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Sathish Kumar Tanneru

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Novel pretreatment methods to improve the properties of pyrolysis oil followed by production of biofuels

By

Sathish Kumar Tanneru

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Novel pretreatment methods to improve the properties of pyrolysis oil followed by production of biofuels

By

Sathish Kumar Tanneru

Approved:

Philip H. Steele
(Major Professor)

Todd E. Mlsna
(Minor Professor)

Abdolhamid Borazjani
(Committee Member/Graduate Coordinator)

Leonard L. Ingram, Jr.
(Committee Member)

Fei Yu
(Committee Member)

George Hopper
Dean
College of Forest Resources

Name: Sathish Kumar Tanneru

Date of Degree: August 15, 2014

Institution: Mississippi State University

Major Field: Forest Resources

Major Professor: Dr. Philip H. Steele

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Candidate for Degree of Doctor of Philosophy

Production of renewable fuels is of growing interest due to the ongoing concerns associated with combustion of fossil fuel contributing to global warming. Biomass-derived bio-oil is a potential alternative replacement for conventional fuels. But negative properties such as lower energy density, higher water content and acidity prevent the direct use of bio-oil as a fuel. It is universally agreed that for production of a viable fuel bio-oils must be significantly upgraded. Present upgrading techniques, such as hydrodeoxygenation and esterification consume high amounts of expensive hydrogen or large volumes of alcohols, respectively. Production of low yields continues to be a challenge for hydrodeoxygenation. Therefore, development of more efficient upgrading methods would be desirable.

The current research was divided into two parts: in the first part the raw bio-oil was pretreated prior to upgrading to reduce coke formation and catalyst deactivation during upgrading. In the second part pretreated bio-oils were further upgraded by several techniques.

The second chapter describes application of an olefination process to raw bio-oil to produce a boiler fuel. In the third chapter, raw bio-oil was pretreated by novel oxidation pretreatment to convert bio-oil aldehydes to carboxylic acids. Aldehydes lead to coke formation and their conversion to carboxylic acids circumvents this issue. Following oxidation pretreatment to raw bio-oil acid anhydride pretreatment was applied to reduce water content which leads to catalyst deactivation during upgrading. The fourth chapter tests esterification of pretreated bio-oil by oxidation to produce boiler fuel with relatively high HHV. The fifth chapter discusses hydrodeoxygenation of oxidized bio-oil produced by oxidation to increase hydrocarbons yield and reduced charring during hydrodeoxygenation. The sixth chapter describes application of catalytic deoxygenation of pretreated bio-oil by oxidation in the presence of pressurized syngas to produce a liquid hydrocarbon mixture. In the seventh chapter we tested direct hydrocracking of pretreated bi-oil by oxidation to produce a liquid hydrocarbon mixture.

The end products were analyzed by following the ASTM methods for HHV, water content, viscosity, density, acid value, elemental analysis. Best performing fuels based on high HHV and low acid value were analyzed by FTIR, GC-MS, DHA, ^{1}HNMR and simulated distillation.

DEDICATION

I would like to dedicate this work and achievement to my lovely parents Bhumaiah Tanneru and Lakshmi Tanneru, my dear brother Shyamkumar Tanneru and my dearest family members for their love, support and motivation during the doctoral program of study and throughout my life.

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RBO	Raw bio-oil
BGY	Billion gallons per year
U.S.	United States
EIA	Energy Information Association
ASTM	American Society for Testing and Materials
HHV	higher heating value
AV	Acid value
RCOOH	Carboxylic acid
RCHO	Aldehyde
OOF	Olefinated organic fraction produced from raw bio-oil
APOP	Consecutive oxidation and butyric acid anhydride - pretreated product
SOAPRBO	Simultaneous oxidation and butyric acid anhydride - pretreated raw bio-oil
DAPRBO	Direct butyric acid anhydride pretreated raw bio-oil
BF1	Boiler fuel produced from raw bio-oil
BF2	Boiler fuel produced from oxidized product
HDO	Hydrodeoxygenation

OP-HTP	Hydrotreated product produced from oxidized product
RBO-HTP	Hydrotreated product produced from raw bio-oil
CDO	Catalytic deoxygenation
WGS	Water gas shift reaction
CH_4	Methane
CO	Carbon monoxide
H_2O	Water
NOx	Nitrogen oxides
SOx	Sulfur oxides
C_2H_6	Ethane
H_2	Hydrogen
CO_2	Carbon dioxide
KOH	Potassium hydroxide
LHM	Liquid hydrocarbon mixture produced from oxidized product
LHM-RBO	Liquid hydrocarbon mixture produced from raw bio-oil
GC-MS	Gas chromatography mass spectroscopy
GC	Gas chromatography
FTIR	Fourier transform infrared spectroscopy
DHA	Detailed hydrocarbon analysis
^{1}H-NMR	Proton nuclear magnetic resonance spectroscopy

TGA	Thermo gravimetric analysis
MJ/kg	Mega joules per kilogram
Psig	Pounds per square inch
mg	Milligram

CHAPTER I

INTRODUCTION

1.1 Introduction

Increasing energy demand and the approach of peak production of petroleum supply have led the world to search for renewable, sustainable and environmentally benign alternative fuels. According to the Renewable Fuels Standard the present use of renewable fuels is 14 billion gallons per year (BGY) and this is projected to increase to 36 BGY by 2022 [25]. Woody biomass is one of the most important renewable energy resources for the production of sustainable liquid fuels [35]. Biomass as a renewable energy source will reduce dependency on conventional fuels and provides significant environmental advantages over fossil fuels. It is greenhouse gas neutral because the CO_2 emitted from the bio-fuels from which it is produced is recycled by photosynthesis [16, 21]. The availability of biomass in the world is 220 billion dry tons per year and is the world's largest and most sustainable energy resource [1]. The present U.S. biomass consumption is 4 quads and is projected to reach 9 quads in 2035 [29]. These advantages make biomass a potential alternative energy source for fossil fuels.

Biomass can be converted into liquid fuels through both thermochemical and biological methods [2]. One of the thermal decomposition methods is fast pyrolysis of lignocellulosic biomass to produce pyrolysis oil that is frequently referred to as bio-oil. Bio-oil conversion to fuels is a potential promising replacement for fossil fuels.

Advantages of liquid bio-oil are the ease of transportation and storage. Production of biomass to bio-oil liquids can reduce the bulk of biomass to 60-70% of the dry weight of biomass. In the case of pine wood, to which the weight of water is often equal or exceeds 100% of the dry weight, the reduction in transportation weight is up to 30-35% of the dry biomass weight. This provides a distinct transportation cost advantage for production of raw bio-oils near the resource with final transportation of liquid bio-oil to conversion facilities [4, 5, 17, 19, 24, 36]. Fast pyrolysis has the potential to convert any biomass type to a liquid fuel. Fast pyrolysis refers to thermal decomposition of biomass in the absence of oxygen at moderate temperatures in the range of 400-650 ^{o}C to produce liquid products of 60-75%, char 15-25% and gases 10-20% dry wt%. Bio-oil is a dark brown and free-flowing miscible mixture of polar organics (70-80 wt%) and water (20-30 wt%). As a fuel, biomass derived bio-oil has environmental advantages when compared to fossil fuels because, on combustion, bio-oil produces half of the NO_x and negligible quantities of SO_x emissions and it is CO_2 neutral when compared to conventional fuels [23, 30]. Direct utilization of raw bio-oil is limited because of its negative physical and chemical properties such as high acidity, high moisture content, low energy density, immiscibility with petroleum products, and polymerization resulting in increased viscosity upon exposure to heat or during long-term storage. The bio-oil contains many reactive species which contribute to unusual attributes. Chemically, bio-oil is a complex mixture of water (15-30%), carboxylic acids (10-25%), aldehydes (10-15%), ketones (1-5%), alcohols (2-5%), sugars (5-15%), phenols (5-10%), furans and pyrans (1-5%) and 10% miscellaneous compounds [5, 12, 15, 24]. It is now universally agreed that bio-oil must be significantly upgraded prior to its use in internal combustion engines [3, 7].

The instability of biomass derived bio-oil is due to the presence of various oxygenated compounds present in the raw bio-oil. It is well known that aldehydes can undergo homo-polymerization, acetalization and oligomerization by reacting with phenols which leads to polymerization that produces high molecular weight thermoplastic resins. Therefore, it is considered that aldehydes may greatly affect the properties of bio-oil mainly in storage, thermal stability and viscosity [8, 11, 33]. Water is the main component (25-35%) of bio-oil and affects the energy density, end-product yields, and causes catalyst deactivation problems in many current bio-oil conversion processes [13, 18, 31]. Most of the research studies on present upgrading technologies such as hydrodeoxygenation (HDO) [11, 14, 37,] and esterification [26, 34] report that these counter-productive polymerization reactions that occur during the upgrading process are a major problem that results in coke formation and low product yields. Therefore, there remains a need to improve both the physical and chemical properties of biomass derived bio-oil. In our current study both oxidation and acid anhydride novel pretreatment methods were developed and tested to improve the efficacy of the upgraded methods.

It has been demonstrated that esterification via alcohol addition will produce a boiler fuel quality product with higher heating value (HHV) of approximately 27-31 MJ/kg. To date researchers have focused on the development of catalysts and with little elucidation of methods to increase energy density via increasing the length of the carbon chain [22, 26, 34]. There is a need to develop more efficient esterification methods and catalysts to reduce excess use of alcohols and to increase the HHV of the esterified product.

Olefination of bio-oil is also a method to produce a boiler fuel [27]. The addition of olefins to the pretreated bio-oil with alcohols as a co-solvent in the presence of a solid acid catalyst produces a highly combustible, low water content and stable oxygen-containing organic fuel where oxygen is not fully removed [6, 38]. Researchers performed their experiments at a micro scale with a high percentage of alcohol and reaction time was relatively long at 3 h. The objective of our current study is to produce a higher-energy olefinated bio-oil useable as boiler fuel with higher HHV and lower acid value with a shorter reaction time than attained by previous researchers.

HDO is a potential upgrading process for reducing heavy molecules into lighter hydrocarbons through the catalytic addition of hydrogen [9]. HDO of bio-oil has been demonstrated to reduce the oxygen content of bio-oil and produces a liquid hydrocarbon mixture that can be utilized as a transportation fuel. HDO of bio-oil with pure pressurized hydrogen in the presence of suitable catalysts has been demonstrated to reduce the oxygen content of bio-oil and produces a liquid hydrocarbon mixture that can be utilized as a transportation fuel. In general, HDO can be performed in one, two, or more steps. It has become traditional to hydroprocess fast pyrolysis oil by an initial 1st-stage hydrotreating step at mild temperatures (200-400 °C) to prevent bio-oil polymerization; typical hydrogen pressure applied for this 1st-stage ranges from 4 to 10 MPa in the presence of a heterogeneous hydrotreating catalyst. In the 2nd stage, a hydrocracking step is performed at more severe temperatures (300-500 °C) and also at high pressure ranges from 10 to 20 MPa in the presence of a heterogeneous hydrocracking catalyst [10, 20, 28, 32, 33].

However, HDO requires a large volume of expensive hydrogen to deoxygenate the bio-oil. In addition, practitioners continue to encounter coke formation and catalyst deactivation as major problems in present bio-oil hydroprocessing processes. Therefore, there is a need to upgrade bio-oil to a fuel by additional methods. New methods may solve the problems encountered during hydroprocessing. In the current research various deoxygenation methods were developed and applied to produce transportation range equivalent hydrocarbons. A study was tested the hydrodeoxygenation of the oxidized bio-oil to produce liquid hydrocarbons using lower amount of hydrogen compared to the current HDO hydrogen consumption by following the traditional two-stage HDO method. In another study, we tested a novel catalytic deoxygenation (CDO) process as an alternative to conventional HDO to produce a quality transportation fuel. In this study the oxidized bio-oil was deoxygenated to liquid hydrocarbons using syngas produced from biomass instead of 100% pure hydrogen to conserve the hydrogen. In our final study, direct hydrocracking of the oxidized bio-oil was tested by eliminating the hydrotreating step from a traditional two-stage HDO to reduce the consumption of the hydrogen during the hydroprocessing.

1.2 Objective

The goal of this research was to produce boiler and transportation fuels by a method that utilizes low volumes of alcohols and hydrogen. A sub-objective is to develop and apply novel bio-oil oxidation and acid anhydride pretreatment methods that greatly increase bio-oil carboxylic acids content and minimize the bound water content of bio-oil.

1.3 References

1. Anon. Survey of energy resources. World energy council, 20th Edition, Elsevier Ltd, Oxford. 2004.

2. Andre, F. Modern biomass conversion technologies. Mitigation and Adaptation Strategies for Global Change. 11, 343–375, 2006.

3. Bridgwater, A.V. Production of high grade fuels and chemicals from catalytic pyrolysis of biomass. Catalysis Today 29, 285-295, 1996.

4. Bridgwater, A.V., Meier, D., Radlein, D., 1999. An overview of fast pyrolysis of biomass. Org. Geochem. 30, 1479-1493.

5. Bandi, A., Baumgart, F., Bridgwater, A. V. Stirling Engine with Flox Burner Fuelled with Fast Pyrolysis Liquid. In Progress in Thermochemical Biomass Conversion. Blackwell Science: Oxford, 1459-1467, 2001.

6. Chatterjee S, Zhang Z, Pittman Jr CU. Acid-catalyzed olefination of bio-oil in the presence of ethanol. Biofuels 2013, 4, 3, 285-294.

7. Czernik, S., Bridgwater, A.V., 2004. Overview of applications of biomass fast pyrolysis oil. Energy Fuels. 18, 590-598.

8. Diebold, J. P. A review of the chemical and physical mechanisms of the storage stability of the fast pyrolysis bio-oils. NREL/SR-570-27613. January, 2000.

9. Elliott, D.C. Historical developments in hydroprocessing bio-oils. Energy & Fuels. 21, 1792-1815, 2007.

10. Elliott, D. C., Hart, T. R., Neuenschwander, G. G., Rotness, L., Olarte, M. V., Zacher, A. H., Solantausta, Y. Catalytic hydroprocessing of fast pyrolysis bio-oil from pine sawdust. Energy and Fuels, 26, 3891-3896, 2012.

11. Gagnon, J., Kaliaguine, S. Catalytic hydrotreatment of vacuum pyrolysis oil from wood, Industrial and Engineering Chemistry Research. 27, 1783-1788, 1988.

12. Girard, P., Blin, J., Bridgwater A.V., Boocock, D.G.G., Meier, D. An assessment of bio-oil toxicity for safe handling and transportation: toxicological and ecotoxicological tests. In: proceedings Science in Thermal and Chemical Biomass Conversion. CPL Press, Newbury, UK, 2005.

13. Guo, Z., Wang, S., Xu, G., Cai, Q. Upgrading of bio-oil molecular distillation fraction with solid acid catalyst. Bioresources 6, 3, 2539-2550, 2011.

14. Hu, Xun., Wang, D.M., Gunawan, R., Lievens, C., Chaiwat, W., Gholizadeh, M., Wu, L., Li, X., Li, C.Z. Polymerization on heating up of bio-oil: A model compound study. AICHE Journal. 2012.

15. Hu, X., Li, C., Xu, Y., Wang, Q. & Zhu, X. On the Thermal Oxidation Stability of Pyrolysis Biomass Oil. International Journal of Renewable Energy Technology. 2, 2, 2011.

16. Huber, G.W., Iborra, S., Corma, A., Synthesis of transportation fuels from biomass: Chem. Catal. Eng. Chem. Rev. 106, 4044–4098.

17. Ingram, L., Mohan, D., Bricka, M., Steele, P.H., Strobel, D., Crocker, D., Mitchell, B., Mohammad, J., Cantrell, K., Pittman, Jr., C.U., 2008. Pyrolysis of wood and bark in an auger reactor: physical properties and chemical analysis of the produced bio-oils. Energy Fuels. 22, 614-625.

18. Lin, W. R., Bartek, R. Removal of bound water from bio-oil. International patent. WO 2012/027428 A1March, 1st, 2012.

19. Maggi, R., Delmon, B. Comparison between 'slow' and 'flash' pyrolysis oils from biomass. 73, 5, 671-667, 1994.

20. McCall MJ, Brandvold TA, Elliott DC. Fuel and fuel blending components from biomass derived pyrolysis oil. US Pat 2012/8,329,969 B2.

21. Mckendry, P., 2002. Energy production from biomass (Part 1): Overview of biomass. Bioresour. Technol. 1, 37–46.

22. Moens, L., Black, S.K., Myers, M.D., Czernik, S. Study of neutralization and stabilization of a mixed hardwood oil, *Energy & Fuels*, **2009**, *23*, 2695-2699.

23. Mohan, D., Pittman, Jr., C.U., Steele, P.H., 2006. Pyrolysis of wood-biomass for bio-oil: a critical review. Energy Fuels. 20, 848-889.

24. Oasmaa, A., Elliott, D.C., Korhonen, J., 2010. Acidity of biomass fast pyrolysis bio-oils. Energy Fuels. 24, 6548-6554.

25. Perlack, R.D., Stokes, B.J., 2011. U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry. ORNL/TM-2011/224. U.S. Department of Energy. Oak Ridge National Laboratory, Oak Ridge, TN. 227p.

26. Shanks, H. Brent., Lohithrn, N. Upgrading of bio-oil: Effect of light aldehydes on acetic acid removal via esterification. Catalysis Communications. 11, 96-99, 2009.

27. Steele HP, Pittman UC, Ingram LL, Gajjela SK, Zhang Z, Bhattacharya P. Method to upgrade bio-oils to fuel and bio-crude. US patent 0192072 A1, Aug. 11, 2011.

28. Steele PH, Tanneru SK, Gajjela SK. Composition and methods for improved fuel production. US Pat 2013/0291431 A1, November 7, 2013.

29. U.S. Energy Information Administration. Annual Energy Review (2010). 2011

30. Wagenaar, B. M., Prins, W., VanSwaaij, W. P. M. Pyrolysis of biomass in the rotating cone reactor: modeling and experimental justification. Chemical Engineering Science. 1994, 49, 5109–5126.

