

The University of Maine  
DigitalCommons@UMaine

---

Electronic Theses and Dissertations

Fogler Library


---

Fall 12-15-2017

# Production of Bio-oil with Different Oxygen Content and Characterization of Catalytic Upgrading to Transportation Fuel

Mubarak Mohammed Khlewee  
*University of Maine*, [mubarak.khlewee@maine.edu](mailto:mubarak.khlewee@maine.edu)

Follow this and additional works at: <https://digitalcommons.library.umaine.edu/etd>

 Part of the [Biochemical and Biomolecular Engineering Commons](#), [Catalysis and Reaction Engineering Commons](#), [Other Chemical Engineering Commons](#), [Thermodynamics Commons](#), and the [Transport Phenomena Commons](#)

---

## Recommended Citation

Khlewee, Mubarak Mohammed, "Production of Bio-oil with Different Oxygen Content and Characterization of Catalytic Upgrading to Transportation Fuel" (2017). *Electronic Theses and Dissertations*. 2816.  
<https://digitalcommons.library.umaine.edu/etd/2816>

This Open-Access Thesis is brought to you for free and open access by DigitalCommons@UMaine. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of DigitalCommons@UMaine. For more information, please contact [um.library.technical.services@maine.edu](mailto:um.library.technical.services@maine.edu).

**PRODUCTION OF BIO-OIL WITH DIFFERENT OXYGEN CONTENT AND  
CHARACTERIZATION OF CATALYTIC UPGRADING TO  
TRANSPORTATION FUEL**

By

Mubarak Khlewee

B.S. Southern Technical University, 2011

A THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

(in Chemical Engineering)

The Graduate School

The University of Maine

December 2017

Advisory Committee:

William J. DeSisto, Professor of Chemical Engineering, Advisor

M. Clayton Wheeler, Professor of Chemical Engineering

Douglas W. Bousfield, Professor of Chemical Engineering

Copyright 2017 Mubarak M. Khlewee

**PRODUCTION OF BIO-OIL WITH DIFFERENT OXYGEN CONTENT AND  
CHARACTERIZATION OF CATALYTIC UPGRADING TO  
TRANSPORTATION FUEL**

By Mubarak Khlewee

Thesis Advisor: Prof. William J. DeSisto

An Abstract of the Thesis Presented  
in Partial Fulfillment of the Requirements for the  
Degree of Master of Science  
(in Chemical Engineering)  
December 2017

The world's increasing population requires an increase in transportation fuel production. The lack of production of transportation fuels due to the shortage of fossil fuel resources combined with concerns about global emissions of carbon dioxide from fossil fuel combustion are the two major issues that have driven researchers to actively pursue alternative sources for oil production. Biomass is being considered as an alternative feedstock to produce fuel and chemicals due to its abundance and renewability. It has many features that make it suitable as a source of transportation fuel production. However, the bio-oil produced by the fast pyrolysis process has many undesirable characteristics that reduce its quality as a transportation fuel. The major problem that causes these negative properties is mainly the oxygenated groups that are present in the bio-oil.

In this research, the goal was to produce a high-quality bio-oil with low or zero oxygen content that could be suitable for use as a transportation fuel. To do that, four different biomass feedstocks were pyrolyzed at the same operating conditions using a process developed by the UMaine group. This process is called formate-assisted fast pyrolysis or FAsP. Oils produced from the fast pyrolysis of these four feedstocks contained oxygen contents of 16, 21, 26 and 27

wt.% and were generated either by formate-assisted pyrolysis or hot-gas filter pyrolysis of pine sawdust. The generated bio-oils were then hydrotreated over an inexpensive commercially available nickel on silica-alumina catalyst and high hydrogen pressure to produce a hydrocarbon fuel. Hydrotreating experiments were conducted in a downflow trickle bed reactor at temperatures between 300-400 °C and reactor pressures between 750-1400 psi with a hydrogen flow rate of 100 sccm over several days. Liquid yields, carbon yields, final product oxygen content, and H:C ratio were determined as a function of time-on-stream.

For the 16 wt.% oxygen content bio-oil, the longest time onstream, 345 hours, was achieved at an average bed temperature of 300 °C, reactor pressure of 1400 psi, hydrogen flow rate of 100 sccm and a weight hourly space velocity of 0.06 hr<sup>-1</sup>. The carbon of the raw bio-oil that ended up in the hydrotreated oil fraction of this experiment was 91.8% with a liquid yield of 95.3%. The highest carbon and hydrogen contents measured for the hydrotreated liquid products from all experiment were 87.0 wt.%, 14.2 wt.% and the lowest were 75.0 wt.%, 10.6 wt.% respectively. Partial deactivation of the catalyst over time was evident due to the quality of the oil product collected, which saw the density, oxygen content and viscosity increase and the H:C ratio and carbon content decrease. The partial deactivation was more pronounced for higher oxygen-containing bio-oil feedstocks and for higher temperatures >300 °C.

Calcium formate pretreatment of biomass prior to pyrolysis produces stable bio-oils with reduced oxygen content. These stable bio-oils can be successfully upgraded into hydrocarbon fuels in a single catalytic hydrotreatment step that ran up to 15 days without significant deactivation and reactor plugging. This improvement eliminates the need for an oil stabilization step prior to hydrotreatment that is required for conventional bio-oil upgrading.

**Keywords:** Transportation fuels, catalysts, upgrading, bio-oil, pyrolysis, calcium formate

## ACKNOWLEDGEMENTS

I would like to express my most sincere gratitude to my advisor, Dr. William J. DeSisto for his kindness, patience, guidance, invaluable encouragement, and dedication throughout my program. I would like also to express thanks and appreciation to my committee members: Dr. M. Clayton Wheeler and Dr. Douglas W. Bousfield for their time and contributions to this research, especially Dr. M. Clayton Wheeler for his invaluable input, timely suggestions, and help in many ways.

I would like to express my heartfelt thanks to Nick Hill for his help in building the experimental apparatus and for offering the technical support with various instruments. Many thanks also go to Elisha Cram (FBRI), Christa Meulenberg (FBRI), and James Hargreaves (FBRI) for their training and help in preparing and interpreting analytical samples. I wish to express my gratitude to the Higher Committee for Education Development in Iraq (HCED) for their generous financial support and funding provided for this research. I would like to acknowledge the Ministry of Oil and Dhi Qar Oil Company in Iraq for their acceptance to come and complete my Master degree at UMaine.

I owe a special gratitude to my parents who have given me endless courage, unwavering support, and unconditional love. I greatly thank my mother who has given her most wonderful years to taking care of me. Most of all, I will be forever grateful to the support and encouragement provided by my loving wife throughout the journey of my academic career, and I would like to dedicate this work to her. She spent nights and days taking care of our lovely kids, encouraging me to pursue my dreams and to achieve my goals, without interrupting my study. Her encouragement and indispensable love made possible what I am now.

# TABLE OF CONTENTS

|   |      |
|---|------|
| ACKNOWLEDGEMENTS .....                                  | iii  |
| LIST OF TABLES .....                                    | viii |
| LIST OF FIGURES .....                                   | x    |
| CHAPTER 1: CONVERSION OF BIOMASS TO BIO-OIL AND BIO-OIL |      |
| CHARACTERIZATIONS .....                                 | 1    |
| 1.1 Introduction .....                                  | 1    |
| 1.2 Lignocellulosic biomass .....                       | 2    |
| 1.3 Thermochemical conversion of biomass .....          | 3    |
| 1.3.1 Pyrolysis .....                                   | 4    |
| 1.4 Chemical composition of bio-oil .....               | 6    |
| 1.5 Physical properties of bio-oil .....                | 8    |
| 1.6 Removal of oxygen during pyrolysis .....            | 12   |
| 1.6.1 Catalytic fast pyrolysis .....                    | 12   |
| 1.6.2 Hot gas filtration .....                          | 13   |
| 1.6.3 Pretreating with calcium compounds .....          | 14   |
| 1.7 Description of research .....                       | 15   |

## CHAPTER 2: A REVIEW OF BIO-OIL UPGRADING INTO TRANSPORTATION

|  |    |
|--|----|
| FUEL: CATALYSTS, OPERATING CONDITIONS, REACTORS AND REACTIONS .....                        | 16 |
| 2.1 Introduction .....   | 16 |
| 2.2 Catalysts, operating conditions and reactor configurations for bio-oil upgrading ..... | 17 |
| 2.2.1 Sulfided catalysts .....   | 17 |
| 2.2.2 Nickel catalysts .....   | 21 |
| 2.2.3 Noble metal catalysts .....  | 26 |
| 2.2.3.1 Pd/C catalyst.....   | 26 |
| 2.2.3.2 Ru/C catalyst .....  | 28 |
| 2.2.3.3 Mono- and bimetallic noble metal catalysts over ZrO <sub>2</sub> .....             | 30 |
| 2.2.4 Other catalysts.....   | 31 |
| 2.3 Catalytic hydrotreatment reactions.....  | 32 |
| 2.4 Catalysts deactivation.....  | 33 |
| 2.5 Summary .....  | 34 |

## CHAPTER 3: FAST PYROLYSIS OF FORMATE ASSISTED PRETREATED PINE

|   |    |
|---|----|
| SAWDUST AT ATMOSPHERIC CONDITION .....  | 36 |
| 3.1 Introduction .....  | 36 |
| 3.2 Material and methods .....  | 37 |
| 3.2.1 Feedstock preparation .....   | 37 |
| 3.2.2 Description of fast pyrolysis system along with fast pyrolysis process..... | 40 |



|   |   |    |
|---|---|----|
| 3.2.3   | Bio-oil characterization.....   | 42 |
| 3.3   | Results and discussion.....   | 43 |
| 3.4   | Conclusion.....   | 49 |
| CHAPTER 4: UPGRADING OF BIO-OILS INTO TRANSPORTATION FUELS..... |   | 50 |
| 4.1   | Introduction .....  | 50 |
| 4.2   | Material and methods.....   | 51 |
| 4.2.1   | Feedstock preparation .....   | 51 |
| 4.2.2   | Description of upgrading system .....   | 51 |
| 4.2.3   | Hydrotreating .....   | 54 |
| 4.2.4   | Hydrotreated bio-oil characterization .....                                     | 55 |
| 4.3   | Results and discussion.....   | 55 |
| 4.3.1   | FAsP oil with 16 wt.% oxygen as a feedstock hydrotreated at 750 psi .....       | 56 |
| 4.3.2   | FAsP oil with 16 wt.% oxygen as a feedstock hydrotreated at 1400 psi .....      | 59 |
| 4.3.3   | FAsP oil with 21 wt.% oxygen as a feedstock.....                                | 61 |
| 4.3.4   | FAsP oil with 26 wt.% oxygen as a feedstock hydrotreated at 750, 1400 psi ..... | 64 |
| 4.3.5   | FAsP oil with 27 wt.% oxygen as a feedstock.....                                | 67 |
| 4.3.6   | Carbon and hydrogen balances .....  | 67 |
| 4.4   | Summary .....   | 74 |
| 4.5   | Conclusion.....   | 76 |
| REFERENCES .....  |   | 78 |

|  |    |
|--|----|
| APPENDIX A. ELEMENTAL ANALYSIS OF BIO-OILS .....   | 84 |
| APPENDIX B. PREPARATION OF BIO-OIL SAMPLES FOR QUANTITATIVE GAS<br>CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS) ANALYSIS ..... | 88 |
| APPENDIX C. GAS SAMPLE ANALYSIS USING SRI'S MULTIPLE GAS<br>ANALYZER .....   | 92 |
| APPENDIX D. KARL-FISHER TITRATION FOR BIO-OILS FRACTIONS .....   | 95 |
| BIOGRAPHY OF THE AUTHOR.....   | 98 |

## LIST OF TABLES

|   |    |
|---|----|
| Table 1. 1 Composition of general lingo-cellulosic materials .....  | 2  |
| Table 1. 2 Pyrolysis products from different lignocellulosic biomass.....   | 5  |
| Table 1. 3 Physical properties of bio-oil derived from wood .....   | 8  |
| Table 1. 4 Comparison between fast pyrolysis and FAsP. ....   | 15 |
| Table 2. 1 Oil product composition from the hydroprocessing of bio-oils.....  | 20 |
| Table 2. 2 Effect of feedstock on the hydrotreating process results. ....   | 26 |
| Table 3. 1 Analysis of pine sawdust .....   | 37 |
| Table 3. 2 Weight percent yields obtained from pyrolysis of 140 gm $\text{Ca}(\text{COOH})_2$ /100 gm<br>of dry, ash-free pine sawdust. ....    | 43 |
| Table 3. 3 Weight percent yields obtained from pyrolysis of 122.5 gm $\text{Ca}(\text{COOH})_2$ /100 gm<br>of dry, ash-free pine sawdust. ....  | 44 |
| Table 3. 4 Weight percent yields obtained from pyrolysis of 70 gm $\text{Ca}(\text{COOH})_2$ /100 gm<br>of dry, ash-free pine sawdust. ....     | 44 |
| Table 3. 5 Weight percent yields obtained from pyrolysis of dry, ash-free pine sawdust<br>without pretreatments.....                            | 45 |
| Table 3. 6 Elemental analysis of the bio-oils obtained from calcium formate loadings as<br>well as pine sawdust without pretreatments.....      | 46 |
| Table 3. 7 Water percentages for the fractions of the bio-oils obtained from the pyrolysis<br>of the four biomass feedstocks.....               | 47 |
| Table 3. 8 Compounds identified by GC-MS (Shimadzu Q2010) in pyrolysis oils obtained<br>from the fast pyrolysis of all biomass feedstocks ..... | 48 |

|  |    |
|--|----|
| Table 4. 1 Results for the hydrotreating of calcium formate pretreated pine sawdust feedstocks.....              | 69 |
| Table 4. 2 Carbon balance for the hydrotreating of calcium formate pretreated pine sawdust feedstocks.....       | 70 |
| Table 4. 3 Hydrogen consumption for the hydrotreating of calcium formate pretreated pine sawdust feedstocks..... | 71 |
| Table A. 1 C, H, N contents of BBOT standard .....   | 85 |
| Table A. 2 C, H, N contents of Lubricant standard .....  | 85 |
| Table C. 1 Temperature programming.....  | 92 |
| Table C. 2 Events programming .....  | 93 |
| Table C. 3 Concentrations of gases used as standards.....  | 94 |

## LIST OF FIGURES

|   |    |
|---|----|
| Figure 1. 1 Thermochemical conversion processes of biomass.....   | 3  |
| Figure 1. 2 Simplified schematic of pyrolysis system shown the location of the hot gas<br>filter housing and filter element.....                                  | 13 |
| Figure 3. 1 IR-35 Infrared Moisture Analyzer (Denver Instrument).....   | 38 |
| Figure 3. 2 Biomass feedstock after achieved the desired moisture content .....   | 39 |
| Figure 3. 3 U.S. Standard Sieve No.14. ....   | 39 |
| Figure 3. 4 Schematic of fast pyrolysis process.....  | 40 |
| Figure 3. 5 Bio-oil collected from the ESP after fast pyrolysis process .....   | 43 |
| Figure 4. 1 Schematic of upgrading process.....   | 51 |
| Figure 4. 2 Temperature controller made by Solo company .....   | 52 |
| Figure 4. 3 HPLC pump with a scale on its top .....   | 53 |
| Figure 4. 4 Reactor set-up.....   | 54 |
| Figure 4. 5 Liquid products collected from the hydrotreating of 87.5% calcium formate<br>loading.....   | 55 |
| Figure 4. 6 Total liquid yield as a function of reaction time for the hydrotreating of the<br>100% calcium formate loading at 750 psi.....                        | 57 |
| Figure 4. 7 Oxygen wt.% and H:C ratio as a function of reaction time for the hydrotreating<br>of the 100% calcium formate loading at 750 psi. ....                | 58 |
| Figure 4. 8 Liquid yield wt.%, Oxygen wt.% and H:C ratio as a function of reaction time<br>for the hydrotreating of 100% calcium formate loading at 750 psi. .... | 58 |
| Figure 4. 9 Total liquid yield as a function of reaction time for the hydrotreating of the<br>100% calcium formate loading at 1400 psi.....                       | 59 |

|  |    |
|--|----|
| Figure 4. 10 Oxygen wt.% and H:C ratio as a function of reaction time for the hydrotreating of the 100% calcium formate loading at 1400 psi. ....                    | 60 |
| Figure 4. 11 Liquid yield wt.%, Oxygen wt.% and H:C ratio as a function of reaction time for the hydrotreating of the 100% calcium formate loading at 1400 psi ..... | 61 |
| Figure 4. 12 Total liquid yield as a function of reaction time for the hydrotreating of the 87.5% calcium formate loading. ....                                      | 62 |
| Figure 4. 13 Oxygen wt.% and H:C ratio as a function of reaction time for the hydrotreating of the 87.5% calcium formate loading. ....                               | 63 |
| Figure 4. 14 Liquid yield wt.%, Oxygen wt.% and H:C ratio as a function of reaction time for the hydrotreating of the 87.5% calcium formate loading. ....            | 63 |
| Figure 4. 15 Total liquid yield as a function of reaction time for the hydrotreating of the 50% calcium formate loading at 1400 psi. ....                            | 65 |
| Figure 4. 16 Oxygen wt.% and H:C ratio as a function of reaction time for the hydrotreating of the 50% calcium formate loading at 1400 psi. ....                     | 66 |
| Figure 4. 17 Liquid yield wt.%, Oxygen wt.% and H:C ratio as a function of reaction time for the hydrotreating of the 50% calcium formate loading at 1400 psi. ....  | 66 |
| Figure 4. 18 Liquid yield wt.% and gases mass flow rates as a function of reaction time for the hydrotreating of the 100% calcium formate loading at 1400 psi. ....  | 72 |
| Figure 4. 19 Liquid yield wt.% and gases mass flow rates as a function of reaction time for the hydrotreating of the 87.5% calcium formate loading at 1400 psi. .... | 73 |
| Figure 4. 20 Liquid yield wt.% and gases mass flow rates as a function of reaction time for the hydrotreating of the 50% calcium formate loading at 1400 psi. ....   | 73 |

|   |    |
|---|----|
| Figure A. 1 Flash 2000 Elemental Analyzer with Mas 200R autosampler ..... | 87 |
| Figure B. 1 Gas Chromatography-Mass Spectrometry (GC-MS) .....            | 91 |
| Figure C. 1 SRI's gas analyzer #1 system overview .....                   | 94 |
| Figure D. 1 Karl-Fisher Titration.....                                    | 97 |

# CHAPTER 1: CONVERSION OF BIOMASS TO BIO-OIL AND BIO-OIL CHARACTERIZATIONS

## 1.1 Introduction

Energy consumption of non-renewable hydrocarbons has largely increased recently due to the growing global worldwide population. The global emissions of CO<sub>2</sub> from fossil fuel combustion and cement production are responsible for the global temperature rise and climate change and have continued to grow by 2.5% per year on average over the past decade (Friedlingstein et al. 2014). As a result of the continuous global warming, climate change is largely irreversible for 1,000 years after emissions stop (Solomon et al. 2014).

Finding another route to produce fuel and chemicals has become imperative. Biomass is being considered as an alternative feedstock to produce transportation fuels. Biomass-derived fuels can be produced within a relatively short cycle. The process of producing bio-oil is relatively inexpensive and considered to be eco-friendly. Biomass has a worldwide abundance and it can be used instead of the world's fossil fuels in a variety of applications. From all biomass sources, Lignocellulosic biomass is the most abundant naturally occurring raw material, where there are more than 400 million dry tons of biomass available each year for potential energy use (Downing et al. 2011). However, methods to convert biomass to fuels have several difficulties.

In this research, the goal was to produce a high-quality bio-oil with low or zero oxygen content that could be suitable for use as a transportation fuel. To do that, we followed two steps. We first produced bio-oils with different oxygen contents using formate-assisted fast pyrolysis (FAsP) process followed by catalytic upgrading to transportation fuel. In Chapter 3, we will



show how we prepared the feedstocks, the pyrolysis system configuration, the operating conditions used, and the physical and chemical compositions of bio-oils produced. In Chapter 4, we will discuss the upgrading process of these bio-oils. This will include the catalyst that we have used, the operating conditions used and the reactor configuration. A Thermo Scientific Model Flash 2000 elemental analyzer (CHNO) was used to determine the elemental composition of the oils. A Shimadzu Q2010 GC-MS was used to characterize the organic fractions of each oil product. Gas products were analyzed using SRI 8610C portable GC. The moisture content in the FAsP oils was performed using Karl-Fisher titration. The pyrolysis and the upgrading processes will be described along with detailed physical and chemical analysis of bio-oil products.

## 1.2 Lignocellulosic biomass

Wood is constructed of three different major components: cellulose, hemicellulose, and lignin. Wood can contain about 40 to 44% of cellulose ( $(C_6H_{10}O_5)_n$ ), 20 to 30% of hemicellulose ( $(C_5H_8O_4)_n$ ) and 18 to 35% of lignin, and all compositions are by dry weight of wood (Carrasco 2013). The composition of the major biomass feedstocks is shown in Table 1.1.

| Plant         | Lignin % | Cellulose % | Hemicellulose % | Extractives | Ash |
|---------------|----------|-------------|-----------------|-------------|-----|
| Willow        | 19.7     | 48.5        | 13.9            | No data     | 1.7 |
| Pine          | 25.9     | 41.7        | 20.5            | 2.7         | 0.3 |
| Eucalyptus    | 27.2     | 46.3        | 14.9            | 1.9         | 1.1 |
| Hybrid Poplar | 25.7     | 41.5        | 17.9            | 4.2         | 1.8 |

Table 1. 1 Composition of general lingo-cellulosic materials (Basu 2010).

### 1.3 Thermochemical conversion of biomass

The thermochemical conversion process is one of the major routes that is being used to convert biomass to fuel and chemicals. In this process, the heat is utilized to chemically decomposes biomass feedstocks and producing viable sources of energy. This process is comprised of four methods which are Combustion, Gasification, Liquefaction, and Pyrolysis. Pyrolysis method will be discussed here. Main thermochemical conversion processes for biomass conversion into fuels and chemicals are listed in Figure 1.1.

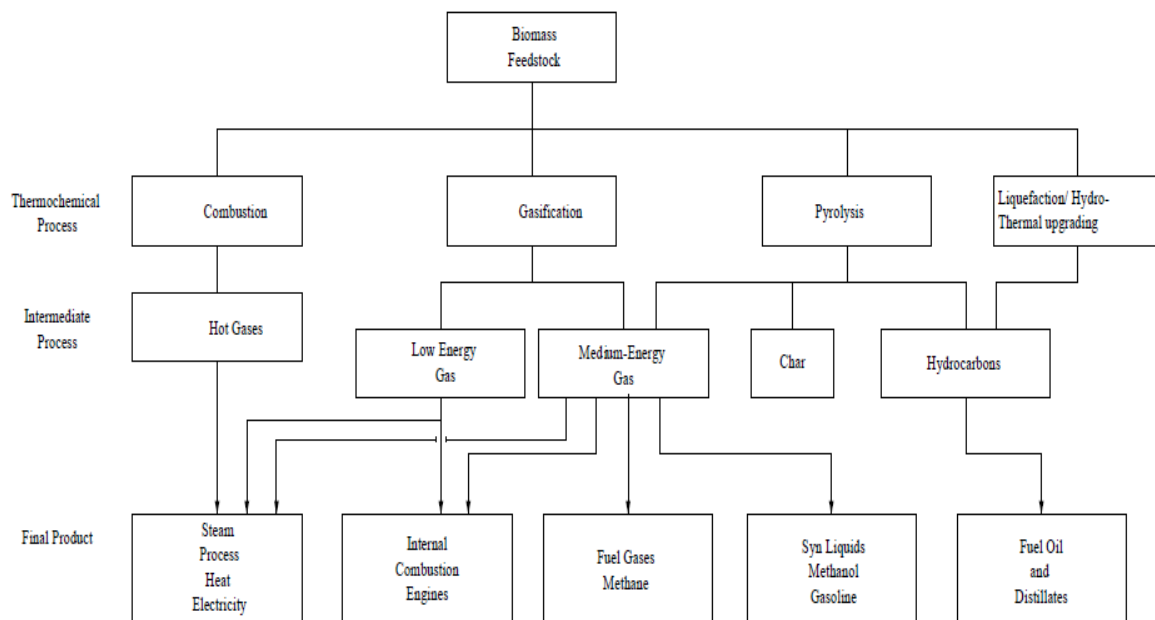


Figure 1. 1 Thermochemical conversion processes of biomass (McKendry et al. 2002).

### 1.3.1 Pyrolysis

Pyrolysis is a process done in an inert atmosphere and in the absence of air. It involves the rapid heating of biomass to temperatures between 450-600 °C, the rapid condensing of pyrolysis vapor and short residence times. Organic vapors, water, gases and char are the pyrolysis products. Pyrolysis oil can be made using many pathways. These pathways can be done either using the conventional slow pyrolysis route or the flash pyrolysis route named also as fast pyrolysis. The slow pyrolysis route is a process done using slow heating rates with long residence time and a temperature range between (400-600 °C). Fast pyrolysis route, on the other hand, takes place at elevated temperature and short residence times. Mohan showed that the fast pyrolysis route can produce 60–75 wt.% of liquid bio-oil, 15–25 wt.% of solid char, and 10–20 wt.% of no condensable gases all depending on the feedstock used (Mohan et al. 2006). On the other hand, the slow pyrolysis route can produce 29.9–47.0 wt.% of liquid bio-oil, 19–33.9 wt.% of solid char, and 22.2–45.8 wt.% of no condensable gases all depending on the feedstock and the temperature used (Phan et al. 2008).

Fast pyrolysis process has the ability to produce a high yield of liquid fuel from any type of biomass feedstock. Liquid bio-oil collected from fast pyrolysis process is the most useful product that can be further upgraded into fuel and valuable-added chemicals (Bridgwater et al. 2000). Despite the advantages that one can get from the fast pyrolysis method, bio-oil has many drawbacks that need to be overcome. The high oxygen content is the major obstacle to pyrolysis oil utilization. In addition to the high oxygen content, bio-oil has high water content and it is highly acidic, etc. To overcome these undesirable characteristics, bio-oil needs an extra step, upgrading step, to remove the oxygenated compounds and enhance its final properties to be used as a substitute for petroleum derived-fuels.

The pyrolysis and the upgraded liquid products can be evaluated using the O:C and H:C ratios. These ratios are important when we need to compare the pyrolysis or the upgraded liquid products quality with the transportation fuels quality (French et al. 2010).

The yields and chemical compositions of the bio-oil obtained from the fast pyrolysis of different biomass feedstocks varied from type to type of wood due to the differences in the compositions of the wood. Yields of the main pyrolysis products, the lignocellulosic material composition, and the chemical composition of produced bio-oil are listed in Table 1.2.

|  | Pine sawdust (softwood) | Mesquite sawdust (hardwood) | Wheat shell |
|--|-------------------------|-----------------------------|-------------|
| Yields of the main pyrolysis products (wt.%)   |                         |                             |             |
| Pyrolysis liquid   | 50.3                    | 38.7                        | 38.0        |
| char   | 28.9                    | 36.6                        | 36.1        |
| Gases  | 20.8                    | 24.7                        | 25.9        |
| Properties of the biomass raw materials (% , dry basis)                                      |                         |                             |             |
| Moisture content   | 10.2                    | 12.5                        | 18.8        |
| Ash  | 0.3                     | 0.6                         | 5.4         |
| Lignocellulosic material composition (% , dry basis)   |                         |                             |             |
| Cellulose  | 35                      | 40-45                       | 10-15       |
| Hemicellulose  | 29                      | 25-30                       | 30          |
| Lignin   | 28                      | 11-28                       | 4-8         |
| Higher heating value (HHV, MJ/Kg)  | 15.4                    | 15.4                        | 14.1        |
| Chemical composition of treated liquid and bio-oil identified by GC-MS (%) (wt.%, dry basis) |                         |                             |             |
| Acids  | 18.71                   | 16.99                       | 18.91       |
| Esters   | 8.29                    | 7.62                        | 8.62        |
| Linear Aldehydes and ketones   | 17.52                   | 9.12                        | 7.34        |
| Cyclic Ketones   | 6.11                    | 5.77                        | 6.06        |
| Furans   | 5.95                    | 6.25                        | 3.44        |
| Alcohols and sugars  | 9.81                    | 8.06                        | 6.04        |
| Ethers   | 0.80                    | 1.22                        | 1.38        |
| Phenols  | 15.74                   | 28.23                       | 19.02       |
| Hydrocarbons and derived   | 0.80                    | 2.15                        | 2.42        |
| Others oxygenated cyclic compounds   | 2.91                    | 3.96                        | 2.64        |
| Nitrogen compounds   | 1.53                    | 1.18                        | 1.48        |

Table 1. 2 Pyrolysis products from different lignocellulosic biomass (Bertero et al. 2012).

