glycerol and water free wt%)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>45.4</td>
<td>44.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H/C&lt;sub&gt;eff&lt;/sub&gt; (glycerol and water free)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.26</td>
<td>0.49</td>
<td>0.67</td>
<td>0.67</td>
</tr>
<tr>
<td>Water (wt%)</td>
<td>51.8</td>
<td>35.3</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Glycerol content**

|                       |          |         |          |                     |
| Initial glycerol (wt%) | -       | 33.7    |          |                     |
| Residual glycerol (wt%) | -     | 15.8    |          |                     |

**Carbon residue**

|                       |          |         |          |                     |
| MCRT (wt%)            | 10.6     | 5.3     |          |                     |
| MCRT (glycerol and water free wt%) | 22.0 | 10.7    |          |                     |

<sup>a</sup> calculated by difference

<sup>b</sup> H/C<sub>eff</sub> = molar H/C − 2 × molar O/C. H/C<sub>eff</sub> 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. H/C<sub>eff</sub> (sugars) ≈ 0, H/C<sub>eff</sub> (aromatics) ≈ 1, H/C<sub>eff</sub> (alkanes) ≈ 2.

Glycerol and water free carbon and oxygen content of PO were similar to those of GPO. However, GPO had higher hydrogen content (on glycerol and water free basis). It appears that the carbon and oxygen content of incorporated glycerol were similar to those of dry PO, as the carbon and oxygen content of GPO (on glycerol and water free basis) did not significantly deviate from those of dry PO. Therefore, almost no excess oxygen was added to dry PO via incorporated glycerol. However, extra hydrogen was introduced into dry PO via incorporated glycerol. Carbon and oxygen content of dehydrated glycerol are similar to those of dry PO while its hydrogen content is higher than the hydrogen content of PO and GPO (on glycerol and water free basis). It seems that glycerol dehydration occurred and incorporated glycerol was partly in the form of dehydrated glycerol. However, if the whole incorporate glycerol was dehydrated glycerol, the hydrogen content of GPO would be 7.1 wt% which is less the measured value by 0.4 wt%.

Theoretical water content of GPO assuming no reaction would be 34.3 wt%. Also, assuming that one mole of water was produced per one mole of converted glycerol, water content increase of PO would be 3.5 wt% resulting in a water content of 37.8 wt%. The difference between this value and the measured value (35.3 wt%) seems to be too small to judge the ongoing reactions based on the change of water content due to the possibility
of instrumental error. On the other hand, assuming that the instrumental measurement was correct, such a small increase (1 wt%) in water content suggests that although esterification reactions might significantly occur during catalytic glycerol pretreatment, the produced water could be consumed again via other reactions (e.g. hydrolysis).

Glycerol content analysis indicates that approximately 50 wt% of glycerol was converted to incorporated glycerol during catalytic glycerol pretreatment. Such a high glycerol conversion significantly increased $H/C_{eff}$ value suggesting that the chemical structure of GPO was considerably deviated from that of PO. Also, micro carbon residue test (MCRT) measured a much lower value for GPO showing that coke formation tendency of GPO was lower than that of PO. Therefore, GPO is likely more stable during processing.

Figure 3-2 shows molar mass distribution of the two feeds. The chromatograms are identical over $M > 1000$ g/mol. It seems that incorporated glycerol did not contribute to molar mass increase of PO via polymerization. However, glycerol incorporation has altered the molar mass distribution of PO over $M < 1000$ g/mol.

![Figure 3-2: Molar mass distribution of PO and GPO](image)

Figure 3-3 shows glycerol and water free distribution of mass and carbon in produced oil fractions, aqueous fractions and gas fractions via HDO and TT of PO and GPO. It is
obtained by combining the mass, elemental composition, water content and residual glycerol content of HDO and TT oil fractions, aqueous fractions and gas fractions.

Figure 3-3: Glycerol and water free distribution of mass and carbon in produced oil fractions, aqueous fractions and gas fractions through HDO and TT of PO and GPO

Higher mass and carbon was obtained from oil fractions of TT in comparison to those of HDO. It seems that polarity increase was higher during TT increasing the amount of transferred compounds from aqueous fractions to oil fractions. However, TT produced a significant amount of char (solids collected together with oil fractions). The amount of produced char was ~ 20 wt% of GPO TT oil fraction and ~ 50 wt% of PO TT oil fraction. Char was considered as a part of TT oil fraction to obtain Figure 3-3. Although higher carbon content can be recovered in oil fractions of TT, they are not likely the potential feeds for further processing (e.g. co-refining via FCC), as their high molar mass components (Figure 3-6) may promote coke formation.

After HDO or TT of GPO, higher amount of organic compounds remained in aqueous fraction in comparison to HDO or TT of PO respectively (Figure 3-3). It seems that the fragments produced via HDO or TT of catalytic glycerol pretreatment derived compounds and/or residual glycerol are hydrophilic leading to higher carbon content of
aqueous fraction. The excess amount of glycerol which was used in GPO production resulted in high concentration of residual glycerol which might increase the concentration of residual glycerol derived fragments in aqueous fraction.

In gas fractions of TT of PO or GPO, higher carbon content was obtained in comparison to those of HDO of PO or GPO respectively indicating that gas production was promoted during TT. Also, via TT or HDO of GPO, the carbon content of produced gas fractions was lower than those of TT or HDO of PO respectively indicating that GPO was more resistant to gasification. Since the dominant component of gas fractions was CO₂, the above pattern was observed in CO₂ production as shown in Table 3-2.

**Table 3-2: CO₂ production via HDO and TT of PO and GPO**

<table>
<thead>
<tr>
<th></th>
<th>HDO (PO)</th>
<th>TT (PO)</th>
<th>HDO (GPO)</th>
<th>TT (GPO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ production [mol CO₂/kg glycerol and water free feed]</td>
<td>2.1</td>
<td>3.0</td>
<td>1.0</td>
<td>1.8</td>
</tr>
</tbody>
</table>

CO₂ production profile suggests that decarboxylation was reduced (de Miguel Mercader et al., 2010) in GPO which resulted in lower CO₂ production during HDO or TT. On the other hand, the amount of produced CO₂ during TT is higher compared to HDO which shows a good correlation with molar mass distribution of their oil fractions (Figure 3-5 and Figure 3-6).

Table 3-3 shows the distribution of residual glycerol in oil fractions and aqueous fractions obtained via HDO and TT of GPO.