31. Wang, S., Gu, Y., Liu, Q., Yao, Y., Guo, Z., Luo, Z., Cen, K. Separation of bio-oil by molecular distillation. Fuel Processing Technology. 90, 738-745, 2009.

32. Wang H, Male J, Wang Y. Recent advances in hydrotreating of pyrolysis bio-oil and its oxygen-containing model compounds. ACS Catal 2013,3:1047-1070.

33. 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. 48, 10324-10334, 2009.

34. Xu, J., Jiang, J., Dai, W., Zhang, T., Xu, Y. Bio-oil upgrading by means of ozone oxidation and esterification to remove water and to improve fuel characteristics. Energy Fuels. 25, 1798-1801. 2011.

35. Yan, J., Alvors, P., Eidensten, L., 1997. A future for biomass: Mechanical Engineering, 117, 94–98.

36. Zanzi, R., Sjostrom, K., Bjornbom, E. Rapid high-temperature pyrolysis of biomass in a free-fall reactor. Fuel 75, 545–550, 1996.

37. Zhang, S. P., Yan, Y. J., Ren, Z., Li, T. Study of hydrodeoxygenation of bio-oil from the fast pyrolysis of biomass. Energy Sources. 25, 1, 57-65, 2003.

38. Zhang Z, Sui S, Wang F, Wang Q, Pittman Jr CU. Catalytic conversion of bio-oil to oxygen-containing fuels by acid-catalyzed reaction with olefins and alcohols over silica sulfonic acid. Energies 2013, 6, 4531-4550.

CHAPTER II

BIO-OIL UPGRADING TO HIGH ENERGY BOILER FUEL BY OLEFINATION

2.1 Abstract

Raw bio-oil produced by fast pyrolysis consists of a complex mixture of various oxygenated compounds. Due to the presence of these oxygenated compounds bio-oil possesses negative properties that have prevented its use directly as a fuel. To overcome these negative properties and improve the bio-oil quality we employed an olefination process to raw bio-oil to produce a high-energy boiler fuel. Three alcohol treatments: 1-butanol alone, 1-octanol alone and a 1-butanol+1-octanol mixture with 1-octene as the olefin were reacted with raw bio-oil via olefination to produce a high-energy olefinated bio-oil as a fuel. The olefinated organic fraction obtained by utilizing 1-butanol+1-octanol mixture produced a higher yield and better quality boiler fuel compared to 1-butanol and 1-octaol alone. The olefinated organic fraction had an acid value of 23.3 mg KOH/g representing a reduction of 74.8% of the raw bio-oil acid value of 92.4 mg KOH/g. Compared to raw bio-oil the olefinated organic fraction of the 1-butanol+1-octanol mixture produced a higher heating value increase of 117.5% from the original 16.0 MJ/kg for raw bio-oil to 34.8 MJ/kg; the water content of the olefinated product decreased by 87.3% and oxygen content decreased by 64.3%. The best olefinated fuel produced was analyzed by GC-MS and FTIR.

Keywords: Bio-oil, fast pyrolysis, boiler fuel, olefination, higher heating value, GC-MS, FTIR.

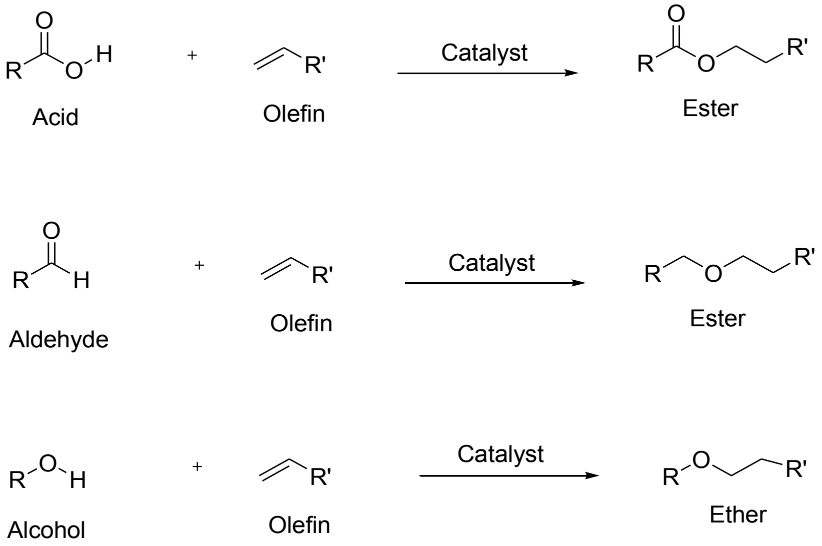
2.2 Introduction

Bio-oil is typically produced by fast pyrolysis of biomass at 400 to 550 ^oC in the absence of oxygen. The yield of bio-oil is relatively high at 60-70% dry-weight basis or higher. Bio-oil is a dark brown colored liquid with pungent phenolic odor [1-3]. As a fuel raw bio-oil has environmental advantages when compared to fossil fuels because on combustion bio-oil produces half the NOx, negligible quantities of SOx emissions and it is CO_2 neutral when compared to petroleum fuels [4,5]. Bio-oil is very complex in chemical composition and contains large numbers of organic compounds such as carboxylic acids, aldehydes, ketones, alcohols, phenols and phenolic derivatives and others. The chemically complex mixture of bio-oil results in each separate bio-oil containing over 200 different organic compounds although over 300 organic compounds have been identified over the range of bio-oils produced [1,3,5]. The presence of oxygenated compounds results in typical bio-oil oxygen content of 40-50 wt%. Due to the presence of a high percentage of oxygen raw bio-oils demonstrate some negative properties such as high water content, lower energy density, high acidity, immiscibility with petroleum products and viscosity increase over time [5-9].

Raw bio-oils are acceptable as boiler fuels and ASTM D7544 10 Standard Specifications for Pyrolysis Liquid Boiler Fuel provides quality standards. The bio-oil boiler fuel quality is determined by ASTM D7544 10 by level of water content, viscosity and HHV. While raw bio-oils can be utilized as boiler fuels treatments to improve current boiler fuel quality would improve market acceptance and speed commercialization [10].

The present methods for upgrading bio-oil to boiler fuel based on catalytic reactions are esterification [12, 17-20] and olefination [13-15]. By these methods total oxygen removal is not required; moreover, that retained in the boiler fuels produces high-energy organic fuels which are combustible and stable oxygenated compounds such as esters, acetals and ethers [11,14,16].

The olefination reaction is one of the potential chemical processes to produce mainly esters and ethers by reacting an olefin with carboxylic acids and aldehydes in the presence of alcohol as a solvent and co-reagent. The olefination reaction scheme is shown below in Scheme 2.1. This reaction produces mainly esters with a maximum HHV of 23-31.9 MJ/kg while reducing the oxygen content considerably such that esterified or olefinated bio-oil is suitable as a heating fuel but not as a transportation fuel [13-17].



Scheme 2.1 Olefination reaction pathway [14,15,17].

Steele et al. applied for a patent (2011) on olefination of bio-oil to produce a high-energy boiler fuel. One embodiment proposed addition of liquid 1-octene and 1-butene as well as adding high boiling point alcohol to the bio-oil. The Steele et al. olefination/esterification experiment was performed by addition of bio-oil (85.7%), butanol (28.6%), and 1-octene (14.3%) with 5 wt% of heterogeneous acidic catalyst at a temperature of 250 °C with pressure of 100 psi helium for 2 h. The patent application also disclosed olefination of bio-oil utilizing 1-butene gas as the olefin source by addition of bio-oil, butanol and gaseous 1-butene at 30 psi of pressure with 5 wt% of acid catalyst at a temperature of 250 °C with pressure of 100 psi helium. For the liquid embodiment to produce olefinated/esterified bio-oil the inventors showed that HHV increased from 17.20 to 32.80 MJ/kg and water content decreased from 28.60 to 6.0 wt% [14].

Zhang et al. (2011) studied the sulfonic acid resin catalytic olefination of bio-oil (1.5 g) with 1-octene (0.25 g or 16.7%) with addition of 1-butanol ranging from 0.25 to 0.75 g (16.7 to 50%) reacted at a temperature ranging from 80 to 150 °C for a reaction time of 3 h. This treatment resulted in an olefinated product with lower acidity (pH value increased from 2.5 to >3.5), reduction of water content 37.2 to less than 7.5% and an increase in HHV to 30.0 MJ/kg from the bio-oil HHV of 12.6 MJ/kg [15].

Zhang et al. (2013) tested the upgrading of bio-oil with the olefins cyclohexene, 1,7-octadiene and 2,4,4-trimethyl pentene along with 1-octene and iso-butanol, t-butanol, and ethanol and 1-butanol as solvents. Researchers performed the olefination reaction in the presence of silica sulfuric acid catalyst at 120 °C for a time of 3 h. Better results were obtained with 1-butanol/1-octene consisting of 0.75 g (50%) 1-butanol and 0.6 g (40%) 1-octene. For this olefinated product acidity was lowered (pH value increased from 2.5 to

>3.5), water content decreased from 37.2 to nearly 7% and the HHV value increased from 12.6 MJ/kg to about 31.9 MJ/kg [16].

Chatterjee et al. (2013) explored the olefination of bio-oil using 1-octene as the olefin and ethanol as the alcohol. They reported that ethanol was not as effective as 1-butanol for promoting 1-octene and bio-oil phase compatibility [13].

Zhang et al. 2011 and 2013 and Chatterjee et al. 2013 performed their experiments at a micro scale with a high percentage of alcohol and reaction time was relatively long at 3 h. The objective of our current study is to produce a higher-energy olefinated bio-oil useable as boiler fuel with higher HHV and lower acid value (AV) with a shorter reaction time than attained by previous researchers.

2.3 Objective

The objective of this study was to apply olefination on the RBO to produce a high energy boiler fuel. The sub-objective is to reduce consumption of the amount of alcohol and olefin used for the olefination process.

2.4 Materials and methods

2.4.1 Materials

1-butanol, 1-octanol and 1-octene were obtained from Sigma Aldrich. Nickel on silica-alumina (Ni/SiO2-Al2O3) and potassium carbonate (K2CO3) were obtained from Alfa Aesar. The bio-oil required for this study was produced with the Mississippi State University (MSU) fast pyrolysis auger reactor located in the Department of Sustainable Bioproducts. The feedstock utilized was clear pine wood particles of 1-3 mm diameter at a moisture content of 8-10% (dry-weight basis) with 65% yield. Raw bio-oil (RBO) was produced by the fast pyrolysis process performed at a temperature of 450 oC with nitrogen carrier gas at a rate of 7 kg/h and with yield of 65%. All described chemicals were used with no further purification.

2.4.2 Methods

All olefination experiments were performed in a stainless steel, high-pressure batch autoclave reactor equipped with an overhead magnetic stirrer, a pressure indicator with a maximum capacity of 5000 psig and a thermocouple for temperature monitoring in the range of 0-500 ^{o}C. The autoclave was equipped with an electrical heating and cooling system to control the temperature inside the reactor. The olefination reaction was applied to RBO by addition of an alcohol, olefin and olefination catalyst.

For this study we tested 1-octene as the olefin with 1-butanol (BtOH), 1-octanol (OtOH) and 1-butanol+1-octanol (BtOH+OtOH) mixture as the alcohol solvents; the catalyst was a mixture of Ni/SiO_2-Al_2O_3 (3 wt%) and K_2CO_3 (5 wt%). Olefination reactions were performed by addition of BtOH (30 wt%) alone, OtOH (30 wt%) alone and the combination of the BtOH+OtOH (30 wt%) mixture (this mixture was prepared by physical addition of 1:1 BtOH and OtOH, i.e., 15 wt% of each) to RBO by using a common 1-octene (10 wt%) as an olefin and a mixture of Ni/SiO_2-Al_2O_3 (3 wt%) and K_2CO_3 (5 wt%) as the catalyst. For the three alcohol solvents a reaction temperature of 250 ^{o}C was applied without pressure while being stirred for 90 min.

Following each reaction described in these results, the reactor was cooled to room temperature and vented to atmospheric pressure. The product from the reaction was collected and the two liquid layers, olefinated organic fraction (OOF) and aqueous fraction were separated by centrifugation for 2-4 h at 4000 rpm. The resultant two phases were removed by separating funnel and yields of all phases and products were calculated.

The alcohol solvent that produced the best qualities and yield of OOF was then chosen for further testing of reaction temperatures and times. The reaction temperatures applied to the solvent selected as the most promising were 225, 250 and 275 ^{o}C; reaction times applied were 60, 90 and 120 min. Again, no pressure was applied during the reaction.

The temperature that produced the best qualities and yield of OOF for the tested best alcohol solvent was then identified. At this temperature reaction times were varied for 60, 90 and 120 min. Again, the reaction time that produced the best qualities and yield of OOF was selected as the optimum time among those tested.

2.5 Data analysis

The RBO and OOFs were characterized using the following ASTM methods. The AVs were determined by ASTM D664 method which was comprised of dissolving 1 g of bio-oil in 50 ml of 35:65 ratio of isopropanol to water mixtures and titrating to a pH of 8.5 with 0.1N KOH solution. The HHVs were determined by Ika-5000 bomb calorimeter by ASTM D240. Water content was determined by Karl-Fisher titration by ASTM E203. Elemental carbon, hydrogen, and nitrogen were determined by EAI CE-440 elemental analyzer with oxygen content determined by difference according to ASTM D5291. The best OOF measured in terms of higher yield and better quality was analyzed by gas chromatography–mass spectrometry (GC-MS) and Fourier transform infrared spectroscopy (FTIR).

2.6 Results and discussion

2.6.1 Olefination of raw bio-oil

The olefination process was applied to the RBO to produce an OOF product with low AV, high HHV and less water content suitable for boiler fuel. Table 2.1 compares AVs, HHVs and water contents of the OOFs obtained from three alcohol treatments (BtOH alone, OtOH alone and a mixture of BtOH+OtOH with 1-octene as the olefin). Table 2.1 indicates that following olefination of RBO with BtOH alone the AV decreased from 92.4 mg KOH/g for raw bio-oil to 31.6 mg KOH/g, a decrease of 64.7%. For the combination of BtOH+OtOH mixture the AV decreased from 92.4 mg KOH/g for raw bio-oil to 23.3 mg KOH/g, a reduction of 74.8%. For OtOH alone the AV decreased from 92.4 mg KOH/g for raw bio-oil to 25.4 mg KOH/g, a decrease of 72.5%.

As shown in the Table 2.1, olefination of the RBO with BtOH alone resulted in a HHV nearly twice as high for OOF with an increase from 16.0 MJ/Kg to 32.5 MJ/Kg, an increase of 103.0%. For the olefination of RBO with the combined BtOH+OtOH mixture the HHV again more than doubled for the OOF with an increase from 16.0 MJ/Kg to 34.8 MJ/Kg, an increase of 117.5%. For the olefination of RBO with OtOH alone the HHV also more than doubled for the olefinated bio-oil product with an increase from 16.0 MJ/Kg to 34.9 MJ/Kg, an increase of 118.1%.

Table 2.1 also shows the water content of the OOF from the OtOH alone treatment was reduced to 6.9 wt% compared to 30.6 wt% for raw bio-oil, a decrease of 77.4%. The OOF obtained from the BtOH+ OtOH mixture treatment had a water content of 3.9 wt% compared to 30.6 wt% for raw bio-oil, this was a decrease of 87.3%. The water content of the OOF from the addition of OtOH alone was reduced to 2.2 wt% compared to the 30.6 wt% for raw bio-oil, a decrease of 92.8%.

Table 2.1 Comparison of AV, HHV, water content between RBO and OOFs obtained from BtOH alone, OtOH alone and BtOH+OtOH mixture with 1-octene as olefin treatments.

Property	RBO	BtOH	BtOH+OtOH	OtOH
AV, mg KOH/g	92.4	31.6	23.3	25.4
HHV, MJ/kg	16.0	32.5	34.8	34.9
Water content, wt%	30.6	6.9	3.9	2.2

Figure 2.1 compares the elemental analysis results measuring carbon, hydrogen, nitrogen and oxygen content (C,H,N,O) of the OOF products produced from treatments (by addition of BtOH alone, OtOH alone and BtOH+OtOH separately) with 1-octene as olefin to that of RBO. The OOF produced from the BtOH alone treatment carbon content increased to 69.5 wt% from 38.4 wt% from that of RBO, an increase of 80.9%. The hydrogen content of OOF from BtOH increased to 10.5 wt% from 7.6 wt% of RBO, an increase of 27.6%. The nitrogen content of OOF from BtOH alone treatment decreased from 0.2 wt% for RBO to 0.1 wt%. The oxygen content of OOF produced from the BtOH alone treatment reduced by 62.9% from RBO of 53.7 wt% to 19.9 wt%.

The carbon content of the OOF obtained from BtOH+OtOH mixture treatment increased to 69.5 wt% from 38.5 wt% of RBO, an increase of 80.5%. Hydrogen content was 26.9% higher for the OOF produced from combined BtOH+OtOH with the value of 10.4 wt% compared to the 7.6 wt% of RBO. Nitrogen decreased from 0.2 wt% for RBO to 0.1 wt%. Oxygen content of OOF from this combined alcohol treatment reduced by 64.3% from 53.7 wt% of RBO to 19.2 wt%.

As shown in Figure 2.1, the carbon content of the OOF produced from OtOH alone increased to 71.0 wt% from 38.5 wt% of RBO, an increase of 84.4%. The hydrogen content increased to 10.1 wt% form 7.6 wt% of RBO. Nitrogen content decreased from 0.2 wt% of RBO to 0.1 wt% for the OOF from OtOH alone treatment. Oxygen content of OOF from OtOH alone treatment reduced by 65.0% from 53.7 wt% of RBO to 18.8 wt%.