## 1.4 Chemical composition of bio-oil

The chemical composition of bio-oil depends upon the chemical composition of the biomass feedstock and the operating conditions used. In general, bio-oils are composed of two main groups, namely, organic and inorganic. The oxygenated groups present in the bio-oils are ketones, aldehydes, carboxylic acids, and alcohols. Aldehydes, ketones, furans, anhydrosugars, sugars, acids, esters and a few hydrocarbons, ethers and alcohol which include phenolic compounds are the major organic groups that are present in the liquid phase obtained from cellulose and hemicellulose pyrolysis (Wei et al. 2012). Bio-oils are also composed of multifunctional compounds, such as hydroxyacetic acid, hydroxyacetaldehyde, hydroxyacetone, and 3-hydroxy- 3-methoxy benzaldehyde (Diebold 2000). In addition to the organic compounds present in the bio-oil, there are also some inorganic compounds that affect pyrolysis oil stability. Potassium, sodium, magnesium and calcium are naturally present in the biomass. These inorganic compounds, especially potassium and calcium catalyze biomass decomposition and char-forming reactions during biomass pyrolysis leading to suspended submicron particles in the pyrolysis oil (Aglevor et al. 1995). The growth of these char particles increases their concentrations in the bio-oils and make them problematic for combustion in different engines (Aglevor et al. 1995).

As mentioned in Diebold 2000, the exact composition of the bio-oil results from a complex interrelationship of:

1. The biomass used as a feedstock including dirt and moisture contents.
2. Organic nitrogen or protein content of the feedstock.
3. The heat transfer rate and the final char temperature during the pyrolysis process.
4. The extent of vapor dilution in the reactor.
5. Vapor residence time and temperature in the reactor.
6. Vapor residence time and temperature in the heated transfer lines from the pyrolysis reactor to the quench zone.
7. Whether the vapors pass through the accumulated char such as in hot gas char filtration.
8. The efficiency of the system that is used to separate the char from the bio-oil vapors before condensation equipment.
9. The efficiency of the condensation equipment that is used to recover the volatile components from the non-condensable gas stream, such as water and low molecular weight esters.
10. Whether the suspended char fines remove from the condensate by filtration.
11. Feedstock water content.
12. The contamination extent of the bio-oil during storage by leaching of the containers.
13. Exposure to air during storage.
14. The length of storage time.
15. The storage temperature.

### 1.5 Physical properties of bio-oil

Bio-oils obtained during pyrolysis of biomass are dark brown, highly viscous with a distinctive smoky odor. In general, the physical properties of bio-oil change with changing the conditions and feedstocks. The grades of bio-oils are determined by characteristics such as oxygen content, density, viscosity, pour point, heating value, flash point, ignition temperature, water content, solids content, sulfur content, ash content, flash point and pour point. Bio-oils are also characterized by aging term, which is defined as the change of physical properties of bio-oils with time. The physical properties of bio-oil are listed in Table 1.3.

|  |            |
|--|------------|
| Moisture content   | 25%        |
| pH   | 2.5        |
| Specific gravity   | 1.20       |
| Elemental analysis (moisture free basis)                       |            |
| C  | 56.4%      |
| H  | 6.2%       |
| N  | 0.2%       |
| S  | < 0.01%    |
| Ash  | 0.1%       |
| O (by difference)  | 37.1%      |
| Higher heating value, HHV (moisture free basis)                | 22.5 MJ/kg |
| Higher heating value, HHV as produced<br>(depends on moisture) | 17.0 MJ/kg |
| Viscosity (at 40°C)  | 30–200 cp. |
| Pour point   | –23°C      |

Table 1. 3 Physical properties of bio-oil derived from wood (Bridgwater et al. 2000).

Bio-oil has more than 300 compounds. Most of them contain oxygen that has a negative effect on bio-oil properties. Some of these oxygenated compounds could be removed through the fast pyrolysis route, but the bio-oil still contains 30-40 wt.% oxygen (Sipila et al. 1998). The highly oxygenated groups cause the bio-oil to be very acidic where the total acid number (TAN) is greater than 100 and make it extremely corrosive (Oasmaa et al. 2010). The viscosity is also affected by these highly oxygenated groups because certain compounds induce polymerization reactions, causing the viscosity of the oil to increase drastically over time (Diebold 2000). Bio-oil becomes a less valuable fuel due to the presence of high oxygen content, which leads to many issues, including utilization and handling. Bio-oil has a much lower energy density than conventional fossil fuel, has poor stability and it is not miscible with hydrocarbons, which are all due to the high oxygen content.

Kim reported that bio-oils contain approximately 15-60% water (Kim et al. 2013). This water content is from the original moisture content present in the biomass feedstock and from the dehydration reactions that take place during the pyrolysis process. It was reported that the high-water content caused by both the pyrolysis reactions and the moisture present in the feed results in lowering the heating value and density. On the other hand, having high water content in the bio-oil results in reducing the oil viscosity which improves bio-oil flow characteristics.

Viscosity is defined as the resistance of the liquid to flow. Bio-oils viscosity can vary over a wide range (35-1000 cP at 40 °C) and that depends on the feedstocks and the conditions by which they create. When bio-oils are stored, their viscosity increase with time and that is defined as an “aging” which is one of the bio-oils characteristics. Through aging, bio-oils suffer from the polymerization or the condensation reactions that take place between the compounds present in the bio-oils, leading to the formation of larger molecules. This increased viscosity is



accelerated by exposure of bio-oils to oxygen and to ultra-violet light or by increasing temperature (Czernik et al. 2004). Scholze concluded that pyrolysis oils suffer strongly accelerated polymerization reactions when they are heated to 80 °C or more. During aging, the viscosity increased from 84.5 cSt after one month to 162.3 cSt after 12 months, whereas the pH and density values remained almost unchanged (Scholze 2002). According to Peacocke, the density of pyrolysis oil decreased with increased temperature where it decreased from 1.205 g/cm<sup>3</sup> at 20 °C to 1.150 g/cm<sup>3</sup> at 80 °C (Peacocke 1994). Viscosity is one of the obstacles that causes instability in the oils. Bridgwater has mentioned that the oil's viscosity could be reduced or controlled by the addition of alcohols such as ethanol or methanol (Bridgwater 2012). Many investigations have done by different authors to study the possibility of changing the stability of oils by adding a catalyst to the fuel during the pyrolysis process (Diebold 1991). Another investigation done by Joseph showed that there are several classes of compounds that give rise to instability, like vinyl compounds (Joseph et al. 2016). It is important to identify the reactive compounds and the reactions that cause the instability of oils during aging because knowing them is contributing to finding different ways to handle them and leading to improve the oil quality.

Acetic and formic acids are two examples of the organic acids that are present in the pyrolysis oil and make it highly acidic. Pyrolysis of untreated biomass results in an oil that has a total acid number (TAN) of greater than 100 and a pH of 2-3 (Oasmaa et al. 2010). Because of this low pH, pyrolysis oils are corrosive to common metal construction materials. Volatile acids form 60-70% of the pyrolysis oil acidity, the acidity is also influenced by other groups of compounds in fast pyrolysis oils which include phenolics, fatty and resin acids, and hydroxy acids (Oasmaa et al. 2010). The pH test method is a useful method to measure the pH of the oils

and knowing which applications may suffer a considerable damage in case of treatment with corrosive oils (Coverdell 2010). In a study done by Oasmaa et al., they concluded that there is a slight increase in acetic and formic acids during the first 2 months of storage and their concentrations remained the same during the stability test at 80 °C for 24 h (Oasmaa et al. 2010). They also reported that there is no any change in the TAN during the aging of fast pyrolysis oil. It is important to know the oils pH and TAN in order to improve the quality of the oil and also determine which compounds are stable and which ones are reactive during studies of bio-oil.

Bio-oil has a lower heating value which is less than 50% of that for a conventional fuel oil. This low heating value is caused primarily by the presence of oxygen and water in the oil. Removal of oxygen and water from bio-oil increases the heating value and improves oil fuel quality.

The application of bio-oil has been limited because of the undesirable characteristics described above. Oxygen removal from bio-oil is the single most important step that will lead to stabilizing and improving bio-oil properties toward final use as a transportation fuel.

## **1.6 Removal of oxygen during pyrolysis**

Fast pyrolysis methods have been modified to remove oxygen in-situ, prior to post-pyrolysis upgrading. These techniques seek to alter the pyrolysis pathways to favor increased deoxygenation either through changing pyrolysis conditions, adding catalysts, or pretreating the feedstock with salts. A review of these techniques is presented below.

### **1.6.1 Catalytic fast pyrolysis**

Pyrolysis of biomass that occurs in the presence of a cracking catalyst such as a zeolite will result in increased gas production producing an oil of lower yield but with less oxygen content (Williams et al. 1995). The catalyst can either be co-fed with the biomass in the pyrolysis reactor or held in a bed downstream of the reactor contacting the vapor/gas stream exiting the reactor. Catalytic fast pyrolysis of biomass generally produces an oil that is rich in aromatics, stable and has a lower oxygen content. Because of the cracking, carbon is lost in the gas stream, resulting in low mass and energy yields. Carlson concluded that the products that are produced through catalytic fast pyrolysis are more stable and have lower oxygen content than those from conventional pyrolysis (Carlson et al. 2009). Despite the fact that the catalytic fast pyrolysis method is considered one of the effective methods for producing stabilized and deoxygenated pyrolysis oil, there are some significant drawbacks. Zeolite catalysts are sensitive to alkali and alkaline earth metals present in biomass feedstocks. These alkali and alkaline earth metals deposited on the catalysts and linearly increased over time leading to a steady decrease in the overall acidity of the catalysts over time (Paasikallio et al. 2014). This drawback makes this method economically unfavorable.

## 1.6.2 Hot gas filtration

Hot gas filtration has been used to remove fine char particles from the vapor/gas stream exiting the pyrolysis reactor. Case recently published that running pyrolysis under conditions of increased residence time and a hot gas filter at temperatures greater than 400 °C resulted in increased cracking reactions producing a lower oxygen content oil (Case et al. 2014b). Further analysis of their oil indicated increased stability relative to conventional oils. This method can produce more stable pyrolysis oil but that depends on the type of hot gas filter used and the operating temperature (Baldwin et al. 2013). Pyrolysis oils produce using hot gas filter have lower solid contents, lower viscosity and alkali metal contents compared to the pyrolysis oils that produce using conventional cyclone separators (Hoekstra et al. 2009). Char filter element after a run is shown in Figure 1.2. The drawbacks of the hot gas filtration method are the low liquid yield and it has not been demonstrated to use it for long time-on-stream.

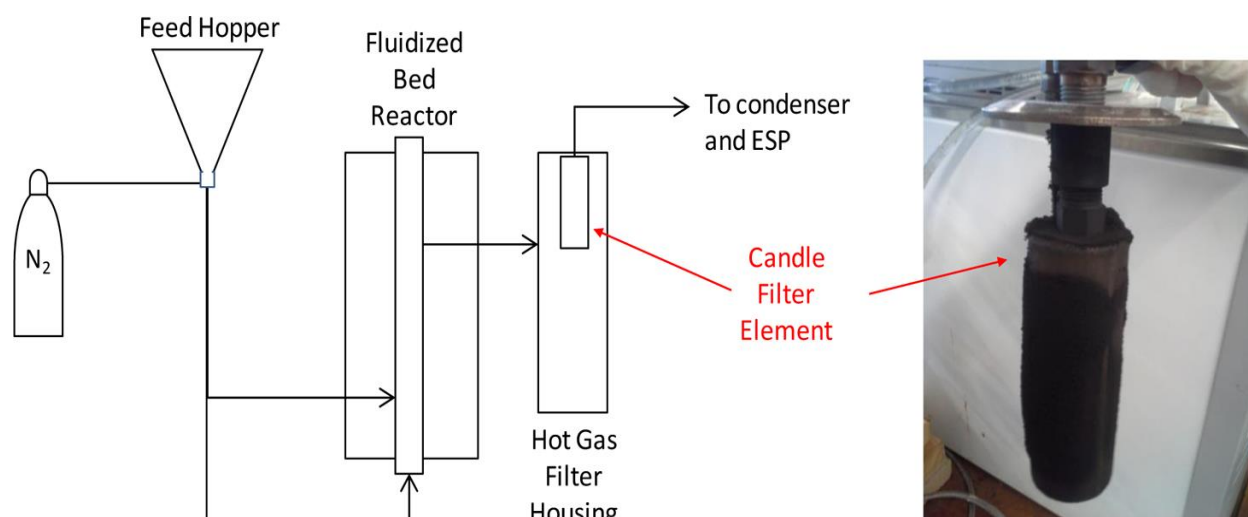


Figure 1. 2 Simplified schematic of pyrolysis system shown the location of the hot gas filter housing and filter element (Case et al. 2014b).

### 1.6.3 Pretreating with calcium compounds

Pretreatment of biomass with calcium compounds prior to fast pyrolysis is a method developed at the University of Maine. Several calcium compounds were tested as pretreatments where they were mixed with pine sawdust first and then pyrolyzed in a fluidized bed pyrolysis reactor at 500 °C with higher residence times (Case et al. 2014a). The addition of calcium formate, carbonate, sulfate, hydroxide and oxide to pine sawdust prior to pyrolysis results in a significant decreasing in the oxygen content and producing more stable oil except for calcium sulfate which was inert during pyrolysis (Case et al. 2014a). In a study done by Wang et al., they concluded that the addition of calcium hydroxide completely prevented the formation of acids, moderately reduced the formation of furans and sugars, and increased ketone and alcohol yields (Wang et al. 2010). They attributed that to the neutralization of carboxylic acid groups that are present in hemicelluloses, leading to the formation of carboxylate salts instead of acids. Their results also showed that there is an increase in the overall liquid yield with the addition of calcium hydroxide. Calcium oxide is another calcium compound that has been studied. It was found that there is a significant decrease in the oxygen content which was from 39 wt.% to 31 wt.% at a high CaO/pine ratio with a slight increase in the overall bio-oil yield (Lin et al. 2010). In Case et al. study, they found that the gas yield is reduced with the addition of calcium hydroxide and calcium oxide compared to untreated pine. Calcium formate is the most important calcium compound because it can contribute to decreasing the oxygen content to about 16 wt.% with high heating rate and high carbon yield compared to the pyrolysis of untreated biomass. The deoxygenation of the liquid product can be done without a decrease in the overall liquid yield or H:C ratio and that is due to the incorporation of hydrogen and carbon from the calcium formate with the biomass (Case et al. 2014a). This method is a straightforward process and done in a

single-step reactor without the usage of the hydrogen gas. It is also a cheap process due to the low cost of calcium compounds (Carlson et al. 2011). Interestingly, it reduces the cost of the upgrading process due to the less oxygen content present in the oil produced from the biomass pretreated with calcium compounds. Table 1.4 shows the comparison between the fast pyrolysis and the formate-assisted pyrolysis (FAsP).

|                           | Fast Pyrolysis (Carrasco 2013) | FAsP (Case et al. 2014a) |
|---------------------------|--------------------------------|--------------------------|
| Oil mass yield, wt.%      | 60                             | 23                       |
| Oxygen content, wt.%      | 35                             | 16                       |
| HHV MJ/Kg                 | 25                             | 32                       |
| O:C (oil)                 | 0.28                           | 0.16                     |
| H:C (oil)                 | 1.15                           | 1.15                     |
| Stability                 | Not stable                     | Stable                   |
| Upgrading (hydrotreating) | Two stages                     | One stage                |

Table 1. 4 Comparison between fast pyrolysis and FAsP.

## 1.7 Description of research

This research study involved preparing bio-oils of different oxygen content using fast pyrolysis methods developed at the University of Maine. These oils were produced using formate-assisted pyrolysis (FAsP) process. The resulting oils of different oxygen contents were then hydrotreated over a commercial nickel / silica-alumina catalyst in a continuous flow, trickle bed reactor for up to 15 days. The effect of hydrotreating operating conditions on oil yield and composition were examined for the different oils. In addition, catalyst robustness was examined. Recommendations are made regarding hydrotreating conditions and oil feed quality on the final product oil yield and composition.

## **CHAPTER 2: A REVIEW OF BIO-OIL UPGRADING INTO TRANSPORTATION FUEL: CATALYSTS, OPERATING CONDITIONS, REACTORS AND REACTIONS**

### **2.1 Introduction**

As discussed in Chapter 1, bio-oils produced from the fast pyrolysis process have many undesirable characteristics that reduce their quality as transportation fuels. The major problem that causes these negative properties is mainly the oxygenated groups that are present in the bio-oil. Besides that, there are a group of complex compounds that are present in the bio-oil which make it very hard to upgrade or to use as a transportation fuel. Through the fast pyrolysis process, these oxygenated groups can be reduced but cannot be totally eliminated, so another process or step should be taken into consideration to remove the remaining oxygenated compounds. The major oxygenated compounds present in the bio-oil are saccharides, alcohols, ketones, aldehydes, carboxylic acids, phenolic compounds, lignin oligomers and water (Brown 2011). Many upgrading methods have been investigated to remove the oxygenated compounds and produce high-quality fuels from bio-oils.

Hydrodeoxygenation, HDO, is the most important process that has been studied extensively and is considered a unique process to produce high energy with oxygen-free content hydrocarbons. The HDO process is normally done in the presence of hydrogen pressure and catalysts at elevated temperatures where the oxygen is rejected in the form of water and some gases. The HDO process can produce bio-oils with high quality and zero oxygen content, but that depends upon many concerns that affect this process. Hydrogen consumption is one of the concerns that the HDO process suffered from as described in Chapter 1. A major concern with the HDO process is the catalyst lifetime. Another major concern is the cost such as the cost of the expensive catalysts and units used. Many catalysts have been studied extensively during the

few past years. Some of them were successful to remove the oxygen content from the oils, some were not. Some of them were deactivated quickly after starting of the hydrotreatment, some of them stood actively for some hours or days. As a result of the usual rapid catalyst deactivation, negative properties appear such as lower product yields and reactor plugging; therefore, the development of an effective catalyst is a very important role in the HDO process. Finding the optimum reaction conditions and catalysts that can tolerate the severe conditions are the main focus for many authors these days. In this study, instead of focusing on optimizing reaction conditions for hydrotreating unstable pyrolysis oils, we examined the effect of feedstock chemical composition on catalyst lifetime, yields, oxygen removal, and hydrogen uptake during HDO. During this study, hydroprocessing experiments were conducted for more than 15 days without stopping.

## **2.2 Catalysts, operating conditions and reactor configurations for bio-oil upgrading**

Many catalysts have been investigated over the past 30 years for bio-oil upgrading. In this section, we are going to present the catalysts that have been used during the HDO process. Because of their importance in this process, we are going to present them in detail.

### **2.2.1 Sulfided catalysts**

The first two catalysts used in the upgrading process were the sulfided catalysts NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub>. They have been tested first by (Elliott et al. 1984). These two sulfided catalysts were used in the petroleum industry first for the purpose of desulfurization and used again in the biomass area. CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst is be able to successfully remove the sulfur



from the petroleum oil down to a few ppm (Prins 2008) and it is the best regarding the deoxygenation activity (Wildschut 2009).

Elliott et al. 1988 have used these two catalysts in a two-step hydroprocessing treatment. They have changed the operating temperature from a low-temperature range (250 to 280 °C) to a high-temperature range (370 to 400 °C). The reason behind this treatment was to eliminate the problems of the polymerization of bio-oils during the start of experiments, as well as the problems with the reactor blockage. These two stages have reduced the problems of the polymerization of bio-oils but coke formation that leads to plug formation was still present.

Wildschut et al. 2009a reported a paper about a hydrotreatment done by comparing sulfided CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts with noble metal catalysts (Ru/C, Pd/C) in a two-stage treatment in a batch system. The first stage was at 250 °C under 100 bar H<sub>2</sub> for 4 hours, while the second one was at 350 °C under 100 bar H<sub>2</sub> for 4 hours too. Ru/C catalyst was the best regarding the deoxygenation activity followed by Pd/C with high oil yield than the two sulfided catalysts. The low amount of sulfur in the feed results in a low yield and makes it difficult to use these catalysts. So, appropriate amounts of sulfur should be added to the feed to maintain the sulfidation state of the catalysts and keep them active.

Horacek et al. 2017 also reported a work on the sulfided catalysts (CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub>). Their work was similar to the work done by Elliott et al. 2012. The reactor was divided into three reaction zones. They tried five reference tests with different operating conditions and different catalysts. In the first reference test, they used the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. In the second, third and fourth reference tests, they used the NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst with different operating conditions. In the fifth test, they used the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst at the bottom of the reactor and the NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst at the top of the reactor. In the first reference test, they used

the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst with temperature ranges of (170–250 °C), (250–350 °C), and (350–450 °C) for the first, second and third zones respectively and WHSV between 0.2-0.4 hr<sup>-1</sup>. The CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst showed a good selectivity towards diesel-like products than the NiMo catalyst. The major problem with the alumina as support is the low stability at high temperature in the presence of water. For the first reference test, the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst deactivated after only 30 hours on-stream with a reactor blockage after 40 hours on-stream.

Elliott 2007 reported a work on the bio-oil hydrotreatment done by Veba Oel AG using the sulfided CoMo and NiMo catalysts. The operating conditions for this work were 17.8 MPa pressure, 350-370 °C temperature and WHSV between 0.25-0.8 g/ g h in a continuous feed bench-scale reactor. 88.0-99.9% was the deoxygenation rates that have been achieved with a relative constant oil yield of 30-35%. During this work, the catalyst experienced considerable deactivation quickly due to the gum-like deposits that blocked the reactor. As a result of that, a stabilization step was necessary to keep the catalyst activity higher because these sulfided catalysts seemed to be deactivated quickly by a single stage treatment.

In a work done by Viljava et al. 2000, they discussed some drawbacks for the presence of sulfur prior to hydroprocessing. They concluded that the hydrodeoxygenation activity of the sulfided catalyst decreased in the presence of H<sub>2</sub>S. The sulfided catalyst was mostly deactivated by coke and high molecular weight products that formed during the hydroprocessing process, water formed during the HDO process also acted as an inhibitor (Delmon et al. 1996).

Elliott et al. 2012 reported a work done using a fixed-bed reactor with a trickle flow where the bio-oil and hydrogen gas entered the top of the catalyst bed and passed through to the exit. Sulfided Ru/C catalyst was used at the top of the reactor at 170 °C with a liquid hourly space velocity (LHSV) of 0.19 whereas the sulfided CoMo or NiMo catalysts used at the bottom

of the reactor at 400 °C and 0.19 LHSV. A sulfiding agent was added to the feed before starting the experiment to maintain 100 ppm sulfide. The upgraded product had an oxygen content ranging between 0.2-2.7 wt.%. For all three tests, a plugging in the front end of the catalyst bed was observed especially in the heat-up zone, that could belong to the catalyst coking in the high-temperature stage, but there is little evidence of this. There was also a pressure buildup across the reactor over time (10-100 hours) due to the polymer formation. The hydrogen consumption using sulfided NiMo catalyst was 572–669 L/L of feed. These three tests were run successfully for 90-99 hours on-stream before reactor plugging happened, which might be caused by the char particles present in the bio-oil. Bio-oils need to be pre-filtered prior to hydroprocessing in order to reduce or remove these particles. The NiMo catalyst produced the more saturated product (higher H:C ratio) than the CoMo catalyst but with higher hydrogen consumption. The compositions of the oil product are listed in Table 2.1.

| test, catalyst  | TOS       | H/C<br>(dry) | C<br>(wt %) | H<br>(wt %) | O<br>(wt %) | N<br>(wt %) | S<br>(wt %) | TAN<br>(mg of KOH/g) | moisture<br>(wt %) | density<br>(g/mL) |
|---|-----------|--------------|-------------|-------------|-------------|-------------|-------------|----------------------|--------------------|-------------------|
| HT162, NiMoS  | 4.5–8.5   | 1.94         | 83.5        | 13.6        | 0.3         | <0.05       | 0.078       | <0.01                | 0.01               | 0.76              |
| HT162, NiMoS  | 24.7–28.7 | 1.73         | 84.6        | 12.3        | 0.2         | <0.05       | <0.005      | <0.01                | 0.01               | 0.80              |
| HT162, NiMoS  | 45.6–57.5 | 1.63         | 86.7        | 11.9        | 0.2         | <0.05       | 0.006       | 0.03                 | 0.02               | 0.83              |
| HT162, NiMoS (0.08 LHSV)  | 81.1–89.0 | 1.53         | 87.3        | 11.2        | 0.3         | <0.05       | 0.014       | 2.7                  | 0.03               | 0.87              |
| HT163, CoMoS/C  | 20.8–24.8 | 1.77         | 86.2        | 12.8        | 0.3         | <0.03       | 0.007       | 0.66                 | 0.01               | 0.82              |
| HT163, CoMoS/C  | 52.9–57.4 | 1.64         | 86.0        | 11.8        | 1.2         | <0.03       | 0.013       | <0.1                 | 0.06               | 0.86              |
| HT163, CoMoS/C (0.08 LHSV)  | 84.9–89.1 | 1.53         | 85.3        | 11.0        | 2.7         | 0.06        | 0.010       | <0.1                 | 0.33               | 0.92              |
| HT164, CoMoS/C  | 7.4–19.4  | 1.76         | 84.6        | 12.5        | 0.3         | <0.05       | 0.018       | <0.1                 | 0.01               | 0.82              |
| HT164, CoMoS/C  | 34.7–38.4 | 1.59         | 85.0        | 11.4        | 0.7         | <0.05       | 0.008       | <0.1                 | 0.02               | 0.86              |
| HT164, CoMoS/C  | 70.4–82.4 | 1.47         | 84.0        | 10.4        | 2.1         | 0.10        | 0.007       | <0.1                 | 0.27               | 0.91              |
| HT166, CoMoS/Al <sub>2</sub> O <sub>3</sub> :F filtered top phase oil | 6.3–18.3  | 1.56         | 86.5        | 11.4        | 1.5         | 0.17        | <0.005      | 0.02                 | 0.20               | 0.88              |

Table 2. 1 Oil product composition from the hydroprocessing of bio-oils (Elliott et al. 2012).

Despite the success that these catalysts have in the petroleum area, there are some drawbacks of using these sulfided catalysts in the biomass area. PNNL reported that the cost of the hydrotreating procedure is very expensive because for example Ru catalysts had to be replaced every 30 days. The reason behind this replacement was due to the coke formation and unstable feedstock. Other drawbacks were the economic scale of sulfur usage and finally the contamination of the product. As a result of these drawbacks, many efforts have been spent by researchers to find alternative catalysts. The nickel and transition metal catalysts were the second options to try which will be discussed in the following sections.