**Table 3-3: Residual glycerol distribution in oil fractions and aqueous fractions from HDO and TT of GPO**

<table>
<thead>
<tr>
<th></th>
<th>GPO</th>
<th>HDO (OF)</th>
<th>HDO (AF)</th>
<th>TT (OF)</th>
<th>TT (AF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual glycerol [g]</td>
<td>23.5</td>
<td>0.5</td>
<td>15.0</td>
<td>1.0</td>
<td>14.0</td>
</tr>
</tbody>
</table>

The table shows that although residual glycerol highly converted during HDO and TT, the converted amounts were very similar. It seems that the conversion of glycerol was mostly affected by the experimental conditions (e.g. temperature) rather than the different reaction routes of HDO or TT. The table also indicates that if an excess amount of
glycerol is used for catalytic glycerol pretreatment, the majority of residual glycerol after upgrading will be present in aqueous fraction.

Table 3-4 shows the properties of produced oil fractions through HDO and TT of PO and GPO.

<table>
<thead>
<tr>
<th></th>
<th>HDO (PO)</th>
<th>TT (PO)</th>
<th>HDO (GPO)</th>
<th>TT (GPO)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Elemental composition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C (glycerol and water free wt%)</td>
<td>69.2</td>
<td>71.8</td>
<td>70.6</td>
<td>69.9</td>
</tr>
<tr>
<td>H (glycerol and water free wt%)</td>
<td>7.6</td>
<td>6.7</td>
<td>7.5</td>
<td>6.6</td>
</tr>
<tr>
<td>O (glycerol and water free wt%)</td>
<td>23.2</td>
<td>21.5</td>
<td>21.9</td>
<td>23.5</td>
</tr>
<tr>
<td><strong>Carbon residue</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCRT (wt%)</td>
<td>19.2</td>
<td>35.4</td>
<td>16.6</td>
<td>36.8</td>
</tr>
<tr>
<td>MCRT (glycerol and water free wt%)</td>
<td>21.8</td>
<td>35.4</td>
<td>20.5</td>
<td>37.9</td>
</tr>
</tbody>
</table>

The oxygen content of oil fractions is similar. It shows that although TT oil fractions are not likely the potential feeds for further processing due to a higher possibility of coke formation promoted by their high molar mass fragments (Figure 3-6), oxygen removal of TT was as efficient as that of HDO. Hydrogen content of HDO oil fractions (on mole basis) is more than that of TT oil fractions. It seems that a part of consumed H$_2$ incorporated in oil fractions as bonded hydrogen and used to saturate double bonds in GPO and PO. This effect will be further discussed via $\frac{\int UVDdv}{\int RIDdv}$ (namely GPC area ratio) in terms of non-aromatic conjugated double bonds. Consumed H$_2$ was also used to remove oxygen from oil fractions in the form of water.

MCRT values seem not to be consistent with the other results. The small difference in the values for oil fractions of HDO is reasonable, as the difference in their molar mass distribution is also small. However, the main inconsistency is in the values for TT oil fractions. Since TT oil fractions contain char to some extent and its distribution is not uniform in them, the inconsistency is most likely due to the existed char in the analysis samples. Therefore, it is difficult to judge oil fractions based on MCRT values.

Van Krevelen plot (Figure 3-4) shows a significant shift of the oil fractions from the feeds. First of all, HDO oil fractions have apparently higher H/C than TT oil fractions
which is expected due to catalytic hydrotreating effects. The effect of catalytic glycerol pretreatment on either HDO or TT is less significant. On the other hand, high oxygen removals were observed via TT of GPO and PO comparable to those via HDO of GPO and PO. However, the high amount of produced char in both cases indicates that TT oil fractions are not as suitable as HDO oil fractions for further processing.

![Van Krevelen plot for PO and GPO and the oil fractions from HDO or TT](image)

**Figure 3-4: Van Krevelen plot for PO and GPO and the oil fractions from HDO or TT**

The area in which HDO oil fractions appear is mostly dependent on the constituents of feed. When the feed is more aqueous with a high concentration of sugars, HDO oil fractions mostly appear in dehydration dominant area. On the other hand, a feed with high concentration of lignin-derived fragments and minimum water content, results in HDO oil fractions appearing hydrodeoxygenation and/or decarboxylation dominant area (de Miguel Mercader, 2011). Since the fast pyrolysis oil used for the experiments of this article had an aqueous nature (water content of 51.8 wt%), the oil fractions are in dehydration dominant area. However, the arrows and regions showed in Figure 3-4 are more helpful when the points are indicating combined H/C and O/C of oil fractions and aqueous fractions. Since, the instrumental error is huge while measuring the hydrogen content of aqueous fractions due to their extremely high water content, it was not viable to include the points of combined H/C and O/C in Figure 3-4.
Figure 3-5 and Figure 3-6 show molar mass distribution of the obtained oil fractions via HDO and TT, respectively. Catalytic glycerol pretreatment seems to be effective on reducing self-polymerization, thereby increasing selectivity toward HDO reactions. This effect is also shown by H$_2$ consumption profile in Table 3-5. Also, self-polymerization highly reduced during TT of GPO. However, dilution effect is likely predominant on self-polymerization reduction as shown in Figure 3-7\(^2\) which compares the molar mass distribution of HDO oil fraction of GPO with that of another feed which is the solution of PO and glycerol (direct loading of glycerol at 50 wt% of PO; HDO was done at the same conditions of HDO of GPO). Although the oil fraction obtained via TT of GPO is comprised of lighter fragments, it still contains a considerable amount of char which may prevent it from being suitable for further processing. However, TT can be an option to upgrade GPO if the experimental conditions are optimized to produce the minimum amount of high molar mass fragments.

![Molar mass distribution of HDO oil fractions](image)

**Figure 3-5: Molar mass distribution of HDO oil fractions**

\(^2\) Obtained at a different configuration of the analysis instrument from the one used for Figures 3-5 and 3-6.
Table 3-5 shows the values of GPC area ratio which are calculated by directly integrating the surface area of GPC chromatograms obtained from UV and RI detectors for the feeds and oil fractions. The above ratio is an indication of relative aromaticity and conjugated double bond content (Hoekstra et al., 2011). The table suggests that GPC area ratio has a similar profile for HDO and TT of the feeds; it decrease from PO or GPO to HDO oil fraction and again increases from HDO oil fraction to TT oil fraction. The table compares GPC area ratio with $H/C_{\text{eff}}$. 
Table 3-5: \( \int \frac{UVDdv}{RIDsdv} \) and H/C\(_{eff} \) of oil fractions and H\(_2\) consumption

<table>
<thead>
<tr>
<th></th>
<th>PO</th>
<th>HDO (PO)</th>
<th>TT (PO)</th>
<th>GPO</th>
<th>HDO (GPO)</th>
<th>TT (GPO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \int \frac{UVDdv}{RIDsdv} \times 10^{-3} )</td>
<td>13</td>
<td>10</td>
<td>56</td>
<td>9</td>
<td>4</td>
<td>21</td>
</tr>
<tr>
<td>H/C(_{eff} )</td>
<td>0.26</td>
<td>0.83</td>
<td>0.69</td>
<td>0.49</td>
<td>0.81</td>
<td>0.63</td>
</tr>
<tr>
<td>H(_2) consumption [mol H(_2)/kg glycerol and water free feed]</td>
<td>-</td>
<td>8.1</td>
<td>-</td>
<td>-</td>
<td>8.6</td>
<td>-</td>
</tr>
</tbody>
</table>