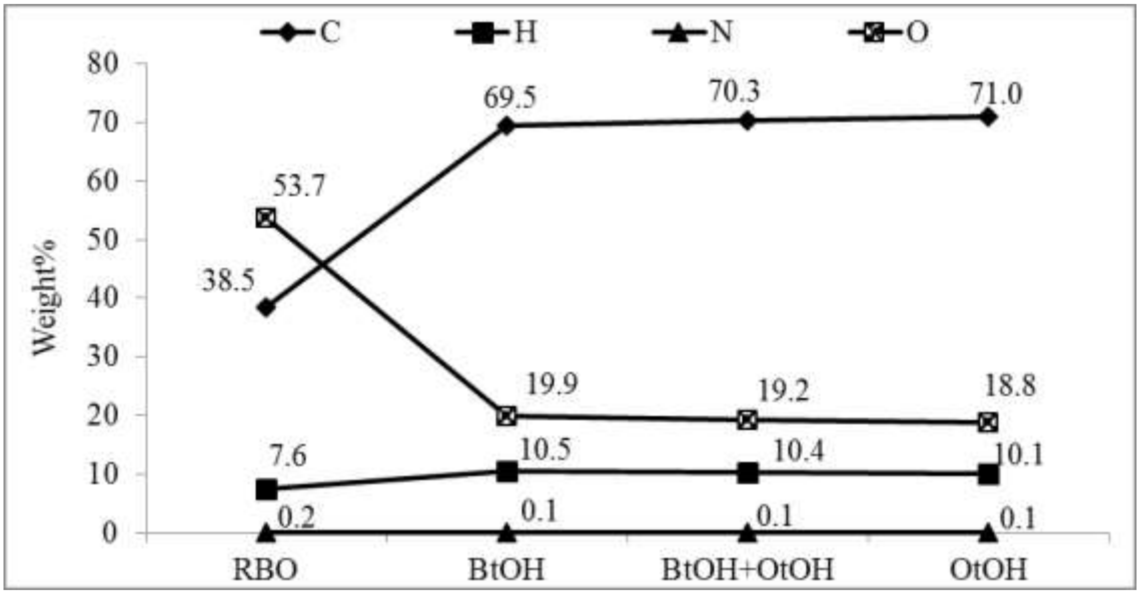


Figure 2.1 Comparison of C, H, N, O weight percentages between RBO and OOF products obtained from BtOH alone, OtOH alone and BtOH+OtOH mixture with 1-octene as olefin treatments.

Figure 2.2 compares the OOF, water, char and gas yields obtained from the olefination of the RBO with three (BtOH alone, OtOH alone and BtOH+OtOH mixture as a solvent) alcohol treatments. As shown in Figure 2.2, the mixture of BtOH+OtOH as a solvent treatment produced a higher yield of OOF product and lower water (aqueous fraction) and gas yields compared to BtOH alone and OtOH alone treatments. The BtOH+OtOH as a solvent treatment produced 13.3% and 6.5% higher yield of OOF compared to the BtOH and OtOH treatments, respectively.

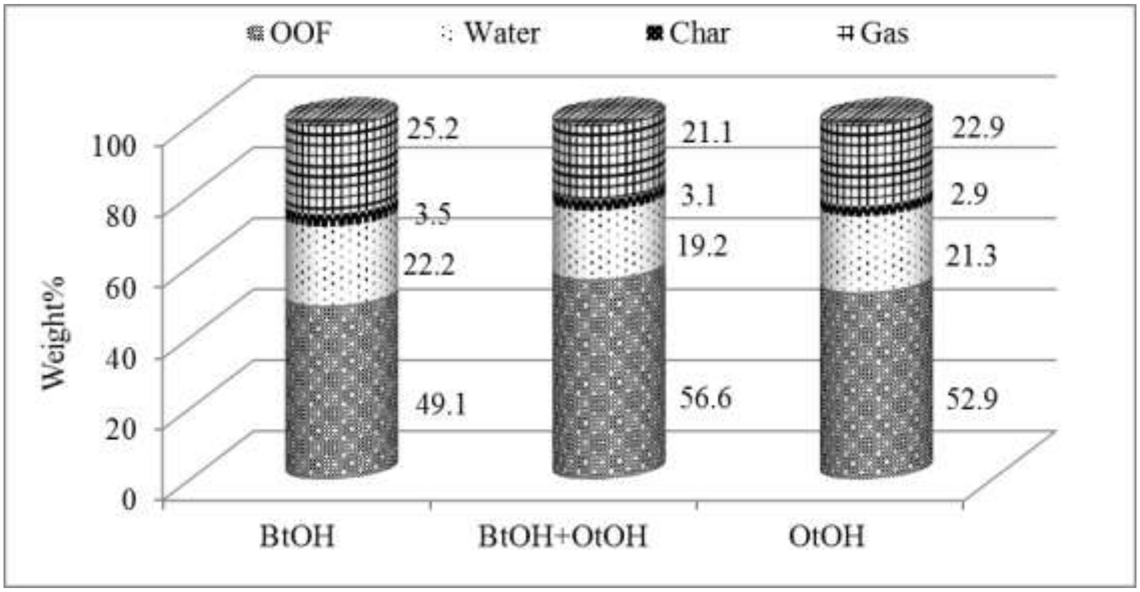


Figure 2.2 Comparison of OOF, water, char and gas yields obtained from BtOH alone, OtOH alone and BtOH+OtOH mixture with 1-octene as olefin treatments at a temperature of 250 °C with no pressure applied for a reaction time of 90 min.

Among all three runs, BtOH+OtOH mixture as an alcohol solvent treatment produced an OOF with higher yield and improved characteristics in terms of reduced AV, higher HHV, lowered water and oxygen content. The OtOH alone treatment produced a very small improvement in the reduction of water content and oxygen. However, the lower yield and high utilization of OtOH (30 wt%) is a much more expensive treatment compared to the mixture of BtOH (15 wt%)+OtOH (15 wt%). Therefore, the OOF obtained from the combined BtOH+OtOH mixture with 1-octene treatment was considered as the best treatment to produce maximum OOF yield. For this (BtOH+OtOH mixture as an alcohol) best treatment, the effect of the reaction temperature was studied. The olefination reactions were conducted at a temperatures ranging from 225-275 ^{o}C at an interval of 25 ^{o}C by following the procedure described in section 2.4.2.

Figure 2.3 shows the effect of reaction temperature on the olefination of RBO by combined BtOH+OtOH as an alcohol solvent treatment. Figure 2.3 shows the HHVs, AVs, water content (H_2O), oxygen content (O) and OOF yield of the three treatments at a temperature 225 ^{o}C, 250 ^{o}C and 275 ^{o}C. As shown in the Figure 2.3, the olefination reaction performed at 250 ^{o}C produced a 55.8 wt% of higher yield of OOF compared to the treatments at 225 ^{o}C with 54.5 wt% yield and at 275 ^{o}C with 53.1 wt% yield. The HHVs of all three treatments had approximately the same values at 34.6, 34.8 and 35.0 MJ/kg at 225 ^{o}C, 250 ^{o}C and 275 ^{o}C, respectively. The AVs of the OOFs produced at 225 ^{o}C, 250 ^{o}C and 275 ^{o}C were 30.1, 23.3 and 21.2 mg KOH/g, respectively. The water content of the OOFs were 4.5, 3.9 and 3.7 wt% for the respective treatment temperatures of 225, 250 and 275 ^{o}C. The oxygen content of the OOFs produced at 225, 250 and 275 ^{o}C were 20.7, 18.8 and 18.7 wt%, respectively.

The OOF produced at the 250 ^{o}C treatment had 22.6% lower AV, 0.6% higher HHV, 13.4% lower water content, 9.2% less oxygen content and 2.4% higher OOF yield when compared to the 225 ^{o}C treatment. Comparing the OOF products produced at the 250 ^{o}C and 275 ^{o}C treatments, the OOF produced at 275 ^{o}C had 9.0% lower AV, 0.6% higher HHV, 5.1% lower water content, 0.5% less oxygen content and 5.1% lower OOF yield when compared to the treatment at 250 ^{o}C. Among these three runs, the olefination reaction performed at 250 °C produced a higher yield of OOF compared to the 225 °C and 275 °C treatments. The effect of the reaction time on the olefination of the RBO was also studied at an optimized reaction temperature of 250 °C. The olefination reactions were conducted with a reaction time in the range of 60-120 min at an interval of 30 min at a temperature of 250 °C by following the procedure described in section 2.4.2.

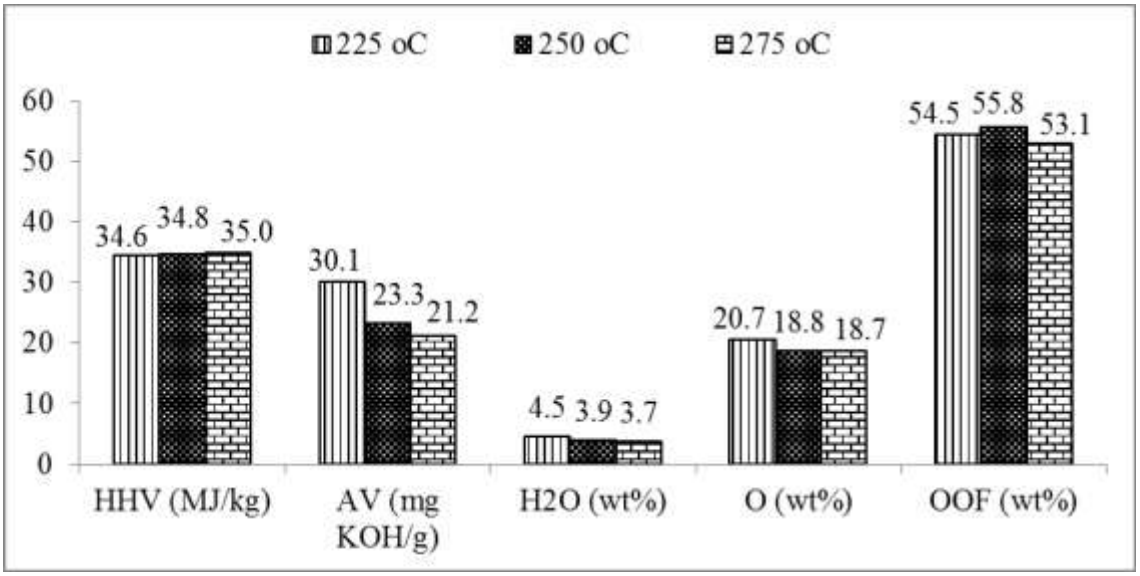


Figure 2.3 Effect of reaction temperature on the olefination of RBO by combined BtOH+OtOH mixture as an alcohol solvent treatment.

The effect of reaction time on the olefination of RBO by combined BtOH+OtOH as an alcohol solvent treatment is shown in the Figure 2.4. The olefination reactions were performed as mentioned in section 2.4.2 at three different time intervals in the range of 60-120 min at a temperature of 250 °C and without external pressure. Figure 2.4 shows the HHV, AV, O_2 and OOF yield of the three treatments performed at 60, 90 and 120 min reaction time intervals. As shown in Figure 2.4, the olefination reaction performed at 250

^{o}C with reaction time for 90 min produced 55.8 wt% of higher yield of OOF compared to the 51.7 wt% and 47.0 wt% OOF yields at reaction time 60 and 120 min, respectively. The HHVs of the OOF produced with reaction time of 90 min had higher value of 34.8 MJ/kg compared to 33.0 MJ/kg at 60 min and 34.2 MJ/kg at 120 min time intervals. The AV of the OOF produced at 90 min contained 23.3 mg KOH/g; whereas both the OOF products produced at the 60 min reaction contained 28.0 mg KOH/g and the 120 min reaction contained 27.1 mg KOH/g higher AV compared to the 90 min reaction time OOF product. The O_2 content of the OOF produced with 60 min of reaction time had 20.0 wt% and OOF's produced at 90 min and 120 min reaction times have approximately the same O_2 of 18.8 wt% and 18.4 wt%, respectively.

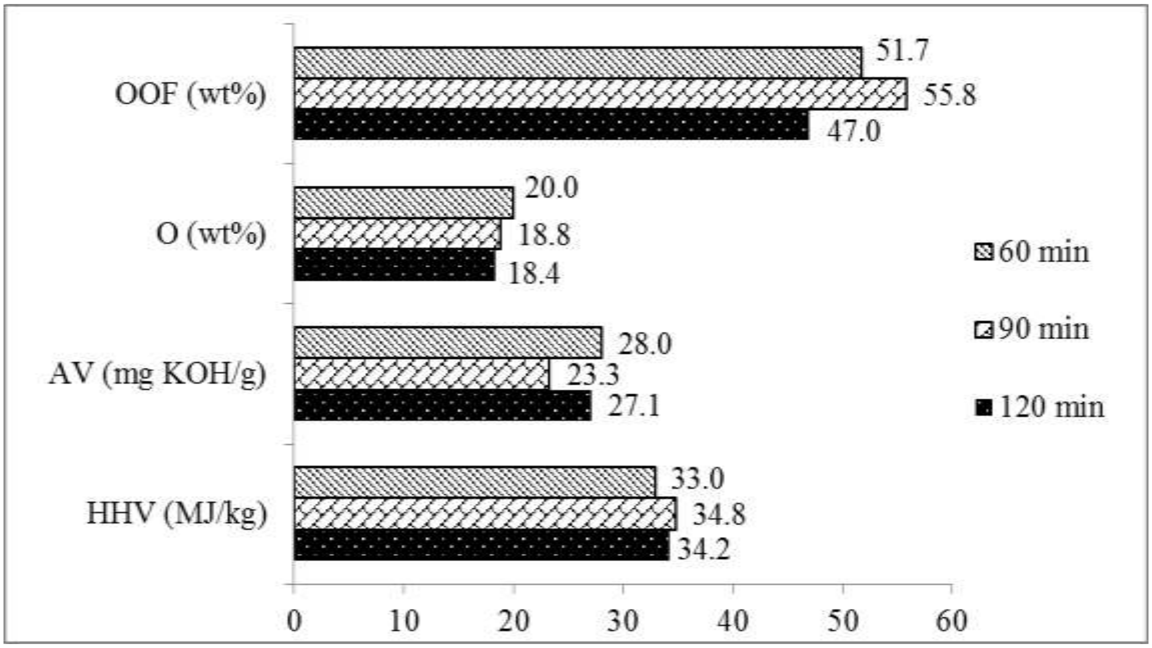


Figure 2.4 Effect of reaction time on the olefination of RBO by combined BtOH+OtOH as an alcohol solvent treatment performed at 250 ^{o}C.

2.6.2 GC-MS analysis

Table 2.2 shows comparison of the chemical composition of RBO and OOF produced from mixed alcohol (BtOH+OtOH) as a solvent treatment by GC-MS analysis. From Table 2.2 it is observed that there is a large difference between RBO and olefinated product chemical composition after the olefination reaction. As shown in Table 2.2, RBO contains mostly oxygenated compounds in the form of alcohols (34.3%), aldehydes and ketones (34.1%), ester and ethers (12.1%), carboxylic acids (15.7%) and others (3%). The presence of all these compounds is attributed to the negative properties of the raw bio-oil. Compared to RBO an olefinated bio-oil contains less alcohol (24.4%) and ketones (1.9%); ester and ethers (26.7%), carboxylic acids (5.2%) and others (3%) were observed to decrease. The reduction of acid content was 66.9 area%. The increase of esters and ethers was observed to be by 120.7 area%. In Table 2.1 the previously discussed decrease in OOF AV compared to that of RBO is also in good agreement with the conversion of carboxylic acids to esters and other oxygenates as shown in Table 2.2 GC-MS results.

Table 2.2 The chemical composition of the RBO and OOF produced from BtOH+OtOH as a solvent treatment at 250 °C for 1.5h.

Components	RBO (Area %)	OOF (Area %)
Acids	15.7	5.2
Esters & Ethers	12.1	26.7
Aldehydes & Ketones	34.1	1.9
Alcohols	34.3	24.4
1-Octene	0	21.3
Other	3	1.3

2.6.3 FTIR spectral analysis

Figure 2.5 compares FTIR spectral data between the RBO and OOF produced from BtOH+OtOH treatment. Characteristic vibrational modes are observed at 3200-3600 cm^{-1} (OH stretching), 2830-2950 cm^{-1} (CH stretching, aliphatic), 1650-1710 cm-1 (C=O stretching) and 1375-1475 cm-1 (C–H vibrations). From Figure 2.5, it is evident that following olefination the OH stretching absorption peak of OOF was decreased due to the conversion of oxygenated compounds such as carboxylic acids, water and alcohols present in the RBO. The increase of the C=O and C-O stretching peak indicates the presence of ester and ether oxygenated compounds present in the OOF. The increase in intensity of C–H aliphatic stretching (2830-2950 cm^{-1}) absorption peak of OOF compared to the RBO spectra indicates the formation of ethers, esters (butyl and octyl) and acetals. The FTIR spectral data shown in Figure 2.5 is in good agreement with the GC-MS spectral properties shown in Table 2.2 and physical and chemical properties as shown in Table 2.1.

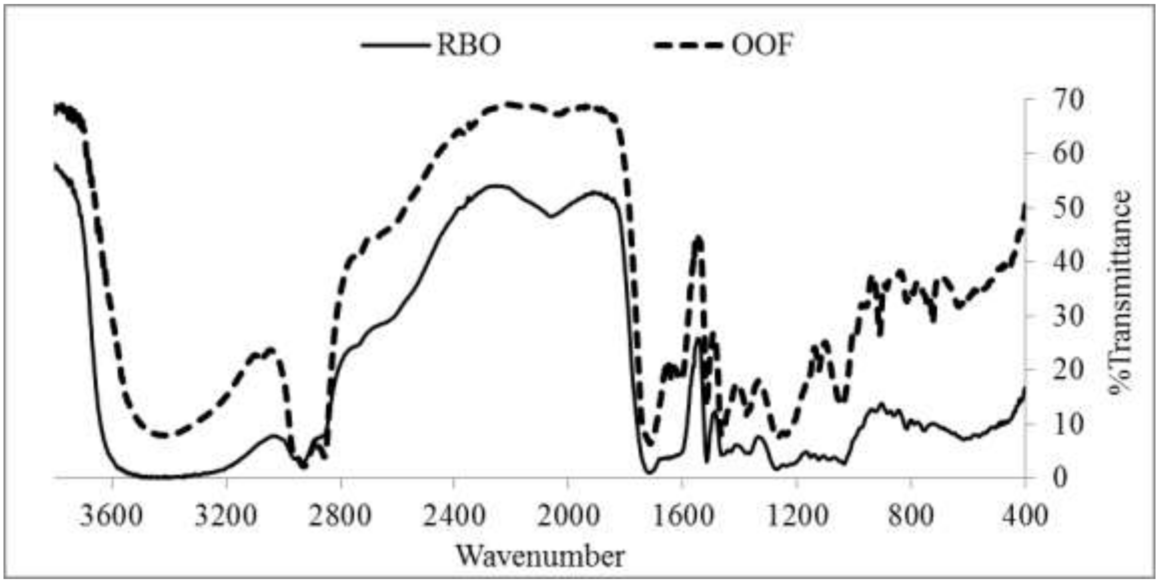


Figure 2.5 Comparison of RBO and OOF produced from BtOH+OtOH as a solvent treatment samples FTIR spectra.