### **2.2.2 Nickel catalysts**

Yang et al. 2014 investigated the hydrodeoxygenation of anisole obtained from the flash pyrolysis of lignocellulosic biomass. This hydrodeoxygenation was done using a series of Ni-containing (20 wt.% loading) catalysts based on carriers as diverse as SBA-15, Al-SBA-15,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, microporous carbon, TiO<sub>2</sub> and CeO<sub>2</sub> in a continuous flow reactor under 3 bar of hydrogen pressure, 290–310 °C of moderate temperature and space velocities of 20.4 and 81.6 h<sup>-1</sup>. In this work, they were trying to see the influence of metal-support interactions on the anisole HDO selectivity toward aromatic products. At 290 °C and 3 bar, Ni/C catalyst gave the highest benzene yield which was 64% with a conversion of 98%. The anisole conversion was almost 100% for the Ni–Al-SBA-15, Ni/SBA-15 and Ni/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. The anisole conversion was 90% for Ni/CeO<sub>2</sub> and 47% for Ni/TiO<sub>2</sub>. The conversion and selectivity of the catalysts above were all under the conditions of 290 °C and 3 bar. Under 290 °C and 3 bar, the hydrodeoxygenation efficiency approached 100% in most of the catalysts except for the Ni/CeO<sub>2</sub> and Ni/C with a <10% production of oxygenated compounds. Finally, they concluded that the

support seems to have a huge effect on the selectivity of the HDO of anisole, where the catalysts based on reducible oxides such as Ni/TiO<sub>2</sub>, Ni/CeO<sub>2</sub> as well as Ni/C showed a high selectivity toward aromatics than others. Higher temperature and lower space velocity were the optimum operating conditions that lead to high aromatic production.

Jin et al. 2014 reported a similar hydrotreatment work to the work done by Yang et al 2014 above except using different reactor set-up, less nickel weight loading, different operating conditions and a new tested support which was SiO<sub>2</sub>. In this work, anisole was investigated using a series of Ni-containing (10 wt.% loading) catalysts based on carriers as diverse as Ni/AC, Ni/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ni/SBA-15, Ni/SiO<sub>2</sub> in a batch set-up under 0.5–3.0 MPa of hydrogen pressure and 180–220 °C of temperature. The anisole conversion was 100% for all four Ni catalysts after 90 min on-stream, and the main products were cyclohexyl methyl ether (CME), cyclohexanol (CHL), cyclohexane (CHE), cyclohexyl ether (CCE). The Ni/AC produced most of the aromatic ring-saturated cyclohexyl methyl ether. The highest activity in the HDO of anisole was showed by Ni/SiO<sub>2</sub> which was 95%. They concluded that the hydrogen pressure and the temperature play a significant role on both anisole conversion and main products distribution, where the conversion increases from 22% to 99% when the pressure goes from 0.5 to 3.0 MPa, while the reaction temperature has a significant effect toward the oxygen-removal.

Phan et al. 2015 published a study on the hydrodeoxygenation of guaiacol using NiMo catalyst based on different supports at 250 °C and a hydrogen pressure of 5 MPa. The supports were  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and SBA-15. NiMo/SBA-15 was the most effective catalyst that displayed the highest activity toward the HDO of guaiacol with a conversion of 90% and an HDO degree of 67.5% with high yields of cyclohexane and other saturated ring compounds. NiMo/CeO<sub>2</sub> also showed higher performances in the HDO reaction of guaiacol.

Ardiyanti et al. 2012a have published a study on the catalytic hydrotreatment of fast pyrolysis oil using non-sulfided bimetallic NiCu/  $\delta$ -Al<sub>2</sub>O<sub>3</sub> catalyst with various Ni/Cu ratios (0.32 to 8.1 w/w). In this study, they started the hydrotreatment reactions with the anisole as a model compound in a continuous fixed bed reactor at 300 °C and a pressure of 10 bar with WHSV values between 3 and 6 h<sup>-1</sup>. Next, they switched to fast pyrolysis oil in a batch autoclave for 1 hour at 150 °C followed by 3 hours at 350 °C all at a pressure of 100 bar. For the anisole hydrotreatment, the catalyst was very active in anisole deoxygenation with a conversion between 66.1 and 95.3 mol%. The main products using the NiCu/  $\delta$ -Al<sub>2</sub>O<sub>3</sub> catalyst for the anisole hydrotreatment were benzene and cyclohexane, while the HDO selectivity was between 70 and 96%. For the pyrolysis oil hydrotreatment, the yield of the product oil obtained over NiCu/  $\delta$ -Al<sub>2</sub>O<sub>3</sub> was between 35 and 42 wt.%. The carbon yield in the upgraded bio-oil was between (64–75 wt.%) and the oxygen content was between 10.4 and 17.1 wt.% (dry basis) after was 40.1 wt.% (dry basis) in the original fast pyrolysis oil with an O:C ratio of 0.08–0.17 and a H:C ratio of 1.0–1.6. In conclusion, they suggested that the bimetallic 16Ni2Cu catalyst (with a Ni to Cu wt.% ratio of eight) was the most active catalyst for the hydrotreatment of both anisole and pyrolysis oil. The hydrogen consumption was 146 L/Kg feed.

Ardiyanti et al. 2012b have used the pyrolysis oil that obtained from the fast pyrolysis of pine wood as a feedstock in this work. In this work, they used the same bimetallic Ni–Cu catalyst that was discussed earlier in Ardiyanti et al. 2012a but over various supports such as CeO<sub>2</sub>–ZrO<sub>2</sub>, ZrO<sub>2</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, rice husk carbon, and Sibunitite with a 7.5 to 9.0 (Ni), 3.1–3.6 wt.% (Cu) for the inorganic supports and a 17.1–17.8 (Ni), 7.1–7.8 (Cu) for the carbon supports. The hydrotreatment of fast pyrolysis oil was done in a batch set-up at 350 °C and 200 bar. The yield of the liquid organic phase was between 36–45 wt.% with an oxygen range between 5.4–16.1

wt.% (dry basis) after it was 40.1 wt.% in the original fast pyrolysis oil. The O:C ratio of the upgraded oil was between 0.08–0.18 while the H:C ratio was between 1.10–1.45. The gases produced during the hydrotreatment were CO, CO<sub>2</sub>, CH<sub>4</sub> and small hydrocarbons where the various supports seem to not have a huge effect on the amount of gas produced. The NiCu/TiO<sub>2</sub> showed the highest activity with the most favorable product oil. The CeO<sub>2</sub>–ZrO<sub>2</sub> support was found to have the highest levels of the carbon deposition on the catalyst whereas the lowest levels were for the ZrO<sub>2</sub> and TiO<sub>2</sub> supports. The hydrogen consumption for all catalysts used was between 85-194 L/Kg feed.

Leng et al. 2013 concluded that the NiFe bimetallic catalyst is the most effective catalyst because it showed an excellent activity toward the oxygen removal for three model compounds of bio-oil (furfuryl alcohol, benzene alcohol and ethyl oenanthatate). The bimetallic catalyst was supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and tested in a tubular quartz reactor. The heating value of the upgraded product increased to 43.9 MJ/kg after it was 37.8 MJ/kg in the original bio-oil with an increase in the pH too. In this study, a loading of 15% Ni to 5% Fe were the optimum values that provided the highest activity and selectivity. At 300 °C, the conversion of furfuryl alcohol and benzene alcohol was more than 85% and about 15% for ethyl oenanthatate. At 400 °C, the conversions of furfuryl alcohol, benzene alcohol and ethyl oenanthatate to 2-methylfuran, toluene and heptane were found to be 100, 95.48 and 97.89% respectively at conditions of 0.01 ml/min flow speed and 1 atm. The flow speed has an opposite effect on the conversions and yields, so the higher flow speeds the lower the conversions and yields. The author suggested that the major reaction pathway during this process is the cleavage of C–O rather than C–C.

Eaton et al. 2015 published a work on thermal deoxygenation (TDO) of neutralized biomass acid hydrolysate (levulinate and formate salt mixtures). Calcium or magnesium

hydroxides were the compounds used to neutralize the acids. A Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was used in a vertical downflow tubular reactor. Mg-derived TDO (Mg-TDO) with an oxygen content of 3.9 wt.% and Ca-derived TDO (Ca-TDO) with an oxygen content of 5.7 wt.% were the oils that they used. The hydroprocessing experiment done using Mg-TDO was under 350 °C, 5.2 MPa H<sub>2</sub> pressure, 100 sccm H<sub>2</sub> flow rate with a feed flow rate varied from 0.02 to 0.05 mL/min and WHSV of 0.12–0.3 h<sup>-1</sup>. The hydroprocessing experiment done using Ca-TDO was under 300 °C, 5.2 MPa H<sub>2</sub> pressure, 200-300 sccm H<sub>2</sub> flow rate with a feed flow rate varied from 0.1–0.3 mL/min and WHSV of 0.06–0.18 h<sup>-1</sup>. The amount of Mg-TDO fed was 425 g processed over 169 hours, while the amount of Ca-TDO fed was 11.2 kg processed over 703 hours both ran without catalyst regeneration. The oil produced through the hydroprocessing experiment of Ca-TDO had less oxygen content and suitable for transportation fuels, where the density was improved from 1.01 kg/dm<sup>3</sup> to 0.89 kg/dm<sup>3</sup> and the H:C ratio increased from 1.1 to 1.65. The major compounds identified in the products were naphthenes, monoaromatics, partially saturated polyaromatics, and only trace oxygenates while alkanes remained minor components. They concluded that the TDO oils that they used are potentially compatible with existing refinery operations and catalysts, where a 700 hours on-stream processing was achieved through these oils without real problems. They also expected that the catalyst lifetime can be improved through these oils to approach the 2-years expected lifetime in industrial catalyst installations.



## 2.2.3 Noble metal catalysts

### 2.2.3.1 Pd/C catalyst

Elliott et al. 2009a reported a catalytic hydrotreatment work focused on the process experimentation undertaken at PNNL using a range of operating parameters such as pressure, temperature and flow rate with different biomass feedstocks. Hydrotreating experiments were done using a Pd/C catalyst in a bench-scale, fixed-bed reactor with lower and higher temperatures of (310 and 375 °C) and LHSV of (0.18 and 1.12). The hydrocracking experiments were the second step that was done using the oil obtained from the first step, hydrotreating step, at 400 °C, 2000 psig, and 0.4 LHSV, using a conventional hydrocracking catalyst. For the hydrotreating results, the biomass feedstock was not the major key that had a huge effect on the yield structure, hydrogen consumption. Table 2.2 shows the effect of feedstocks on the hydrotreating results at 340 °C, 2000 psig with large excess hydrogen flow and 0.14–0.25 LHSV.

| Bio-oil                 | Oil yield, g/g dry feed | Aqueous yield, g/g wet feed | Gas yield, g/g carbon feed | Hydrogen consumption, liter/liter feed | Relative exotherm versus setpoint |
|-------------------------|-------------------------|-----------------------------|----------------------------|--|-----------------------------------|
| Mixed wood              | 0.62                    | 0.48                        | 0.062                      | 205                                    | +6°C                              |
| Corn stover light phase | 0.45                    | 0.68                        | 0.071                      | 82                                     | +0°C                              |
| Corn stover heavy phase | 0.78                    | 0.31                        | 0.073                      | 128                                    | +3°C                              |
| 2nd corn stover         | 0.45                    | 0.61                        | 0.066                      | 76                                     | +3°C                              |
| Poplar (hot-filtered)   | 0.59                    | 0.46                        | 0.060                      | 252                                    | +2°C                              |

Table 2. 2 Effect of feedstock on the hydrotreating process results.

Carbon dioxide was the main gas product produced with a small amount of methane for all tests. From the tests that they did, plugging of the catalyst bed was the major problem. The

plugging was at the front end of the catalyst bed, especially in the heat-up zone. A pressure buildup was seen over time between 10-100 hours depending on the operating conditions. The pressure buildup was due to the formation of polymer as they mentioned. For the next step, hydrocracking step, high oil and gas yields were observed in these experiments with high amounts of hydrocarbon gases rather than carbon dioxide. The hydrogen consumption was much higher in these experiments than the hydrotreating experiments. In the hydrocracking step, catalyst coking was observed with no pressure buildup across the reactor.

Cheng et al. 2017 reported a work done using the same catalyst, Pd/C, in a batch reactor with different temperatures (200 °C, 250 °C and 300 °C). The high reaction temperatures, 250 °C and 300 °C, seemed to have good results by increasing the hydrocarbon content of biofuels. A temperature of 250 °C produced biofuels with the highest heating value, highest hydrocarbons content and lowest water content. However, the two temperatures, 250 and 300 °C, contributed to decreasing the biofuel yields and increasing the gas yields. In general, the oxygen content was decreased from 48.78 wt.% to values ranging (30.20- 36.85 wt.%). The major oxygenated compounds such as aldehydes, ketones, acids and phenols were reduced in the upgraded biofuels compared to the raw feedstock. Catalyst deactivation was the problem identified, which was mainly attributed to the coke deposition on the catalyst, which was leading to the blocking of the catalyst pores masked active sites on the catalyst surface.

Wildschut et al. 2009b conducted a catalytic hydrotreatment study using D-glucose, D-cellobiose, and D-sorbitol at 250 °C temperature, 4.3 hours reaction time and 100 bar hydrogen pressure using Ru and Pd on carbon catalysts in water. The Pd/C catalyst was used with the D-glucose on the similar operating conditions described above. H<sub>2</sub>, CO, CO<sub>2</sub>, ethane and propane were the main gases produced by Pd/C. The clues of this study indicated that the Pd/C catalyst

was less active than the Ru/C catalyst under the same operating conditions. It took 3.5 hours to reach the full conversion of D-glucose, while it took only 1 hour to reach the full conversion of D-glucose for Ru/C.

### **2.2.3.2 Ru/C catalyst**

Elliott et al. 2009b reported a hydrotreatment work using Ru and Pd catalysts over various temperatures 150, 200, 250, and 300 °C in a batch reactor. Guaiacol, Furfural and Acetic acid were the three model compounds that represented the bio-oil in this study. For the hydrotreating of guaiacol, furfural and acetic acid at 150 °C and 200 °C, the primary products were 2-methoxycyclohexanol, small amounts of ethanol and THF-MeOH respectively. For the 250 °C hydrotreating, the major products were cyclohexanol, high amounts of ethanol and MTHF respectively. For the 300 °C hydrotreating, the main products were phenol, low amounts of ethanol and MTHF respectively. For the acetic acid as a feed using Ru/C as a catalyst, the conversion was too low for the temperatures below 200 °C and the gas production was too high for the temperatures higher than 250 °C. In general, they concluded that the ruthenium catalyst seems to be a more effective catalyst for hydrogenations in this study than palladium.

Sanna et al. 2015 investigated the Ru/C and Pt/C catalysts with the continuous flow hydrogenation of the water-soluble fraction of bio-oil (WSBO). Single and two stage processes have been discussed in this study. Ru/C catalyst has been used with a temperature range from 75 to 175 °C in a single stage continuous flow reactor. At 75 and 100 °C, 2-furanone, furfural, 5-HMF, hydroxyacetaldehyde and methyl-cyclopentanedione were the only reactants that have been converted into products which were comprised of 15% of the identified reactants. At 125 °C, hydroxy acetone, catechol, phenol, levoglucosan and sugars were the reactants that have been

converted into products which represented 56% of the reactants. At 150 °C, all the reactants have almost been converted (90%) except for the acetic acid and phenol. At 175 °C, plugging of the reactor was identified after 8 hours on-stream which was due to the coke reactions. They concluded that the coke was generated as a result of the carbon that was deposited in the free section of the reactor at 150 and 175 °C, which was generated at the beginning of the experiment. In the two stages step, two different reactors in series were used where the Ru/C was used in the first stage and either Ru/C or Pt/C was used in the second stage. 26-28% more of the feed was converted using two-stage processes than the single stage process. At 250 °C, the liquid yield with Ru/C was decreased to 38% after it was 70% at 220 °C. At 1445 psi, the amount of hydrogen required was decreased from 7 wt.% at 750 psi to 4 wt.% of hydrogen all at 250 °C using Ru/C. The amount of carbon converted to the gas phase decreased to about 20% using higher space velocities with Ru/C and operating conditions of (6 h<sup>-1</sup>, 750 psi, 250 °C). This yielded a decrease in the carbon yield of the desired products to 16% less than the first stage process. As a result of the low yield of the desired products, this paper suggested that the high-temperature hydrogenation of water-soluble bio-oil cannot be done with this catalyst and 125 °C is the low hydrogenation temperature that can be used with Ru/C.

Wildschut et al. 2010 reported a paper on the Ru/C catalyst that has been used for the hydrogenation of the pyrolysis oil at a temperature of 350 °C and a pressure of 200 bar in a batch reactor. Three different phases have been observed in the liquid product after reaction with substantial amounts of coke and char, as well as gas phase organics. There was an increase in the oil yield during the first hour on-stream until 4 hours where it reached the maximum which was 65 wt.%. The oil yield then started to decrease for longer times (>4 hours) where it dropped down to 10 wt.% after 6 hours on-stream due to the formation of gaseous phase components such

as methane, ethane, propane, CO/CO<sub>2</sub> with methane and CO<sub>2</sub> as the main gas phase products. The carbon content was 84 wt.% during the first 4 hours on-stream and decreased to 70 wt.% between 4 to 6 hours. The H:C and O:C ratios were increased as a function of reaction time with an O:C ratio of 0.02 to 0.07 and an H:C ratio of 1.05 to 1.32 when going from 1 hour to 6 hours reaction times.

### **2.2.3.3 Mono- and bimetallic noble metal catalysts over ZrO<sub>2</sub>**

Gutierrez et al. 2009 tested zirconia-supported (ZrO<sub>2</sub>) mono- and bimetallic noble metal (Rh, Pd, Pt) catalysts for the hydrogenation of guaiacol at 100 °C and 8 MPa for 5 hours. They used guaiacol again for the hydrodeoxygenation at 300 °C and 8 MPa for 3 hours. Hydrogenation and hydrodeoxygenation steps were all done in a batch reactor. The guaiacol was the selected model compound for wood-based pyrolysis oil. The conversion of guaiacol at (100 °C and 8 MPa for 5 hours) was 13.8% for the monometallic Pd and Pt catalysts, while it was 100% for the ZrO<sub>2</sub>-supported Rh and RhPt catalysts. Hydrogenated oxygen-containing compounds were the main compounds that have been produced by all catalysts used in this study at 100 °C. The carbon deposition was higher for the Rh catalyst and lower for the less active catalysts (PdPt, Pd, Pt). The O:C ratio obtained with all the catalysts was 0.29 mol/mol while the H:C ratio obtained with Rh and RhPt catalysts was 1.95 mol/mol. For the HDO process at 300 °C, the conversion of guaiacol was 100% for all noble metal catalysts. Rh and RhPd catalysts were the best catalysts regarding the lowest O:C ratio. In this study, they tested a combination of Pd and Pt in the bimetallic PdPt catalyst and the combination of Pd or Pt with Rh. The first combination, PdPt, showed bad results while the second one, RhPd or RhPt, showed good results where the conversion increased to 98.7% on the RhPt catalyst and to 32.7% on the RhPd catalyst. This

paper concluded that the Rh-containing catalysts are the most active noble metal catalysts regarding both the HDO and hydrogenation of guaiacol and for both lower and higher temperatures.

Ardiyanti et al. 2011 investigated the same catalysts listed above in Gutierrez et al. 2009 except for changing the operating conditions to the following (350 °C, 20 MPa total pressure, and 4 hours reaction time) and the feedstock to the fast pyrolysis oil obtained from fast pyrolysis of lignocellulosic biomass. The yield of the upgraded oils was between 37.3–46.7 wt.% with an O:C ratio between 0.07–0.10 and an H:C ratio between 0.99–1.19. The oxygen content was between 7.7-11.0 wt.% (dry basis) compared to 40.1 wt.% for the feed. Pd/ZrO<sub>2</sub> showed the highest activity followed by Rh/ZrO<sub>2</sub> which produced the best product properties. Pt/ZrO<sub>2</sub> showed less activity compared to the Rh and Pd analogs. The hydrogen consumption for all catalysts used was between 54-186 L/Kg feed.

#### **2.2.4 Other catalysts**

Adjaye et al. 1994 investigated the following catalysts: HZSM-5, silicalite, H-mordenite, H-Y and silica-alumina for the upgrading of bio-oil in a fixed bed micro-reactor operated at 1 atm, 3.6 WHSV and temperatures of 330 and 410 °C. In this study, the overall performance followed the order: HZSM-5 > H-mordenite > H-Y > silica-alumina, silicalite.

Zhao et al. 2011 investigated the following catalysts Ni<sub>2</sub>P/SiO<sub>2</sub>, Fe<sub>2</sub>P/SiO<sub>2</sub>, MoP/SiO<sub>2</sub>, Co<sub>2</sub>P/SiO<sub>2</sub> and WP/SiO<sub>2</sub> for the upgrading of guaiacol gas phase in a packed bed reactor operated at 1 atm and a temperature range of 200–300 °C. The activity for HDO of guaiacol followed the order: Ni<sub>2</sub>P>Co<sub>2</sub>P>Fe<sub>2</sub>P, WP, MoP.

Mortensen et al. 2013 investigated 23 different catalysts for the upgrading of phenol in a batch reactor operated at 275 °C and 100 bar H<sub>2</sub>. Ni/ZrO<sub>2</sub> was the only active non-noble metal catalyst whereas the Ni/C was inactive for the HDO of phenol. The order of catalysts regarding the HDO activity were as follows: Ni/ZrO<sub>2</sub> > Ni-V<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub> > Ni-V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> > Ru/C > Ni/Al<sub>2</sub>O<sub>3</sub> > Ni/SiO<sub>2</sub> >> Pd/C > Pt/C.

Bui et al. 2012 studied a series of silica-supported metal phosphides for the upgrading of 2-methyltetrahydrofuran (2-MTHF) in a packed-bed reactor operated at 300 °C and 1 atm. The activity order was as follows: Ni<sub>2</sub>P > WP > MoP > CoP > FeP > Pd/Al<sub>2</sub>O<sub>3</sub>.

Echeandia et al. 2010 investigated the Ni–W catalysts supported on activated carbon for the upgrading of 1 wt.% phenol hydrodeoxygenation in n-octane in a fixed-bed reactor operated at temperatures of 423 to 573 K and a hydrogen pressure of 1.5 MPa. Ni–W/AC catalyst was considered as a promising candidate for HDO processes and can result in better catalytic performance. Catalysts supported on activated carbon resulted in a lower coke formation compared to the classical alumina support.

### **2.3 Catalytic hydrotreatment reactions**

There is a complex reaction network appears during the catalytic upgrading of bio-oil. Mortensen et al. 2011 listed the reactions that occurred during the hydrotreating as well as the reasons that can be attributed to the high diversity of compounds in the feed. The reactions that take place for both zeolite cracking and HDO are cracking, decarbonylation, decarboxylation, hydrocracking, hydrodeoxygenation, hydrogenation, and polymerization.

## 2.4 Catalysts deactivation

Many papers have been published recently regarding the deactivation of the catalysts used in the upgrading of the bio-oils obtained from the biomass sources. Furimsky et al. 1999 listed the reasons behind the deactivation of the catalysts. The first reason for the catalyst's deactivation is attributed to the poison that adsorbs on active catalyst sites, resulting in either incapacitating the site or competition with the reactants of a given reaction. This kind of deactivation is due to the reactant, reaction intermediates or products, as well as the extraneous compounds present in the feed such as  $N_2$  compounds and water. The second reason is attributed to the coke deposition on the catalysts. This kind of deactivation is caused by polymerization reactions leading to blocking of the catalyst pores, and it can be analyzed using TGA method (Thermogravimetric analysis). The third reason is attributed to the metals present in the feed that will deposit on the catalyst surface and cause deactivation. The last reason of the catalyst's deactivation as mentioned in Furimsky et al. 1999 is due to the changes in catalyst structure, metal sintering, which is due to the temperature change after a prolonged period of reaction time causes a reduction in the interfacial sites between the metal particles and the support. Metal sintering can be tested using transmission electron microscopy (TEM) technique. Leaching the active metal of catalyst into the liquid phase is another reason for catalyst's deactivation. It can be tested using ICP analysis method.



## 2.5 Summary

Many catalysts have been employed during the hydrodeoxygenation process. Each catalyst used had some drawbacks with some success and that depended on the feedstocks used, the operating conditions and the catalyst strength towards the reactions happened during the process. Regarding sulfided catalysts, CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst was a good HDO catalyst due to the high deoxygenation activity and good selectivity to diesel-like products.

Regarding nickel catalysts, Ni/TiO<sub>2</sub>, Ni/CeO<sub>2</sub> as well as Ni/C showed high selectivity toward aromatics than others for the hydrodeoxygenation of anisole under 290 °C and 3 bar. Ni/SiO<sub>2</sub> catalyst showed the highest activity in HDO of anisole under 5–30 bar of hydrogen pressure and 180–220 °C of temperature. Ni<sub>2</sub>P was the best catalyst for the hydrodeoxygenation of guaiacol and 2 methyl tetrahydrofuran under 300 °C and 1 atm. Ni/ZrO<sub>2</sub> was the best catalyst regarding the HDO of phenol under 275 °C and 100 bar H<sub>2</sub>. NiMo/SBA-15 and NiMo/CeO<sub>2</sub> were the most effective catalysts that displayed the highest activity toward the HDO of guaiacol under 250 °C and a hydrogen pressure of 50 bar. The bimetallic NiCu/  $\delta$ -Al<sub>2</sub>O<sub>3</sub> (with a Ni to Cu wt.% ratio of eight) was the most active catalyst for both anisole and pyrolysis oil hydrotreatments. NiCu/TiO<sub>2</sub> showed the highest activity with the most favorable product oil using pyrolysis oil as a feedstock under 350 °C and a pressure of 200 bar.

Regarding noble metal catalysts, Ru/C catalyst was the best for the D-glucose hydrotreatment under 250 °C temperature and 100 bar hydrogen. Ruthenium catalyst seems to be a more effective catalyst for hydrogenations in a study used Guaiacol, Furfural and Acetic acid as three model compounds under various temperatures 150, 200, 250, and 300 °C. Rh-containing catalysts (Rh/ ZrO<sub>2</sub> and RhPd or RhPt/ ZrO<sub>2</sub>) were the most active noble metal catalysts regarding both the HDO and hydrogenation of guaiacol and for the lower (100 °C, 80 bar) and

higher temperatures (300 °C, 80 bar). Pd/ZrO<sub>2</sub> showed the highest activity followed by Rh/ZrO<sub>2</sub> where they produced the best product properties for pyrolysis oil hydrotreatment under 350 °C, 200 bar total pressure.

A Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was the catalyst used by Eaton et al. 2015 on thermal deoxygenation (TDO) of neutralized biomass acid hydrolysate (levulinate and formate salt mixtures) under 300 °C, 5.2 MPa H<sub>2</sub>, 200-300 sccm H<sub>2</sub> flow rate with a feed flow rate varied from 0.1–0.3 mL/min and WHSV of 0.06–0.18 h<sup>-1</sup>. This catalyst showed a unique HDO activity for 700 hours on-stream processing with an 11.2 kg of material processed.

There are tradeoffs in choosing a catalyst. Some catalysts can remove the whole oxygen from the oils used as feedstocks, but they are either expensive or cannot be regenerated again. Some of them are cheap and active but the problem is with the low oil yield. Based on these tradeoffs and the issues associated with the catalysts described in this chapter, we chose the same catalyst used by Eaton et al. 2015 for our oxygenated pyrolysis oils due to many reasons:

1. It is active, cheap and does not regenerate through experiments.
2. It stands actively for long time-on-stream.
3. Higher amounts of material can be processed through it.
4. It yields higher oil yields with lower density.
5. It yields products with lower oxygen content and higher H:C ratio.

## **CHAPTER 3: FAST PYROLYSIS OF FORMATE ASSISTED PRETREATED PINE SAWDUST AT ATMOSPHERIC CONDITION**

This chapter describes the fast pyrolysis experiments along with the materials, methods, operating conditions and instruments used in this research study.