It shows that although GPC area ratio has the lowest value for HDO oil fractions, H/C\(_{eff} \) has the highest value. It can be concluded that the relative aromaticity of HDO oil fractions has the highest value (shown by H/C\(_{eff} \) values) and their overall chemical structure is deviated from sugars to aromatics (H/C\(_{eff} \) for sugars \( \approx 0 \) and for aromatics \( \approx 1 \)). On the other hand, HDO oil fractions most likely have the lowest non-aromatic conjugated double bond content, as the consumed H\(_2\) was partly used to saturate those bonds. TT oil fractions also seem to be aromatic while having a higher concentration of non-aromatic conjugated double bonds. H\(_2\) consumption is likely linked to GPC area ratio as well, as higher H\(_2\) consumption has resulted in lower GPC area ratio. It seems that higher H\(_2\) consumption increased the amount of saturated non-aromatic conjugated double bond leading to a lower GPC area ratio.

3.4. Conclusions

The effects of stabilizing fast pyrolysis oil via catalytic glycerol pretreatment on upgrading were studied. Non-stabilized fast pyrolysis oil was also upgraded to obtain benchmarks. Three major conclusions can be drawn by summarizing the observed effects:

The carbon content of aqueous fractions obtained after upgrading stabilized oil was higher due to production of hydrophilic fragments from stabilization derived fragments and/or residual glycerol during upgrading which led to lower carbon content of oil fractions. To maximize the yield of oil fractions (main products), reducing the initial concentration of alcohol may be helpful. However, reduction in alcohol concentration may alter the extent of other effects of stabilization.
Although the hydrogen content of stabilized oil was higher and it consumed more H₂ during HDO, HDO oil fractions had similar molar H/Cs which could be due to the interaction of aqueous fractions. Molar O/Cs were also similar indicating that oxygen removal from oil fractions did not affected by stabilization. It seems that the most effective parameters on altering the elemental composition of oil fractions are experimental conditions (e.g. temperature and residence time).

Molar mass distribution analysis indicated that the produced oil fractions via HDO or TT of stabilized oil contained lighter fragments. However, direct HDO of fast pyrolysis oil and glycerol solution (at the same ratio used for stabilization) implied that dilution plays an important role during upgrading in reducing the molar mass of oil fractions. Therefore, dilution while being beneficial via reducing molar mass decreased the carbon content of oil fractions.

Different alcohols may affect stabilization and upgrading to different extent, as their reactivity towards fast pyrolysis oil can be significantly different. It will be beneficial to reduce the concentration of alcohol to maximize the yield of oil fraction while maintaining the positive effects of stabilization. As such, in our future study, various alcohols (methanol, ethanol and glycerol) at a much lower concentration will be tested to examine the effects of catalytic alcohol pretreatment on stabilization and subsequent upgrading.
3.5. References


CHAPTER 4. THE EFFECTS OF STABILIZING FAST PYROLYSIS OIL VIA CATALYTIC ALCOHOL PRETREATMENT ON HYDRODEOXYGENATION: ALCOHOL VARIATION AT MINIMIZED DILUTION

4.1. Introduction

Lignocellulosic biomass is a potential resource for fuels, hydrocarbons for petrochemical synthesis and hydrogen currently derived from petroleum (Ibáñez et al., 2012). Pyrolysis increases energy density of lignocellulosic biomass, providing feasibility for further processing at the same time (Venderbosch et al., 2010). In order to minimize transportation cost, pyrolysis plants can be built at the nearest point to the origin of biomass and pyrolysis oil can be transported to processing facilities.

Pyrolysis oil has a high oxygen content comprised of oxygen of water and oxygenated compounds resulting in a similar elemental composition to that of biomass rather than petroleum (Mohan et al., 2006; Bridgwater, 2004). The oxygen content leads to a lower heating value (LHV) of around that of biomass and half that of petroleum derived fuels (Oasmaa & Czernik 1999; Wildschut et al., 2009). It also makes pyrolysis oil immiscible with petroleum based fuels (Joshi & Lawal, 2012; Baldauf et al., 1994). The oxygenated compounds (aldehydes, ketones, carboxylic acids, alkenes and guaiacol-type fragments) cause pyrolysis oil to be chemically unstable (Fisk et al., 2009; Hu et al., 2012). Carboxylic acids and phenolics are also responsible for the high acidity of pyrolysis oil. The lack of chemical stability mainly appears in the form of self-polymerization during storage and processing (Hu et al., 2012; Diebold & Czernik, 1997). Self-polymerization of pyrolysis oil during processing can lead to reactor plugging and coke formation (Elliott & Neuenschwander, 1996). The above drawbacks prevent pyrolysis oil from being suitable for direct use as a transportation fuel, thereby emphasizing the requirement for upgrading.

3 A version of this chapter will be submitted to Energy & Fuels.
The process of producing transportation fuels from pyrolysis oil can be integrated with the existing infrastructure via incorporating a stabilization process in pyrolysis plant and an upgrading process in standard petroleum refinery. Pyrolysis oil can be stabilized via a mild pretreatment after production at pyrolysis plant. Then, stabilized pyrolysis oil is transported to the standard petroleum refinery in which the upgrading process is incorporated. The upgrading process which is performed via hydrodeoxyg enation (HDO) reduces the oxygen content of stabilized pyrolysis oil, thereby improving its miscibility with petroleum based fuels (Elliott, 2007). Upgraded oil is blended with conventional petroleum fractions (e.g. vacuum gas oil) and undergoes co-refining (e.g. FCC) to produce transportation fuels.

The advantages of this process are as follow:

1) Increasing the stability of pyrolysis oil to reduce self-polymerization during storage and processing.

2) Decreasing the capital cost of producing transportation fuels from pyrolysis oil due to using the existing infrastructure for stabilization and upgrading.

3) Reduction in hydrogen gas consumption during upgrading, as for co-refining upgraded pyrolysis oil with a petroleum fraction, complete oxygen removal of pyrolysis oil is not necessary (de Miguel Mercader et al., 2011).

It is reported that fast pyrolysis oil can be treated with alcohol to increase stability via reducing the amount of reactive compounds (majorly carboxylic acids) (Zhang et al., 2006; Lohitharn and Shanks, 2009; Hilten et al., 2010). It is expected that increase in stability will decrease self-polymerization during storage and/or processing. In our previous study (chapter 3), glycerol at a relatively high concentration was used for stabilizing fast pyrolysis oil. Subsequently, stabilized oil was processed via HDO or thermal treatment (TT). It was observed that the major expected effect of stabilization
(self-polymerization reduction) was induced by dilution due to the relatively high concentration of glycerol rather than reactivity reduction due to stabilization.