2.7 Summary

The olefination of RBO with three alcohols (BtOH alone, OtOH alone and a BtOH+OtOH mixture) with 1-octene as the olefin treatment was tested and results were compared. All three treatments produced high-energy boiler fuel with improved fuel characteristics. However, the combined BtOH+OtOH as an alcohol solvent treatment produced an OOF with higher yield of 56.6% that was, respectively, 13.3% and 6.5% higher than the yields for the BtOH and OtOH treatments alone. The highest reduction of AV for the RBO was also achieved by the BtOH+OtOH mixture treatment. The BtOH+OtOH mixture treatment had an AV of 23.3 mg KOH/g compared to the 92.4 mg KOH/g AV of RBO, a reduction of 74.8%. The HHV of the OOF produced by the BtOH+OtOH treatment was more than doubled to 34.8 MJ/Kg from 16.0 MJ/Kg for RBO, an increase of 117.5%. As compared to RBO the OOF obtained from the

BtOH+OtOH treatment water content was reduced by 87.3%; the oxygen content of OOF from the combined alcohol treatment was reduced by 64.3%. From a GC-MS comparison between the RBO and the best OOF produced by this method it was observed that the reduction of acid content was 66.9 area% and the increase of esters and ethers was 120.7 area%.

2.8 Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

2.9 References

1. Mohan D, Pittman CU, Steele PH. Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. Energy Fuels 2006, 20, 3, 848-889.

2. Huber GW, Iborra S, Corma A. Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. Chem. Rev. 2006, 106, 9, 4044-4098.

3. Bridgwater AV, Peacocke GVC. Fast pyrolysis processes for biomass. Renewable and Sustainable Energy Reviews 2000, 4, 1, 1-73.

4. Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. Biomass and Bioenergy 2012, 38, 68-94.

5. Czernik S, Bridgwater AV. Overview of Applications of Biomass Fast Pyrolysis Oil. Energy Fuels 2004, 18, 2, 590-598.

6. Elliott DC. Historical Developments in Hydroprocessing Biooils. Energy Fuels 2007, 21, 3, 1792-1815.

7. Tanneru KS, Steele PH. Pretreating bio-oil to increase yield and reduce char during hydrodeoxygenation to produce hydrocarbons. Fuel 2014, May 13, DOI: 10.1016/j.fuel.2014.05.026.

8. Steele PH, Tanneru SK, Gajjela SK. Composition and methods for improved fuel production. US Pat 2013/0291431 A1, November 7, 2013.

9. Mahfud FH, Melian-Cabrera I, Manurung R, Heeres JJ. Biomass to fuels upgrading of flash pyrolysis oil by reactive distillation using a high boiling alcohol and acid catalysts, process Safety and Environmental Protection 2007, 85, 466-472.

10. ASTM D7544:2010 Standard Specifications for pyrolysis liquid biofuel, specification reported here *www.astm.org/Standards/D7544.htm*

11. Xu J, Jiang J, Dai W, Zhang T, Xu Y. Bio-oil upgrading by means of ozone oxidation and esterification to remove water and to improve fuel characteristics: Energy Fuels 2011**,** *25*, 1798-1801.

12. Tanneru KS, Parapati RD, Steele PH. Boiler fuel produced from pyrolysis oil by oxidation followed by esterification. Energy. June 4, 2014.

13. Chatterjee S, Zhang Z, Pittman Jr CU. Acid-catalyzed olefination of bio-oil in the presence of ethanol. Biofuels 2013, 4, 3, 285-294.

14. Steele HP, Pittman UC, Ingram LL, Gajjela SK, Zhang Z, Bhattacharya P. Method to upgrade bio-oils to fuel and bio-crude. US patent 0192072 A1, Aug. 11, 2011.

15. Zhang Z, Wang Q, Tripathi P, Pittman Jr CU. Catalytic upgrading of bio-oil using 1-octene and 1-butanol over sulfonic acid resin catalysts. Green Chemistry 2011, 13, 940-949.

16. Zhang Z, Sui S, Wang F, Wang Q, Pittman Jr CU. Catalytic conversion of bio-oil to oxygen-containing fuels by acid-catalyzed reaction with olefins and alcohols over silica sulfonic acid. Energies 2013, 6, 4531-4550.

17. Yang C, He C. Gold(I)-catalyzed intermolecular addition of phenols and carboxylic acids to olefins. J. Am. Chem. Soc. 2005, 127, 19, 6966-6967.

18. Shanks HB, Lohithrn N. Upgrading of bio-oil: Effect of light aldehydes on acetic acid removal via esterification: Catalysis Communications, 2009, 11, 96-99.

19. Weerachanchai P, Tangsathitkulchai C, Tangsathitkulchai M. Effect of reaction conditions on the catalytic esterification of bio-oil: Korean J. Chem. Eng, 2012, *29*(2), 182- 189.

20. Wang J, Chang J, Fan J. Catalytic esterification of bio-oil by ion exchange resins. Jounal of fuel chemistry and technology 2010, 38, 5.

CHAPTER III

NOVEL OXIDATION AND ACID ANHYDRIDE PRETREATMENTS FOR FAST PYROLYSIS OIL

3.1 Abstract

Biomass can be converted into liquid fuels by both thermal and biological methods. One of the thermal decomposition methods is fast pyrolysis of lignocellulosic biomass to produce pyrolysis oil that is frequently referred to as bio-oil. The raw bio-oil produced from fast pyrolysis is limited to use as a heating fuel due to its negative properties such as thermal instability, lower heating value and high water content. The negative properties of bio-oil largely result from its high oxygen content (40-50%) resulting from the numerous oxygenated compounds of which it is comprised. Aldehydes and other primary oxygenated compounds are contained in bio-oil that result in coke formation when catalytic hydrodeoxygenation to produce hydrocarbons. This coke and the high-water content (25-35%) contained in bio-oil both lead to rapid catalyst deactivation during hydrodeoxygenation.

This study explored the potential for pretreating bio-oil with oxidation and/or addition of acid anhydride to reduce the coking and catalyst deactivation that occurs during hydrodeoxygenation of bio-oil. The oxidation pretreatment applied to bio-oil converts aldehydes and phenols to carboxylic acids resulting in a highly acidic product. Acid anhydride is known to convert water to carboxylic acids thereby reducing water content. Both oxidized and acid anhydride pretreated bio-oils were analyzed by the ASTM methods for higher heating value, viscosity, density, total acid value and elemental analysis. Best pretreated bio-oils were also analyzed by GC-MS and FTIR.

Keywords: Pyrolysis oil, pretreatment, oxidation, acid anhydride pretreatment, HHV, GC-MS and FTIR.

3.2 Introduction

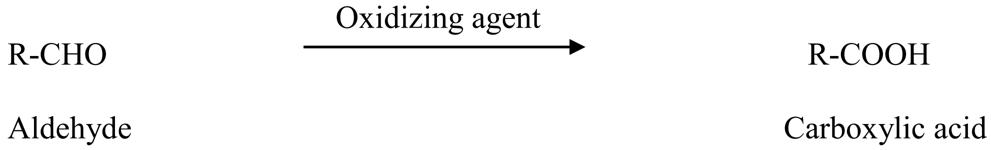
Fast pyrolysis is a thermal application that produces liquid products usually referred to as bio-oil. Bio-oil can be utilized as a precursor feedstock for the potential production of fuels. During the past two decades considerable efforts have been dedicated to the development of techniques for the production of bio-oil by fast pyrolysis (Maggi et al. 1994, Zanzi et al. 1996, Bridgwater 1996, Wagenaar et al. 1994, Bridgwater et al. 1999, Mohan et al. 2006, Oasmaa et al. 2010). Fast pyrolysis refers to thermal decomposition of biomass in the absence of oxygen at moderate temperatures in the range of 400-650 ^{o}C to produce liquid products of 60-75%, char of 15-25% and gases of 10-20% dry wt%. Fast pyrolysis requires very short vapor residence times of approximately 2 sec, or less (Maggi et al. 1994). Bio-oil is a dark brown and free-flowing miscible mixture of polar organics (70-80 wt%) and water (20-30 wt%). Chemically, bio-oil is a complex mixture of water (15-30%), carboxylic acids (10-15%), aldehydes (10-20%), ketones (1-5%), alcohols (2-5%), sugars (5-15%), phenols (5-10%), furans and pyrans (1-5%) and 10% miscellaneous compounds (Oasmaa et al. 2010, Huber et al. 2006, Girard and Blin 2005, Bridgwater et al. 1999, Mohan et al. 2006).

The typical bio-oil produced from woody biomass through the fast pyrolysis process has a heating value in the range of 15-17 MJ/kg, total acid value of 86-92 mg

KOH/g, pH is approximately 2-3, and water content of 25-35 wt%. Table 1 also shows that the elemental composition of bio-oil contains, in dry wt% terms, approximately 52-58% carbon, 5.5-7.0% hydrogen and 0-0.2% nitrogen. Bio-oil contains many highly oxygenated compounds that result in a total oxygen content of 30-50%. The presence of these highly oxygenated chemical compounds is the main reason for bio-oil negative properties such as low volatility, low heating value, and immiscibility with fossil fuels, high acidity, and polymerization of the liquids upon heating or during storage over time (Bridgwater 1996, Mohan et al. 2006, Ingram et al. 2008).

Bio-oils have been tested in combustion engines such as boilers, turbines, diesel and Stirling engines to produce heat and electrical power. Tests were conducted with neat bio-oil or bio-oil in dual-fuel mode. The main problems with boilers, turbines and diesel engines using bio-oils as a fuel were ignition difficulties resulting from low heating value and high water content, engine corrosion due to high acidity and coking because of the thermally unstable bio-oil compounds. With the exception of Stirling engines, researchers reported some engine damage in each case. Stirling engines operated satisfactorily without engine damage in heat and power production, but electrical power production was limited (Czernik and Bridgwater 2004, Bandi et al. 2001). Researchers concluded that utilization of bio-oils as engine or transportation fuels will require significant upgrading by some method.

Bio-oil aldehydes play a vital role in bio-oil instability, over time or with heating. Aldehydes readily react with phenols and sugars to form higher molecular weight resins and oligomers via polymerization and condensation; oligomerization reactions lead to coke formation (Gagnon et al. 1988, Diebold 2000, Zhang et al. 2003, Shanks et al. 2009, Hu et al.2012). Aldehydes present in the bio-oil can be converted to carboxylic acids by subjecting them to oxidation (Xu et al. 2011). Scheme 3.1 symbolizes the conversion of all bio-oil aldehydes to carboxylic acids in the presence of an oxidizing agent reaction pathway.



$$\underset{\text{Aldehyde}}{\text{R-CHO}} \xrightarrow{\text{Oxidizing agent}} \underset{\text{Carboxylic acid}}{\text{R-COOH}}$$

Scheme 3.1 Oxidation reaction pathway of bio-oil aldehydes to carboxylic acids (Xu et al. 2011).

Shanks et al. (2009) studied the impact of reactive oxygenated groups such as aldehydes on the esterification of organic acids using organic-inorganic mesoporous silica functionalized with propylsulfonic acid (SBA-15-SO_3H) catalyst. A bio-oil model compound was prepared by mixing acetaldehyde, propionaldehyde and acetic acid. To examine the effect of aldehydes (acetaldehyde and propionaldehyde) on esterification of acetic acid with ethanol using molar ratio of (ethanol/acetic acid) 2.7, researchers conducted the esterification of acetic acid with and without aldehydes at three different temperatures of 100 ^{o}C, 70 ^{o}C and 50 ^{o}C. The conversion of acetic acid to ethyl esters was not affected by the presence of aldehydes at 100 ^{o}C. However, at 70 ^{o}C and 50 ^{o}C, the acetic acid to esters conversion in the absence of aldehydes was higher than when aldehydes were present. They also found that the impact of aldehydes on esterification of acetic acid at 50 ^{o}C was even higher when compared at 70 ^{o}C. At 70 ^{o}C, the acetic acid conversion to esters in the presence of aldehydes was lowered by 6% when compared to the same reaction without aldehydes. At 50 °C, the acetic acid conversion in the presence of aldehydes was lowered by 28% when compared to the same reaction without aldehydes. It was also observed that excess of ethanol was consumed due to the formation of acetals by acetalization reactions in the presence of aldehydes. Researchers concluded that there is a significant effect of aldehydes and temperatures on the esterification of carboxylic acids.

Xu et al. (2011) introduced an ozone oxidation pretreatment method to bio-oil derived from rice-husks. At laboratory scale using an ozone generator (WJ-H-Y5) ozone was generated at 5 g/h. All the oxidation pretreatment reactions were performed by continuously introducing the ozone into a batch glass reactor at a temperature range of 20-22 °C for 10 h. This pretreatment method converted the more reactive aldehydes present in bio-oil into organic acids. Researchers found that the pretreated bio-oil acid value increased from 45.4 to 118.4 mg/KOH, heating value from 9.5 to 9.9 KJ/g and density from 1.13 to 1.17 g/cm^3. The pretreated and RBOs were esterified by addition of butanol and $NaHSO_4$ at 116 °C for 3-4 h in a 250 ml round bottom flask equipped with a water receiver (Dean-Stark trap) on which a reflux condenser was mounted. This oxidation of bio-oil followed by esterification improved the fuel quality compared to direct RBO esterification without pretreatment. The gross calorific value of RBO (9.5 KJ/g) increased to 25.0 KJ/g for esterified bio-oil without pretreatment; for esterified bio-oil with pretreatment the increase was to 27.4 KJ/g. Water content of the RBO was 45.0%; for esterified bio-oil without pretreatment water was reduced to 2.4% and with pretreatment and esterification water content was 1.5%. In addition, densities of the esterified bio-oils without and with pretreatment decreased from 1.13 for RBO to 0.94

and 0.92 kg/m^3, respectively; viscosity decreased from 14.4 mm^2/s for RBO while that for esterified bio-oils without pretreatment was reduced to 9.6 mm^2/s and with pretreatment was reduced to 9.1 mm^2/s.

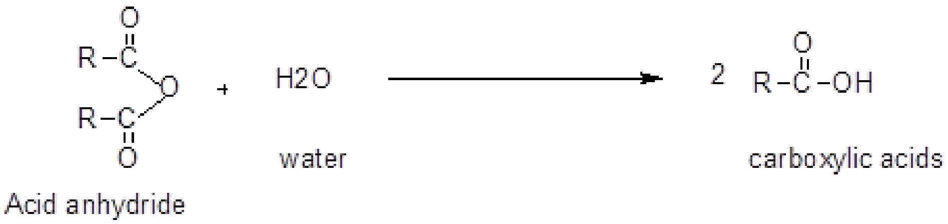
Bio-oil contains 25-35 wt% of “bound water” which is water that is physically and/or chemically bound within the bio-oil so that it does not separate from the bio-oil. The presence of a high quantity of water contributes to catalyst deactivation that often occurs during catalytic bio-oil upgrading. Water removal, as a means of pretreatment, will improve the bio-oil’s properties of heating value, viscosity and density and reduce the risk of catalyst poisoning during bio-oil upgrading, especially in the case of noble metal catalyst application (Lin et al. 2012).

Wang et al. (2009) separated water from the crude bio-oil derived from pine biomass by molecular distillation. Molecular distillation is a vacuum distillation below the pressure of 0.01 Torr to ensure temperatures are well below the compound’s normal boiling points. RBO was first centrifuged and filtered to remove solid impurities. This filtered bio-oil was fractionated by the molecular distillation process into light, middle and heavy fractions at 70, 100 and 130 ^{o}C at a pressure of 60 Pa. Based on the analysis of properties, the light fraction contained 50-70% water; the middle fraction had low water content of 1-2%; the heavy fraction, without volatile compounds, was similar to a black solid in appearance and contained a negligible water percentage. Researchers observed that rising distillation temperature resulted in the increased yield of light and middle fractions and the reduced yield of the heavy fraction. The heating and pH values of all three fractions were observed to increase compared to RBO.

Guo et al. (2011) also applied molecular distillation technology to remove water from bio-oil to produce a bio-oil with high carboxylic acid and ketone fraction. The first molecular distillation process was performed under 80 °C and 1600 Pa to produce bio-oil fraction 1. The residual heavy fraction was subjected to a second molecular distillation at 80 °C and 340 Pa to produce bio-oil fraction 2. These two fractions were mixed to form a new bio-oil which was esterified by adding n-propanol in the presence of a lanthanum-promoted solid acid catalyst in a stainless steel autoclave under atmospheric pressure at a temperature of 90 °C for 2 h. Researchers successfully decreased the acid content of the RBO from its initial 18.4% to 2.7% in the upgraded bio-oil. The ester content increased from 0.72% for RBO to 31.2% for esterified bio-oil.

Lin et al. (2012) developed a two-step process to remove bound water from bio-oil. They first combined the bio-oil with an azeotrope agent. The azeotrope agent contained one or more C_6-C_{10} water-insoluble hydrocarbons. Researchers then subjected this treated bio-oil product to distillation with an azeotropic distillation column which contained both overhead and bottom columns. The azeotropic distillation process was performed at a top column pressure in the range of 10 to 750 mmHg and a bottom column temperature in the range of 30 to 140 °C. Researchers obtained an overhead stream comprised of high water content. A lower second stream consisted of a water-depleted bio-oil. They also observed that the water-rich overhead stream comprised about 75 wt% of the bound water originally present in RBO.