### **3.1 Introduction**

The conversion of biomass to transportation fuel requires a solid-to-liquid transformation while also removing oxygen and adding hydrogen. Thermal conversion pathways involving pyrolysis first create an oxygenated hydrocarbon liquid called bio-oil. The bio-oil is then hydrotreated over a catalyst and high-pressure hydrogen to produce a hydrocarbon fuel. In this chapter, four different biomass feedstocks were pyrolyzed at the same operating conditions (temperature around 500 °C, a pressure of 1 atm and a total N<sub>2</sub> flow rate of 6 L/min.) using a process known as formate-assisted fast pyrolysis or FAsP, which is a new process devolved by UMaine group. These feedstocks had different calcium formate/pine sawdust mass loadings and contained oxygen contents of 16, 21, 26, and 27 wt.%. The bio-oils obtained through this process have less oxygen content and are more stable compared to conventional pyrolysis oils. This process reduces the cost of the downstream upgrading process, which then requires less hydrogen consumption and needs a simpler upgrading system set-up.

## 3.2 Material and methods

### 3.2.1 Feedstock preparation

Bio-oils were generated from pine sawdust pretreated with different quantities of calcium formate salt. The pine sawdust (*Pinus strobus*) was obtained from the University of Maine Advanced Structures and Composite Center (AEWC). Calcium formate salt in solid form was purchased from GEO Specialty Chemicals. Four different biomass feedstocks were prepared. The calcium formate mass loadings were different in three of them while the fourth was pine sawdust without pretreatments. The mass loadings for the three feedstocks were as follows: 140 gm (100% calcium formate loading), 122.5 gm (87.5% calcium formate loading) and 70 gm (50% calcium formate loading) each to 100 gm pine sawdust. The element analysis of pine sawdust is given in Table 3.1.

|                     |        |
|---------------------|--------|
| <b>Moisture (%)</b> | 10-13  |
| <b>Ash (%)</b>      | 0.309  |
| <b>C</b>            | 0.451  |
| <b>H</b>            | 0.068  |
| <b>N</b>            | <0.005 |
| <b>O</b>            | 0.481  |
| <b>HHV (MJ/kg)</b>  | 18.07  |

Table 3. 1 Analysis of pine sawdust.

The feedstocks were all prepared in the same manner as follows: calcium formate was incorporated with the pine sawdust by forming a solution/suspension with the salt in deionized water, and then incorporated the dry sawdust. The mixture then sat in a beaker for at least 12 hours with a temperature around 25 °C. The pretreated pine was then oven dried to approximately 5-10% moisture content. IR-35 Infrared Moisture Analyzer (Denver Instrument) shown in Figure 3.1 was the analyzer used to check the moisture content in all biomass feedstocks.



Figure 3. 1 IR-35 Infrared Moisture Analyzer (Denver Instrument).

A mixture of pine sawdust pretreated with calcium formate is shown in Figure 3.2 below.



Figure 3. 2 Biomass feedstock after achieved the desired moisture content.

Finally, the solid material was ground and sieved to achieve a particle size smaller than 1.5 mm for feed consistency. A U.S. standard sieve No. 14 shown in Figure 3.3 was used to achieve the desired particle size.



Figure 3. 3 U.S. Standard Sieve No.14.

### 3.2.2 Description of fast pyrolysis system along with fast pyrolysis process

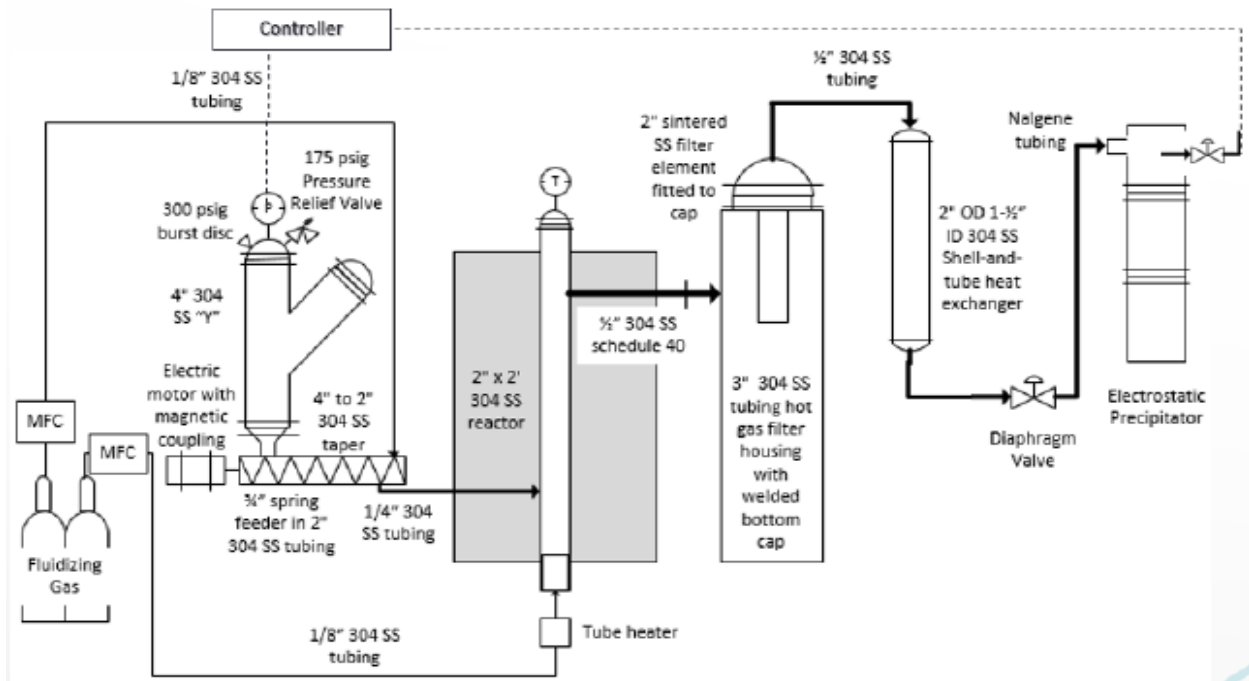


Figure 3. 4 Schematic of fast pyrolysis process (Case 2015).

The schematic as shown in Figure 3.4 was used in this study with some modifications made to achieve the desired operating conditions. In this schematic, nitrogen, supplied by two tanks, was fed to the fluidized bed reactor and the biomass feeder, called a hopper feed. Both were controlled by rotameters. The first nitrogen pathway supplied nitrogen to the hopper and was used to carry the biomass feedstock present in the hopper to the fluidized bed reactor through a stainless-steel tube. The second nitrogen pathway supplied nitrogen to the bottom of the fluidized bed reactor which was first heated by a tube heater and then used to provide a fluidization to the 40-60 mesh sand, which is used as a heat transfer medium in the reactor. The hopper is a cylindrical feed compartment that has a rotating spring that is used to facilitate the biomass feedstock flow rate into the reactor. The hopper also has a pressure gauge on its top that is used to monitor the pressure during the experiments.

The fluidized bed reactor is 1.75 in. in diameter and 12 in. in length, with a total volume of 0.473 L. The reactor temperature is measured using two K-type thermocouples located on the vertical axis measured 3.0 and 9.5 in. from the top of the reactor. One of these thermocouples is used to measure the temperature at the inlet of the biomass to the reactor, while the other is used to measure the temperature at the outlet of the products to the hot gas filter. The fluidized bed reactor is heated in a heating furnace consisting of three heating zones. The fluidized bed reactor is described in detail elsewhere (DeSisto et al. 2010).

The char separator is 2.87 in. in diameter and 24 in. in length with a total volume of 2.54 L. The filter element inside the char separator is made from stainless steel and is 6 in. long and 1 in. OD. The temperature of the char separator is measured by a K-type thermocouple inserted into the vessel and it is controlled by a variac and heating bands. The condenser is made from stainless steel and it is a tube and shell type heat exchanger. The water provided to the condenser is chilled using a Thermo Scientific RTE 740 chiller.

In all experiments, the untreated and pretreated sawdust were pyrolyzed as follows: the pine/calcium formate mixture was metered through a screw feeder and pneumatically fed into the reactor using a total nitrogen flow rate of 6 L/min. The feed rate was approximately between 1.0-2.5 g/min, and up to 1.25 kg of material could be processed in a run. The pyrolysis temperature was 500 °C. Immediately downstream of the reactor, char was separated using a hot gas filter (HGF) also maintained at 500 °C where the char is collected in the bottom of the housing vessel and the outside of the filter element. The total vapor residence time in the fluidized bed reactor and the HGF was 10.5 sec, with about 84% of that time in the HGF. After the vapor passed through the hot gas filter, the liquid water was collected in a condenser operated at 3 °C followed by an electrostatic precipitator (ESP) to collect aerosols by an electrical charge supplied by a



stainless-steel rod placed vertically inside the ESP. The pyrolysis exhaust gas was periodically measured using an SRI 8610C portable GC. The exhaust gas flow rate was measured using a dry gas meter.

### **3.2.3 Bio-oil characterization**

The ESP oil shown in Figure 3.5 was then used for further hydrodeoxygenation in this work and will be discussed in Chapter 4. The moisture content in the FAsP oil was determined using Karl-Fisher titration (see Appendix D). Carbon, hydrogen, and nitrogen analysis of the FAsP oil was determined using a Thermo Scientific Model Flash 2000 elemental analyzer (see Appendix A) and oxygen content was calculated by difference. A Shimadzu Q2010 GC-MS was used to characterize the composition of the oils (see Appendix B). Gas products were analyzed using an SRI 8610C portable GC (see Appendix C). The yields of the bio-oil and aqueous fractions were calculated by subtracting the weights of the ESP and condenser before and after pyrolysis experiments, while the char yield was calculated by subtracting the mass of calcium carbonate produced from calcium formate from the weight of the total solid materials after pyrolysis.

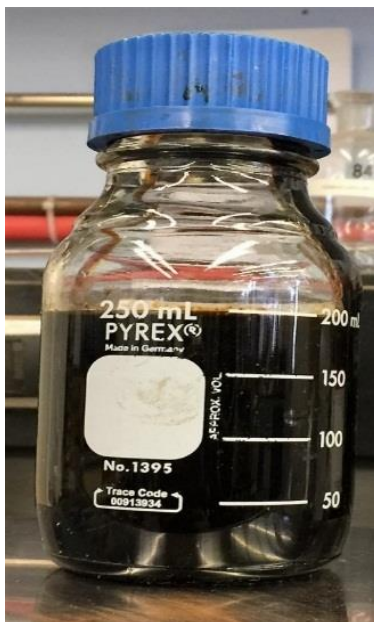


Figure 3. 5 Bio-oil collected from the ESP after fast pyrolysis process.

### 3.3 Results and discussion

|                         | run 1 | run 2 |
|-------------------------|-------|-------|
| Residence time (s)      | 9.95  | 9.17  |
| ESP yield (wt.%)        | 9%    | 12%   |
| Char yield (wt.%)       | 15%   | 16%   |
| Gas yield (wt.%)        | 46%   | 41%   |
| Condenser yield (wt.%)* | 30%   | 31%   |

\*Water phase only with negligible amount of oil

Table 3. 2 Weight percent yields obtained from pyrolysis of 140 gm  $\text{Ca}(\text{COOH})_2$  /100 gm of dry, ash-free pine sawdust.

From the two runs shown in Table 3.2, the 100% calcium formate loading (140 gm  $\text{Ca}(\text{COOH})_2$  /100 gm pine sawdust) produced mostly gases where the average gas yield for the two runs was 43%. The aqueous fraction collected from the condenser yielded the second-highest percentage produced with an average of 31% for the two runs. The average bio-oil yield

was 10%. The char yield was the lowest yield achieved through this pyrolysis with an average yield of 16%. The total average residence time for these two runs was 9.56 seconds.

|                         | run 1 |
|-------------------------|-------|
| Residence time (s)      | 10.43 |
| ESP yield (wt.%)        | 14%   |
| Char yield (wt.%)       | 12%   |
| Gas yield (wt.%)        | 42%   |
| Condenser yield (wt.%)* | 32%   |

\*Water phase only with negligible amount of oil

Table 3. 3 Weight percent yields obtained from pyrolysis of 122.5 gm  $\text{Ca}(\text{COOH})_2$  /100 gm of dry, ash-free pine sawdust.

From Table 3.3, the liquid phase yields obtained through the pyrolysis of the 87.5% calcium formate loading were 14% for the bio-oil collected from the ESP and 32% for the water collected from the condenser. The gas yield was the highest with 42% and the char yield was the lowest with 12%. The total residence time was 10.43 seconds.

|                         | run 1 | run 2 |
|-------------------------|-------|-------|
| Residence time (s)      | 10.88 | 10.73 |
| ESP yield (wt.%)        | 15%   | 14%   |
| Char yield (wt.%)       | 8%    | 8%    |
| Gas yield (wt.%)        | 37%   | 44%   |
| Condenser yield (wt.%)* | 39%   | 34%   |

\*Water phase only with negligible amount of oil

Table 3. 4 Weight percent yields obtained from pyrolysis of 70 gm  $\text{Ca}(\text{COOH})_2$  /100 gm of dry, ash-free pine sawdust.

Table 3.4 shows the pyrolysis of 50% calcium formate loading (70 gm  $\text{Ca}(\text{COOH})_2$  /100 gm pine sawdust). The gas yield was still the highest yield obtained with an average of 41% for the two runs followed by the condenser yield with an average of 37% for the two runs. The

highest bio-oil yield produced through this loading was 15%. The char yield was the lowest yield achieved through this pyrolysis with an average yield of 8%. The total average residence time for these two runs was 10.81 seconds.

|                         | run 1 | run 2 |
|-------------------------|-------|-------|
| Residence time (s)      | 11.43 | 10.73 |
| ESP yield (wt.%)        | 17%   | 16%   |
| Char yield (wt.%)       | 12%   | 13%   |
| Gas yield (wt.%)        | 46%   | 45%   |
| Condenser yield (wt.%)* | 25%   | 25%   |

\*Water phase only with negligible amount of oil

Table 3. 5 Weight percent yields obtained from pyrolysis of dry, ash-free pine sawdust without pretreatments.

The yields shown in Table 3.5 are determined based on the pyrolysis of pine sawdust without pretreatments. The order of the yields for this pyrolysis was as follows: gas > condenser > ESP > char with average yields of 46%, 25%, 17% and 13% for the two runs, respectively. The highest bio-oil yield produced through this pyrolysis was 17%. The total average residence time for these two runs was 11.08 seconds.

Based on the results listed in the tables above, the bio-oil yields increased as we reduced the calcium formate loading in the feedstock, with a maximum of 17% for the pyrolysis of pine sawdust without pretreatments. The gas yield was higher and approximately the same for the pyrolysis of 100% calcium formate loading and the pyrolysis of pine sawdust without pretreatments followed by the pyrolysis of 87.5% calcium formate loading and finally the pyrolysis of 50% calcium formate loading. The aqueous yield was approximately the same for the pyrolysis of 100% and 87.5% calcium formate loadings while it increased to 37% for the pyrolysis of 50% calcium formate loading and decreased to 25% for the pyrolysis of pine

sawdust without pretreatments. The lowest char yield obtained was for the pyrolysis of 50% calcium formate loading (70 gm Ca(COOH)<sub>2</sub> /100 gm pine sawdust), which was 8%. More important, the bio-oil yield obtained through the pyrolysis of 100% calcium formate loading was lower than other bio-oil yields obtained through the pyrolysis of different biomass feedstocks; however, a trade-off of 50% reduction in O:C ratio was observed.

|                          | Pine Feed | Pine sawdust without pretreatments | 50% calcium formate loading | 87.5% calcium formate loading | 100% calcium formate loading |
|--------------------------|-----------|------------------------------------|-----------------------------|-------------------------------|------------------------------|
| C (wt.%)                 | 45.10     | 64.26                              | 65.89                       | 71.51                         | 74.96                        |
| H (wt.%)                 | 6.80      | 7.20                               | 7.08                        | 7.41                          | 7.45                         |
| N (wt.%)                 | 0         | 1.22                               | 0.52                        | 0.11                          | 0.81                         |
| O (wt.%) (by difference) | 48.10     | 27.31                              | 26.51                       | 20.97                         | 16.78                        |
| O:C                      | 0.80      | 0.31                               | 0.30                        | 0.22                          | 0.16                         |
| H:C                      | 1.80      | 1.34                               | 1.29                        | 1.24                          | 1.19                         |
| HHV (MJ/Kg)*             | 16.52     | 26.17                              | 26.74                       | 29.90                         | 31.59                        |

\*HHV calculated based on equation 3 from Demirbas et al. 2008

Table 3. 6 Elemental analysis of the bio-oils obtained from calcium formate loadings as well as pine sawdust without pretreatments.

The elemental analysis of the bio-oils obtained through the fast pyrolysis process was done using a Thermo Scientific Model Flash 2000 elemental analyzer and the oxygen was calculated by subtracting the carbon, hydrogen, and nitrogen from the total mass. From Table 3.6, we can see that the carbon weight percent and the higher heating value are a function of the percentage of calcium formate in the biomass feedstock, where they decrease as the calcium formate loadings decrease in the feedstock. However, the oxygen contents increase as the calcium formate loadings decrease in the feedstock. The oxygen content of the bio-oil obtained through the pyrolysis of 100% calcium formate loading, 16 wt.%, is consistent with the oxygen

content obtained from a work done by Case et al. 2014a using the same biomass feedstock and operating conditions. The differences in the yields between this work and the work done by Case et al. 2014a can be attributed to the modifications in pyrolysis reactor system as well as the changes in the nitrogen flow rate, which lead to the change in the residence time.

|                                    | Water content % |
|------------------------------------|-----------------|
| 100% calcium formate loading       | 2.2             |
| 87.5% calcium formate loading      | 4.2             |
| 50% calcium formate loading        | 4.4             |
| Pine sawdust without pretreatments | 8.0             |

Table 3. 7 Water percentages for the fractions of the bio-oils obtained from the pyrolysis of the four biomass feedstocks.

The moisture content of the fast pyrolysis oils was performed using Karl-Fisher titration. From Table 3.7, the lowest water content was in the bio-oil obtained from the pyrolysis of 100% calcium formate loading. The water content was approximately the same in the bio-oils obtained from the pyrolysis of 87.5% and 50% calcium formate loadings; however, it doubled for the bio-oil obtained from the pyrolysis of biomass feedstock done without calcium formate pretreatments. In general, these water contents are lower compared to the water contents present in conventional pyrolysis oils which are between 15–25% (Bridgwater 2012).

Gas products were analyzed using an SRI 8610C portable GC. The compositions of the gases produced (CO, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>+) were higher and approximately the same for the pyrolysis of 100% calcium formate loading and the pyrolysis of pine sawdust without pretreatments followed by the pyrolysis of 87.5% calcium formate loading and finally the pyrolysis of 50% calcium formate loading.

The most abundant compounds present in the pyrolysis oils are shown in Table 3.8 below.

| Compound identified by GC-MS     | 100% calcium formate loading | 87.5% calcium formate loading | 50% calcium formate loading | Pine sawdust without pretreatments |
|----------------------------------|------------------------------|-------------------------------|-----------------------------|------------------------------------|
| cyclopentanone                   | identified                   | identified                    | ---                         | ---                                |
| 2- cyclopentanone -1-one         | identified                   | ---                           | ---                         | ---                                |
| 2-methyl-2-cyclopentene-1-one    | identified                   | identified                    | identified                  | identified                         |
| 3-methyl-2- cyclopentene -1-one  | identified                   | identified                    | identified                  | ---                                |
| phenol                           | identified                   | identified                    | ---                         | identified                         |
| 3-Ethylphenol                    | identified                   | identified                    | identified                  | identified                         |
| 2,6-Dimethylphenol               | identified                   | identified                    | identified                  | identified                         |
| 2,3-Dimethylphenol               | identified                   | ---                           | identified                  | identified                         |
| 3,4,5 trimethylphenol            | identified                   | identified                    | identified                  | identified                         |
| 2-Methoxy-6-methylphenol         | identified                   | identified                    | ---                         | ---                                |
| Phenol, 2-methoxy-3-(2-propenyl) | ---                          | identified                    | identified                  | ---                                |
| 2-Methoxy-4-vinylphenol          | ---                          | identified                    | identified                  | ---                                |
| m-cresol                         | identified                   | ---                           | ---                         | ---                                |
| O-cresol                         | identified                   | identified                    | identified                  | identified                         |
| 2-Methoxy-p-cresol               | ---                          | identified                    | identified                  | identified                         |
| Catechol                         | identified                   | identified                    | identified                  | identified                         |
| 4-Methylcatechol                 | identified                   | ---                           | identified                  | identified                         |
| 4-Ethylcatechol                  | ---                          | ---                           | identified                  | identified                         |
| 4-Propylcatechol                 | ---                          | identified                    | identified                  | identified                         |
| 4-methoxybenzyl - alcohol        | ---                          | identified                    | ---                         | ---                                |
| retene                           | identified                   | identified                    | identified                  | identified                         |
| hyroxyacetone                    | ---                          | identified                    | identified                  | identified                         |
| methylcyclopentene               | ---                          | identified                    | ---                         | ---                                |
| 3-Methylcyclopentane-1,2-dione   | ---                          | ---                           | identified                  | identified                         |
| Guaiacol                         | ---                          | ---                           | identified                  | identified                         |
| Furfural                         | identified                   | ---                           | identified                  | ---                                |
| 5-Methylfurfural                 | ---                          |                               | identified                  | identified                         |
| Acetic acid                      | ---                          | identified                    | ---                         | ---                                |
| butyl ester                      | ---                          | identified                    | ---                         | ---                                |
| Acetone                          | identified                   | identified                    | ---                         | ---                                |
| 1,3,5,7-Cyclooctatetraene        | ---                          | ---                           | ---                         | identified                         |
| ortho-Phthalaldehyde             | ---                          | ---                           | ---                         | identified                         |
| Benzene, 1,2-propadienyl         | ---                          | ---                           | ---                         | identified                         |
| Propionic acid                   | ---                          | ---                           | ---                         | identified                         |
| 1,4-Butanediol                   | ---                          | ---                           | ---                         | identified                         |
| Oxiranemethanol Acetate          | ---                          | ---                           | ---                         | identified                         |

Table 3. 8 Compounds identified by GC-MS (Shimadzu Q2010) in pyrolysis oils obtained from the fast pyrolysis of all biomass feedstocks.

### 3.4 Conclusion

Four biomass feedstocks were pyrolyzed successfully under the operating conditions of 1 atm and 500 °C (reactor and hot gas filter) with a nitrogen flow rate of 6 L/min and a biomass flow rate between 1.0-2.5 gm/min. The order of the solid, gas, and liquid yields in all pyrolysis experiments were as follows: gas > water > oil > char. A significant yield of oil can be produced through a pyrolysis of feedstock with lower amounts of calcium formate or none. However, lower amounts of calcium formate present in the feedstock can lead to an increase in the oxygen content. The pyrolysis of 100% calcium formate loading (140 gm Ca(COOH)<sub>2</sub> /100 gm pine sawdust) produces the lowest oxygen content with the most stable bio-oil in a single-step reactor. The bio-oil yield obtained through the 100% calcium formate loading was lower than other bio-oils obtained from different biomass feedstocks; however, a trade-off of 50% reduction in O:C ratio was observed. The advantage of using the full amount of calcium formate (100% calcium formate loading) is not only attributed in the reduction in the oxygen content but also in an increase in the carbon yield and the higher heating value for the final bio-oil. Adding calcium formate to the pine sawdust by the manner described above reduces the oxygen content from 48 to 16 wt.% and changes the physical and chemical properties of the bio-oil produced without the need to use expensive materials such as the hydrogen and catalysts. This loading produces low oxygen content bio-oil without the need to run at elevated pressures, which eliminates the need for an extra unit cost.

Finally, the lower oxygen content oils obtained through the fast pyrolysis of the four biomass feedstocks cannot be used as transportation fuels due to the issues discussed in detail in section 1.5. As a result of that, an extra upgrading process is needed in order to improve their quality to that of conventional fuel. The upgrading process will be discussed in the next chapter.



## CHAPTER 4: UPGRADING OF BIO-OILS INTO TRANSPORTATION FUELS

This chapter describes the hydrotreating experiments along with the materials, methods, operating conditions and instruments used in this research study.

### 4.1 Introduction

The goal of this chapter is to investigate the upgrading of the pyrolysis oils with different oxygen contents to hydrocarbon fuels by catalytic hydrodeoxygenation (HDO) and examine the effect of feedstock chemical composition on catalyst lifetime, yields, oxygen removal, and hydrogen uptake during HDO. Hydrotreatment of bio-oil is very sensitive to oxygen content and chemical composition of the bio-oil. Bio-oils with different oxygen contents (16, 21, 26 and 27 wt.%) were hydrotreated in a downflow trickle bed reactor. A commercial nickel on silica-alumina catalyst was tested with different pyrolysis generated bio-oil feedstocks. Hydrotreating experiments were conducted at temperatures between 300-400 °C and reactor pressures between 750-1400 psi with a hydrogen flow rate of 100 sccm over several days. The catalyst activity was tested during several experiments using different operating conditions. Experiments ran up to several days and would end due to reactor plugging or running out of feedstock. Data collected included liquid yields and CHNO (Thermo Scientific Model Flash 2000 elemental analyzer) quantities in the oil fraction of the liquid.

## 4.2 Material and methods

### 4.2.1 Feedstock preparation

Six bio-oil feedstocks were hydrotreated to remove the remaining oxygen content and enhance their final quality. The biomass feedstock, 100% calcium formate loading, was pyrolyzed twice to generate two bio-oil feedstocks. The first bio-oil feedstock was hydrotreated at a hydrogen pressure of 750 psi while the second was hydrotreated at a hydrogen pressure of 1400 psi. The same was done for the two bio-oil feedstocks generated from the pyrolysis of 50% calcium formate loading biomass feedstock. The bio-oils generated from the pyrolysis of 87.5% calcium formate loading biomass feedstock and the pyrolysis of pine sawdust only were hydrotreated at 1400 psi. The preparation of biomass feedstocks for fast pyrolysis process was described in section 3.2.1, and the generation of these bio-oils was described in section 3.2.2.

### 4.2.2 Description of upgrading system

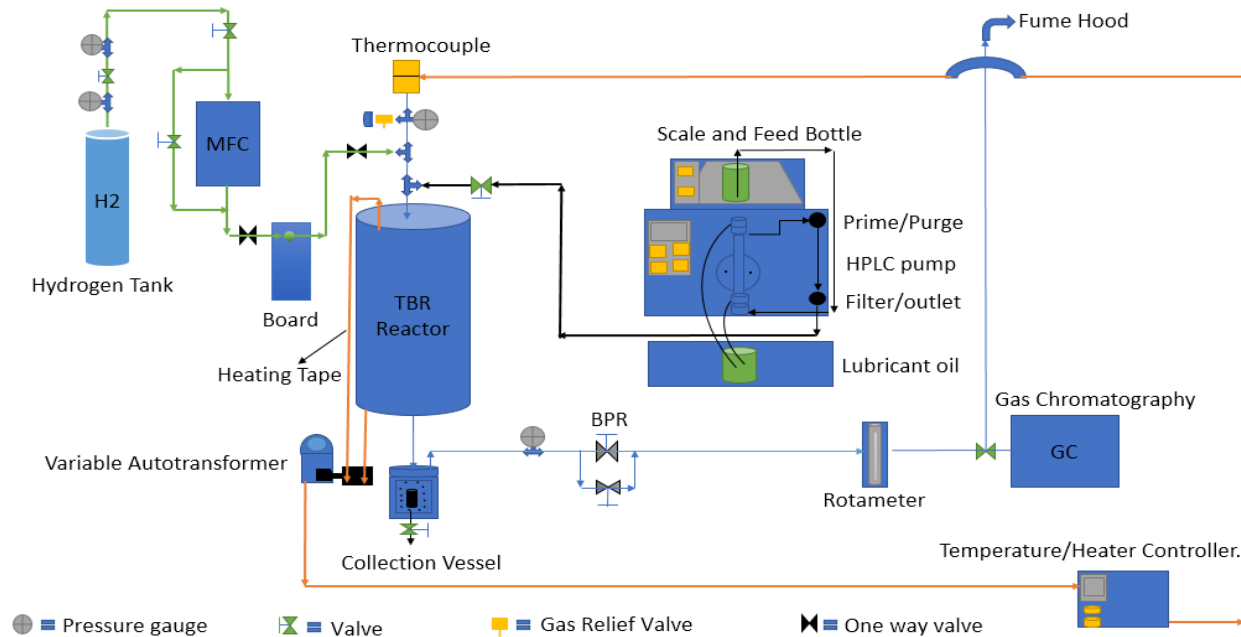


Figure 4. 1 Schematic of upgrading process.