This research is examining the effects of alcohol variation on catalytic alcohol pretreatment (stabilization) and subsequent HDO (upgrading) at minimized dilution effect conditions. Here, TT was only used once to test the resistance of stabilized pyrolysis oil at self-polymerization promoting conditions. Fast pyrolysis oil was stabilized utilizing methanol, ethanol and glycerol via catalytic alcohol pretreatment. Stabilized oil samples were called MPO, EPO and GPO respectively. NPO was the product of stabilization without any alcohol at the same conditions of catalytic alcohol pretreatment. The feeds were upgraded via HDO while feeding hydrogen at semi-batch mode. Upgraded oils were compared subsequently.

4.2. Material and Methods

The hardwood sawdust fast pyrolysis oil (PO) used for this study was supplied by BTG with a water content of 28 wt% and a heating value of 17.2 MJ/kg. It was much more stable in comparison to the fast pyrolysis oil used for chapter 3. The stirred autoclave used for stabilization and upgrading (Parr Instrument Company; nominal internal volume of 500 mL) was a part of the setup developed for semi-batch injection of hydrogen into the autoclave while maintaining its pressure at a desired level. To produce MPO, EPO or GPO, typically 275 g of PO and 5 wt% (on wet PO basis) methanol, ethanol or glycerol (respectively) were loaded into the autoclave and 3 wt% (on wet liquid mixture basis) fresh dry Amberlyst 35 (Rohm and Haas; used without any pretreatment) was added to the liquid mixture. To produce NPO, no alcohol was used while adding 3 wt% (on wet PO basis) the same catalyst to PO. Then, the autoclave was sealed and a leak test was performed at 30 barg of nitrogen for 20 min. If no leak was observed, the nitrogen was vented while removing the air from the inside of autoclave. The autoclave was flushed twice by nitrogen at 30 barg to remove any residual air and filled with nitrogen at 2 barg as the initial pressure. The stirrer speed was set at 360 rpm and heating started at an approximate rate of 2 °C/min. The temperature set point was 100 °C. The retention time of liquid was 2 h including the heating time. After 2 h, heating was stopped and a cooling
water bath was used to quench the autoclave to room temperature. The gas was collected in a gas bag for analysis and the autoclave was opened to collect the liquid product. Since a very small amount of gas was produced, its composition analysis is not included here. The stirrer was kept on at 180 rpm until the whole gas was collected to remove any dissolved gas from the liquid. No phase separation of the liquid was observed. The liquid product was collected and the spent catalyst was separated by centrifuge at 4500 rpm and 30 min.

The following is the overview of HDO experiments. We intended to observe the possible effects of stabilization in different regimes.

300 °C: semi-batch mode of hydrogen; 100 barg of hydrogen (initial pressure); 150 bar of hydrogen (semi-batch mode pressure); 3 h

350 °C: semi-batch mode of hydrogen; 100 barg of hydrogen (initial pressure); 200 bar of hydrogen (semi-batch mode pressure); 3 h

200 °C: batch mode; 100 barg of hydrogen (initial pressure); 3 h

Hydrogen was always injected into the autoclave from a supply vessel (Swagelok, nominal volume of 300 mL) while recording its pressure and temperature by a PC (Figure 4-1). The recorded data in combination with the data obtained from analysis of each HDO gas fraction was used to calculate the amount of consumed hydrogen.
For each HDO run, typically 150 g of the feed was loaded into the autoclave and 3.33 wt% (on wet feed basis) Ru/C (Sigma/Aldrich; Ru loading: 5 wt%; used without any pretreatment) was added to the feed as the catalyst. The autoclave was sealed and stirring was started at 360 rpm. The leak test was performed at 150 barg of hydrogen for 20 min. If no leak was detected, the hydrogen was vented while removing a part of residual air from the inside of autoclave. Then, the residual air was completely removed from the inside of autoclave, supply vessel and lines using a vacuum pump. The heating rate was ~11 °C/min for all of HDO runs.

PO, MPO, EPO, GPO and NPO were the feeds for the set of HDO runs at 300 °C. During these runs, the autoclave was operated in batch mode initially for 1 h including the heating time. To fill the autoclave with 100 barg of hydrogen (initial pressure), the supply vessel was filled up to ~250 barg of hydrogen. Then, R1 was set to 100 barg and V1 was opened to let the hydrogen into the lines. Subsequently, V2 was opened to fill the autoclave with hydrogen at 100 barg. However, due to safety and volume limitation of the supply vessel, the initial filling of autoclave was done in three steps (first injection,
refilling supply vessel, second injection). Then, heating was started and the autoclave was kept in batch mode for 1 h (V2 and V1 were closed). Once more, the supply vessel was refilled up to ~ 250 barg to provide the maximum pressure difference during semi-batch mode. After 1 h, R1 was set to 150 barg and V1 was open to increase the pressure of lines to 150 barg. Afterwards, V2 was opened and the pressure of the autoclave increased to 150 barg. The pressure was maintained at 150 barg for the next 2 h to continuously compensate consumed hydrogen (V2 and V1 were kept open). The temperature was maintained at 300 ºC. Figure 4-2 and Figure 4-3 show samples of typical P-t and T-t graphs respectively.

![Figure 4-2: Pressure vs. time](image)

![Figure 4-3: Temperature vs. time](image)

After an overall retention time of 3 h, V2 and V1 were closed and heating was stopped. The cooling loop inside the autoclave was used to quench the content of the autoclave with ice cooled water for 30 min. During internal cooling, the stirrer was kept on at 360 rpm. After 30 min, the temperature of autoclave reached ~ 75 ºC and for further cooling to room temperature, the cooling loop was switched to an ice cooled water bath to
continue cooling from outside. The stirrer speed was reduced to 180 rpm and kept at this speed until the whole gas was collected to remove any dissolved gas from the liquid. The gas was collected at room temperature in a gas bag for analysis. The autoclave was opened to collect the liquid product. Phase separation was observed in the liquid product. To improve phase separation, the liquid product was poured in centrifuge vials and underwent centrifugation for 30 min at a speed of 4500 rpm. Afterwards, two phases were obtained; an organic phase (namely oil fraction; OF) which contained oxygen lean (semi-hydrophobic) fragments and the spent catalyst and an aqueous phase (namely aqueous fraction; AF) which contained water and hydrophilic fragments. The obtained fractions were separated for analysis.

The same methodology of HDO runs at 300 ºC was applied to HDO runs at 350 ºC. The differences in experimental conditions are the temperature set point (350 ºC) and the pressure of hydrogen in semi-batch mode (200 barg). The feeds for these runs were PO and MPO.