As shown in Scheme 3.2, one mole of acid anhydride hydrolyzes with one mole of water present in bio-oil to give two moles of corresponding carboxylic acids. With this treatment, the water content in the bio-oil will decrease depending on the ratio of acid anhydride to bio-oil and the bio-oil carboxylic acid content will also increase. This will further help to increase the product yield and the energy density of the upgraded bio-oil due to the presence of a higher acid content.



Scheme 3.2 The chemical reaction pathway of an acid anhydride pretreatment to bio-oil bound water to give two moles of carboxylic acid.

Very limited research has been performed to convert the more reactive aldehydes to carboxylic acids or to remove bound water from bio-oil. Therefore, there remains a need to develop efficient pretreatment methods to convert aldehydes to carboxylic acids and to lower bound water content in bio-oil.

3.3 Objective

The objective of this study was to develop pretreatment methods to modify the chemical composition and properties of biomass derived bio-oil. This research was divided into three phases by applying two pretreatment methods: in the first phase, an oxidation pretreatment was performed to convert the aldehyde functional groups to carboxylic acids. In the second phase, an acid anhydride pretreatment was performed to convert bio-oil bound water to carboxylic acids. In the third phase both methods were employed both simultaneously and consecutively.

3.4 Research materials and methods

3.4.1 Materials

Hydrogen peroxide (H_2O_2) 50 wt% solution in water, oxone (potassium monopersulfate triple salt) and butyric anhydride were obtained from Sigma-Aldrich. All chemicals were used with no further purification. Oxygen gas was obtained from nexAir. Ozone used in this study to oxidize the raw bio-oil was produced by pumping the pure oxygen (obtained from nexAir) through an OZV-8 ozone generator with 8 g/h ozone flow directly into the pretreatment reaction vessel.

Raw bio-oil (RBO) required for this research was produced from loblolly pine wood chips with a size of 1-3 mm and moisture content of 8-10%, dry-basis. Bio-oil was produced by fast pyrolysis performed at a temperature of 450 ^{o}C with nitrogen carrier gas at a rate of 7-kg/h with the auger-feed pyrolysis reactor located in the Department of Sustainable Bioproducts, Mississippi State University (MSU). Several pyrolysis runs were required to produce bio-oils for experiments. The mass balance for these runs varied but yields of the products ranged from 60-65% for bio-oil, 10-15% of non-condensable gases and 20-25% char on dry biomass basis. The mean RBO yield for all of these runs was 62.1%.

3.4.2 Methods

3.4.2.1 RBO oxidation pretreatment by oxone and H_2O_2 individually and combined

All the optimization reactions of oxidation pretreatment of bio-oil were conducted in a 250 ml round-bottom flask equipped with an electronic stirrer in a closed hood. Once the pretreatment by oxidation conditions was optimized further experiments with the optimized conditions were performed in a stainless steel, high-pressure batch autoclave (Parr Instruments and Co) reactor equipped with an overhead magnetic stirrer, a pressure indicator with a maximum capacity of 5000 psig and a thermocouple for temperature monitoring in the range of 0-500 ºC. The autoclave was equipped with an electrical heating and cooling system to control reactor temperature. The oxidation of RBO was tested with three oxidizing agents: oxone alone, H_2O_2-alone and a combination of oxone and H_2O_2 (oxone/H_2O_2). The oxidation reactions were performed at an ambient reaction temperature and pressure.

The oxidation of RBO by oxone alone was tested by addition of 2.5, 5.0, 7.5 and 10 wt% of oxone. The oxidation of RBO by H_2O_2-alone was tested by addition of 2.5, 5.0, 7.5 and 10 wt% of H_2O_2. The pretreatment with the highest acid value (AV) was selected as having the best performance unless the increase in AV for higher reagent addition was considered negligible. A choice of highest AV without consideration of the amount of reagent consumed would result in an optimal AV value but not an optimal choice based on catalyst cost. Magnitude of AV was utilized as the selection criteria because it indicated the highest production of carboxylic acids, which in turn represented an increased conversion of aldehydes and some other oxygenated compounds. The oxidation of RBO was also tested by combination of the best oxone-alone treatment oxone wt% and the best H_2O_2-alone treatment H_2O_2 wt%. This oxone/H_2O_2 solution was prepared by dissolving the desired wt% of oxone in the desired wt% of commercial 50 wt% H_2O_2 solution in water. The effect of the reaction time on the oxidation pretreatment was tested at 30, 60, 90 and 120 min at the optimum pretreatment reaction conditions. In the remainder of this study, for clarity of understanding, the pretreated RBO by oxidation will be termed *oxidized product.*

Following the oxidation pretreatment of RBO, the oxidized product with high carboxylic acid content was further pretreated with acid anhydride treatment to reduce water content in the oxidized product.

3.4.2.2 RBO oxidation pretreatment by ozone and H_2O_2 individually and combined

The oxidation of RBO was also tested with ozone alone, H2O2-alone and a combination of ozone and H2O2 (ozone/H2O2). These three (ozone-alone, H2O2-alone and ozone combined with H2O2) RBO oxidation pretreatments were performed in a 250 ml round bottom flask equipped with an electronic stirrer in a closed hood. Oxidation reactions were performed at ambient temperature and pressure. The oxidation of RBO by ozone-alone was performed by pumping 3-5 psig ozone into the pretreatment reaction vessel followed by stirring for 60 min at room temperature. For the H2O2-alone results for the 2.5, 5.0, 8.7 and 10.0% utilization ratios the treatment percentage that produced the highest AV level was selected for further testing for the combination of ozone and H2O2 treatment. The oxidation of RBO by H2O2-alone was performed by addition of 10 wt% of commercial 50 wt% H2O2 solution in water followed by stirring for 60 min at room temperature and without pressure. The oxidation of RBO was also conducted for a mixture of ozone/H2O2 by pumping 3-5 psig ozone into the round bottom flask containing a mixture of RBO and 10 wt% of commercial 50 wt% H2O2 solution in water followed by stirring for 60 min at room temperature. Again, the pretreatment with the highest AV was selected as having the best performance because it indicated the highest production of carboxylic acids, which in turn represented an increased conversion of aldehydes and other oxygenated compounds. The effect of reaction time at 0, 15, 30, 45, 60, 75 and 90 min on the oxidation of RBO with ozone/H2O2 oxidizing agent was tested. The RBO pretreated by best ozone/H2O2 treatment produced product was referred to as the oxidized product-II.

3.4.2.3 Pretreatment of RBO and oxidized product by acid anhydride

The pretreatment of the oxidized product by acid anhydride was performed in the same Parr batch autoclave described in section 3.4.2.1. In this study, butyric anhydride was selected as the acid anhydride for testing. The effect of weight percent of butyric acid anhydride pretreatment of the oxidized product (conversion of oxidized product's water to carboxylic acids) was tested at 5, 15, 25 and 35 wt%. The best butyric anhydride treatment level was selected based on the butyric acid anhydride pretreated oxidized product (APOP) that had the lowest water content. The effects of reaction temperature at 30, 60, 90 and 120 ^{o}C and reaction times of 30, 60, 90 and 120 min on the acid anhydride pretreatment of the oxidized product were also tested.

As a control, simultaneous oxidation and butyric acid anhydride pretreatment of the RBO (SOAPRBO) and direct butyric acid anhydride pretreatment of the RBO (DAPRBO) were also tested. The SOAPRBO and DAPRBO products properties such as water content, acid value and HHV were compared to the APOP obtained by oxidation followed by acid anhydride treatments performed separately to identify the best pretreatment method.

3.5 Data analysis

The RBO, oxidized product, oxidized product-II, APOP, DAPRBO and SOAPRBO were characterized by following ASTM methods. The densities were determined by Anton Parr DMA 35n portable density meter by ASTM D4052 method. Viscosities were determined by Ubbelohde capillary viscometer at 40 ^{o}C water bath temperature by ASTM D445 method. Higher heating values (HHV) were determined by Ika-5000 bomb calorimeter by ASTM D240 method. The acid values (AV) were determined by dissolving 1 g of bio-oil in 50 ml of 35:65 ratio of isopropanol to water mixtures and titrating to a pH of 8.5 with 0.1N KOH solution by ASTM D664 method. The pH values were determined by addition of 1 g of bio-oil to 50 ml of 35% of isopropanol mixture. The pH values were determined by ASTM E70 method. Elemental carbon, hydrogen, and nitrogen were determined by EAI CE-440 elemental analyzer with oxygen content determined by difference according to ASTM D5291 method. Water content was determined by Karl-Fisher titration by ASTM E203. The GC-MS analysis of the fuels was performed with a Hewlett-Packard HP 5890-Series II GC equipped with a Hewlett-Packard HP 5971 series MS. FTIR spectra were obtained by Varian 3500 FTIR analyzer with standard potassium bromide disk technique and spectra were analyzed by Varian-Resolutions software.

3.6 Results and discussion

3.6.1 RBO oxidation pretreatment by oxone and H_2O_2 individually and combined

Figure 3.1 compares the AVs of the oxidized products produced from oxone-alone and H_2O_2-alone oxidizing agents' treatments to the RBO. All the results reported were taken average of three replicas of each experiment. As a benchmark value for comparison of the RBO oxidation treatments on the resultant oxidized products it is noted that the AV of the RBO was 92.4 mg KOH/g. As shown in Figure 3.1, the AVs of the oxidized products produced by 2.5, 5, 7.5 and 10 wt% oxone-alone treatments were 102.0, 114.7, 115.6 and 116.0 mg KOH/g, respectively. The AV of the oxidized product increased by 10.4% for the 2.5 wt% oxone treatment compared to RBO. The increase was 12.5% when the oxone-alone treatment increased from 2.5 wt% to 5.0 wt%. For the oxone wt% increase to 7.5 wt% and 10.0 wt% the AV increase was a negligible 0.8% and 0.4%, respectively. Therefore, RBO pretreated by 5.0 wt% of oxone was considered as the best treatment due to the small gains in AV increase as a result of the 7.5 and 10.0 wt% treatments.

As also shown in Figure 3.1, the AVs of the oxidized products produced from 2.5, 5.0, 7.5 and 10 wt% H_2O_2-alone treatments were 111.3, 112.8, 116.2 and 118.4 mg KOH/g, respectively. Compared to the RBO AV of 92.4 mg KOH/g the AV of the 2.5% H_2O_2-alone treatment resulted in a 20.4% increase in AV making a treatment at this level certainly worthwhile. For the increase in H_2O_2 alone 2.5 to 5.0, 5.0 to 7.5 and 7.5 to 10.0 wt% the respective AV percentage increases were 1.3, 3.0 and 2.0%. It was observed there was a considerable effect on the AV by increasing the amount of H_2O_2 to 10 wt%; therefore, RBO pretreated by 10 wt% H_2O_2 was considered the best treatment.

The RBO pretreated by oxone-alone and H_2O_2-alone was influential on AV increase but this increase was likely not high enough to repay the expense of oxidation treatment.

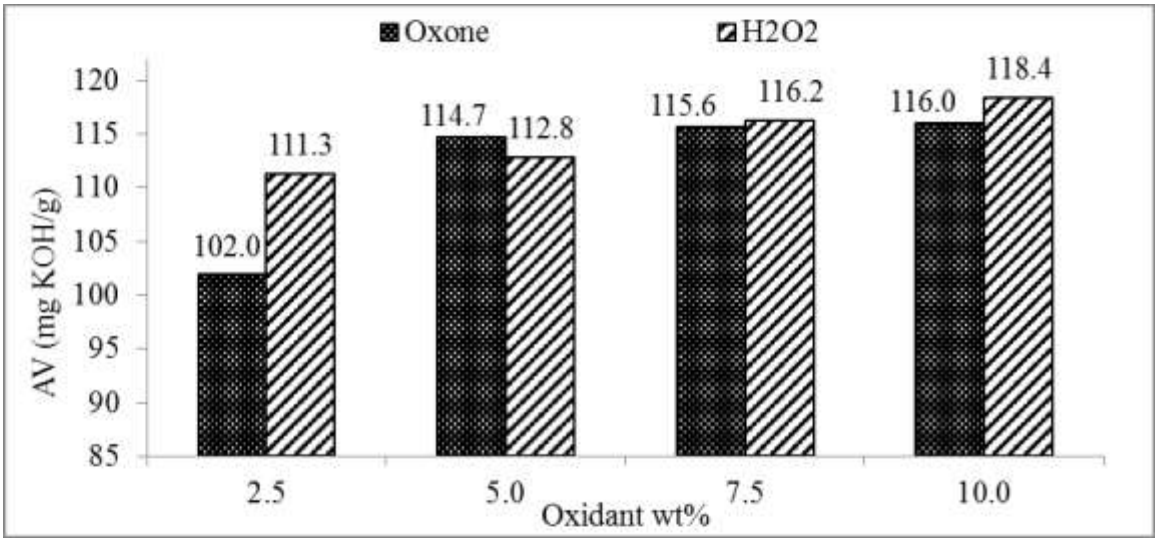


Figure 3.1 AVs comparison of the RBO and oxidized products produced from oxone-alone, H_2O_2-alone oxidizing agents' treatments to the RBO.

Table 3.1 shows that the pretreatment of RBO using (0.15 mol)oxone+(0.07mol)H_2O_2 (combination of 5wt% oxone plus 10wt% H_2O_2; oxone and H_2O_2 are in 2:1 mol ratio were utilized) resulted in a much higher AV than for use of these two oxidants individually. Table 3.1 shows the physical and chemical properties of the oxidized product produced from the 5wt%oxone+10.0wt% H_2O_2 treatment. As shown in Table 3.1 the acid number increased from 90.2 for RBO to 156.9 mg KOH/g for the combined oxidant pretreatment. Viscosity decreased by 45.1%; water content increased by about 11%. The increase in water content may be due to the addition of 50wt% aqueous H_2O_2 reagent. The HHV of the acidified product decreased from 16.0 to 15.4 MJ/kg probably due to the water content increase. Density decreased from 1.2 to 1.1 g/ml and pH was reduced to 2.6 from 3.1. Oxygen content increased somewhat from 53.6 to

56.9 wt%. The increased oxygen content likely resulted from both increased acid and water content.

Table 3.1 Comparison of RBO and oxidized product physical and chemical properties.

Properties	**RBO**	**Oxidized product**
Density, g/mL	1.2	1.1
HHV, MJ/kg	16.0	15.4
Oxygen, wt%	53.6	56.9
AV, mg KOH/g	90.2	156.9
pH	3.1	2.6
Water content, vol%	30.4	33.7
Kinematic viscosity, 40°C, cSt	12.0	8.6
Yield (wt%)	-	99%

Figure 3.2 compares the AVs, water and oxygen contents of the oxidized products produced from 5wt%oxone+10.0wt% H_2O_2 treatment at reaction times of 0, 30, 60, 90 and 120 min. As shown in Figure 3.2, the AVs of the oxidized products were 110.5, 141.8, 154.6, 160.4 and 161.2 mg KOH/g at 0, 30, 60, 90 and 120 min, respectively. The oxidized products produced had approximately the same 31.8, 33.2, 33.5, 33.8 and 33.8 wt%s of water content at the respective 0, 30, 60, 90 and 120 min treatments. The oxygen contents of the oxidized products were 55.8, 56.4, 56.5, 56.7 and 57.0 at 0, 30, 60, 90 and 120 min, respectively. The HHVs of the oxidized products were not able to be

determined by calorimeter because the high water content did not allow ignition. The AVs of the oxidized product increased as the reaction time increased from 0 to 90 min (from 110.5 to 160.4 mg KOH/g). For the 120 min treatment the AV of the oxidized product increased by only 0.5%. For this reason AV increase of the oxidized product produced at a reaction time of 90 min was considered as the best result.

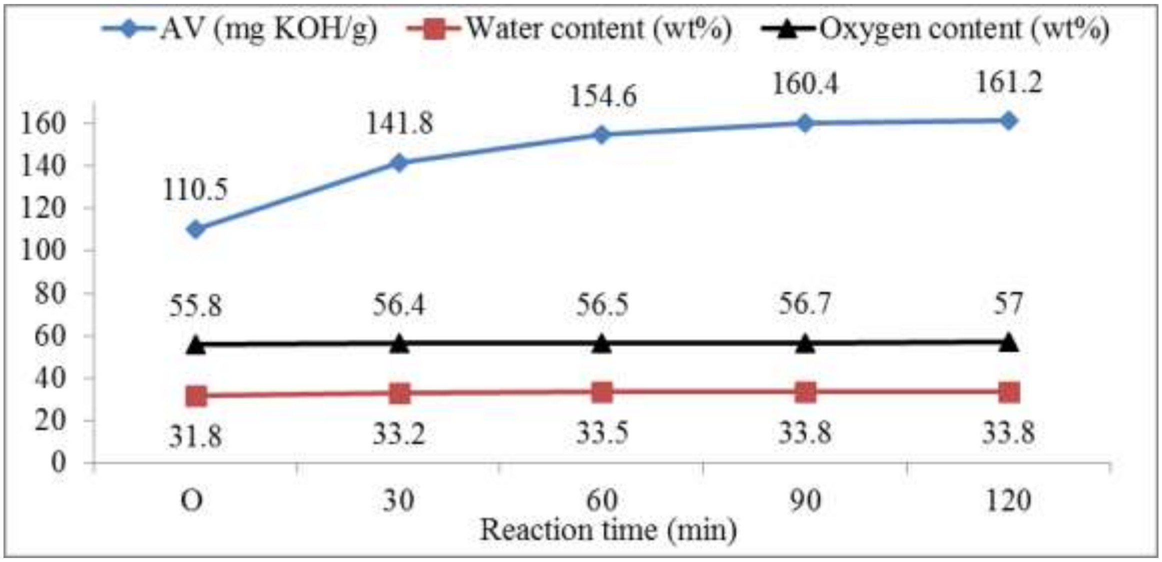


Figure 3.2 Compares the AVs, HHVs, water contents and oxygen contents of the oxidized products produced at reaction times of 0, 30, 60, 90 and 120 min.