Figure 4.1 shows a simplified schematic of the hydroprocessing unit used in this thesis work. In this schematic, hydrogen is introduced concurrently with the liquid feed at the top of the trickle bed reactor. The hydrogen flow rate is controlled by a mass flow controller. The trickle bed reactor is a cylindrical vessel that is 12.7 mm in diameter and 457 mm in length with a total volume of 0.058 L. The temperature of the bed is monitored using a thermocouple that is inserted down in the center of the bed. The thermocouple is controlled by a variac, which is controlled by a temperature controller that is shown in Figure 4.2. The trickle bed reactor is heated by a heating tape wrapped around the reactor. The reactor has a pressure gauge on its top, which is used to monitor the pressure during the experiments. A back-pressure regulator is used to control the reactor pressure.



Figure 4. 2 Temperature controller made by Solo company.

The HPLC pump (High-Pressure Liquid Chromatography) shown in Figure 4.3 is used to facilitate the bio-oil flow rate into the reactor. It has four buttons named as mode, prime, up, and down. The mode button is used to switch between the high pressure, the low pressure, and the bio-oil flow rate. The prime button is used to pull all bubbles out of the lines by using a syringe.

The up and down buttons are used to increase or decrease the pump pressure or the bio-oil flow rate. The maximum pressure that the pump can reach is 6000 psi and the highest bio-oil flow rate is 10 ml/min. Isopropanol is used to lubricate the pump's shift.

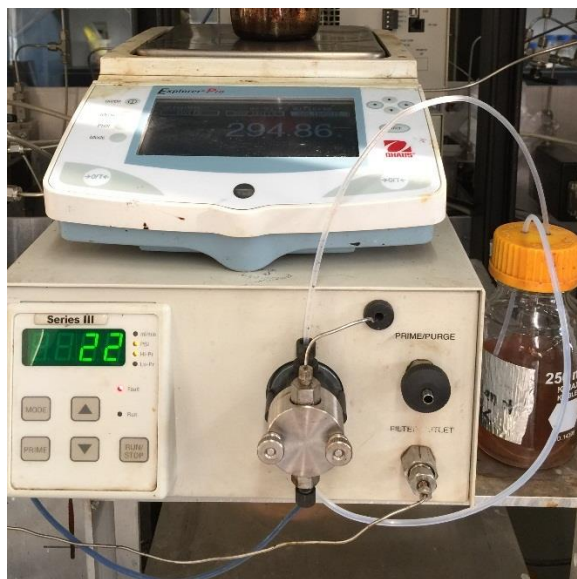


Figure 4. 3 HPLC pump with a scale on its top.

The HDO products (Liquid and gases) produced from the reactions occurred between the hydrogen and the bio-oil on the catalyst surface were allowed to pass through the reactor to the 150 ml collection vessel where the liquid phase products were collected. The gas products then passed through a pressure regulator and rotameter located after the sample collection vessel to the gas chromatography for analysis or sent to the fume hood.

### 4.2.3 Hydrotreating

Hydrotreatment of bio-oils was conducted using a  $66\% \pm 5\%$  nickel on silica-alumina ( $\text{Ni/SiO}_2\text{-Al}_2\text{O}_3$ ) catalyst (Alfa Aesar) powder loaded into a vertical downflow tubular reactor as illustrated in Figure 4.4 as described previously in Eaton et al. 2015. The reactor consisted of an electrically heated 12.7 mm ID x 457 mm long stainless-steel tube. Bio-oil and hydrogen were co-fed to the top of the reactor at 0.01 ml/min and 100 sccm, respectively. The bio-oil feed rate corresponded to a weight hourly space velocity of  $0.06 \text{ hr}^{-1}$ . The reactor was operated between 300-400 °C and 750-1400 psi. Liquid phase products were collected in a sample collection vessel and gas products were vented through a pressure regulator followed by a rotameter. The catalyst was activated with a continuous flow of  $\text{H}_2$  at 100 sccm, 350 °C (heating rate of 1.5 °C/min), and atmospheric pressure for at least 12 hours. Samples were collected every 12 hours for runs up to 345 hours with up to 182.35 gm of material processed.

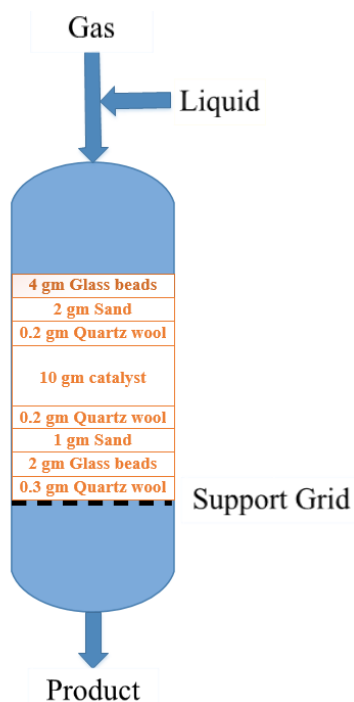


Figure 4. 4 Reactor set-up.

#### 4.2.4 Hydrotreated bio-oil characterization

The moisture content in the hydrotreated liquid products was performed using Karl-Fisher titration (see Appendix D). Carbon, hydrogen, and nitrogen analysis of the hydrotreated oil was done using a Thermo Scientific Model Flash 2000 elemental analyzer (see Appendix A) and oxygen was calculated by difference. A Shimadzu Q2010 GC-MS was used to characterize the composition of the hydrotreated oils (see Appendix B). Gas products were analyzed using an SRI 8610C portable GC. The liquid product yield was calculated by weighing the sampling bottles before and after. Some hydrotreated liquid products are shown in Figure 4.5.



Figure 4. 5 Liquid products collected from the hydrotreating of 87.5% calcium formate loading.

#### 4.3 Results and discussion

Bio-oil feedstocks were hydrotreated over a commercially available Ni/silica-alumina catalyst in a trickle bed reactor for up to 345 hours, similar to previous work on hydrotreating bio-oils with this catalyst (Eaton et al. 2015). Liquid yields, carbon yields, final product oxygen content, and H:C ratio were determined as a function of time-on-stream.

#### **4.3.1 FAsP oil with 16 wt.% oxygen as a feedstock hydrotreated at 750 psi**

During the hydrodeoxygenation, the feedstock could undergo several reactions. Ideally, the oxygenated oil would react to form a deoxygenated oil plus water as a by-product. However, cracking reactions could produce permanent gases. Also, coke could be formed as a solid by-product that will plug the reactor and deactivate the catalyst. The hydrotreatment of this feedstock was done over the nickel/silica-alumina catalyst with operating conditions of 300 °C reactor temperature, 750 psi reactor pressure, and 100 sccm of H<sub>2</sub>. At temperatures greater than 300 °C, the reactor was prone to plugging due to excessive coking. This coking could have occurred because of the feed polymerizing before hydrodeoxygenation could occur.

Based on these initial results, an experiment of 300 hours was conducted under the conditions listed above. A total of 152.67 gm of 16 wt.% oxygen FAsP oil was fed to the reactor. The liquid yield (oil plus water) was measured periodically by dividing the mass of liquid collected during a 12-24 hours interval by the mass of the amount fed during that same interval. The initial yield is low because the reactor is taking time to fill. In addition, we have observed that this catalyst has increased cracking activity during start-up, also observed in Eaton et al. 2015, possibly due to the reduction in acid sites on the alumina via mild coking. By 50 hours, the reactor was at liquid yield greater than 70% and remained relatively constant through 300 hours as shown in Figure 4.6.

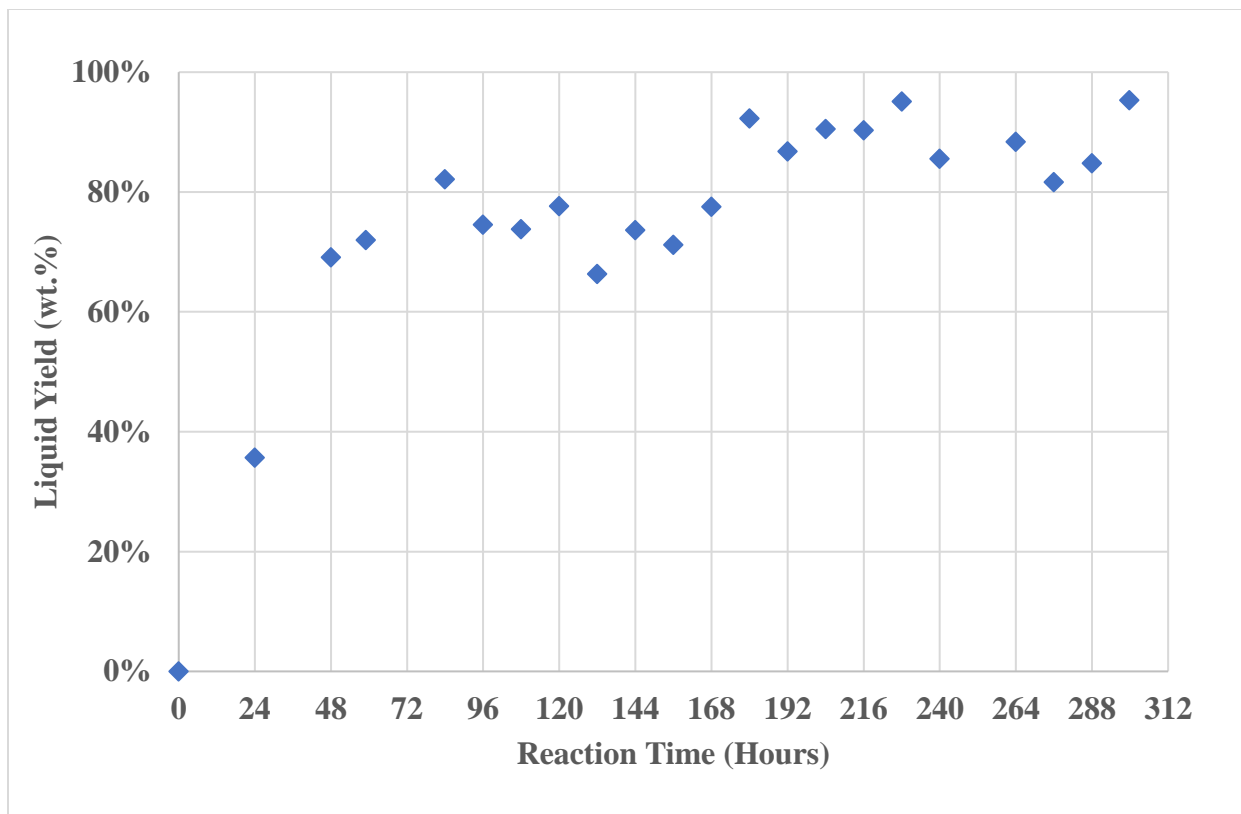


Figure 4. 6 Total liquid yield as a function of reaction time for the hydrotreating of the 100% calcium formate loading at 750 psi.

Figure 4.7 shows the change in oxygen content of the oil fraction of the liquid samples collected over the course of the experiment. It is clear that a slow, but steady, increase in oxygen content within the collected oil occurred. This increase was from approximately 0.5 to 4 wt.% over the course of 300 hours of run time. In addition to the oxygen increase, a slow but steady decrease in H:C ratio was measured. The H:C ratio decreased from approximately 2 to 1.5. The increase in oxygen and decrease in hydrogen contents are consistent with a slow and steady degradation of the HDO catalyst. The coloration of the collected oil samples was progressively darker with increased run time. The high H:C ratio was due to the high hydrogenation occurred during this experiment.



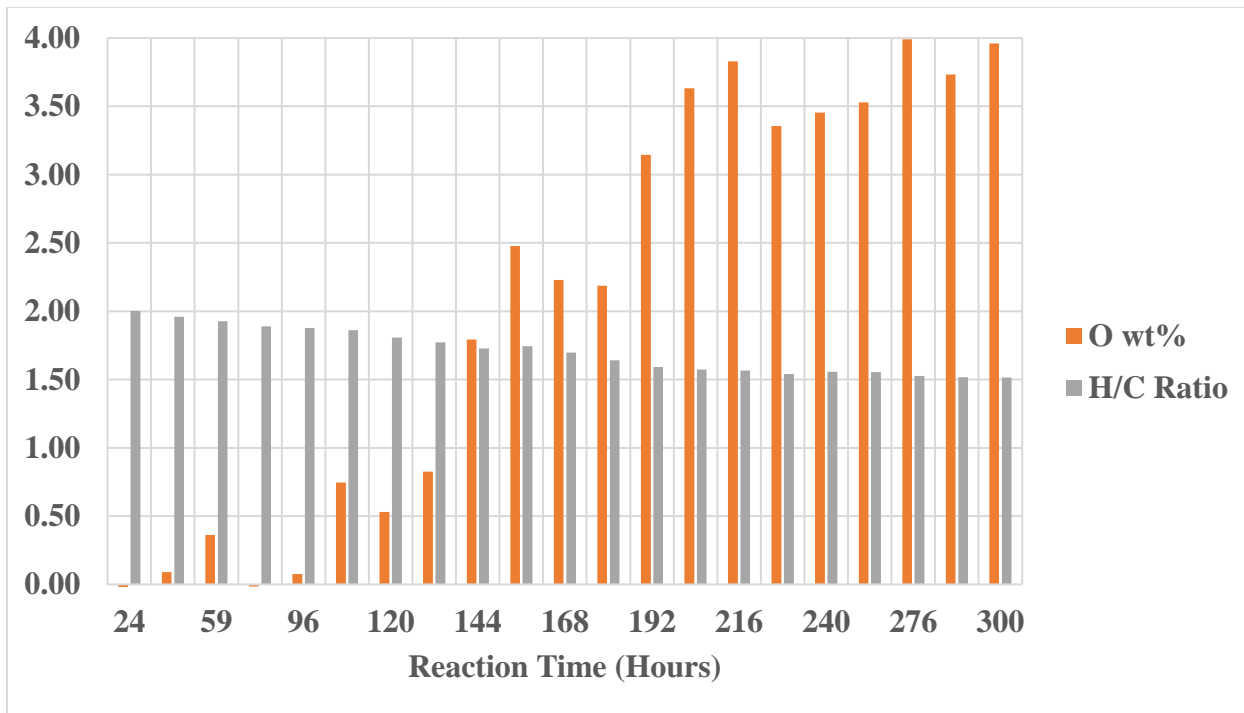


Figure 4. 7 Oxygen wt.% and H:C ratio as a function of reaction time for the hydrotreating of the 100% calcium formate loading at 750 psi.

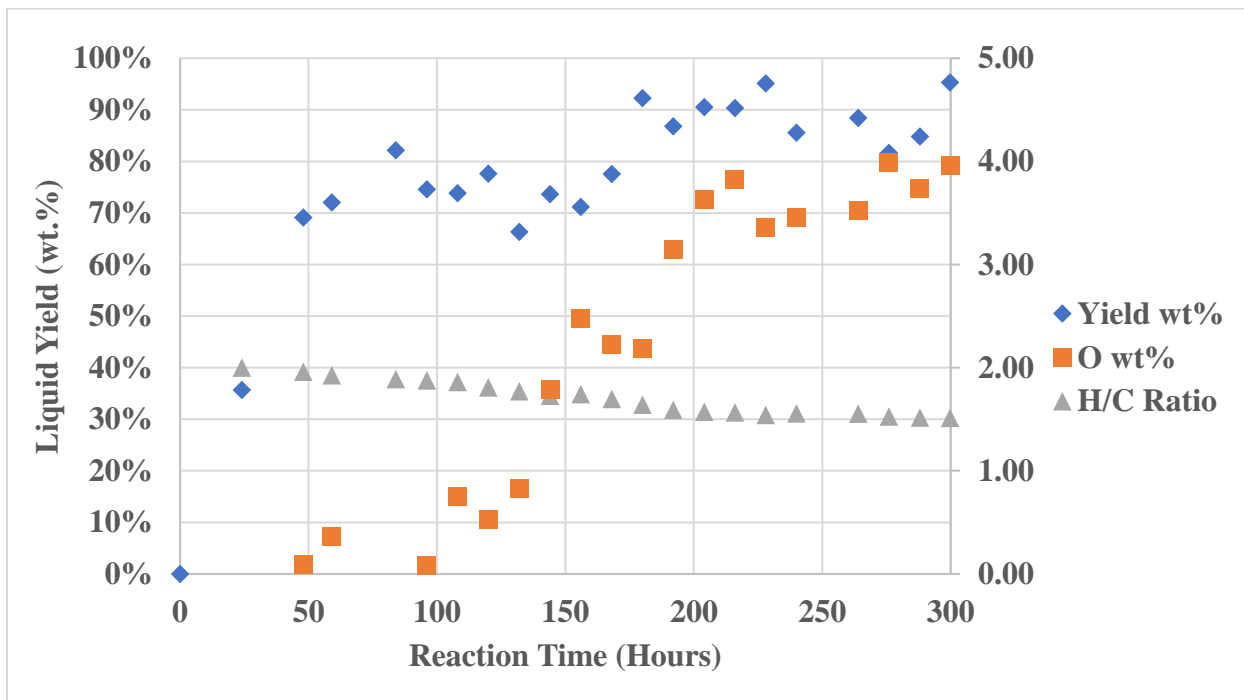


Figure 4. 8 Liquid yield wt.%, Oxygen wt.% and H:C ratio as a function of reaction time for the hydrotreating of 100% calcium formate loading at 750 psi.

### 4.3.2 FAsP oil with 16 wt.% oxygen as a feedstock hydrotreated at 1400 psi

A multi-day experiment was conducted revealing that good overall liquid yields of low oxygen content (oil plus water) could be achieved over the nickel/silica-alumina catalyst at 300 °C reactor temperature, 1400 psi reactor pressure, and 100 sccm of H<sub>2</sub>.

An experiment of 345 hours was conducted under the conditions listed above. A total of 182.35 gm of 16 wt.% oxygen FAsP oil was fed to the reactor. The liquid yield (oil plus water) was measured in the same way described above. The initial yield is low also because the reactor is taking time to fill. By 120 hours the reactor was at a liquid yield of 100% and remained relatively constant through 345 hours as shown in Figure 4.9. In this experiment, most of the bio-oil fed was converted to liquid product with less gas yield. A 153.36 gm was the liquid product collected from a total of 182.35 gm of bio-oil fed means that 84% of the bio-oil fed was retained in the liquid product and 16% was converted to gas or coke.

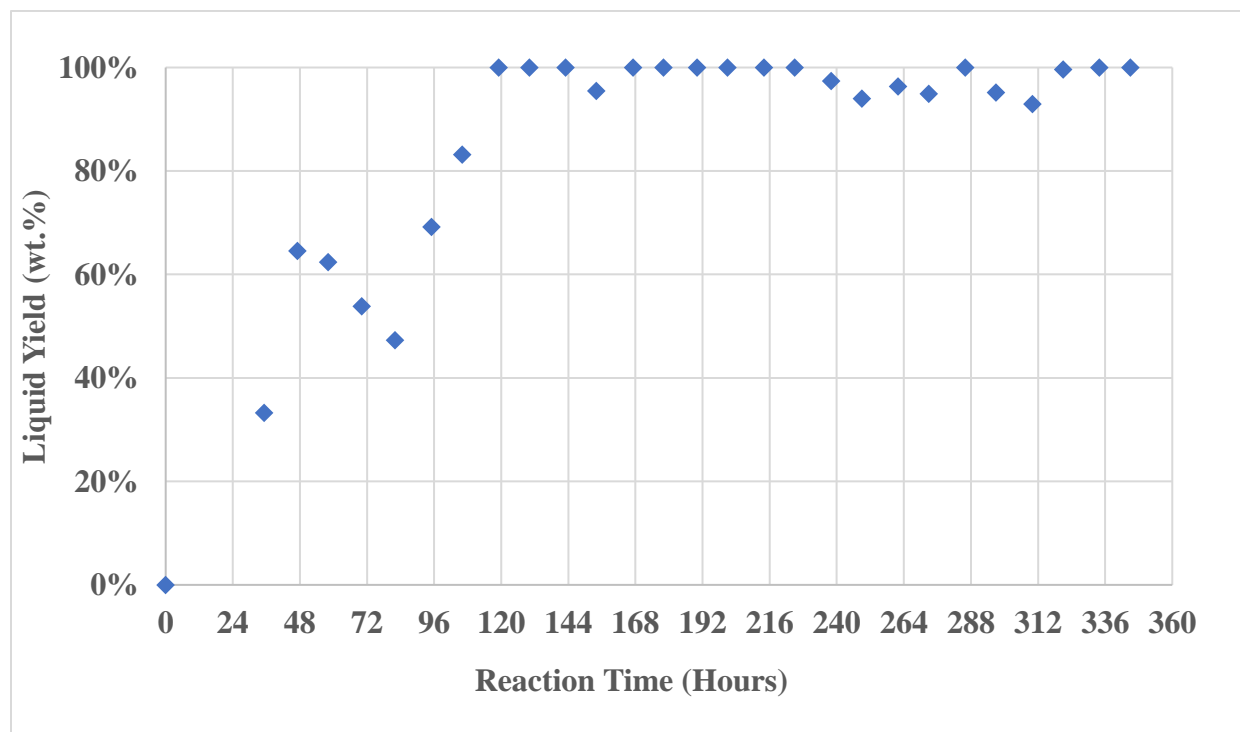


Figure 4. 9 Total liquid yield as a function of reaction time for the hydrotreating of the 100% calcium formate loading at 1400 psi.

Figure 4.10 shows the change in oxygen content of the oil fraction of the liquid samples collected over the course of the experiment. An increase in the oxygen content within the collected oil was noticed. This increase was from approximately 0.55 to 6.20 wt.% and it was slow but steady over the course of 345 hours of run time. In addition to the oxygen increase, there was a slow decrease in the H:C ratio. This decrease was from approximately 1.91 to 1.59. The increase in oxygen and decrease in hydrogen contents are a clear evidence that the catalyst got a slow and partial deactivation with time.

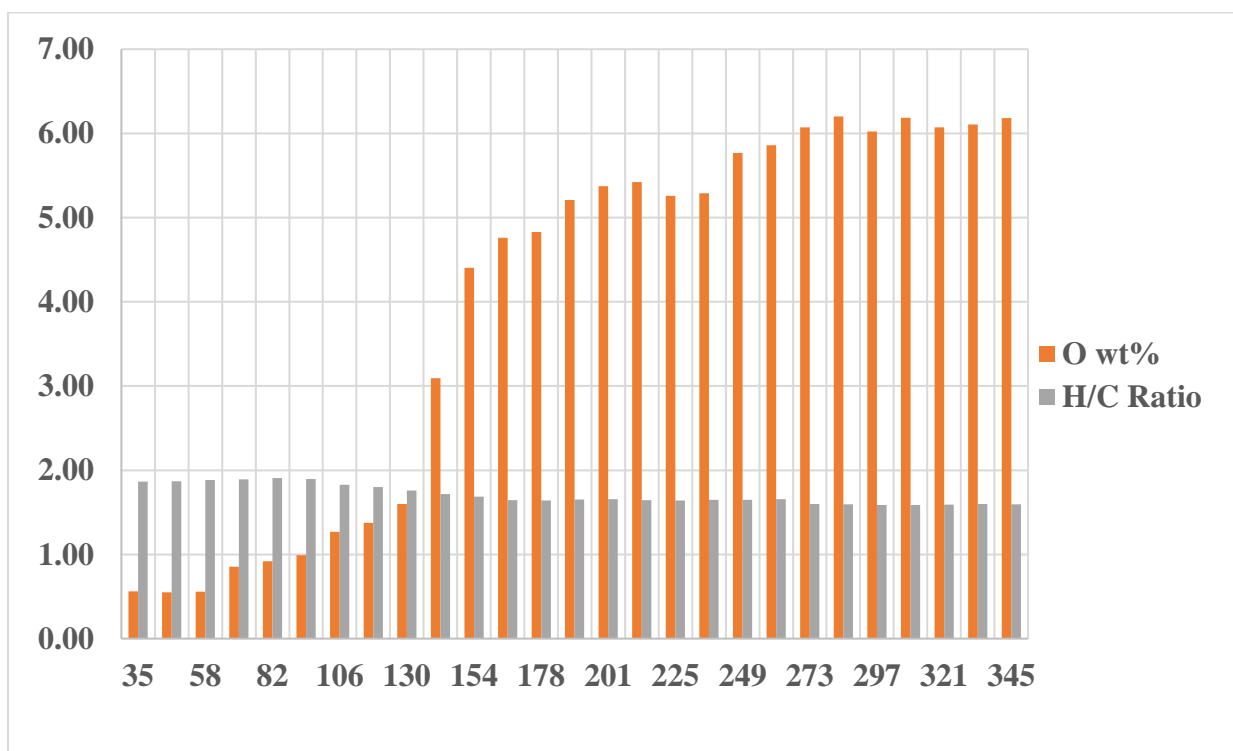


Figure 4. 10 Oxygen wt.% and H:C ratio as a function of reaction time for the hydrotreating of the 100% calcium formate loading at 1400 psi.

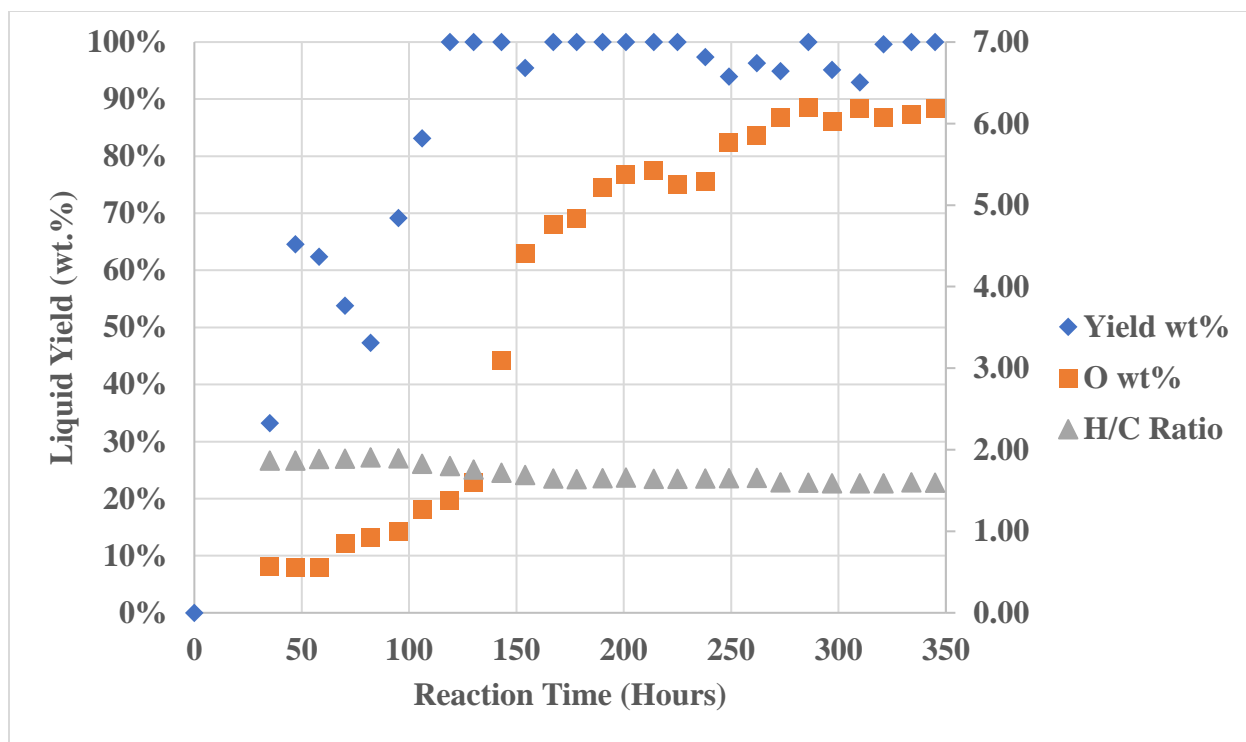


Figure 4. 11 Liquid yield wt.%, Oxygen wt.% and H:C ratio as a function of reaction time for the hydrotreating of the 100% calcium formate loading at 1400 psi

### 4.3.3 FAsP oil with 21 wt.% oxygen as a feedstock

An experiment of 336 hours was conducted under the conditions of 300 °C reactor temperature, 1400 psi reactor pressure, and 100 sccm of H<sub>2</sub>. A total of 178.87 gm of 21 wt.% oxygen FAsP oil was fed to the reactor. The liquid yield (oil plus water) was measured in the same way described above. By 60 hours the reactor was at a liquid yield of greater than 70% and increased to reach 93% through 336 hours as shown in Figure 4.12. The lowest liquid yield measured was during the first 48 hours on-stream where it was approximately 60%. This happened because the reactor is taking time to fill and due to the cracking activity during start-up. A 142.23 gm was the liquid product collected from a total of 178.87 gm bio-oil fed. The remaining amount of bio-oil fed was probably converted to gas or coke.