For HDO runs at 200 ºC, the method used for initially filling the autoclave at 300 ºC and 350 ºC with hydrogen at 100 barg was applied, but the reactor was kept at batch mode until the end of runs. PO and MPO were the feeds for this set of HDO runs.

PO and MPO also underwent TT at 200 ºC. The initial pressure of nitrogen was 50 barg. The retention time of the feeds inside the autoclave was 75 min including the heating time. The same heating rate of HDO runs (11 ºC/min) was used to reach the temperature set point.

4.3. Results and Discussion

Elemental composition and alcohol content of the feeds are shown in Table 4-1.
Elemental composition of the feeds on wet and residual alcohol included basis is similar. It seems that the only considerable difference is the higher hydrogen content of GPO in comparison to that of the other feeds due to low molar mass of hydrogen. This difference is magnified in dry and residual alcohol free elemental composition of the feeds. Although carbon contents on dry and residual alcohol free basis are similar, hydrogen contents are very different. It can be seen that for MPO and EPO, hydrogen content decreased by 0.4 wt% while for GPO, it increased by 0.2 wt%. High hydrogen content of GPO is coupled with high glycerol consumption during production of GPO. It seems that the amount of hydrogen introduced to dry PO by incorporated glycerol in GPO was higher than the hydrogen content of replaced portion. This phenomenon happened in reverse order for methanol and ethanol in MPO and EPO respectively. Alcohol incorporation and water production significantly affected $\text{H/C}_{\text{eff}}$ value of the feeds. Elemental composition of NPO is the same as that of PO. Water content of the feeds is calculated theoretically as follows:

1) water content of PO is the reference value and the produced water via reactions during stabilization results in increase in this value.
2) the number of moles of produced water in MPO, EPO and GPO is equal to the number of moles of consumed methanol, ethanol and glycerol respectively. However, more than one mole of water can be produced per one mole of consumed glycerol resulting in different possible water contents of GPO. The value shown in Table 4-1 is based on one mole of produced water per one mole of consumed glycerol. Three possibilities for GPO according to three different possible water contents are shown in Van Krevelen plot as GPO-1, GPO-2 and GPO-3 representing one, two and three moles of water per one mole of glycerol respectively (Figure 4-4).

3) two extremes can be assumed for NPO; no water production which results in the same water content as PO or the highest water production due to reactions of an R-OH type alcohol which results in the same water content as MPO. However, above extremes lead to very similar points in Van Krevelen plot as shown in Figure 4-4.

The exact loading of alcohols before stabilization in analyzed feed samples per 150 g of feed (the typical amount of feed for HDO experiments) is shown in Table 4-1. The measured amount of residual alcohols after stabilization per 150 g of feed is also shown in Table 4-1. Methanol conversion was higher than ethanol conversion (on mole basis) which shows that the reactions between PO and methanol were more kinetically favored likely due to higher loading of methanol on mole basis and/or higher reaction rate constant. Glycerol conversion was extremely high in comparison to methanol and ethanol. It seems that glycerol conversion was due to other reactions than esterification (the major expected reaction for methanol and ethanol) induced by its hydroxyl sites.

Table 4-2 shows properties of the oil fractions produced via HDO of PO, MPO, EPO, GPO and NPO at 300 °C and 150 bar of semi-batch H₂. The alcohol content of oil fractions and aqueous fractions obtained after HDO of the feeds are also shown in Table 4-2. It is assumed that no water exists in HDO oil fractions and the produced water via HDO plus the initial water of the feeds exists in HDO aqueous fractions.
Table 4-2: Properties of HDO oil fractions at 300 °C

<table>
<thead>
<tr>
<th>Elemental composition</th>
<th>PO</th>
<th>MPO</th>
<th>EPO</th>
<th>GPO</th>
<th>NPO</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (wt%)</td>
<td>71.2</td>
<td>69.3</td>
<td>68.6</td>
<td>69.2</td>
<td>71.0</td>
</tr>
<tr>
<td>H (wt%)</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
<td>8.1</td>
<td>8.3</td>
</tr>
<tr>
<td>O (wt%)(^a)</td>
<td>20.4</td>
<td>22.3</td>
<td>23.0</td>
<td>22.7</td>
<td>20.7</td>
</tr>
<tr>
<td>C (alcohol free wt%)</td>
<td>71.2</td>
<td>69.7</td>
<td>69.0</td>
<td>69.9</td>
<td>71.0</td>
</tr>
<tr>
<td>H (alcohol free wt%)</td>
<td>8.4</td>
<td>8.3</td>
<td>8.3</td>
<td>8.1</td>
<td>8.3</td>
</tr>
<tr>
<td>O (alcohol free wt%)(^a)</td>
<td>20.4</td>
<td>22.0</td>
<td>22.7</td>
<td>22.0</td>
<td>20.7</td>
</tr>
<tr>
<td>H/C(_{eff}) (alcohol free)</td>
<td>0.99</td>
<td>0.96</td>
<td>0.94</td>
<td>0.93</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Residual alcohol in oil fractions and aqueous fractions

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<tr>
<th></th>
<th>Initial alcohol in feed (g/150g of feed)</th>
<th>Residual alcohol in aqueous fraction (g/150g of feed)</th>
<th>Residual alcohol in oil fraction (g/150g of feed)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OG (^b)</td>
<td>OG (^b)</td>
<td>OG (^b)</td>
</tr>
<tr>
<td>OG</td>
<td>6.37</td>
<td>6.49</td>
<td>0.25</td>
</tr>
<tr>
<td>OG</td>
<td>0.84</td>
<td>1.74</td>
<td>1.63</td>
</tr>
<tr>
<td>OG</td>
<td>0.98</td>
<td>3.93</td>
<td>2.15</td>
</tr>
</tbody>
</table>

\(^a\) calculated by difference

\(^b\) OG: only glycerol; the effect of unknown peak persisted in oil and aqueous fractions. The same calculation method was applied to GPO oil and aqueous fraction, here by comparing with NPO oil and aqueous fraction. No methanol or ethanol was observed.

Elemental composition of HDO oil fractions on wet and residual alcohol included basis is similar. The only significant difference is the lower hydrogen content of GPO HDO oil fraction in comparison to that of the other HDO oil fractions. It is again coupled with glycerol backward conversion (production) during HDO of GPO. As shown by alcohol content of GPO HDO oil fraction and aqueous fraction, a part of incorporated glycerol in GPO was released during HDO due to interaction with H\(_2\). However, methanol and ethanol were further consumed during HDO of MPO and EPO respectively. The conversion of methanol during HDO was extremely higher than that of ethanol even on mass basis. It is coupled with CO\(_2\) production during HDO of MPO as shown in Figure 4-5, indicating that the high conversion of methanol resulted in high CO\(_2\) production via gasification. In contrast, ethanol was very resistant to gasification and the converted ethanol during HDO most likely remained in EPO HDO aqueous fraction.