3.6.1.1 GC-MS analysis of the RBO and oxidized product

Table 3.2 shows the GC-MS analyzed chemical composition of RBO and oxidized product produced from pretreatment of RBO using 5wt%oxone+10.0wt%H_2O_2 (0.15 mol oxone plus 0.07 mol H_2O_2) at the 90 min reaction time at ambient temperature and pressure. Approximately 50 chemical compounds were identified by EPA/NIST library search not confirmed by comparison to authentic compounds using GC-MS chromatogram in both samples. The chemical compound name and their area percentages are given in Table 3.2. The total area percentages of the major fifty compounds present in RBO and oxidized product were 98.12% and 99.9%, respectively. As shown in Table 3.2 it can be noted that, after the pretreatment of RBO, its chemical composition as measured by GC-MS area percentage was changed considerably. The carboxylic acids of the oxidized product increased to 37.6 area% from the 9.8 area% for RBO, an increase of 283.7%. The oxidized product aldehydes and ketones content decreased to 1.5 and 9.6 area% from 11.1 and 36.8 area% for RBO, respectively. The aldehydes of the RBO were decreased by 86.5% due to the conversion of aldehydes to carboxylic acids during the oxidation pretreatment. The esters and ethers were reduced to 3.4 area% for the oxidized product from 12.1 area% of RBO. The alcohols and phenols contained in the RBO at 39.3 area% decreased to 32.6 area% for the oxidized product. The remaining RBO compounds increased from 2.1 area% to 15.3 area% for the oxidized product.

Table 3.2 RBO and oxidized product chemical composition analysis by GC-MS with area percentages.

Raw bio-oil		**Oxidized product**	
Compound name	Area%	Compound name	Area%
Acids		**Acids**	
Acetic acid	5.1	Acetic acid	6.01
Heptanoic acid	1.42	Glyceric acid	1.69
Benzoic acid, 4-hydroxy-3-methoxy-	0.75	1,3-butadiene-1-carboxylic acid	0.71
Benzene acetic acid, alpha-hydroxy-	1.96	pentanoic acid, 1,1-dimethylpropyl	1.05
benzene acetic acid, 4-hydroxy-3-methyl	0.54	2-Oxiranecarboxylic acid	1.95
Esters & Ethers		Butanoic acid, 2-ethyl-,1,2,3-propyl	0.66
acetic acid, 1-methylethyl ester	1.82	2-propenoic acid, 2-methyl-,ethyl	0.6
pentanoic acid, ethyl ester	0.92	Heptanoic acid	0.8
n-heptyl hexanoate	0.94	hexanoic acid	18.97
Hexanoic acid, 1-methylhexyl ester	1.85	3-hydroxy-4-methoxybenoic acid	0.82
1-propene, 1-methyoxy-2-methyl-	0.93	propanoicacid ,2, 2-dimethyl-	0.94
Furan, 2-ethoxy-2,3-dihydro-4-methyl	0.58	benzeneacetic acid, 4-hydroxy-3-methyl	1.67
2,6-Dimethoxytoluene	0.9	octanoic acid, 2-tetrahydrofurylmethyl-	0.98
3-methoxy-4-methylaniline	1.25	propanoicacid , dibutyl-, diethyl	0.77

Table 3.2 (Continued)

4,4'-Dimethoxy-biphenyl-2-carboxyl-	0.98	**Esters & Ethers**	
Aldehydes & Ketones		Acetic acid, hydroxy-, methyl ester	0.8
furfural	1.94	butanoic acid, propyl ester	1.65
2-cyclopenten-1-one, 2-hydroxyl-	1.42	furan, 2-ethyltetrahydro-5-methoxy	0.92
2-furancarboxaldehyde, 5-methyl-	0.63	**Aldehydes & Ketones**	
2-cyclopenten-1-one, 2-hydroxy-3-methyl	1.84	2-butanone, 4-hydroxy-3-methyl-	0.5
Glutaraldehyde	1.16	2 (5H)-Furanone	0.5
4H-Pyran-4-one, 3,5-dihydroxy-2-methyl-	0.58	2-Furancarboxaldehyde, 5-methyl-	0.51
cyclopentanecarboxaldehyde	0.82	1,2-Cyclopentanedione, 3-methyl	1.79
2-Furancarboxaldehyde, 5-methyl-	1.78	5-octen-4-one, 7-methyl-	1.29
5-methyl-2-thiophenecarboxaldehyde	0.55	vanillin	1.01
Ethanone, 1-(4-hydroxy-3-methoxyphenol)	20.81	ethanone, 1-(4-hydroxy-3-methoxyphenol	0.5
4-hydroxy-2-methylacetophenone	1.27	4-hydroxy-2-methylacetophenone	1.21
Benzaldehyde, 3-hydroxy-, oxime	0.74	4-methyl.delta.-naphthoflavone	3.8
4-hydroxy-2-mehoxycinnamaldehyde	0.71	**Alcohols**	
9,12-octadecadienal	0.6	2-Propanone, 1-hydroxy	1.37

Table 3.2 (Continued)

2-propanone, 1-94-hydroxy-3-methoxy)-	0.84	p-Dioxane-2,3-diol	1.1
vanillin	1.09	2- Furabethanol, beta-methoxy-	3.22
Alcohols	3.63	2-Aminoresorcinol	1.11
2-Propanone, 1-hydroxy	1.14	Phenol, 4-methyl	0.51
phenol, 2-methyl-	0.72	Phenol, 2-methoxy	3.19
phenol, 4-methyl-	4.15	phenol, 2-methoxy-4-methyl-	7.82
phenol, 2-methoxy-	0.59	cyclopentanol, 1-methyl-	0.63
4-mercaptophenol	10.81	1,2-Benzenediol,3-methyl	1.11
Phenol, 2-methoxy-4-methyl-	0.93	Phenol, 4-ethyl-2-methoxy	1.92
1,2-Benzenediol, 3-methyl-	2.61	2-Methoxy-4-vinylphenol	1.2
phenol, 4-ethyl-2-methoxy-	1.31	Eugenol	1.33
1,2-Benzenediol, 4-methyl-	3.63	Phenol, 2-methoxy-4-propyl	0.67
Eugenol	1.78	1-butene, 1-methoxy-	0.81
1-propene, 1-methyoxy-2-methyl-	0.93	Phenol, 2-methoxy-4-(1-propenyl)	4.65
phenol, 2-methoxy-4-(1-propenyl)-	1.65	homovanillyl alcohol	0.96
Phenol, 2-methoxy-3-(2-propenyl)-	3.28	phenol, 4-amino-2,5-dimethyl-	0.99
phenol, 2-methoxy-4-propyl-	3.16	**Other**	
homovanillyl alcohol	0.98	tricyclo [5.2.2.0 (2,6)] undacen-11-O	10.62
phenol, 2-methoxy-4-(methoxymethyl)-	0.65	pyridine, 2-fluoro-	0.64
Ethyl, 4-hydroxy-7-trifluoromethyl-quinoline	0.98	3,4-anhydro-d-galactosan	0.91

Table 3.2 (Continued)

Other		cyclohexane, 1,2,4,5-tetraethyl-	0.65
3,4-anhydro-d-galactosan	2.1	5-nitro-3-phenyl-1H-indazole	1.22
Total	98.12	4-formyl-1-1,3(2H)-dihydroimidazole-	1.23
		Total	99.96

3.6.1.2 FTIR analysis of the RBO and oxidized product

Figure 3.3 shows the comparison of RBO and oxidized product FTIR spectra. These spectra identified the functional groups present in the product types. Characteristic vibrational modes were observed at 3200-3600 cm^{-1} (OH stretch), 2800-3100 cm^{-1} (CH aliphatic stretch), 1600-1750 cm^{-1} (C=O stretch), 1350-1470 cm^{-1} (CH bending) and 1000-1250 cm^{-1} (C-O stretch). It was observed that C=O stretching was decreased and OH stretching was intensified, indicating that carbonyl compounds (mainly aldehydes and ketones) were converted to carboxylic acids. The findings of the FTIR spectra were in good agreement with the physical and chemical properties described in Table 3.1 and GC-MS analysis as shown in Table 3.2.

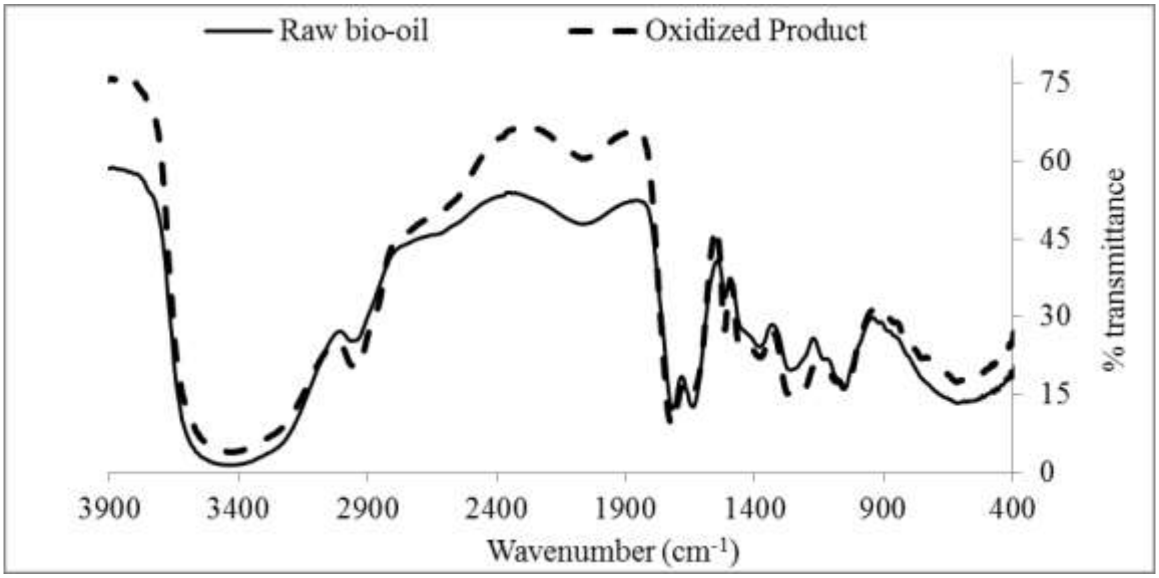


Figure 3.3 FTIR spectra comparing RBO and oxidized product.

3.6.2 RBO oxidation pretreatment by ozone and H_2O_2 individually and combined

Figure 3.4 compares AVs of the pretreated products obtained from 1-h pretreatments of RBO with ozone alone, H_2O_2-alone and the ozone/H_2O_2 combination. Figure 3.4 indicates that after pretreatment of RBO with ozone-alone pretreatment the AV increased from 90.3 of RBO to 107.7 mg KOH/g; with H_2O_2-alone pretreatment the AV increased from 90.3 to 118.3 mg KOH/g. For the combined ozone/H_2O_2 pretreatment AV increased from 90.3 to 161.9 mg KOH/g. The 161.9 mg KOH/g AV for the ozone/H_2O_2 pretreatment represented respective 50.3% and 36.8% increases in AV above the values for the ozone-alone and H_2O_2-alone pretreatments.

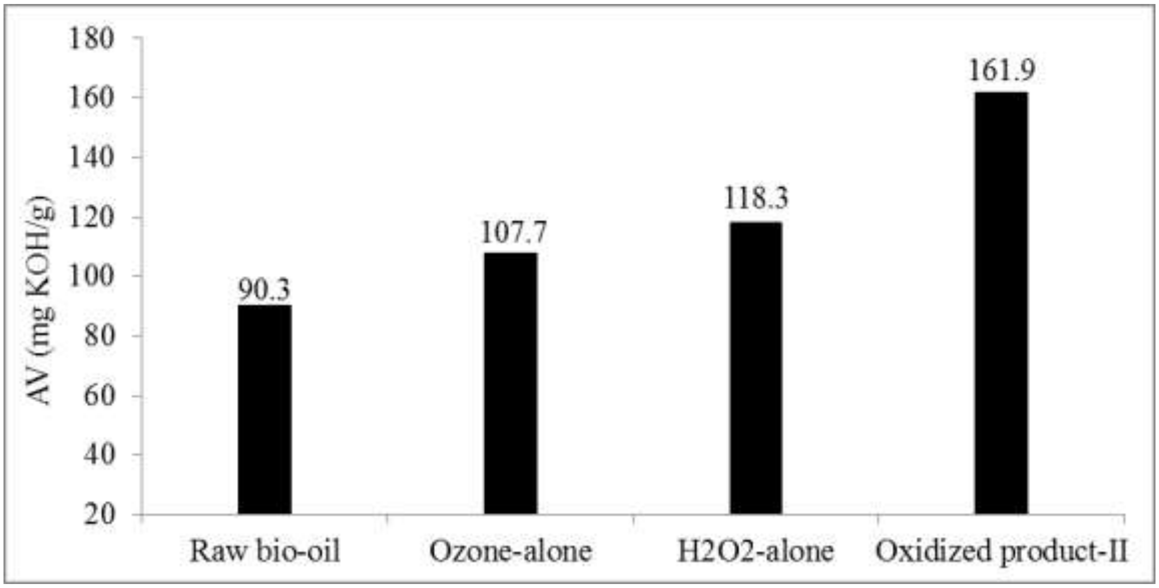


Figure 3.4 Effect on AVs of ozone-alone, H_2O_2-alone and combined ozone/H_2O_2 oxidation pretreatments applied to RBO over a time period of 1 h.

The high AV of the oxidized product-II indicated the conversion of aldehydes and other oxygenated compounds to carboxylic acids. Therefore, the best pretreatment for oxidation of RBO utilizing ozone and based on highest AV obtained was the ozone/H_2O_2 combined pretreatment.

3.6.2.1 Effect of reaction time on the ozone/H2O2 pretreatment to RBO

Figure 3.5 shows the effect of combined ozone/H_2O_2 pretreatment on RBO AV over time and tested at 15 min time intervals over a zero to 90 min time range. The AV of the oxidized product-II at time zero was 110.4 mg KOH/g; the AV of oxidized product-II after 90 min reaction time was 162.5 mg KOH/g. However, after 1h the AV of the oxidized product-II remained essentially constant for the 75 and 90 min time periods.

Therefore, ozone/H_2O_2 pretreatment performed for reaction time 1 h was considered the best treatment.

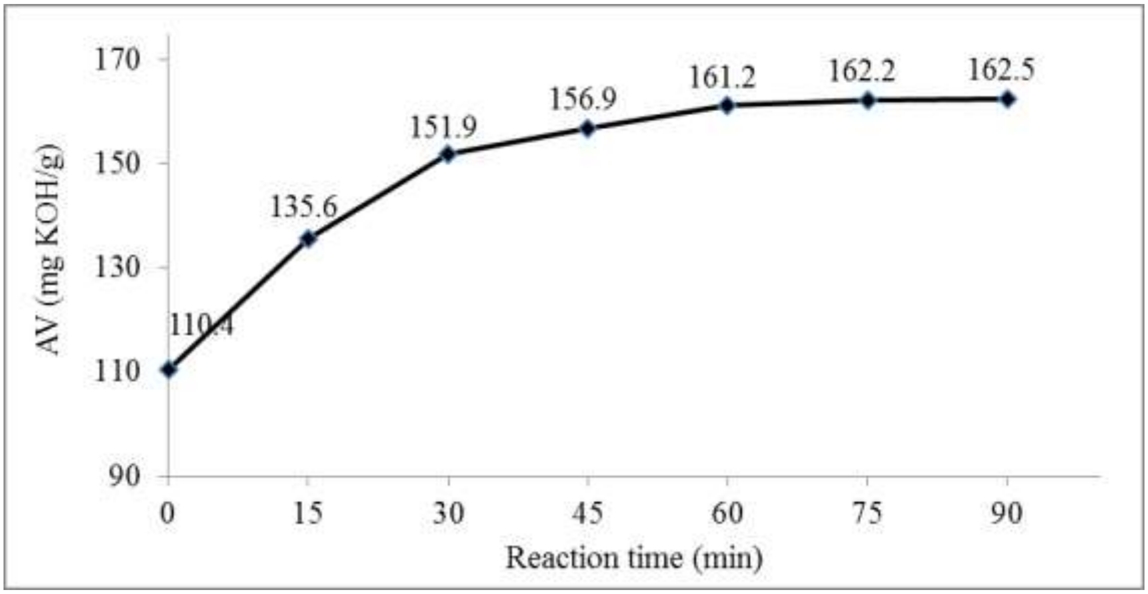


Figure 3.5 Effect of ozone/H_2O_2 pretreatment on AV of oxidized product-II over time as measured at 15-min intervals from zero to 90 min.

3.6.2.2 FTIR analysis of the RBO and oxidized product-II

Figure 3.6 compares the FTIR spectra of RBO and oxidized product-II for ozone/H_2O_2 at the best to 60 min reaction time. Characteristic vibrational modes were observed at 1650-1710 cm-1 (C=O stretching) and 3600-3000 cm-1 (HO stretching). It was observed that C=O stretching was decreased and OH stretching was intensified, indicating that carbonyl compounds (mainly aldehydes and ketones) were converted to carboxylic acids.