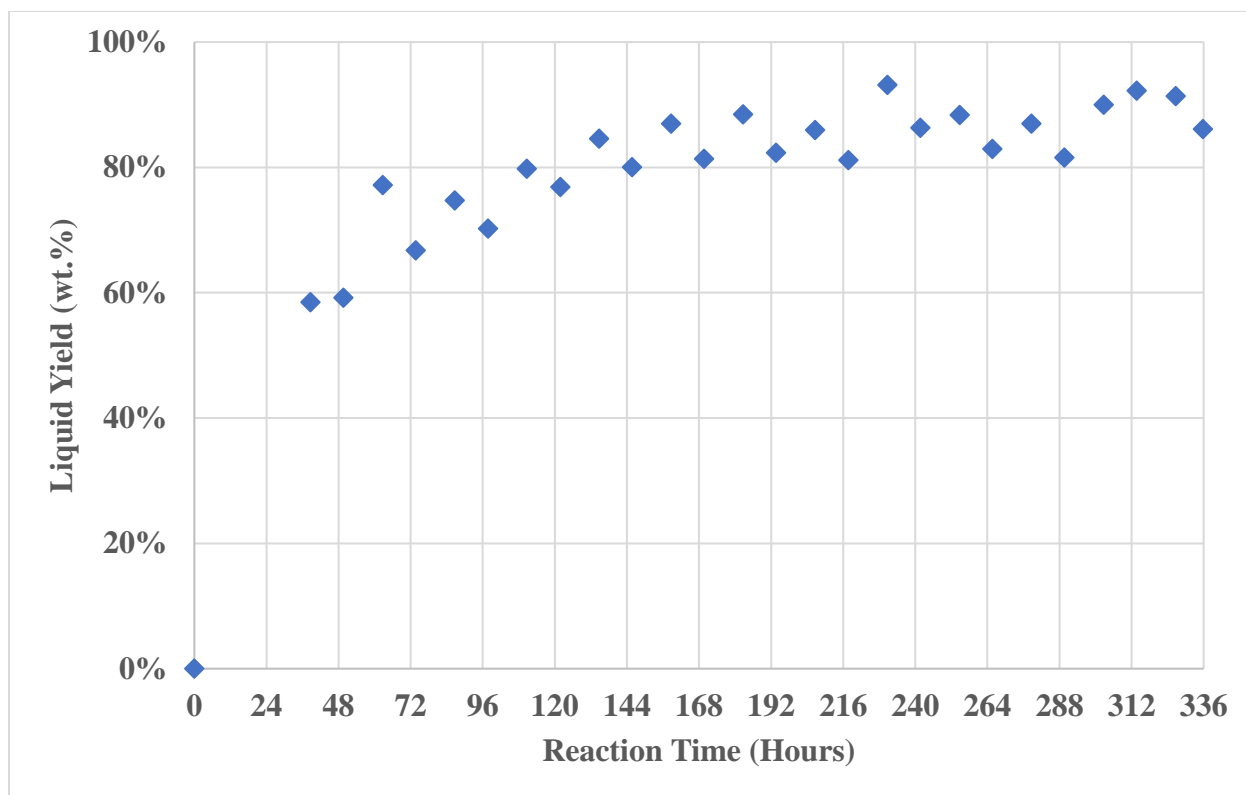


Figure 4. 12 Total liquid yield as a function of reaction time for the hydrotreating of the 87.5% calcium formate loading.

Figure 4.13 shows the change in oxygen content of the oil fraction of the liquid samples collected over the course of the experiment. There was a slow increase in the oxygen content and a slow decrease in the H:C ratio over the course of the 336 hours of run time. The oxygen content increased from approximately 0.28 to 5.51 wt.% while the H:C ratio decreased from approximately 1.98 to 1.58. The coloration of the collected oil samples was also progressively darker with increased run time. By 146 hours, the oil fractions product got a slow increase in the oxygen content indicating that the catalyst started to get partial deactivation after this time-on-stream.

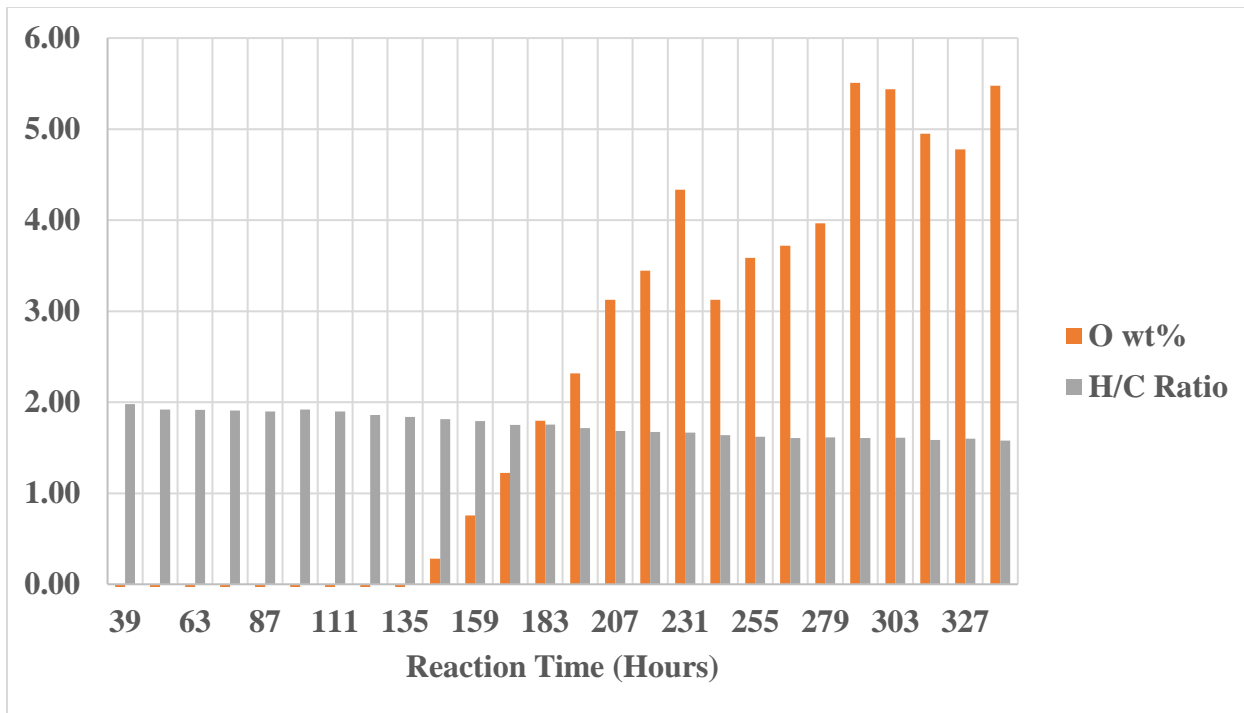


Figure 4. 13 Oxygen wt.% and H:C ratio as a function of reaction time for the hydrotreating of the 87.5% calcium formate loading.

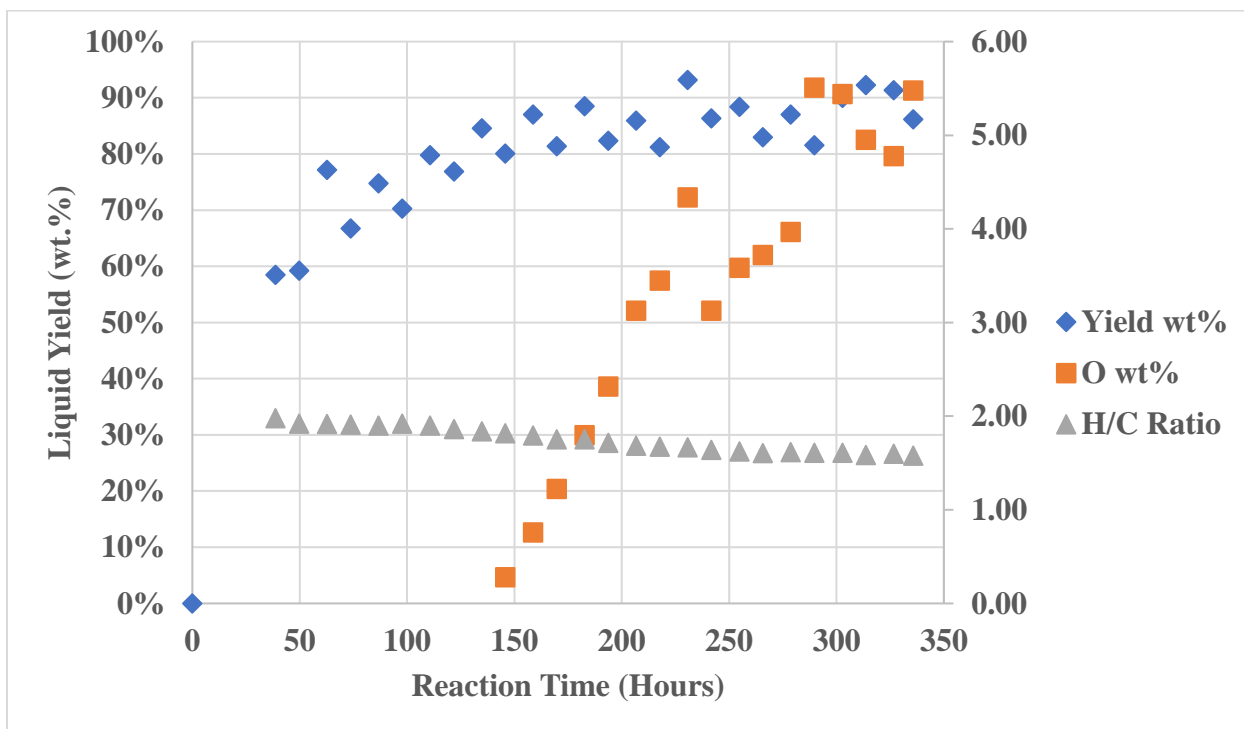


Figure 4. 14 Liquid yield wt.%, Oxygen wt.% and H:C ratio as a function of reaction time for the hydrotreating of the 87.5% calcium formate loading.

#### **4.3.4 FAsP oil with 26 wt.% oxygen as a feedstock hydrotreated at 750, 1400 psi**

Initial experiments attempting HDO of FAsP oil (26 wt.% oxygen) involved repeating the successful experiment with the 16 wt.% oxygen oils over the same nickel/silica-alumina catalyst run at 300 °C and 750 psi. These experiments resulted in the catalyst bed and reactor being plugged with carbon/coke deposits within 70-80 hours of operation. Overall liquid yields with this feedstock under these conditions were consistently below 50% indicating that significant fractions of carbon in the feedstock were being converted either to permanent gas or char/coke.

Increasing the reactor pressure to 1400 psi resulted in increasing the time to reactor plugging to 200 hours of operation with a total of 97.62 gm oil fed. In addition, the liquid yields were above 70% for a significant portion of the run, as shown in Figure 4.15. In this experiment, the liquid yield rose steadily from 35 to 60 wt.% over the first 120 hours of run time, and then increased to above 70 wt.% where it remained until flow stopped due to plugging at near 200 hours of run time. The low liquid yield measured at the beginning of the hydrotreating was probably due to the cracking activity during start-up.

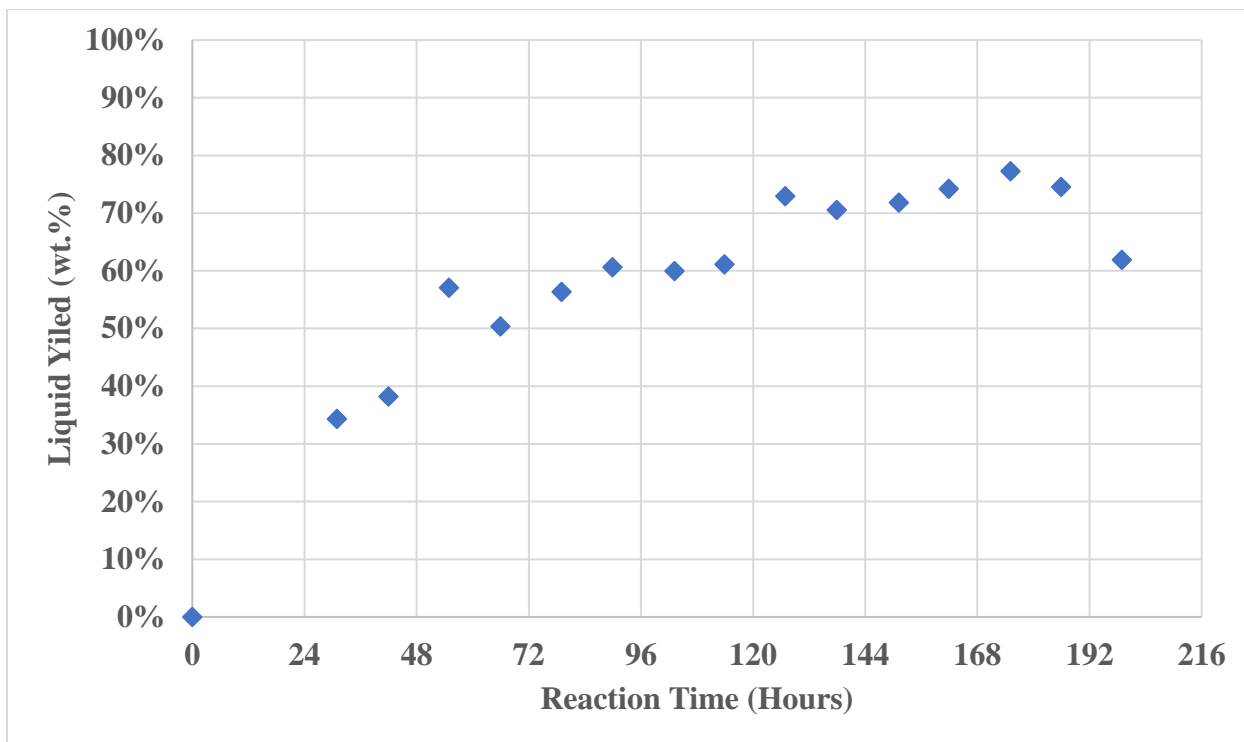


Figure 4. 15 Total liquid yield as a function of reaction time for the hydrotreating of the 50% calcium formate loading at 1400 psi.

Figure 4.16 shows the change in oxygen content of the oil fraction of the liquid samples collected over the course of the experiment. The oxygen content remained quite low, below 1.5 wt.% until 130 hours where the oil contained significantly more oxygen, between 5 and 14 wt.%. The H:C ratio remained fairly constant throughout the experiment.



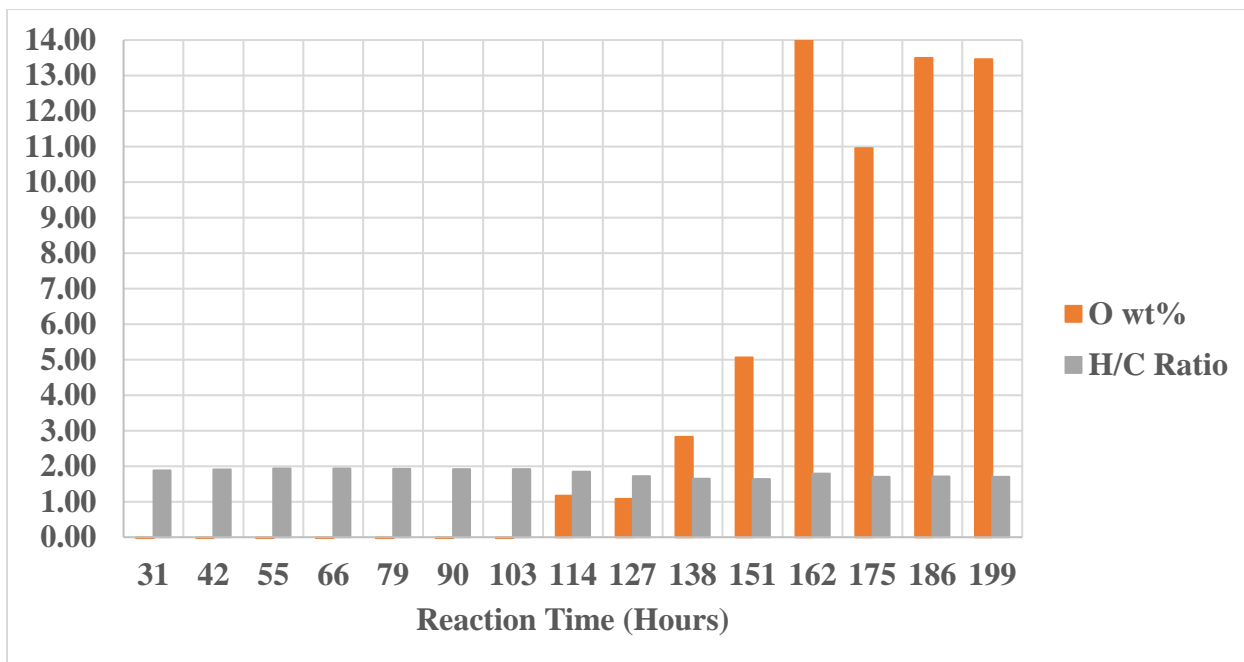


Figure 4. 16 Oxygen wt.% and H:C ratio as a function of reaction time for the hydrotreating of the 50% calcium formate loading at 1400 psi.

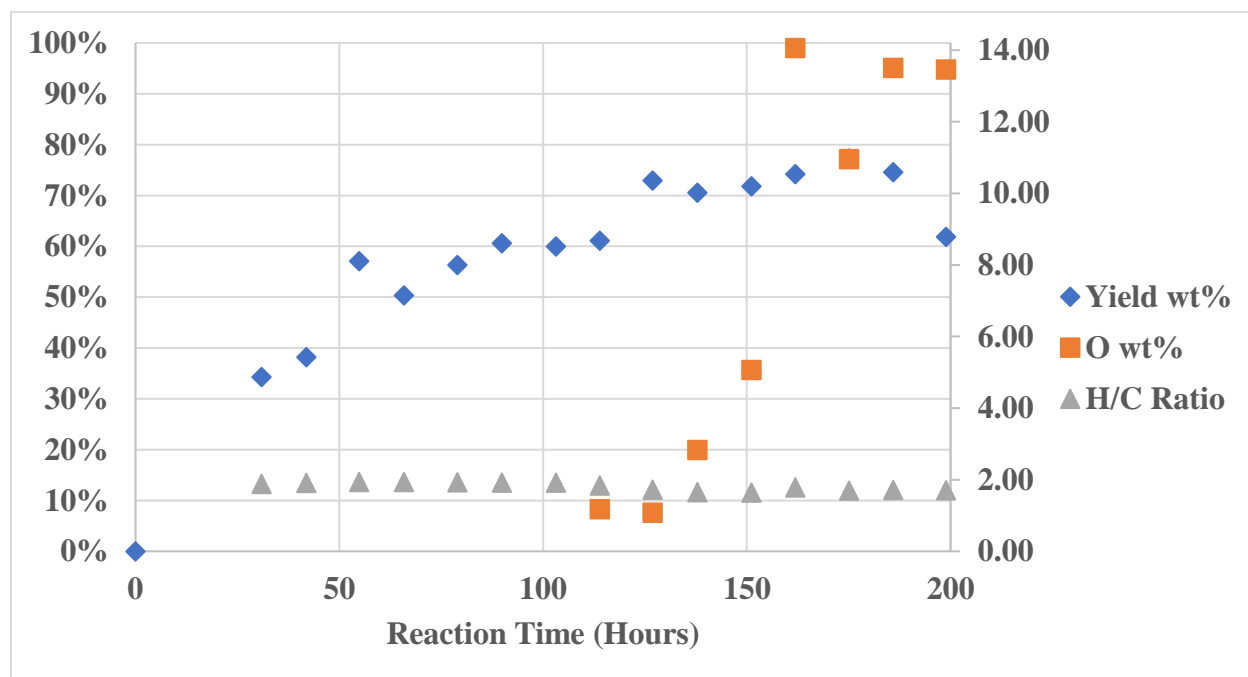


Figure 4. 17 Liquid yield wt.%, Oxygen wt.% and H:C ratio as a function of reaction time for the hydrotreating of the 50% calcium formate loading at 1400 psi.

#### **4.3.5 FAsP oil with 27 wt.% oxygen as a feedstock**

Hydroprocessing of this feedstock under the operating condition of 300 °C reactor temperature, 1400 psi reactor pressure, 100 sccm hydrogen flow rate, and 0.01 ml/min feed flow rate over the same nickel/ silica-alumina catalyst resulted in a reactor blockage with carbon/coke deposits within 24-48 hours of operation. Overall liquid yields with this feedstock under these conditions were consistently below 22% indicating that significant fractions of carbon in the feedstock were being converted either to permanent gas or char/coke.

#### **4.3.6 Carbon and hydrogen balances**

The elemental analysis of the bio-oils obtained from the fast pyrolysis of the biomass feedstocks (100% calcium formate loading, 50% calcium formate loading, 87.5% calcium formate loading) was done using a Thermo Scientific Model Flash 2000 elemental analyzer, and the oxygen was calculated by subtracting the carbon, hydrogen, and nitrogen from the total mass. The balance calculations for the carbon and hydrogen were done on the hydrotreated oil and water layers as well as the dry bio-oils fed.

The carbon and hydrogen mass yields in the bio-oil fed are calculated by multiplying the mass of the dry bio-oil fed by the carbon and hydrogen weight percentages present in the bio-oil fed. The carbon and hydrogen mass yields in the hydrotreated oil or water layers for a particular sample are calculated by multiplying the mass of the hydrotreated oil or water layers by the carbon and hydrogen weight percentages measured in the hydrotreated oil or water layers. The amount of hydrogen consumed (uptake from the cylinder) is calculated by multiplying the density of the hydrogen by the volume of the hydrogen consumed, which is calculated by

multiplying the volumetric flow rate of the hydrogen fed to the reactor by the time of taking a sample.

The total carbon mass yield in a hydrotreated sample is calculated by adding the mass of the carbon measured in the oil layer to the mass of the carbon measured in the water layer. The total hydrogen mass yield is calculated in an analogous way to the total carbon mass yield described above. The total hydrogen fed to the reactor is calculated by adding the mass of the hydrogen in the bio-oil fed to the mass of the hydrogen taken from the cylinder, which is described in the previous paragraph.

Gas products were analyzed using an SRI 8610C portable GC. For  $H_2$  converted to gas, we first multiply methane, ethane, propane, butane, pentane, and hexane mole flow rates by 2, 3, 4, 5, 6 and 7 respectively to get the hydrogen mole flow rate in each one of them. This is done because we need 2 hydrogen molecules to produce methane, 3 hydrogen molecules to produce ethane, 4 hydrogen molecules to produce propane, 5 hydrogen molecules to produce butane, 6 hydrogen molecules to produce pentane and 7 hydrogen molecules to produce hexane. Then, we multiply the hydrogen mole flow rate by its molecular weight to get the hydrogen mass flow rate in each one of them and finally we sum all of the hydrogen mass flow rates to know how much hydrogen ended up in the gas product.

For carbon converted to gas, we first multiply methane, ethane, propane, butane, pentane, and hexane mole flow rates by 1, 2, 3, 4, 5 and 6, respectively to get the carbon mole flow rate in each one of them. This is done because we need 1 carbon molecule to produce methane, 2 carbon molecules to produce ethane, 3 carbon molecules to produce propane, 4 carbon molecules to produce butane, 5 carbon molecules to produce pentane and 6 carbon molecules to produce hexane. Then, we multiply the carbon mole flow rate by its molecular weight to get the carbon

mass flow rate in each one of them and finally we sum all of the carbon mass flow rates to know how much carbon ended up in the gas product.

| Bio-oil Feedstocks            | H <sub>2</sub> , psi | Time-on-stream (hour) | Mass yield of product oil, wt.% | Mass yield of aqueous fraction, wt.% | Mass* yield of product gas, wt.% | Mass Balance, % |
|-------------------------------|----------------------|-----------------------|---------------------------------|--------------------------------------|----------------------------------|-----------------|
| 50% calcium formate loading   | 1400                 | 151-162               | 52.4%                           | 21.6%                                | 11.3%                            | 85.3%           |
| 87.5% calcium formate loading | 1400                 | 255-266               | 66.5%                           | 16.4%                                | 5.3%                             | 88.2%           |
| 100% calcium formate loading  | 750                  | 240-264               | 66.8%                           | 21.2%                                | -----                            | 88.1%           |
| 100% calcium formate loading  | 1400                 | 321-334               | 79.4%                           | 15.9%                                | 2.3%                             | 97.5%           |

Table 4. 1 Results for the hydrotreating of calcium formate pretreated pine sawdust feedstocks.

\* Yields of the main gaseous species

Based on the amount of the bio-oil fed and the summary of the hydrotreating results shown in Table 4.1, the mass yield of the oil fraction collected from the hydrotreating of the 100% calcium formate loading at 1400 psi was the highest mass yield measured, which was 79.4%. The lowest mass yield measured for the oil fraction was 52.4% resulted from the hydrotreating of the 50% calcium formate loading at 1400 psi. In contrast, the yields of the aqueous fraction and product gas were higher for the hydrotreating of the 50% calcium formate loading at 1400 psi (21.6% and 11.3%, respectively) and lower for the hydrotreating of the 100% calcium formate loading at 1400 psi (15.9% and 2.3%, respectively). In conclusion, the oil fraction yield increased as the oxygen content decreased in the oil feedstock whereas the aqueous and gas yields increased as the oxygen content increased in the feedstock.

| Bio-oil Feedstocks            | H <sub>2</sub> , psi | Time-on-stream (hour) | Carbon yield of product oil, % | Carbon yield of aqueous fraction, % | Carbon* yield of product gas, % | Carbon Balance, % |
|-------------------------------|----------------------|-----------------------|--------------------------------|-------------------------------------|---------------------------------|-------------------|
| 50% calcium formate loading   | 1400                 | 151-162               | 61.3%                          | 0.1%                                | 14.1%                           | 75.5%             |
| 87.5% calcium formate loading | 1400                 | 255-266               | 82.4%                          | 0.1%                                | 6.0%                            | 88.5%             |
| 100% calcium formate loading  | 750                  | 240-264               | 79.4%                          | 0.1%                                | -----                           | 79.5%             |
| 100% calcium formate loading  | 1400                 | 321-334               | 91.8%                          | 0.2%                                | 2.5%                            | 94.5%             |

Table 4. 2 Carbon balance for the hydrotreating of calcium formate pretreated pine sawdust feedstocks.