Figure 4-4 is Van Krevelen plot of the feeds and HDO oil fraction at 300 °C. It also includes the points of GPO with two or three moles of produced water per one mole of converted glycerol.
Figure 4-4: Van Krevelen plot of feeds and HDO oil fractions at 300 °C

Figure 4-4 shows that although there is significant difference between the feeds, HDO oil fractions are similar. However, the difference between GPO HDO oil fraction and EPO HDO oil fraction may be considerable. The main phenomenon to consider in Figure 4-4 is the routes from the feeds to their HDO oil fraction. HDO of PO, MPO, EPO and NPO resulted in oil fractions with lower O/C and higher H/C. However, GPO HDO oil fraction had a lower H/C than GPO even if GPO was a mixture of GPO-1 and GPO2. GPO-3 is not most likely the state of GPO due to no observed polymerization in molar mass distribution of GPO in comparison to the other feeds as shown in Figure 4-6. The glycerol released during HDO of GPO seems to be responsible for the lower H/C of GPO HDO oil fraction. The point shown for NPO is the extreme state with R-OH alcohol type reaction. The other extreme state will be the exact point of PO.
Figure 4-5: CO$_2$ production and H$_2$ consumption via HDO at 300 °C

Figure 4-5 shows that H$_2$ consumption is coupled with CO$_2$ production. The highest H$_2$ consumption and lowest CO$_2$ production was observed for HDO of GPO and EPO. In contrast, the lowest H$_2$ consumption and highest CO$_2$ production was observed for HDO of NPO. It appears that NPO can be a potential feed for in-situ HDO using hydrogen transfer catalysts due to the lowest H$_2$ consumption. Although GPO had high H$_2$ consumption during HDO, it seems that a part of consumed H$_2$ was used to release incorporated glycerol which resulted in the low H/C of GPO HDO oil fraction. High CO$_2$ production was observed for HDO of MPO which is linked to high methanol conversion.

It seems that the linkage between H$_2$ consumption and CO$_2$ production majorly reflects the ongoing reactions in HDO aqueous fractions, as the hydrogen content of HDO oil fractions is similar. However, HDO aqueous fractions are expected to be very different (due to various possible PO and alcohol derived hydrophilic compounds). Unfortunately, it was not feasible to measure hydrogen content of HDO aqueous fractions due to their extremely high water content leading to huge instrumental errors. CO$_2$ production did not show any correlation with self-polymerization, while it did in our previous work. It seems that in presence of excess H$_2$ and weak dilution effect of used alcohol, thermal reactions which are responsible for promoting self-polymerization and producing CO$_2$ at the same time, are effective at the same extent. Since, the aqueous fractions are different due to
different hydrophilic PO and/or alcohol derived fragments, the extent of CO$_2$ produced varies considerably. Comparing H$_2$ consumption and CO$_2$ production during HDO of GPO and PO here with those during HDO of GPO and PO in chapter 3 (Table 3-5 and Table 3-2), it can be observed that H$_2$ consumption and CO$_2$ production are affected by stabilization. Although dilution effect is minimized here while it dominated in chapter 3, the same profile for H$_2$ and CO$_2$ was observed.

**Table 4-3: Gas composition of HDO gas fractions at 300 °C [g/kg feed]**

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<tr>
<th></th>
<th>PO</th>
<th>MPO</th>
<th>EPO</th>
<th>GPO</th>
<th>NPO</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO production</td>
<td>3.15</td>
<td>4.29</td>
<td>0.44</td>
<td>0.32</td>
<td>4.18</td>
</tr>
<tr>
<td>CO$_2$ production</td>
<td>62.18</td>
<td>48.12</td>
<td>28.70</td>
<td>32.04</td>
<td>70.75</td>
</tr>
<tr>
<td>CH$_4$ production</td>
<td>2.52</td>
<td>2.50</td>
<td>2.74</td>
<td>1.26</td>
<td>2.97</td>
</tr>
<tr>
<td>Higher alkanes production</td>
<td>2.09</td>
<td>1.68</td>
<td>1.14</td>
<td>0.71</td>
<td>2.36</td>
</tr>
</tbody>
</table>

Gas composition of HDO gas fractions varies to a high extent. The amounts of CO produced via HDO of MPO and NPO are the highest. However, CO$_2$ production was higher during HDO of NPO. It can be seen that methanol conversion has affected CO$_2$ production instead of CH$_4$ production at 300 °C, as the amount of CH$_4$ produced via HDO of MPO and PO are similar. The minimum CO production was observed to happen while HDO of EPO and GPO. HDO of GPO led to the lowest values for produced amounts of CH$_4$ and higher alkanes. It seems that PO and glycerol derived fragments via stabilization are more resistant to methanation and hydrocracking (Wildschut et al., 2010). They are likely present in GPO HDO aqueous fraction.

Molar mass distribution of the feeds and HDO oil fractions at 300 °C are shown in Figure 4-6 and Figure 4-7 respectively.
Figure 4-6: Molar mass distribution of feeds

Figure 4-7: Molar mass distribution of HDO oil fractions at 300 °C

Figure 4-6 shows that the feeds have similar molar mass distribution at the higher range (M > 1100 g/mol) suggesting that self-polymerization did not happen during stabilization even for NPO. However, at the lower range (100 < M < 1100 g/mol), incorporation of different alcohols has created different molar mass distribution patterns for the feeds. Figure 4-7 indicates that although the molar mass of HDO oil fractions is lower than that of the feeds, the difference between them is not very considerable. However, MPO seems to produce a slightly lighter HDO oil fraction. Figure 4-8 compares the molar mass distribution of MPO, MPO HDO oil fraction and aqueous fraction at 300 °C.
Figure 4-8: Molar mass distribution of MPO, MPO HDO oil fraction and aqueous fraction at 300 ºC

It can be observed that MPO HDO aqueous fraction is comprised of very light compounds. The figure indicates that the summation of molar mass distribution of MPO HDO oil fraction and aqueous fraction is at a lower range than molar mass distribution of MPO (the above distributions are similar when phase separation dominates). It can be concluded that HDO coupled with hydrocracking decreased the overall molar mass of MPO and the other feeds (Ardiyanti et al., 2012).

Figure 4-9 shows dry and residual alcohol free mass and carbon balance closures obtained after HDO of the feeds.
Figure 4-9: Dry and residual alcohol free mass and carbon distribution of HDO fractions at 300 °C

The highest mass and carbon content was obtained from HDO oil fractions. The significant difference in the amount of produced gas (majorly in the form of CO₂) via HDO of different feeds is also reflected in Figure 4-9. The carbon content of HDO aqueous fraction of MPO, EPO and GPO is slightly higher than that of PO and NPO which is due to higher concentration of hydrophilic compounds derived through alcohol and PO interaction.