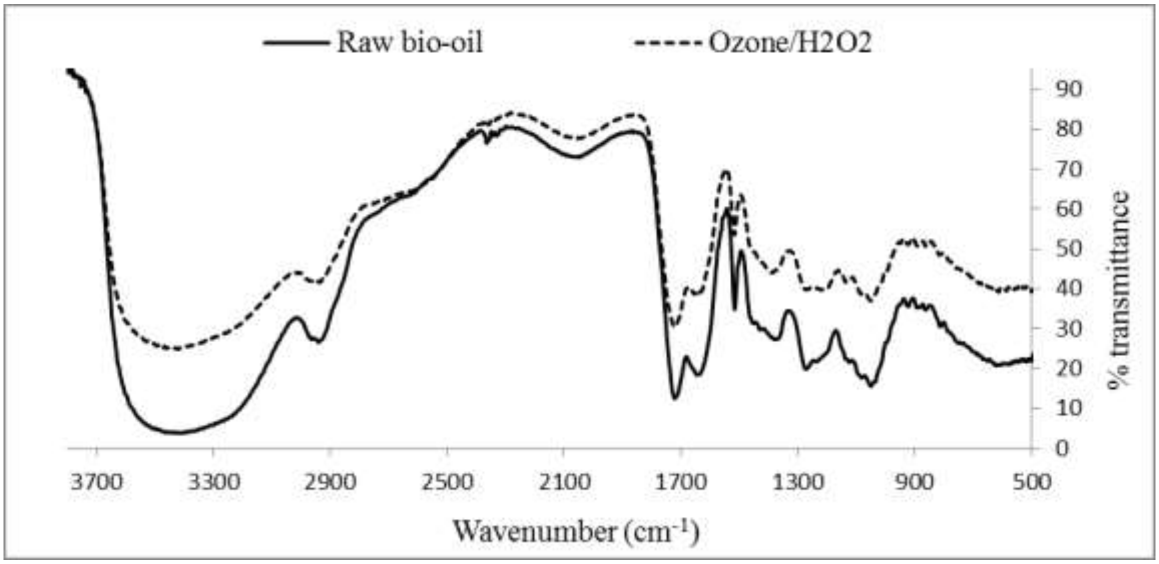


Figure 3.6 FTIR spectrum comparison of RBO and oxidized product-II.

Table 3.3 shows a comparison of physical and chemical properties between RBO and oxidized product-II. The AV of oxidized product-II increased to 165.4 mg KOH/g from 90.2 mg KOH/g the value of RBO. The total AV increased by 83.16 %, which indicated the oxidation of aldehydes, ketones and phenols to carboxylic acids. The viscosity decreased from 12.0 to 9.2 cSt and water content increased from 30.4 to 33.5%. The HHV of the oxidized product increased from 16.0 to 16.4 MJ/kg. Density decreased from 1.2 to 1.0 g/ml and pH was reduced to 2.3 from 3.1. Oxygen content increased somewhat, from 53.9 to 55.3 wt%. This oxygen content increase likely resulted from both increased acidity and water content of oxidized product-II.

Table 3.3 Comparison of some physical and chemical properties of RBO and oxidized product-II.

Properties	**RBO**	**Oxidized product-II**
HHV, MJ/Kg	16.0	16.4
AV (mg KOH/g)	90.2	165.4
Water content (%)	30.4	33.5
Density, g/ml	1.2	1.0
Kinematic viscosity, 40 °C, cSt	12.0	9.2
pH	3.1	2.3
Elemental analysis (%)		
C	38.4	37.6
H	7.6	7.6
N	0.2	0.2
O	53.7	54.6
Yield (wt%)	-	99%

3.6.2.3 GC-MS analysis of the RBO and oxidized product-II

Table 3.4 shows the chemical composition of RBO and oxidized product-II analyzed by GC-MS. Approximately 50 chemical compounds were identified by GC-MS in both samples. The chemical compound name and their area percentages are given. The total area percentages of the major fifty compounds present in RBO and oxidized product-II were 98.12 and 100.0%, respectively. As shown in Table 3.4 it is very clear that, after the pretreatment of RBO by ozone/H_2O_2, its chemical composition as measured by GC-MS area percentage changed considerably. The carboxylic acids of the oxidized product-II increased to 49.56 area% from the 9.8 area% for RBO, an increase of 405.7%. The oxidized product-II aldehydes and ketones decreased to 0.62 and 2.07 area% from 11.1 and 36.8 area% of RBO, respectively. The aldehydes of the RBO were decreased by 94.4% due to the conversion of aldehydes to carboxylic acids during the oxidation pretreatment. Esters-ethers were reduced to 6.25 area% for oxidized product-II from 12.1 area% of RBO. The alcohols and phenols of the RBO decreased from 39.3 area% to 23.1 area% for oxidized product-II. The other RBO compounds increased from 2.1 area% for RBO to 18.4 area% for oxidized product-II.

Table 3.4 RBO and oxidized product-II chemical composition analysis by GC-MS with area percentages for the compounds.

RBO		**Oxidized product-II**	
Compound name	Area%	Compound name	Area%
Acids		**Acids**	
Acetic acid	5.1	Acetic acid	14.46
Heptanoic acid	1.42	1-Butaneboronic acid	0.47
Benzoic acid, 4-hydroxy-3-methoxy-	0.75	Pentanoic acid, 4-oxo-	1.29
Benzeneacetic acid, alpha-hydroxy-	1.96	d-(+)-Glyceric acid	0.14
benzeneacetic acid, 4-hydroxy-3-methyl	0.54	Hexanoic acid	0.87
Esters & Ethers		Guanidineacetic acid	1.02
acetic acid, 1-methylethyl ester	1.82	d-(+)-Glyceric acid	0.47
pentanoic acid, ehtyl ester	0.92	Propanoic acid, 2-methyl-, tert-butyl	0.67

Table 3.4 (Continued)

n-heptyl hexanoate	0.94	Sulfurous acid, 2-methyl-4-methoxy	0.35
Hexanoic acid, 1-methylhexyl ester	1.85	3-Butenoic acid, 2,2-dimethyl-	1.53
1-propene, 1-methyoxy-2-methyl-	0.93	Heptanoic acid	17.39
Furan, 2-ethoxy-2,3-dihydro-4-methyl	0.58	Benzeneacetic acid, 4-hydroxy-3-methyl	0.87
2,6-Dimethoxytoluene	0.9	Sulfurous acid, dodecyl 2-pentyl	4.04
3-methoxy-4-methylaniline	1.25	N-Methylmaleamic acid	0.73
4,4'-Dimethoxy-biphenyl-2-carboxyl-	0.98	Hexanedioic acid, bis(2-ethylhexyl	4.75
Aldehydes		1-Phenanthrenecarboxylic acid, 1,2	0.34
furfural	1.94	Butanedioic acid, 2,3-dibromo-	0.17
2-furancarboxaldehyde, 5-methyl-	0.63	**Esters & Ethers**	
Glutaraldehyde	1.16	Acetic acid, hydroxy-, methyl ester	1.37
cyclopentanecarboxaldehyde	0.82	Acetic acid, 1-methylethyl ester	0.92
2-Furancarboxaldehyde, 5-methyl-	1.78	Acetic acid, fluoro-, ethyl ester	0.57
5-methyl-2-thiophenecarboxaldehyde	0.55	Furan, tetrahydro-2,5-dimethoxy-	0.45
vanillin	1.39	Oxalic acid, isohexyl pentyl ester	0.62
9,12-octadecadienal	0.6	Sulfurous acid, hexyl nonyl ester	2
Benzaldehyde, 3-hydroxy-, oxime	0.74	4-Nitrobenzoic acid, dodecyl ester	0.18

Table 3.4 (Continued)

4-hydroxy-2-mehoxycinnamaldehyde	0.71	Decanoic acid, decyl ester	0.14
4-hydroxy-2-methylacetophenone	1.27	**Aldehydes**	
Ketones		1-Cyclohexene-1-acetaldehyde, 2,6,	0.2
4H-Pyran-4-one, 3,5-dihydroxy-2-methyl-	0.58	Formaldehyde, dimethylhydrazone	0.42
2-propanone, 1-94-hydroxy-3-methoxy)-	0.84	**Ketones**	
2-cyclopenten-1-one, 2-hydroxy-3-methyl	1.84	2-Propanone, 1,3-difluoro-	0.44
2-cyclopenten-1-one, 2-hydroxyl-	1.42	2-Propanone, 1-cyclopropyl-	0.13
Ethanone, 1-(4-hydroxy-3-methoxyphenol)	19.55	Butyrolactone	1.5
Alcohols		**Alcohols**	
2-Propanone, 1-hydroxy	3.63	2-Propanone, 1-hydroxy-	2.49
phenol, 2-methyl-	1.14	Cyclopentanol	0.57
phenol, 4-methyl-	0.72	Silanol, trimethyl-	0.32
phenol, 2-methoxy-	4.15	2(R),3(S)-1,2,3,4-Butanetetrol	1.12
4-mercaptophenol	0.59	Tricyclo[5.2.2.0(2,6)]undecan-11-ol	2.34
Phenol, 2-methoxy-4-methyl-	10.81	2-Furanmethanol	0.19
1,2-Benzenediol, 3-methyl-	0.93	Phenol, 2-methoxy-	2.15
phenol, 4-ethyl-2-methoxy-	2.61	Phenol, 4-ethyl-2-methoxy-	0.92
1,2-Benzenediol, 4-methyl-	1.31	Propenylguaethol	11.62
Eugenol	1.78	Homovanillyl alcohol	0.34
1-propene, 1-methyoxy-2-methyl-	0.93	Benzenemethanol, 2-(dimethylamino)	0.55

Table 3.4 (Continued)

phenol, 2-methoxy-4-(1-propenyl)-	1.65	1,2-Benzenediol,4-(2-aminopropyl)-	0.49
Phenol, 2-methoxy-3-(2-propenyl)-	3.28	**Other**	
phenol, 2-methoxy-4-propyl-	3.16	Cyanogen chloride	0.28
homovanillyl alcohol	0.98	Methane, nitro-	0.48
phenol, 2-methoxy-4-(methoxymethyl)-	0.65	1,2-Butadiene, 3-methyl-	0.39
Ethyl, 4-hydroxy-7-trifluoromethyl-quinoline	0.98	2(1H)-Pyridinone, 3-hydroxy-	0.98
phenol, 2-methoxy-4-(1-propenyl)-	1.65	1-Propene, 3,3-diethoxy-	2.48
Other		1-Octadecanamine, N-methyl-	0.74
3,4-anhydro-d-galactosan	2.1	2,6-Dimethoxytoluene	0.88
Total	98.12	Ethanethioamide, N-phenyl-	0.55
		1,6-Anhydro-.beta.-D-glucopyranose	11.62
		Total	100

3.6.3 Acid anhydride pretreatment of oxidized product and RBO

Table 3.5 shows the physical and chemical properties of the RBO and APOP produced by addition of 25 wt% of butyric acid anhydride at the reaction temperature of 90 °C at a reaction time of 90 min without any pressure applied. As shown in Table 3.5, density decreased from 1.2 to 1.0 g/ml. The AV increased from 90.2 for RBO to 272.8 mg KOH/g for the APOP produced by consecutive oxidation and butyric acid anhydride pretreatment. The APOP water content reduced to 18.7 from 30.4 for raw bio-oil, a decrease by 38.5%. The HHV of the APOP increased from 16.0 of raw bio-oil to 19.8

MJ/kg and oxygen content of APOP was also decreased somewhat for raw bio-oil from 53.6 to 44.2 wt% probably due to the water content decrease. pH was reduced to 1.8 from 3.1. Viscosity of APOP decreased to 6.5 from 12.0 for raw bio-oil.

Table 3.5 Comparison of RBO and APOP physical and chemical properties.

Properties	**RBO**	**APOP**
Density, g/mL	1.2	1.0
HHV, MJ/kg	16.0	19.8
Oxygen, wt%	53.6	44.2
AV, mg KOH/g	90.2	272.8
pH	3.1	1.8
Water content, vol%	30.4	18.7
Kinematic viscosity, 40°C, cSt	12.0	6.5

Figure 3.7 compares the AVs and water contents of the APOPs produced at 5, 15, 25 and 35 wt% of butyric acid anhydride reagent addition to the oxidized product produced from pretreatment of combined oxone/H_2O_2 at ambient temperature and pressure at 90 min reaction time. As shown in Figure 3.7, the AVs of the APOPs were 196.7, 235.0, 272.8 and 304.4 mg KOH/g at 5, 15, 25 and 35 wt% butyric anhydride addition, respectively. The AVs of APOPs consistently increased as the butyric acid anhydride wt% increased from 5 to 35 wt%. The APOPs produced had 29.0, 23.6, 18.7 and 21.5 wt% water content at respective 5, 15, 25 and 35 wt% treatments. The water

contents of the APOPs decreased from 29.0 wt% to 18.7 wt% as the butyric acid anhydride wt% increased from 5 to 25 wt%; at 35 wt% the water content of APOP increased to 21.5 wt% from the 18.7 value for the 25 wt% addition of butyric acid anhydride. Therefore, based on the lower water content APOP produced the addition of butyric acid anhydride at 25 wt% treatment was considered the best treatment.

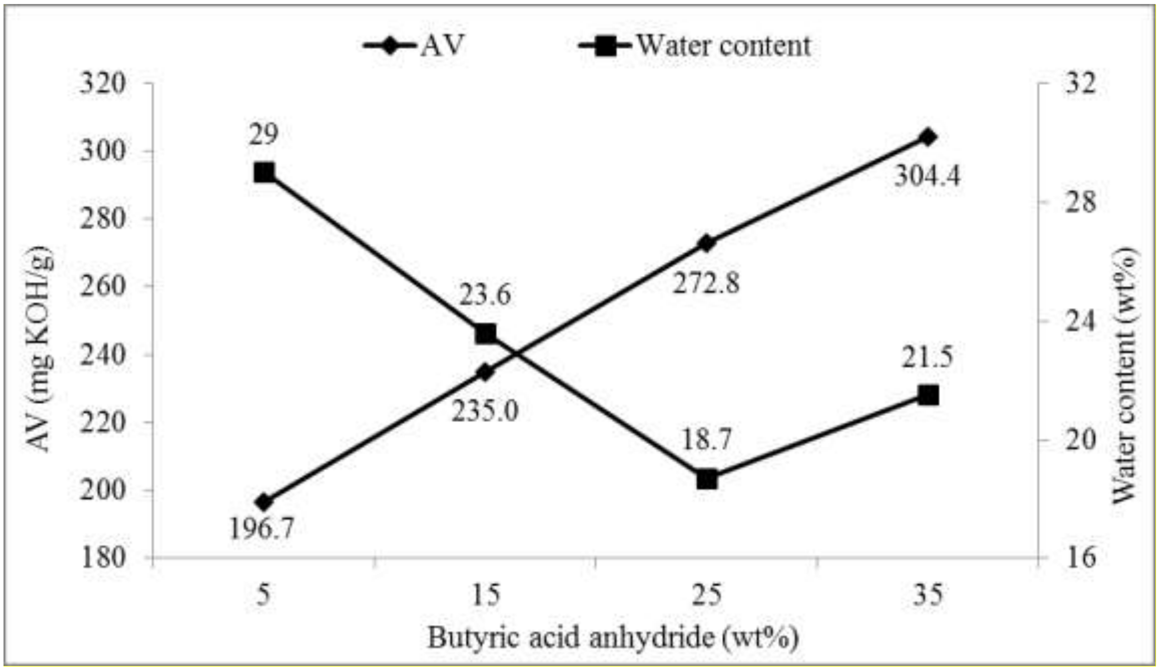


Figure 3.7 Effect of the butyric acid anhydride wt% on the AVs and water contents of APOPs produced at a reaction time 90 min at a reaction temperature 90 ºC.

Figure 3.8 compares the AVs and water contents of the APOPs produced at reaction times of 30, 60, 90 and 120 min using the addition of 25 wt% of butyric acid anhydride pretreatment of oxidized product. As shown in Figure 3.8, the AVs of the APOPs were 247.0, 255.8, 272.8 and 275.3 mg KOH/g at 30, 60, 90 and 120 min, respectively. The AVs of APOPs increased as the reaction time increased from 30 to 120 min. The APOPs produced had 27.3, 23.4, 18.7 and 24.2 wt% water content at respective 30, 60, 90 and 120 min treatments. The water contents of the APOPs decreased from 27.3 wt% to 18.7 wt% as the reaction time increased from 30 to 90 min. The water content of the APOP at the reaction time of 120 min increased to 24.2 wt%. Therefore, based on the lower water content APOP the reaction time of 90 min was considered the best treatment.

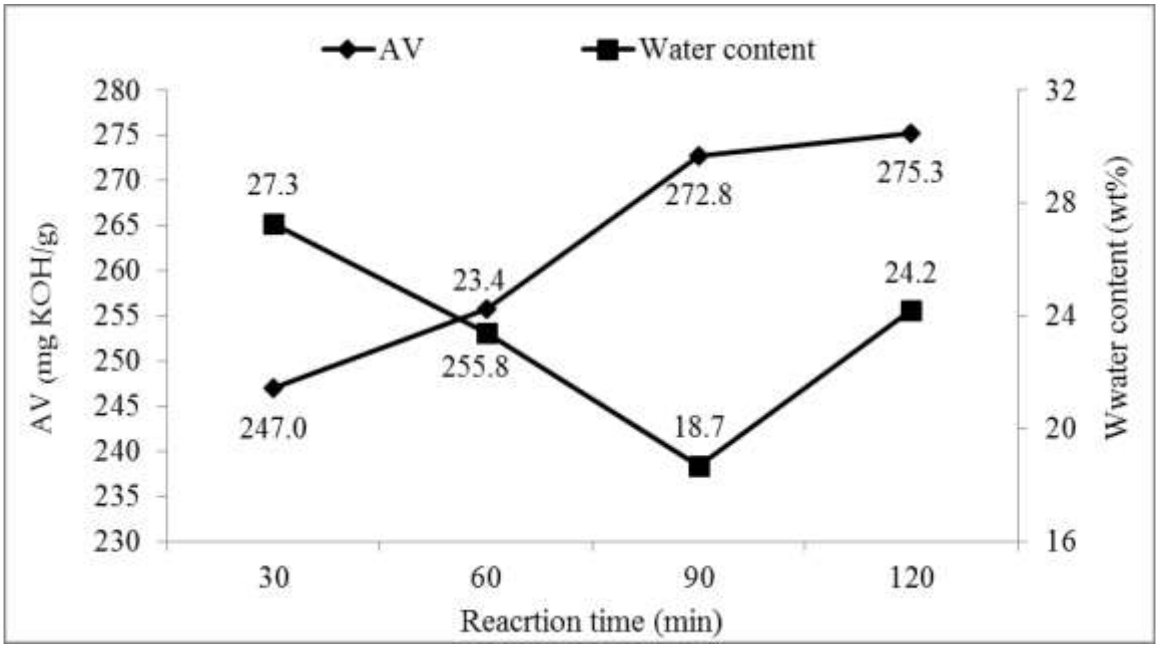


Figure 3.8 Effect of the reaction time on the AVs and water contents of APOP.