\* Carbon yields in the main gaseous species

Based on Table 4.2, the carbon weight percentage was high in the oil fraction collected from the hydrotreating of the 100% calcium formate loading at 1400 psi (91.8%) and low in the oil fraction collected from the hydrotreating of the 50% calcium formate loading at 1400 psi (61.3%). The carbon weight percentage was approximately the same in the oil fractions collected from the hydrotreating of the 100% calcium formate loading at 750 psi and the 87.5% calcium formate loading at 1400 psi. The carbon weight percentages in the aqueous fractions were negligible (0.1-0.2%) and were approximately the same for all experiments. The carbon weight percentage was higher in the gases produced from the hydrotreating of the 50% calcium formate loading at 1400 psi (14.1%) and lower in the gases produced from the hydrotreating of the 100% calcium formate loading at 1400 psi (2.5%). Most of the bio-oil carbon ended up in the oil fraction product and increased as the oxygen content decreased in the oil feedstock whereas the carbon that ended up in the gas product increased as the oxygen content increased in the oil feedstock, which might be caused by the high oxygen content present in this feedstock that might reduce the catalyst activity.

| Bio-oil Feedstocks            | H <sub>2</sub> , psi | Time-on-stream (hour) | H <sub>2</sub> Consumed, g of H <sub>2</sub> in oil product per g of dry bio-oil fed | H <sub>2</sub> Consumed, g of H <sub>2</sub> in aqueous fraction per g of dry bio-oil fed | H <sub>2</sub> Consumed, * g of H <sub>2</sub> in gas product per g of dry bio-oil fed |
|-------------------------------|----------------------|-----------------------|--|---|--|
| 50% calcium formate loading   | 1400                 | 151-162               | 0.061  | 0.026   | 0.025  |
| 87.5% calcium formate loading | 1400                 | 255-266               | 0.079  | 0.020   | 0.012  |
| 100% calcium formate loading  | 750                  | 240-264               | 0.077  | 0.025   | -----  |
| 100% calcium formate loading  | 1400                 | 321-334               | 0.091  | 0.019   | 0.005  |

Table 4. 3 Hydrogen consumption for the hydrotreating of calcium formate pretreated pine sawdust feedstocks.

\* Hydrogen yields in the main gaseous species

Table 4.3 shows the amount of hydrogen consumed in the oil fraction, aqueous fraction, and gas product per 1 g of dry bio-oil fed. The amounts of hydrogen consumed in the aqueous fraction and gas product were higher for the hydrotreating of the 50% calcium formate loading at 1400 psi (0.026 and 0.025 g respectively) and lower for the hydrotreating of the 100% calcium formate loading at 1400 psi (0.019 and 0.005 g respectively). On the other hand, the hydrogen consumption was higher in the oil fraction collected from the hydrotreating of the 100% calcium formate loading at 1400 psi (0.091 g) and lower in the oil fraction collected from the hydrotreating of the 50% calcium formate loading at 1400 psi (0.061 g).

The gas analysis was conducted on the experiments done at 1400 psi as shown in Figures 4.18, 4.19 and 4.20 below. The weight percentages of the carbon and hydrogen converted to gas were higher for the hydrotreating of the 50% calcium formate loading followed by the 87.5% calcium formate loading, while the lower weight percentages of carbon and hydrogen converted to gas were achieved for the hydrotreating of the 100% calcium formate loading.

We conclude that the decrease in the liquid yield at the beginning of the hydroprocessing in all hydrotreating experiments was due to the higher amounts of gases produced (cracking activity during start-up). The mass flow rates of the gases produced through all hydrotreating experiments were higher at the beginning especially for methane, which was the most abundant component, and decreased with increased the reaction time until reach almost zero flow rates for the 100, 87.5% calcium formate loadings and less than 0.4 (gm/sample time, hour) for the 50% calcium formate loading. The main gaseous species produced from all experiments were methane, ethane, propane, butane, pentane and hexane with trace amounts of CO and CO<sub>2</sub>.

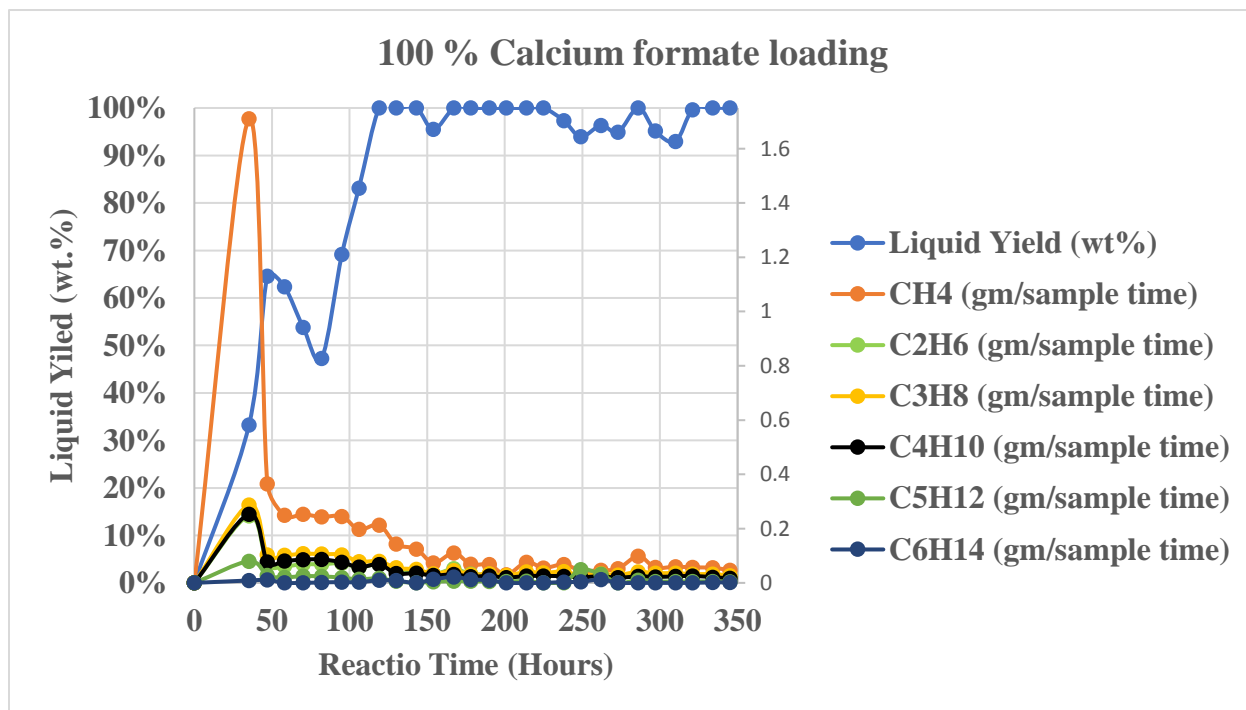


Figure 4. 18 Liquid yield wt.% and gases mass flow rates as a function of reaction time for the hydrotreating of the 100% calcium formate loading at 1400 psi.

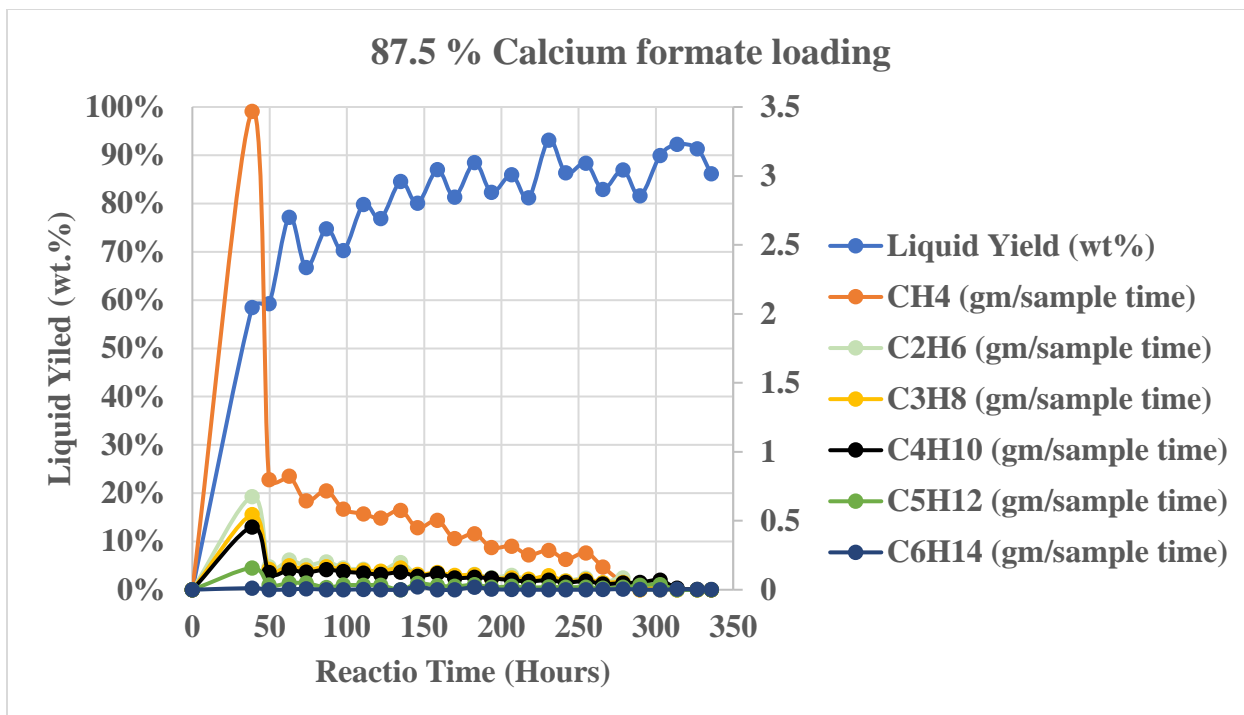


Figure 4. 19 Liquid yield wt.% and gases mass flow rates as a function of reaction time for the hydrotreating of the 87.5% calcium formate loading at 1400 psi.

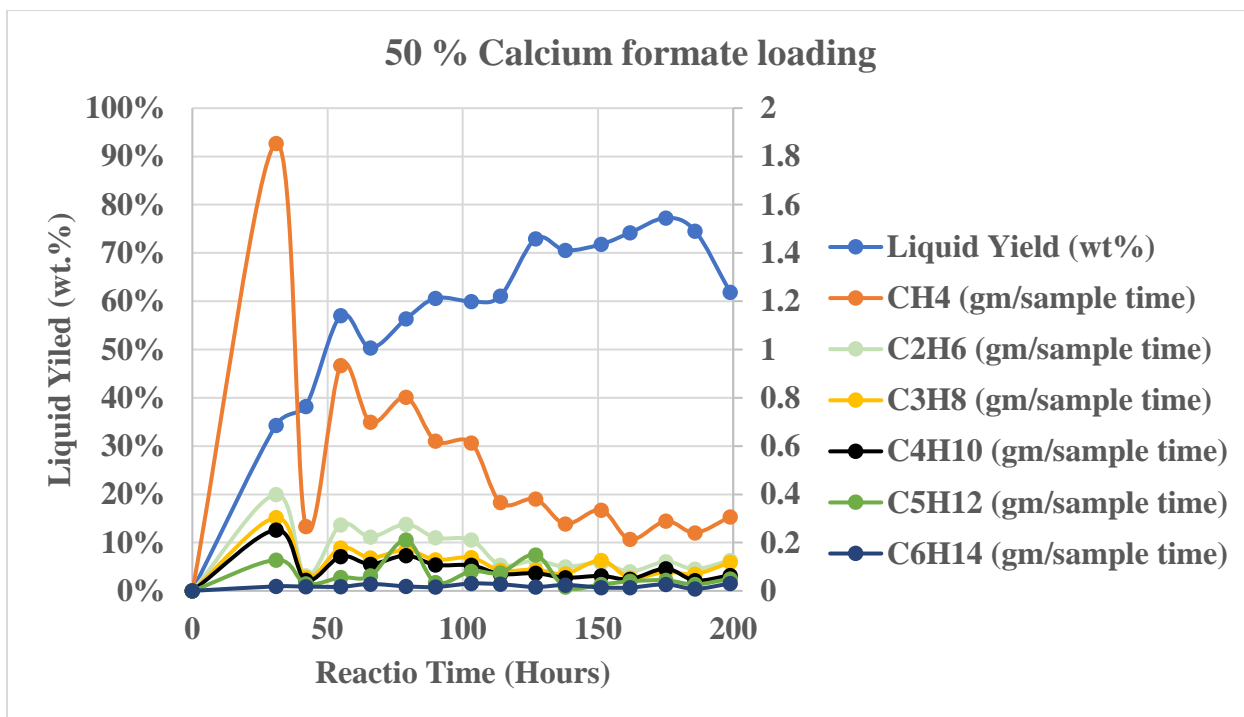


Figure 4. 20 Liquid yield wt.% and gases mass flow rates as a function of reaction time for the hydrotreating of the 50% calcium formate loading at 1400 psi.



#### 4.4 Summary

For the 16 wt.% oxygen content bio-oil hydrotreated at 750 psi H<sub>2</sub>, the longest time onstream operation (300 hours) was achieved at an average bed temperature of 300 °C, reactor pressure of 750 psi, and 100 sccm H<sub>2</sub>. The highest carbon and hydrogen contents measured for the hydrotreated liquid products from this experiment were 86.0 wt.%, 14.2 wt.% and the lowest were 84.0 wt.%, 10.6 wt.% respectively. The oil phase collected within the first 24 hours of the experiment had an oxygen content of 0 wt.%, while the oil phase collected toward the end of the experiment had an oxygen content between 3-4 wt.%. For the 16 wt.% oxygen content bio-oil hydrotreated at 1400 psi H<sub>2</sub> with same other operating conditions, the longest time onstream operation (345 hours) was achieved at an average bed temperature of 300 °C, reactor pressure of 1400 psi, and 100 sccm H<sub>2</sub>. The highest carbon and hydrogen contents measured for the hydrotreated liquid products from this experiment were 86.0 wt.%, 13.6 wt.% and the lowest were 83.0 wt.%, 11.0 wt.% respectively. The oil phase collected within the first 24 hours of the experiment had an oxygen content between 0-0.5 wt.% while the oil phase collected toward the end of the experiment had an oxygen content between 5.2-6.2 wt.%.

For the 21 wt.% oxygen content bio-oil, the longest time onstream operation (336 hours) was achieved at an average bed temperature of 300 °C, reactor pressure of 1400 psi, and 100 sccm H<sub>2</sub>. The highest carbon and hydrogen contents measured for the hydrotreated liquid products from this experiment were 87.0 wt.%, 14.2 wt.% and the lowest were 83.0 wt.%, 11.0 wt.% respectively. The oil phase collected within the first 24 hours of the experiment had an oxygen content of 0 wt.% while the oil phase collected toward the end of the experiment had an oxygen content between 4.5-5.5 wt.%. For the 26 wt.% oxygen content bio-oil, the longest time onstream operation (200 hours) was achieved at an average bed temperature of 300 °C, reactor

pressure of 1400 psi, and 100 sccm H<sub>2</sub>. The highest carbon and hydrogen contents measured for the hydrotreated liquid products from this experiment were 87.0 wt.%, 14.0 wt.% and the lowest were 75.0 wt.%, 11.0 wt.% respectively. The oil phase collected within the first 24 hours of the experiment had an oxygen content of 0 wt.% while the oil phase collected toward the end of the experiment had an oxygen content between 10.9-14.0 wt.%.

The hydrotreating experiments done using bio-oil feedstocks containing 16 and 21 wt.% oxygen had the highest times-on-stream (345 hours and 336 hours respectively) and stopped due to the running out of feedstocks and without any pressure buildup across the reactor. The hydrotreating experiments done using bio-oil feedstocks containing 26 and 27 wt.% oxygen had the lowest times-on-stream (200 hours and 48 hours respectively) and stopped due to reactor plugging. The major compounds identified by the GC-MS (Shimadzu Q2010) were alkylated cyclohexane whereas Alkanes were the minor components. Only trace oxygenates were identified in the product such as cyclopentanone.

In summary, partial deactivation of the catalyst over time was evident due to the quality of the oil product collected, which saw the density, oxygen content and viscosity increase and the H:C ratio and carbon content decrease. The partial deactivation of the catalyst might be caused by one of the reasons discussed in section 2.3, i.e. poisoning, coke deposition, metals present in the feed and changes in catalyst structure. The partial deactivation was more pronounced for higher oxygen-containing bio-oil feedstocks and for higher temperatures >300 °C.

## 4.5 Conclusion

The results obtained from this work suggest that the bio-oils generated from the biomass feedstocks (calcium formate pretreated with pine sawdust) can be successfully upgraded into hydrocarbon fuels using experiments that ran up to 15 days without any problems and without the need for a stabilization step. Oils produced from the hydrotreating of the 100%, 87.5% and 50% calcium mass loadings have physicochemical properties comparable to petroleum oil. The low oxygen bio-oil feedstock, 16 wt.%, is able to be hydrotreated better than high oxygen bio-oil feedstock because it has less or none complex oxygenated compounds, less water content and more stable.

A hydrogen pressure of 750 psi was not a suitable hydrotreating pressure to use for higher oxygen-containing bio-oil feedstocks. A reactor temperature of 350 °C was not the perfect hydrotreating temperature to use for all oxygen-containing bio-oil feedstocks. A hydrogen pressure of 750 psi and a temperature of 350 °C accelerated the polymerization reactions, which resulted in rapid plug formation. Instead, 1400 psi and 300 °C were the optimum operating conditions that prevented the occurrence of reactor plugging and pressure drop across the reactor. A 16 wt.% oxygen bio-oil operated at 1400 psi gave the highest oil and carbon yields with the lowest gas and aqueous yields.

From this study, we learned that the oxygen content present in the bio-oils generated from the fast pyrolysis of the feedstocks described earlier had a huge effect on the upgrading process. As the oxygen content increased, the hydrotreating problems increased as well. We also learned that the changes in the temperature, pressure and the compositions of the bio-oils used as feedstocks can alter the physical and chemical properties of the products. The quality of the products achieved during all hydrotreating experiments was the highest using low oxygen bio-oil

feedstock with high hydrogen pressure (1400 psi) and intermediate bed temperature (300 °C). Finally, we learned that the cheap nickel on silica-alumina catalyst is an excellent HDO catalyst compared to other HDO catalysts mentioned in Chapter 2 because it showed the highest deoxygenation activity with less consumption of hydrogen. It did not require supplemental sulfur. It had the long lifetime because it stood actively for more than 15 days removing more than 10 wt.% oxygen and if the necessary feedstocks were available we would reach probably more than 30 days on-stream time. It yielded oils with higher carbon and hydrogen wt.% and none or lower oxygen content. High oil with low aqueous and gas yields could produce through it. Finally, it yielded higher H:C ratio which was between 2-1.6 and it is approximately within the range of the diesel (~1.8) and kerosene (~1.95) products. In future work, we are interested in improving the catalyst lifetime by studying the deactivation mechanisms, trying another catalyst, decreasing the hydrogen consumption, and enhancing the product quality.

## REFERENCES

1. Friedlingstein, P., Andrew, R.M., Rogelj, J., Peters, G.P., Canadell, J.G., Knutti, R., Luderer, G., Raupach, M.R., Schaeffer, M., van Vuuren, D.P. and Le Quere, C. "Persistent Growth of CO<sub>2</sub> Emissions and Implications for Reaching Climate Targets". *Nature Geosci.* 2014, 7 709-714.
2. Solomon, S., Plattner, G.K., Knutti, R. and Friedlingstein, P. "Irreversible Climate Change Due to Carbon Dioxide Emissions". *Proc. Nat. Acad. Sci.* 2014, 106(6) 704-1709.
3. Downing, M.; Eaton, L. M.; Graham, R. L.; Langholtz, M. H.; Perlack, R. D.; Turhollow Jr, A. F.; Stokes, B.; Brandt, C. C. U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry. Oak Ridge National Laboratory, Oak Ridge, TN. 2011.
4. Carrasco, J.L. "Techno-Economic Analysis of Pyrolysis of Forest Residues ", Master Thesis, University of Maine, USA. 2013. (10).
5. Basu, P., "Biomass Gasification and Pyrolysis and Torrefaction: Practical Design and Theor ". 2013: Elsevier Science, p. 10-51
6. McKendry, P. (2002) Energy production from biomass (part 2): conversion technologies. *Biores. Technol.* 83: 47-54.
7. Mohan, D.; Pittman, C. U.; Jr.; Steele, P. H. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy & Fuels.* 2006, 20(2), 848-889.
8. Anh N. Phan, Changkook Ryu, Vida N. Sharifi, Jim Swithenbank. Characterisation of slow pyrolysis products from segregated wastes for energy production. *J. Anal. Appl. Pyrolysis* 81 (2008) 65–71
9. Bridgwater AV, Peacocke GVC. Fast pyrolysis process for biomass. *Renew Sustain Energy Rev* 2000; 4:1–73.
10. French, R.; Czernik, S. Catalytic pyrolysis of biomass for biofuels production. *Fuel Process. Technol.* 2010, 91, 25–32.
11. Bertero, M., G. de la Puente, and U. Sedran, Fuels from bio-oils: Bio-oil production from different residual sources, characterization and thermal conditioning. *Fuel*, 2012. 95: p. 263-271.
12. Wei, X., et al., Characterization of the water-insoluble pyrolytic cellulose from cellulose pyrolysis oil. *Journal of Analytical and Applied Pyrolysis*, 2012. 97: p. 49-54.

13. Diebold, J. P. A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-Oils; Report No. NREL/ SR-570-27613; National Renewable Energy Laboratory: Golden, CO, 2000; <http://www.osti.gov/bridge>.
14. Agblevor, F.A.; Besler, S.; and Evans, R.J. (1995) "Influence of Inorganic Compounds on Char Formation and Quality of Fast Pyrolysis Oils," abstracts of the ACS 209th National Meeting, Anaheim, CA, April 2-5.
15. Sipila, K.; Kuoppala, E.; Fagemas, L.; Oasmaa, A., Characterization of biomassbased flash pyrolysis oils. *Biomass and Bioenergy* 1998, 14, (2), 103-113.
16. Oasmaa, A.; Elliott, D. C.; Korhonen, J., Acidity of Biomass Fast Pyrolysis Biooils. *Energy & Fuels* 2010, 24, 6548-6554.
17. Kim, K.H., et al., Comparison of physicochemical features of biooils and biochars produced from various woody biomasses by fast pyrolysis. *Renewable Energy*, 2013. 50: p. 188-195.
18. Czernik, S.; Bridgwater, A. V., Overview of applications of biomass fast pyrolysis oil. *Energy & Fuels* 2004, 18, (2), 590-598.
19. Scholze, B. Long-term Stability, Catalytic Upgrading, and Application of Pyrolysis Oils - Improving the Properties of a Potential Substitute for Fossil Fuels. PhD thesis, University of Hamburg, 2002.
20. G.V.C. Peacocke, PhD Thesis, Aston University, 1994
21. Bridgwater, A.V., "Review of Fast Pyrolysis of Biomass and Product", *Biomass and Bioenergy*, 2012. 38 p. 68-94.
22. J.P. Diebold, In: A.V. Bridgwater and G. Grassi (Eds.), *Biomass Pyrolysis Liquid Upgrading and Utilization*, Elsevier, London, 1991, p. 341
23. Joseph, J., Rasmussen, M. J., Fecteau J. P., Kim, S., Lee, H., Tracy, K. A., Jensen, B. L., Frederick, B. G., Stemmler, E. A. (2016) Compositional changes to low water content bio-oils during aging: An NMR, GC/MS, and LC/MS Study. *Energ Fuels*. 30: 4825-4840.
24. Coverdell, A. A comprehensive look at the acid number test. *Mach. Lubr.* 2010, January; [http://www.machinerylubrication.com/article\\_detail.asp? articleid 1052](http://www.machinerylubrication.com/article_detail.asp?articleid 1052).
25. P.T. Williams, P.A. Horne, J. *Anal. Appl. Pyrolysis*, 31, 1995, p. 39
26. Carlson, T.; Tompsett, G.; Conner, W.; Huber, G., Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks. *Topics in Catalysis* 2009, 52, (3), 241-252.

27. Paasikallio, V.; Lindfors, C.; Kuoppala, E.; Solantausta, Y.; Oasmaa, A.; Lehto, J.; Lehtonen, J., Product quality and catalyst deactivation in a four day catalytic fast pyrolysis production run. *Green Chemistry* 2014, 16, (7), 3549-3559.
28. b- Case, P. A., Wheeler, M. C., Desisto, W. J. (2014) Effect of Residence Time and Hot Gas Filtration on the Physical and Chemical Properties of Pyrolysis Oil, *Energy Fuels* 28:3964-3969.
29. Baldwin, R. M.; Feik, C. J. Bio-oil stabilization and upgrading by hot gas filtration. *Energy & Fuels*, 2013, 27 (6), 3224-3238.
30. Hoekstra E, Hogendoorn KJ, Wang X, Westerhof RJ, Kersten SR, van Swaaij WP, et al. Fast pyrolysis of biomass in a fluidized bed reactor: in situ filtering of the vapors. *Ind Eng Chem Res* 2009; 48:4744–56.
31. a- Case, P. A., Wheeler, M. C., Desisto, W. J. (2014) Formate assisted pyrolysis of pine sawdust in-situ oxygen removal and stabilization of bio-oil. *Biores Technol.* 173:177-184.
32. Wang, Z.; Wang, F.; Cao, J.; Wang, J., Pyrolysis of pine wood in a slowly heating fixed-bed reactor: Potassium carbonate versus calcium hydroxide as a catalyst. *Fuel Processing Technology* 2010, 91, (8), 942-950.
33. Lin, Y. Y.; Zhang, C.; Zhang, M. C.; Zhang, J. A., Deoxygenation of Bio-oil during Pyrolysis of Biomass in the Presence of CaO in a Fluidized-Bed Reactor. *Energy & Fuels* 2010, 24, 5686-5695.
34. Carlson, T. R.; Cheng, Y. T.; Jae, J.; Huber, G. W., Production of green aromatics and olefins by catalytic fast pyrolysis of wood sawdust. *Energy & Environmental Science* 2011,4, (1), 145-161.
35. Brown, R.C., ed. *Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals, and Power.* ed. C.V. Stevens. 2011, John Wiley & Sons.
36. Elliott, D.C.; Baker, E.G. Upgrading Biomass Liquefaction Products through Hydrodeoxygenation. *Biotechnol. Bioeng. Symp.* 1984, suppl. 14, 159.
37. R. Prins. *Handbook of Heterogeneous Catalysis*, chapter 13.2: Hydrotreating, pages 2695\_2718. John Wiley & Sons, Inc.: New York, 2008.
38. J. Wildschut. *Pyrolysis Oil Upgrading to Transportation Fuels by Catalytic Hydrotreatment.* PhD thesis, Rijksuniversiteit Groningen, 2009.
39. E. G. Baker and D. C. Elliott, *Catalytic upgrading of biomass pyrolysis oils*, Elsevier Appl Sci Publ Ltd, Barking Essex, 1988, pp. 883–895.