The effects of stabilization on HDO were further studied at extreme condition for self-polymerization; self-polymerization promoting conditions at lower temperatures and self-polymerization preventing conditions at higher temperatures (de Miguel Mercader et al., 2011). The experimental conditions are as follows:

1) more favorable conditions for HDO reactions (350 °C, 200 bar of semi-batch H₂ and 3 h)

2) less favorable conditions for HDO reactions (200 °C, 100 bar of batch H₂ and 3 h)

3) self-polymerization promoting conditions via TT (200 °C, 50 bar of N₂ and 75 min)
The feed chosen for this part is MPO due to:

1) relatively better performance towards reducing self-polymerization during HDO at 300 ºC

2) less dilution effect in comparison to EPO and GPO due to conversion of residual methanol into CO₂ and CH₄ (specially at high temperatures)

Table 4-4 presents the composition of gas fractions obtained via HDO of PO and MPO at 200, 300 and 350 ºC. H₂ consumption of each route is also shown in Table 4-4.

**Table 4-4: Composition of HDO gas fractions and H₂ consumption at 200, 300 and 350 ºC [g/kg feed]**

<table>
<thead>
<tr>
<th></th>
<th>PO (200 ºC)</th>
<th>MPO (200 ºC)</th>
<th>PO (300 ºC)</th>
<th>MPO (300 ºC)</th>
<th>PO (350 ºC)</th>
<th>MPO (350 ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO production</td>
<td>0.00</td>
<td>0.00</td>
<td>3.15</td>
<td>4.29</td>
<td>1.13</td>
<td>4.74</td>
</tr>
<tr>
<td>CO₂ production</td>
<td>26.10</td>
<td>17.14</td>
<td>62.18</td>
<td>48.12</td>
<td>71.69</td>
<td>101.20</td>
</tr>
<tr>
<td>CH₄ production</td>
<td>1.76</td>
<td>4.75</td>
<td>2.52</td>
<td>2.50</td>
<td>9.69</td>
<td>14.81</td>
</tr>
<tr>
<td>Higher alkanes production</td>
<td>0.09</td>
<td>0.20</td>
<td>2.09</td>
<td>1.68</td>
<td>7.60</td>
<td>9.08</td>
</tr>
</tbody>
</table>

CO produced during HDO of PO decreased from 300 to 350 ºC while it remained constant for MPO which is likely due to conversion of methanol. CO₂ production via HDO of PO was higher at 200 and 300 ºC while it extensively increased during HDO of MPO at 350 ºC. Table 4-5 shows methanol content of MPO HDO oil fractions and aqueous fraction at 200, 300 and 350 ºC. The overall methanol content slightly decreased at 350 ºC compared to 300 ºC. However, a higher methanol conversion was expected due to the extensive increase in CO₂. It appears that at 350 ºC, a part of CO₂ was produced due to conversion of incorporated methanol (in HDO fractions) via thermal reactions. The majority of residual methanol was detected in aqueous fraction at 350 ºC showing that the polarity of oil fraction significantly decreased compared to 300 ºC.

The amount of CH₄ derived through HDO of MPO decreased from 200 to 300 ºC while it extremely increased from 300 to 350 ºC leading to an even higher value than that of PO. It is most likely due to promoted methanation effect of the catalyst at 350 ºC and/or methanol conversion. Hydrocracking significantly increased from 300 to 350 ºC as
shown by higher concentration of higher alkanes in gas fractions. The effect of hydrocracking is reflected in reduction of molar mass of HDO oil fractions obtained at 350 °C shown in Figure 4-10.

Table 4-5: Methanol content of MPO HDO fractions and H/C\textsubscript{eff} of PO and MPO oil fractions at 200, 300 and 350 °C

<table>
<thead>
<tr>
<th></th>
<th>200 °C</th>
<th>300 °C</th>
<th>350 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol in HDO AF [g]</td>
<td>4.43</td>
<td>0.99</td>
<td>1.49</td>
</tr>
<tr>
<td>methanol in HDO OF [g]</td>
<td>1.73</td>
<td>0.84</td>
<td>0.20</td>
</tr>
<tr>
<td>MPO HDO OF H/C\textsubscript{eff}</td>
<td>0.90</td>
<td>0.96</td>
<td>1.18</td>
</tr>
<tr>
<td>PO HDO OF H/C\textsubscript{eff}</td>
<td>0.99</td>
<td>0.99</td>
<td>1.12</td>
</tr>
<tr>
<td>MPO HDO OF HHV (MJ/kg)</td>
<td>27.20</td>
<td>32.10</td>
<td>37.26</td>
</tr>
<tr>
<td>PO HDO OF HHV (MJ/kg)</td>
<td>29.25</td>
<td>32.96</td>
<td>36.60</td>
</tr>
</tbody>
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The dilution effect of methanol at 200 °C is the highest, as both of the fractions have the highest methanol content. H/C\textsubscript{eff} of MPO HDO oil fraction increased from 200 to 350 °C resulting in a higher value than that of PO HDO oil fraction at 350 °C. MPO HDO oil fraction has a higher HHV at 350 °C which is due to its higher hydrogen content while having similar oxygen content to PO HDO oil fraction. Figure 4-12 provides more information on hydrogen and oxygen content of each HDO oil fraction.

Figure 4-10 compares molar mass distribution of HDO oil fractions of PO and MPO at 200, 300 and 350 °C.
Figure 4-10: Molar mass distribution of PO and MPO HDO oil fractions at 200, 300 and 350 °C

Figure 4-11 compares molar mass distribution of TT oil fractions of PO and MPO at 200 °C.

Figure 4-11: Molar mass distribution of PO and MPO TT oil fractions at 200 °C

Hydrocracking has reduced the molar mass of HDO oil fractions at 350 °C. However, their molar mass distribution is the same. Also, the chromatograms are the same at 200 °C for oil fractions of HDO or TT. It seems that dilution is effect only at relatively high alcohol concentrations. At 200 °C, HDO oil fractions have a very similar molar mass distribution to that of the feeds indicating that phase separation is likely the predominant
phenomenon. TT produced oil fractions of very high molar mass showing that self-polymerization was promoted.

**Figure 4-12: Van Krevelen plot of PO and MPO HDO oil fractions at 200, 300 and 350 °C**

Figure 4-12 shows that MPO HDO oil fraction has a higher H/C than PO HDO oil fraction at 350 °C while having a similar O/C. It seems that oxygen removal via CO₂ production was considerable via HDO of MPO at 350 °C. Also, higher H/C could be due to in-situ hydrogen production via methanol decomposition. Oxygen removal was significantly improved with temperature (decreasing O/C), decreasing hydrogen content (H/C) at the same time which is due to producing water.
Mass loss increased from 200 to 350 °C which is due to production of water. The carbon content of aqueous fractions decreased with temperature indicating that their carbon was transferred either to oil fractions or gas fractions. MPO aqueous fraction has higher carbon content at 200 and 300 °C which is due to higher concentration of methanol and/or PO derived hydrophilic compounds. However at 350 °C, the carbon contents of aqueous fractions become almost the same indicating that the higher temperature was effective on altering aqueous fractions. It seems that at 350 °C, the higher carbon content of MPO gas fraction is coupled with MPO oil fraction as the carbon content of PO and MPO aqueous fractions are almost the same.

4.4. Conclusions

The effects of stabilizing fast pyrolysis oil via catalytic alcohol pretreatment on HDO were studied. The alcohol concentration was minimized to reduce the dilution effect and clarify the effects of stabilization. The conclusions can be divided into alcohol-independent conclusions and alcohol-dependent conclusions as follows:
4.4.1. Alcohol-independent conclusions

Molar mass distribution of HDO (or TT) oil fractions was not affected at various experimental conditions. It may be concluded that at high temperatures during upgrading, the effect of stabilization on self-polymerization is minimum, as stabilization derived fragments (e.g. esters) may decompose at high temperatures (e.g. due to hydrocracking). Therefore, stabilization may be effective on reducing self-polymerization at low temperatures (e.g. during storage). Previously in chapter 3, it was observed that dilution (due to relatively high concentration of alcohol) reduced the molar mass of HDO and TT oil fractions during upgrading at high temperature. Therefore, in order to reduce self-polymerization during upgrading, dilution seems to be more advantageous than stabilization. However, the solvent can possibly be of no/less reactive nature.

4.4.2. Alcohol-dependent conclusions

Gas composition, H\textsubscript{2} consumption and molar H/C of the feeds and HDO oil fractions were affected by stabilization and alcohol variation. At the reference temperature (300 °C), stabilization increased H\textsubscript{2} consumption and reduced CO\textsubscript{2} production. However, this profile was reversed at 350 °C due to conversion of methanol. Methanol conversion was beneficial, as it increased molar H/C of HDO oil fraction at 350 °C likely due to in-situ hydrogen production. Although alcohol variation altered molar H/C of the feeds, it had no significant effect on HDO oil fractions at the reference temperature. Glycerol conversion during stabilization was extremely higher than methanol and ethanol (probably due to more hydroxyl groups). Its behavior during HDO was also different from methanol and ethanol such that despite further conversion, it was released. This different behavior changed the pathway from GPO to GPO HDO oil fraction on Van Krevelen plot in comparison to the other feeds.
4.5. References


CHAPTER 5. OVERALL CONCLUSIONS AND OUTLOOK

5.1. Overall conclusions

Pyrolysis oil is a potential resource for fuels which are derived from petroleum currently. However, its high oxygen content must be minimized to achieve similar properties to those of petroleum derived fuels. The high oxygen content also provides a reactive nature for pyrolysis oil leading to self-polymerization during storage and processing (e.g. via hydrodeoxygenation). Reducing self-polymerization during processing is critical, as it appears in the form of coke and char formation deactivating the catalyst and plugging the reactor. A mild pretreatment (stabilization) after production seems to be beneficial to reduce the reactivity of pyrolysis oil, thereby reducing self-polymerization. In literature, stabilization with alcohol (esterification) is raised as a promising route to reduce the reactivity of pyrolysis oil. This research which was conducted in two parts investigated the effects of stabilization with alcohol on processing via hydrodeoxygenation or thermal treatment.

The main outcome of the first part was that the major expected effect of stabilization on processing (self-polymerization reduction) was induced by dilution due to the relatively high concentration of used alcohol (glycerol) rather than reactivity reduction due to stabilization. However, stabilization had other effects such as decreasing CO\textsubscript{2} production and increasing H\textsubscript{2} consumption during processing. The alcohol concentration used in literature was also high. Although the high concentration of alcohol may increase the stability of pyrolysis oil during storage, it must be minimized to improve the economics of stabilization.

Since different alcohols may affect stabilization and subsequent processing to different extent due to their different reactivity toward pyrolysis oil, the second part of the research examined the effects of alcohol variation while minimizing the alcohol concentration to clarify the effects of stabilization.

Alcohol variation and various experimental conditions did not considerably affect molar mass distribution (associated with self-polymerization) of HDO (or TT) oil fractions. It
may be concluded that at high temperatures during upgrading, the effect of stabilization on self-polymerization is minimum, as stabilization derived fragments (e.g. esters) may decompose (e.g. due to hydrocracking). Therefore, stabilization may be effective on reducing self-polymerization at low temperatures (e.g. during storage). Combining this outcome with the main outcome of the first part, it may be concluded that in order to reduce self-polymerization during upgrading, dilution seems to be more advantageous than stabilization.

However, other properties such as gas composition, H₂ consumption and molar H/C of the feeds and HDO oil fractions were affected by alcohol and temperature variation. Methanol was observed to be beneficial at higher temperatures of processing due to increasing molar H/C of HDO oil fraction likely due to in-situ hydrogen production (resultant of incorporated methanol decomposition).

With current state of the art and results obtained, stabilization is not recommended while self-polymerization reduction is intended at high temperatures during upgrading. However, at low temperatures (e.g. during storage), it may reduce self-polymerization preventing viscosity increase and phase separation of pyrolysis oil. Dilution effect of the alcohol as a solvent showed to be more effective on reducing self-polymerization during upgrading. However, utilizing an alcohol as a solvent at a high concentration will make upgrading more expensive. There may be less expensive routes to induce dilution effect instead of introducing and consuming alcohol (e.g. via recycling a part of upgraded oil). Furthermore, since no significant reduction in the acidity of pyrolysis oil was observed after stabilization, direct utilization of stabilized oil as a fuel for combustion (e.g. in engines) will also be limited due to the negative effects of its corrosivity on injection nozzles.

Stabilization had positive effects other than self-polymerization reduction at high temperatures as incorporated methanol decomposition increased the hydrogen content of upgraded oil increasing the heating value consequently. However, the upgraded oil may be more expensive.
5.2. Recommendations for future work

To continue the pathway of the research conducted for this thesis, it is recommended to study the effects of utilizing upgraded oil as the solvent on self-polymerization reduction during upgrading. Because, if it is shown that the positive effect of dilution during upgrading is independent of the reactivity of solvent (alcohols in this study), the overall economics of process can be significantly improved via recycling a part of upgraded oil and utilizing as the solvent. Furthermore, a continuous flow setup can be developed to replace the semi-batch setup improving the viability of scaling up the process.

Although noble metal catalysts are shown to be very successful in hydrodeoxygenation, utilizing them at large scales may be limited, as they are expensive leading to increase in the price of upgraded oil. Further research is needed to develop a less expensive hydrodeoxygenation catalyst or to significantly improve the activity of current catalysts to minimize the catalyst loading for hydrodeoxygenation.
Appendices

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