40. a-Wildschut, J.; Mahfud, F. H.; Venderbosch, R. H.; Heeres, H. J., Hydrotreatment of Fast Pyrolysis Oil Using Heterogeneous Noble-Metal Catalysts. *Industrial & Engineering Chemistry Research* 2009, 48, (23), 10324-10334.
41. Jan Horacek; David Kubicka. Bio-oil hydrotreating over conventional CoMo & NiMo catalysts: The role of reaction conditions and additive. *Fuel*, Volume 198, 15 June 2017, Pages 49-57. <https://doi.org/10.1016/j.fuel.2016.10.003>.
42. Elliott, D. C. Historical development in hydroprocessing bio-oils. *Energy & Fuel*, 2007, 21, 1792-1815.
43. T.-R. Viljava\_, R.S. Komulainen, A.O.I. Krause. Effect of H<sub>2</sub>S on the stability of CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts during hydrodeoxygenation. *Catalysis today*. 2000, 60; 83-92.
44. B. Delmon, G.F. Froment, *Catal. Rev. Sci. Eng.* 38 (1996) 69.
45. Elliott DC, Hart TR, Neuenschwander GG, Rotness LJ, Olarte MV, Zacher AH, et al. Catalytic hydroprocessing of fast pyrolysis bio-oil from pine sawdust. *Energy Fuels*. 2012; 26:3891–6.
46. Yongxing Yang, Cristina Ochoa-Hernández, Víctor A. de la Pena O'Shea, Patricia Pizarro, Juan M. Coronado, David P. Serrano. Effect of metal–support interaction on the selective hydrodeoxygenation of anisole to aromatics over Ni-based catalysts. *Applied Catalysis B: Environmental* 145 (2014) 91– 100.
47. Shaohua Jin, Zihui Xiao, Chuang Li, Xiao Chen, Lei Wang, Jiacheng Xing, Wenzhen Li, Changhai Liang. Catalytic hydrodeoxygenation of anisole as lignin model compound over supported nickel catalysts. *Catalysis Today* 234 (2014) 125–132.
48. Binh M. Q. Phan • Quan L. M. Ha • Nguyen P. Le • Phuong T. Ngo • Thu H. Nguyen • Tung T. Dang • Luong H. Nguyen • Duc A. Nguyen • Loc C. Luu. Influences of Various Supports,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and SBA-15 on HDO Performance of NiMo Catalyst. *Catal Lett* (2015) 145:662–667. 10.1007/s10562-014-1412-4.
49. a-A.R. Ardiyanti, S.A. Khromova, R.H. Venderbosch, V.A. Yakovlev, H.J. Heeres. Catalytic hydrotreatment of fast-pyrolysis oil using non-sulfided bimetallic Ni-Cu catalysts on a  $\delta$ -Al<sub>2</sub>O<sub>3</sub> support. *Applied Catalysis B: Environmental* 117– 118 (2012) 105– 117.
50. b-Ardiyanti, A. R.; Khromova, S. A.; Venderbosch, R. H.; Yakovlev, V. A.; Melian-Cabrera, I. V.; Heeres, H. J., Catalytic hydrotreatment of fast pyrolysis oil using bimetallic Ni-Cu catalysts on various supports. *Applied Catalysis a-General* 2012, 449, 121-130.



51. Leng S, Wang X, He X, Liu L, Liu Y, Zhong X, et al. Ni Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: a universal catalyst for the hydrodeoxygenation of bio-oil and its model compounds. *Catalysis Communications* 2013; 41 :34–7.
52. Scott J. Eaton, Sedat H. Beis, Sampath A. Karunarathne, Hemant P. Pendse, and M. Clayton Wheeler. Hydroprocessing of Biorenewable Thermal Deoxygenation Oils. *Energy and Fuels* Volume: 29 Issue: 5 Pages: 3224-3232
53. a-D. C. Elliott, T. R. Hart, G. G. Neuenschwander, L. J. Rotness and A. H. Zacher, Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products, *Environ. Prog. Sustain. Energy*, 2009, 28(3), 441–449.
54. S. Cheng, et al., In situ hydrodeoxygenation upgrading of pine sawdust bio-oil to hydrocarbon biofuel using Pd/ C catalyst, *Journal of the Energy Institute* (2017), <http://dx.doi.org/10.1016/j.joei.2017.01.004>
55. b-Wildschut, J.; Arentz, J.; Rasrendra, C. B.; Venderbosch, R. H.; Heeres, H. J., Catalytic Hydrotreatment of Fast Pyrolysis Oil: Model Studies on Reaction Pathways for the Carbohydrate Fraction. *Environmental Progress & Sustainable Energy* 2009, 28 (3), 450-460.
56. b-Elliott DC, Hart TR. Catalytic hydroprocessing of chemical models for bio-oil. *Energy Fuels* 2009; 23:631–7.
57. Aimaro Sanna, Tushar P. Vispute, George W. Huber. Hydrodeoxygenation of the aqueous fraction of bio-oil with Ru/C and Pt/C catalysts. *Applied Catalysis B: Environmental* 165 (2015) 446–456.
58. Wildschut J, Muhammad I, Mahfud F, Melian Cabrera I, Venderbosch RH, Heeres E. Insights in the hydrotreatment of fast pyrolysis oil using a ruthenium on carbon catalyst. *Energy & Environmental Science* 2010; 3:962–70.
59. A. Gutierrez, R.K. Kaila, M.L. Honkela, R. Slioor, A.O.I. Krause. Hydrodeoxygenation of guaiacol on noble metal catalysts. *Catalysis Today* 147 (2009) 239–246.
60. A.R. Ardiyanti, A. Gutierrez, M.L. Honkela, A.O.I. Krause, H.J. Heeres. Hydrotreatment of wood-based pyrolysis oil using zirconia-supported monoand bimetallic (Pt, Pd, Rh) catalysts. *Applied Catalysis A: General* 407 (2011) 56– 66.
61. J. D. Adjaye and N. N. Bakhshi. Upgrading of a wood-derived oil over various catalysts. *Biomass and Bioenergy* Vol. 7, No. 1-6, pp. 201-211, 1994.
62. H.Y. Zhao, D. Li, P. Bui, S.T. Oyama. Hydrodeoxygenation of guaiacol as model compound for pyrolysis oil on transition metal phosphide hydroprocessing catalysts. *Applied Catalysis A: General* 391 (2011) 305–310.

63. Mortensen, P.M.; Grunwaldt, J.-D.; Jensen, P.A.; Jensen, A.D. Screening of catalysts for hydrodeoxygenation of phenol as a model compound for bio-oil. *ACS Catal.* 2013, 3, 1774–1785.
64. Bui, P.; Cecilia, J.A.; Oyama, S.T.; Takagaki, A.; Infantes-Molina, A.; Zhao, H.; Li, D.; Rodríguez-Castellón, E.; López, A.J. Studies of the synthesis of transition metal phosphides and their activity in the hydrodeoxygenation of a biofuel model compound. *J. Catal.* 2012, 294, 184–198.
65. Echeandia, S.; Ariasa, P. L.; Barriola, V. L.; Pawelec, B.; Fierrob, J. L. G. Synergy effect in the HDO of phenol over Ni–W catalysts supported on active carbon: Effect of tungsten precursors. *Applied Catalysis B: Environmental.* 2010, 101, 1–12.
66. Edward Furimsky, Franklin E. Massoth. Deactivation of hydroprocessing catalysts. *Catalysis Today* 52 (1999) 381-495.
67. Mortensen, P. M.; Grunwaldt, J. D.; Jensen, P. A.; Knudsen, K. G.; Jensen, A. D., A review of catalytic upgrading of bio-oil to engine fuels. *Applied Catalysis A: General* 2011, 407, (1-2), 1-19.
68. Case, P. A. (2015) Fundamentals of pyrolysis of pretreated biomass (Doctoral dissertation). Retrieved from Fogler Library Digital Commons <http://digitalcommons.library.umaine.edu/cgi/viewcontent.cgi?article=3369&context=td>
69. DeSisto, W. J., Hill, N., Beis, S. H., Mukkamala, S., Joseph, J., Baker, C., Ong, T. H., Stemmler, E. A., Wheeler, M. C., Frederick, B. G., van Heiningen, A. (2010) Fast Pyrolysis of Pine Sawdust in a Fluidized-Bed Reactor. *Energ Fuels.* 24:2642-2651.
70. Demirbas, A., Relationships proximate analysis results and higher heating values of lignites. *Energy Sources Part A-Recovery Utilization and Environmental Effects* 2008,30, (20), 1876-1883.

## APPENDIX A. ELEMENTAL ANALYSIS OF BIO-OILS

The Flash 2000 Elemental Analyzer is used for the determination of carbon, hydrogen, nitrogen, sulfur and oxygen in liquids. Flash 2000 Elemental Analyzer with Mas 200R autosampler is shown in Figure A.1.

Catalyst-packed quartz tubes should be cleaned every 50-80 analyses and must be replaced every 150-250 analyses. The moisture trap should be checked when the quartz tubes are replaced or cleaned. Manufacturer's instrument manual (saved on Desktop > folder "CHNSO Documents > Flash 2000 Operating manual") should be checked for more information regarding these components.

1. Required PPE (goggles, gloves, lab coat)
2. To open the software, go to:
  - a. Desktop > Click on EagerXperience software > Open the CHNO analyzer
3. To remove the standby, click on:
  - a. Edit > Edit elemental analyzer parameters > Clear the standby box > Send
  - b. This should set the appropriate flow rates and temperatures for the desired analysis
4. To check the leak test, click on:
  - a. View > View elemental analyzer status > Click on "special functions" tab > Leak test
  - b. Start > yes to perform autozero > New window will pop-up
  - c. The test should take 90 seconds and both flow rates should be less than 5 ml/min in order to complete your analysis
  - d. Stop > Done
5. To edit the sample table, click on:
  - a. Edit > Sample table > Enter the names of your samples

- b. Enter the weights for your samples by click on the green arrow in the weight cell to receive the weights from the balance

6. To prepare the samples:

- a. Wipe and rinse the sample preparation surface, Spatula, Microbalance plate, Capsule sealing and Forceps using Acetone
- b. Standard checks should be run before running your samples:
  - i. From sample type, chose unknown
  - ii. For pyrolysis oils obtained from fast pyrolysis, BBOT standards should be used
  - iii. For oils obtained from hydrotreating experiments, Lubricant oil standards should be used
  - iv. The C, H, N contents of BBOT standards should come in the expected ranges as below:

|            |              |
|------------|--------------|
| Carbon %   | 71.79-73.25% |
| Hydrogen % | 6.03-6.151%  |
| Nitrogen % | 6.445-6.575% |

Table A. 1 C, H, N contents of BBOT standard.

- v. The C, H, N contents of lubricant oil standards should come in the expected ranges as below:

|            |              |
|------------|--------------|
| Carbon %   | 81.25-82.9%  |
| Hydrogen % | 13.48-13.76% |
| Nitrogen % | 1.079-1.101% |

Table A. 2 C, H, N contents of Lubricant standard.

- c. Prepare bio-oil samples for analysis:
- i. Turn on the Helium gas flow to 50 ml/min
  - ii. Place an empty capsule on the balance
  - iii. Close the balance door by waving your hand on the right side of the balance display screen
  - iv. Wait until the weight is stabilized by disappearing the black circle > Press –T– button to zero the capsule weight
  - v. remove the capsule from the balance using forceps
  - vi. In the capsule adds between 1-2 mg of each sample, using spatula for pyrolysis oils obtained from fast pyrolysis because they are too viscous
  - vii. In the capsule adds between 1-2 mg of each sample, using syringes for oils obtained from hydrotreatments experiments because they are less viscous
  - viii. Put the capsule back on the balance to make sure that it is in the target weight
  - ix. Remove the capsule form the balance and put it in the capsule sealing device
  - x. Allow sample to purge with helium inside capsule sealing device for 30-60 seconds > Seal capsule using sealing device
  - xi. Remove the capsule after sealing and put it back in the balance
  - xii. Close the balance door
  - xiii. wave your hand over the left side of the balance display screen, the weight of your sample after that will pop-up in the weight cell in the sample table
  - xiv. The row that says “Act” in the sample table is the first sample that will be run in the sequence

- xv. Insert a blank row into the sample table after the last sample in the sequence by hitting “shift” + “insert” at the same time
  - i. Hold the capsule and put it in the first autosampler position available
  - ii. Any capsule fall on the ground, throw it away in the trash
  - iii. Click start to start run
  - iv. Each bio-oil sample should be run in at least triplicate
  - v. 360 seconds is the approximate time to analyze each sample of pyrolysis oils
  - vi. 720 seconds is the approximate time to analyze each sample of hydrotreated oils
  - vii. Results of the analysis can be viewed by clicking on the “summarize results” button



Figure A. 1 Flash 2000 Elemental Analyzer with Mas 200R autosampler.

## **APPENDIX B. PREPARATION OF BIO-OIL SAMPLES FOR QUANTITATIVE GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS) ANALYSIS**

This instrument is used to qualify and quantify the presence and concentration of compounds present in liquid bio-oils obtained from different techniques. Gas Chromatography-Mass Spectrometry (GC-MS) is shown in Figure B.1

### **Before starting:**

1. Required PPE (goggles, chemical resistance gloves, lab coat)
2. Check the ethyl acetate solution that uses as a solvent. It is the first vial from the right of the auto-sampler
3. Make sure that vial uses to receive discharged solutions is empty. It is the second vial from the right of the auto-sampler
4. Materials should be prepared to start: 5 mL vials, compatible GC vials and caps, Micropipettes + pipette tips or wire trols, spatula, Ethyl Acetate (solvent), Bio-oil samples

### **Preparation of bio-oil samples:**

1. Add the following to a 2mL GC vial:
2. 200  $\mu$ L bio-oil solution
3. 1.6 mL Ethyl Acetate
4. Cap the vial and shake to mix well before placing vials on the auto-sampler for analysis

### **Procedure for analysis:**

1. Open the real time analysis window
2. Go to File
3. Open
4. Method file
5. Choose your method file
6. Open
7. Click on Acquisition that located on the main menu bar
8. Download > Download initial parameters
9. It takes 30 minutes to reach the desired temperature, 250 °C
10. While waiting for the desired temperature, click on Batch processing button located on the left side of the instrument screen
11. Fill your samples information in the table
12. The sample name, sample ID, and Data file should be the same
13. You have to change the method file and others into your desired information
14. After filling the sample table, click on:
  - a. File
  - b. Save Batch file as
  - c. Put your desired name and location
15. Put your sample by order in the auto-sampler
16. Click on set button on the instrument screen
17. Click start on the left side of the instrument screen to start run
18. The total run time for one sample is approximately 45 min



### **Display results:**

1. Go to Postrun analysis window
2. File > Open data file
3. Find your sample name > Open
4. We can go through sample peaks and use the tools provide inside
5. On results window, zoom in from plus sign located on the right of the results window
6. Go back by right click inside the results window, then click undo zoom
7. Right-click then click on initial zoom to go to the original zoom
8. Double click in the center of the peak. Right-click and choose similarity search to show the compound name, Mw, formula and structure

### **Compare between results:**

1. Go to Postrun analysis window
2. Click on Data Comparison located on the left side of the instrument screen
3. Click on File > Open data file
4. Find your sample name > Open
5. We can go through samples peaks and use the tools provide inside to compare
6. On results window
7. Zoom in from plus sign located on the right of the results window
8. Go back by right click inside the results window, then click undo zoom
9. Right-click then click on initial zoom to go to the original zoom
10. Double click in the center of the peak. Right-click and choose similarity search to show the compound name, Mw, formula and structure

**To get the peak area:**

1. Open Postrun analysis window
2. Zoom in the peak and let the beginning and the end of the peak appear
3. Click on the integrate icon from the special menu which is below the main menu bar
4. Click on the beginning of the peak
5. Continue placing the mouse without remove your hand until reaching the end of the peak, then click on the end of the peak
6. Now you get two vertical lines, one on the beginning and the other on the end of the peak
7. Go to the left side and click qualitative button
8. The area will appear on the top of the peak in the results window

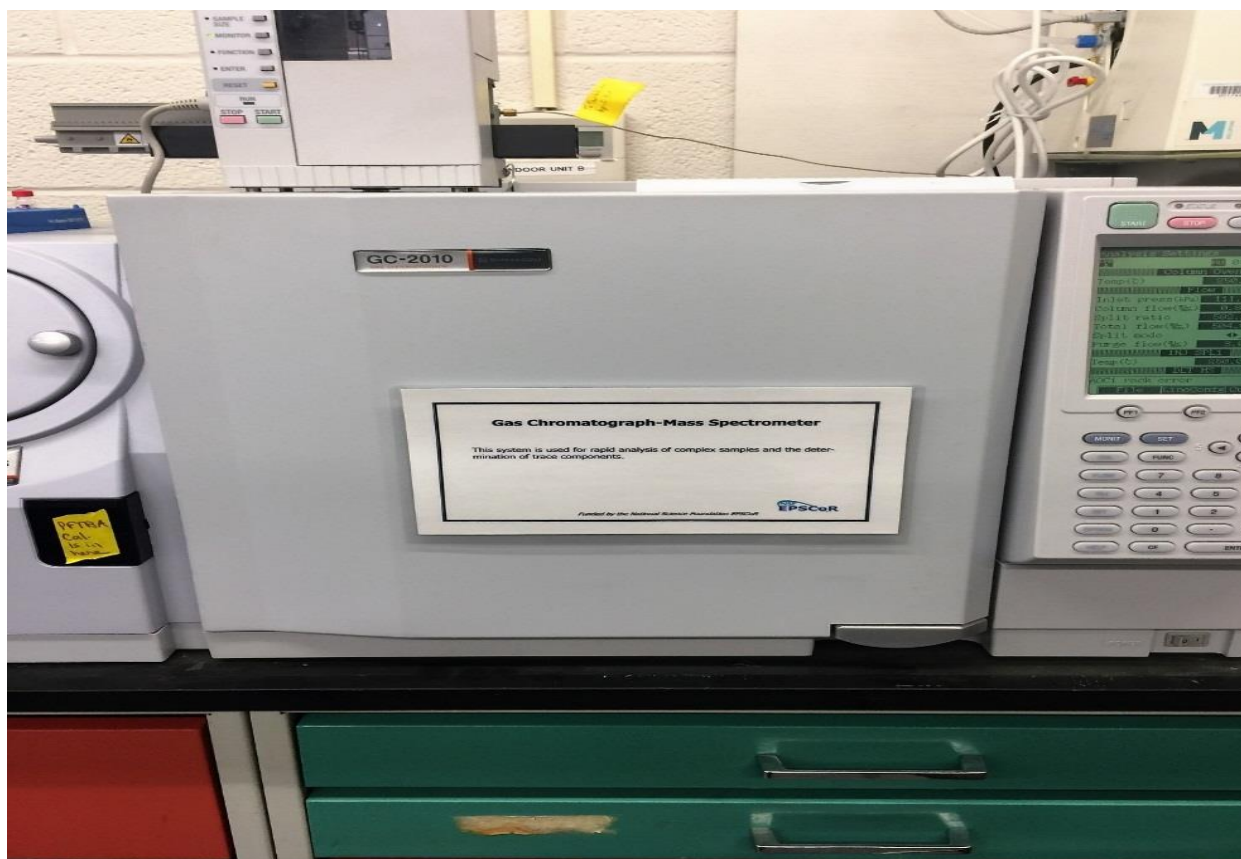


Figure B. 1 Gas Chromatography-Mass Spectrometry (GC-MS).

**APPENDIX C. GAS SAMPLE ANALYSIS USING SRI'S MULTIPLE GAS  
ANALYZER**

**Gas analyzer is equipped with:**

1. TCD detector
2. FID-Methanizer
3. Two packed columns
4. 10-port gas sampling valve and loop
5. Air compressor
6. 4 or 6 channel PeakSimple Data system
7. Columns: a 2-meter Molecular Sieve 13X and a 2-meter Silica gel (HayeSep-D Column)

**Procedure:**

1. Turn the laptop on
2. open Peak435-32bit program
3. Turn on both carrier (He) and Hydrogen gas flow
4. Helium and Hydrogen flow should be at pressure of 40 psi
5. Turn the instrument on
6. Insert the temperature into the program by Right click on channel 1 > Temperature > Add  
the numbers listed below > OK

| Initial Temp | Hold | Ramp | Final Temp |
|--------------|------|------|------------|
| 36           | 16   | 0    | 36         |

Table C. 1 Temperature programming.

7. Insert the events into the program by Right click on channel 1 > Events > Add the numbers listed below > OK

| Time  | Event    |
|-------|----------|
| 0.000 | ZERO     |
| 0.000 | B ON ()  |
| 0.050 | G ON ()  |
| 8.500 | A ON ()  |
| 8.500 | B OFF () |

Table C. 2 Events programming.

8. If there is a water droplet coming out of the small tube on the side of the GC, FID-Methanizer is working
9. In the back of the GC, there are 6 lights that should be green. Carrier 1(helium 1), carrier 2 (helium 2), hydrogen 1, hydrogen 2, air 1, air 2
10. Wait for 30 min. for the instrument to come to steady temperature before injecting calibration gas samples
11. The Standard Scott gas mixture used as calibration gas was purchased from Sigma Aldrich (Product #A0905360, Cat. No. 23462)

| Component       | Gas concentration in moles (%) |
|-----------------|--------------------------------|
| Acetylene       | 1.01                           |
| Carbon Dioxide  | 1.00                           |
| Carbon monoxide | 1.00                           |
| Ethane          | 1.01                           |
| Ethylene        | 1.01                           |
| Methane         | 1.01                           |
| Nitrogen        | 93.6                           |

Table C. 3 Concentrations of gases used as standards.

A system overview of the Multiple gas analyzer is shown in Figure C.1

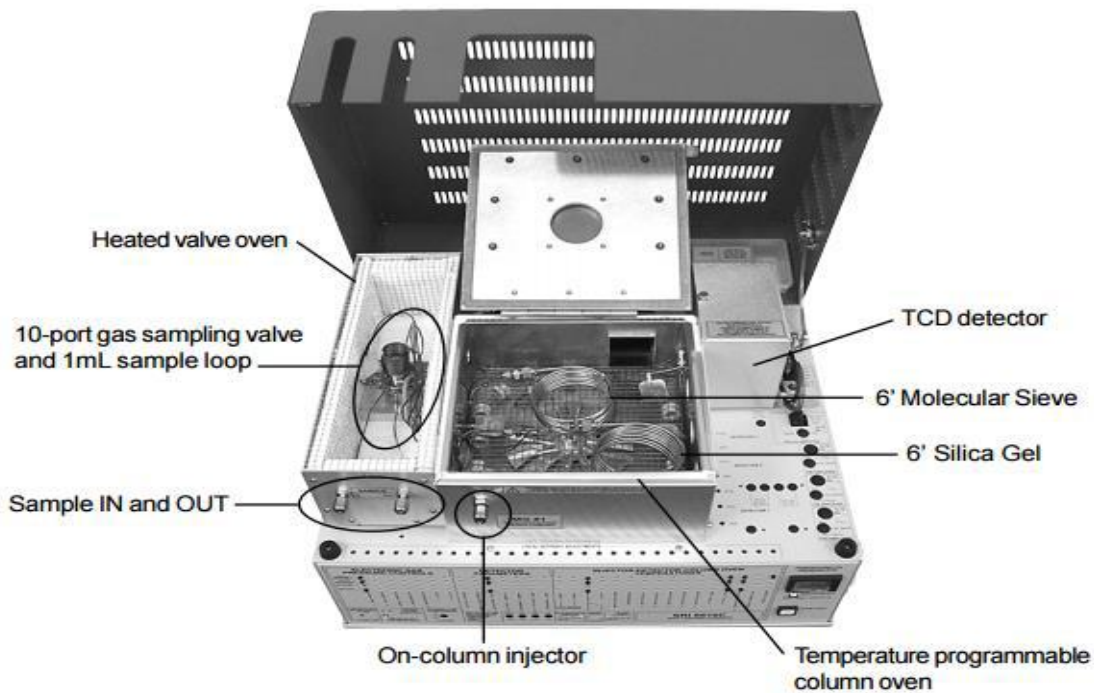


Figure C. 1 SRI's gas analyzer #1 system overview.

## APPENDIX D. KARL-FISHER TITRATION FOR BIO-OILS FRACTIONS

### **Before starting:**

1. Required PPE (goggles, chemical resistance gloves, lab coat)
2. Make sure that all tubes are connected to the Composite (solvent) that you will use
3. If your sample contains high water content, then use Composite 5
4. If your sample contains low water content, then use Composite 2
5. Clean the syringe very well
6. Discharge the old solution from the waste bottle as follows:
  - a. Click the stop icon on the top left of the instrument screen
  - b. Discharge the old solution by press on the right button located below the glass vessel
  - c. Fill the glass vessel with a new solution by press on the left button located below the glass vessel. Make sure that the added solution covers the magnetic stirrer
7. Make sure also that you have enough Composite for whatever samples you use

### **If you are using the Composite for the first time, then you must do standards as follows:**

1. Open the program icon which is tiamo 1.2
2. Take a small tube of standard water > Fill the syringe with it and remove the air > Put the syringe on the scale
3. Go to the left side of the instrument screen. Click Method – File – Open
4. Select the method which is “KF Titer with water std 2” or “KF Titer with water std 5” based on the Composite used
5. Go to program workplace fill > On the sample ID put determination 1 titer value > On certified water content put 10 > On sample size put 1.0 gm for both sides
6. Click start and wait until conditioning be ok

7. Record the weight of the syringe first
8. Click start again > Inject one ml of the water standard in the glass vessel quickly
9. Put the syringe back on the weight > Record the new weight after injection
10. Subtract the two weights and put the number in the square window that will appear after clicking the start icon > Click Enter from the keyboard
11. Wait until finishing the sequence and the conditioning be ok
12. Before each injection, click start located in top left of the instrument screen
13. Inject again and subtract the two weights “before and after the injection”
14. Do it three times
15. After the third time and when the conditioning be ok, click stop
16. Check the results which should be all within the standard value

**Preparation and analysis of standard solution:**

1. Go to Method – File – Open > click on “KF Sample with composite 2” or “KF Sample with composite 5” based on the Composite used
2. Go to program workplace fill > On sample ID put water standard 10mg/g (1%)
3. On sample size put 1.0 g for both sides
4. Take a small tube of standard water > Fill the syringe with it and remove the air
5. Put the syringe on the scale
6. Click start and wait until conditioning be ok > Record the weight of the syringe first
7. Click start again > Inject one ml of the water standard in the glass vessel quickly
8. Put the syringe back on the weight > Record the new weight after injection
9. Subtract the two weights and put the number in the square window that will appear after clicking the start icon > Click Enter from the keyboard

10. Wait until finishing the sequence and the conditioning be ok
11. Before each injection, click start located in top left of the instrument screen
12. Inject again and subtract the two weights “before and after the injection”
13. Do it three times
14. After the third time and when the conditioning be ok, click stop > Check the results:
  - a. Go to left side of the instrument screen and click on the Database icon
  - b. The injections results should be all within the expected standard value

**Preparation and analysis of Bio-oil samples:**

1. Take a small amount of your sample and put it in the syringe to clean the syringe first, then discharge it, after that put 3 ml of your oil in the syringe for 3 injections
2. For any sample (bio-oil for example) repeat the points from 1 to 14 above with replacing water with bio-oil



Figure D. 1 Karl-Fisher Titration.



## **BIOGRAPHY OF THE AUTHOR**

Mubarak M. Khlewee was born in Dhi Qar, Iraq. He graduated from Al Markaziyah High School in Dhi Qar in June 2006. In June 2011, he graduated from Southern Technical University (Engineering Technical College) in Basra with a Bachelor of Science degree in Fuel and Energy Engineering. After graduation, he worked for the geophysical company BGP, which specializes in seismic surveys, for one year as a supervisor engineer. He is currently employed by the Dhi Qar oil company in Iraq in the production division as an oil production engineer where he has worked since 2012. Mubarak is working on an article that is in preparation. He enrolled in the Chemical Engineering graduate program at the University of Maine in January 2016. Mubarak is a candidate for the Master of Science degree in Chemical Engineering from the University of Maine in December 2017.