Figure 3.9 compares the AVs and water contents of the APOPs produced at reaction temperatures 30, 60, 90 and 120 °C for the addition of 25 wt% of butyric acid anhydride for a reaction time of 90 min. The AVs of the APOPs were 268.0, 271.9, 272.8 and 275.3 mg KOH/g at 30, 60, 90 and 120 °C, respectively. The AVs of the APOPs increased very little, but reaction temperature increased from 30 to 120 °C. The APOPs produced had respective 23.8, 23.2, 18.7 and 25.4 water content wt% values for the 30, 60, 90 and 120 °C treatments. The water contents of the APOPs decreased from 23.8 wt% to 18.7 wt% as the reaction temperature increased from 30 to 90 °C. The water content of the APOP at the reaction temperature of 120 °C increased to 25.4 wt%. Therefore, in light of the small difference in APOP AV value increase above the optimum temperature of 90 °C for lowest water content wt%, 90 °C was considered as the best treatment.

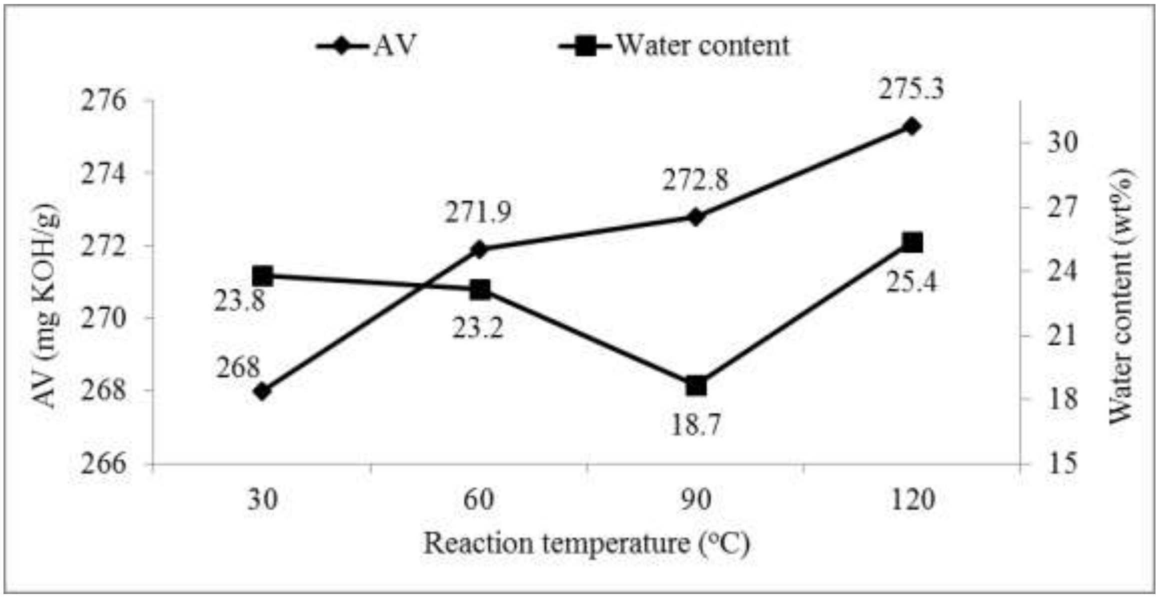


Figure 3.9 Effect of the reaction temperature on the AVs and water contents of APOP.

After testing the effects of the butyric acid anhydride wt%, reaction time and reaction temperature on the butyric acid anhydride pretreatment of the oxidized product, the pretreatment performed at a reaction temperature of 90 °C for a reaction time 90 min by addition of 25 wt% of butyric acid anhydride was considered as the optimum treatment. At this optimal butyric acid anhydride pretreatment reaction conditions both simultaneous (SOAPRBO) and consecutive (APOP) oxidation and butyric acid anhydride pretreatments were then performed. As a control, the direct butyric acid anhydride pretreatment of RBO was also performed and AVs and water contents of the resulting product (DAPRBO) were compared with SOAPRBO and APOP.

Figure 3.10 compares the AVs and water contents of the APOP, DAPRBO and SOAPRBO produced by butyric acid anhydride pretreatment at optimal reaction conditions. As shown in Figure 3.10, the AVs of the APOP, DAPRBO and SOAPRBO were 272.8, 205.9 and 263.1 mg KOH/g, respectively. The APOP AV, at 272.8 mg KOH/g was 32.5% higher compared to the DAPRBO value; in comparison to the 263.1 AV value for SOAPRBO the APOP AV was 3.7% higher. The water content of the APOP at 18.7 wt% was 14.2% lower than the DAPRBO value of 21.8 wt%; compared to the APOP water content wt% the SOAPRBO value, at 26.6 wt%, was 29.7% lower. Therefore, the water content of the butyric acid anhydride pretreatment performed with consecutive oxidation with oxone and H_2O_2 with added butyric acid anhydride was found to be the best pretreatment. This is as compared to the oxidation with oxone/H_2O_2 and simultaneous butyric acid anhydride direct butyric acid anhydride addition treatments.

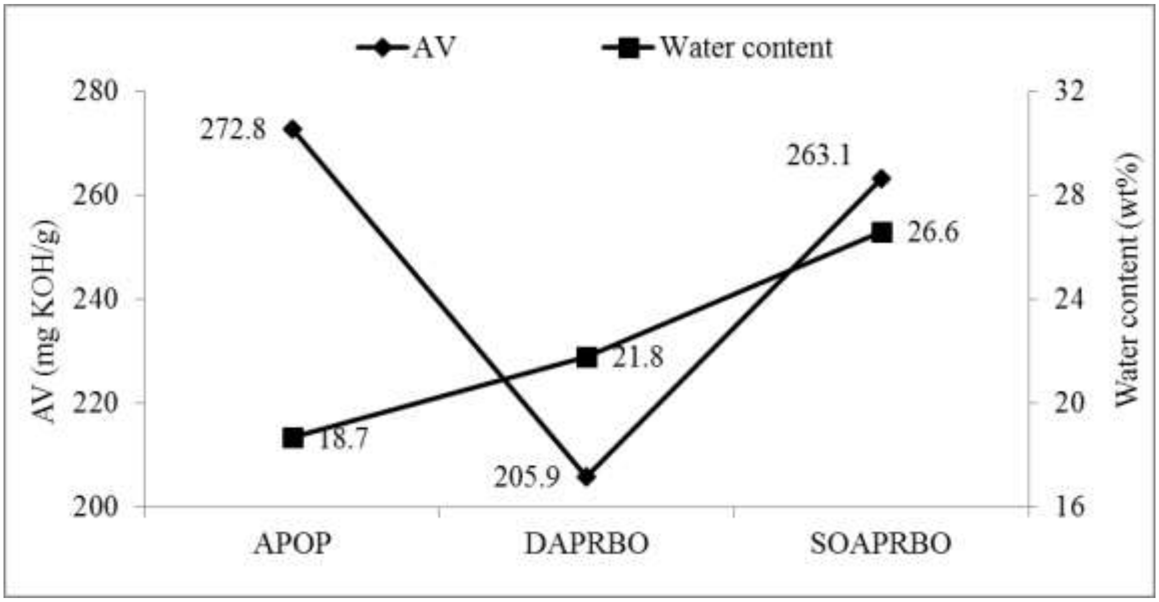


Figure 3.10 Comparison of the AVs and water contents of APOP, DAPRBO and SOAPRBO.

3.6.3.1 GC-MS analysis of the RBO and APOP

Table 3.6 shows the chemical composition of RBO and APOP analyzed by GC-MS. Approximately 50 chemical compounds were identified by GC-MS in both RBO and APOP. The chemical compound name and their area percentages are given in Table3.6. The total area percentages of the major fifty compounds present in RBO and APOP were 98.12 and 100.0%, respectively. As shown in Table 3.6 following the butyric acid anhydride pretreatment of the oxidized product the resulting APOP chemical composition as measured by GC-MS area percentage was changed considerably compared to the RBO. The carboxylic acids of the APOP increased to 44.08 area% from the 9.8 area% for RBO, an increase of 349.8%. The increase was especially high in carboxylic acids. As shown in Table 3.6 butanoic acid alone produced 34.98 area% due to the conversion of butyric acid anhydride by reacting with the water present in the oxidized product. The

APOP aldehydes and ketones content decreased to 1.31 and 1.56 area% from 11.1 and 36.8 area% for RBO, respectively. The aldehydes of the RBO were decreased by 88.2%. The esters-ethers were increased to 22.3 area% for the APOP from 12.1 area% of RBO. The alcohols and phenols contained in the RBO at 39.3 area% decreased to 17.08 area% for the APOP due to the considerable formation of esters during pretreatment. The remaining RBO compounds increased from 2.1 area% to 13.67 area% for the APOP.

Table 3.6 RBO and APOP chemical composition analysis by GC-MS with area percentages.

RBO		**APOP**	
Compound name	Area%	Compound name	Area%
Acids		**Acids**	
Acetic acid	5.1	Acetic acid	3.27
Heptanoic acid	1.42	Butanoic acid	34.98
Benzoic acid, 4-hydroxy-3-methoxy-	0.75	Pentanoic acid, 1,1-dimethylpropyl	0.5
Benzeneacetic acid, alpha-hydroxy-	1.96	d-(+)-Glyceric acid	0.22
benzeneacetic acid, 4-hydroxy-3-methyl	0.54	Benzeneacetic acid, 4-hydroxy-3-methyl	0.84
Esters & Ethers		Acetic acid, 2-acetoxymethyl-1,2,3	0.22
acetic acid, 1-methylethyl ester	1.82	Pentadecanoic acid, 14-methyl-, me	0.33
pentanoic acid, ethyl ester	0.92	Z-8-Methyl-9-tetradecenoic acid	0.39
n-heptyl hexanoate	0.94	Benzeneacetic acid, 4-hydroxy-3-methyl	0.23

Table 3.6 (Continued)

Hexanoic acid, 1-methylhexyl ester	1.85	Hexanedioic acid, bis(2-ethylhexyl)	2.41
1-propene, 1-methyoxy-2-methyl-	0.93	Butanoic acid, 2-(cyano)(2,4,6-tri	0.69
Furan, 2-ethoxy-2,3-dihydro-4-methyl	0.58	**Esters & Ethers**	
2,6-Dimethoxytoluene	0.9	Acetic acid, hydroxy-, methyl ester	0.52
3-methoxy-4-methylaniline	1.25	Butanoic acid, methyl ester	18.69
4,4'-Dimethoxy-biphenyl-2-carboxyl-	0.98	Hexanoic acid	0.19
Aldehydes		2-Methoxytetrahydrofuran	0.4
furfural	1.94	Butanoic acid, anhydride	0.81
2-furancarboxaldehyde, 5-methyl-	0.63	Methyl 3,3-dimethoxypropionate	0.36
Glutaraldehyde	1.16	Butanoic acid, 1-methylbutyl ester	0.91
cyclopentanecarboxaldehyde	0.82	Chloroacetic acid, 10-undecenyl ester	0.42
2-Furancarboxaldehyde, 5-methyl-	1.78	**Aldehydes**	
5-methyl-2-thiophenecarboxaldehyde	0.55	2-Furancarboxaldehyde, 5-methyl-	0.41
vanillin	1.39	Vanillin	0.65
9,12-octadecadienal	0.6	Benzaldehyde, 2,4-dihydroxy-	0.25
Benzaldehyde, 3-hydroxy-, oxime	0.74	**Ketones**	
4-hydroxy-2-mehoxycinnamaldehyde	0.71	Ethanone, 1-(2-furanyl)-	0.59

Table 3.6 (Continued)

4-hydroxy-2-methylacetophenone	1.27	1,2-Cyclopentanedione, 3-methyl-	0.97
Ketones		**Alcohols**	
4H-Pyran-4-one, 3,5-dihydroxy-2-methyl-	0.58	2-Propanone, 1-hydroxy-	1.61
2-propanone, 1-94-hydroxy-3-methoxy)-	0.84	3-Furanmethanol	0.25
2-cyclopenten-1-one, 2-hydroxy-3-methyl	1.84	Phenol	0.36
2-cyclopenten-1-one, 2-hydroxyl-	1.42	Phenol, 3-methyl-	0.66
Ethanone, 1-(4-hydroxy-3-methoxyphenol)	19.55	Phenol, 2-methoxy-	2.92
Alcohols		Phenol, 2-methoxy-4-methyl-	4.36
2-Propanone, 1-hydroxy	3.63	Phenol, 4-ethyl-2-methoxy-	1.47
phenol, 2-methyl-	1.14	Eugenol	0.82
phenol, 4-methyl-	0.72	Phenol, 2-methoxy-4-propyl-	0.98
phenol, 2-methoxy-	4.15	2-Buten-1-ol, 2-methyl-	0.72
4-mercaptophenol	0.59	Homovanillyl alcohol	0.6
Phenol, 2-methoxy-4-methyl-	10.81	Cyclopentanol, 1-methyl-	1.45
1,2-Benzenediol, 3-methyl-	0.93	2-Butanol, 3-(2,2-dimethylpropoxy)	0.37
phenol, 4-ethyl-2-methoxy-	2.61	2,3-Methylenedioxyanisole	0.22
1,2-Benzenediol, 4-methyl-	1.31	1,4-Benzenedimethanol, .alpha.-methyl	0.29
Eugenol	1.78	**Other**	
1-propene, 1-methyoxy-2-methyl-	0.93	Propanamide, N,N-dimethyl-	0.3
phenol, 2-methoxy-4-(1-propenyl)-	1.65	2-Thiazolamine, 4,5-dihydro-	0.19
Phenol, 2-methoxy-3-(2-propenyl)-	3.28	2,4-Dihydroxypyridine	1.65

Table 3.6 (Continued)

phenol, 2-methoxy-4-propyl-	3.16	4-Methyl-1,4-heptadiene	0.2
homovanillyl alcohol	0.98	Levoglucosenone	0.75
phenol, 2-methoxy-4-(methoxymethyl)-	0.65	Propane, 1,1-dimethoxy-2-methyl	0.57
Ethyl, 4-hydroxy-7-trifluoromethyl-quinoline	0.98	3,4-Anhydro-d-galactosan	0.34
Other		Thiazole, 4-ethyl-2-methyl-	1.06
3,4-anhydro-d-galactosan	2.1	1,6-Anhydro-.beta.-D-glucopyranose	7.27
Total	98.12	Lactose	1.12
		3,6-Dimethyl-2,3,3a,4,5,7a-hexahyd	0.22
		Total	100

3.6.3.2 FTIR analysis of the RBO and APOP

Figure 3.11 shows the comparison of RBO and APOP FTIR spectra. These spectra identified the functional groups present in the product types. Characteristic vibrational modes were observed at 3200-3600 cm^{-1} (OH stretch), 2800-3100 cm^{-1} (CH aliphatic stretch), 1600-1750 cm^{-1} (C=O stretch), 1350-1470 cm^{-1} (CH bending) and 1000-1250 cm^{-1} (C-O stretch). It was observed that both C=O stretching and OH stretching were intensified, indicating that carboxylic acids content was increased considerably compared to the RBO during the pretreatment of the RBO. The findings of the FTIR spectra were in good agreement with the physical and chemical properties described in Table 3.5 and GC-MS analysis.

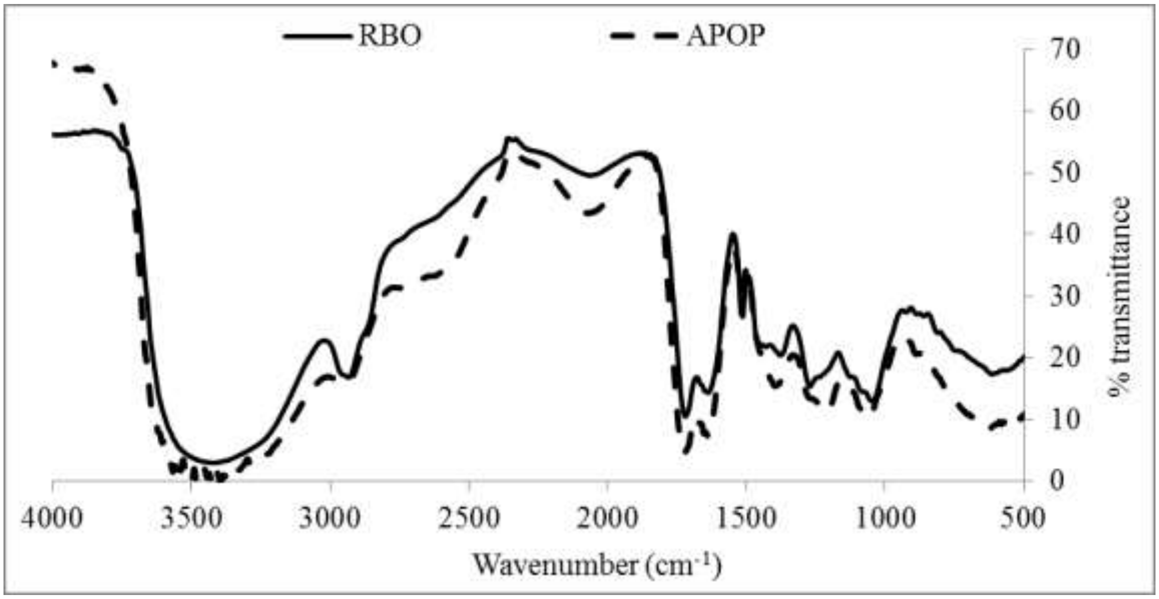


Figure 3.11 Compares RBO and APOP FTIR spectra.

3.7 Summary

Aldehydes are the major chemical compounds contained in RBO that produce coke during HDO upgrading to fuels. The coking causes catalyst deactivation as a result of char deposition on catalyst surface. Eventual reactor plugging occurs as the catalyst carbonization totally plugs the reactor. Oxidation of RBO by individual oxidation using oxone, ozone and H_2O_2 treatments comprised the first phase of the study. Combinations of oxone/H_2O_2 and ozone/H_2O_2 were shown to be superior in producing high AV values (indicating high conversion of aldehydes to carboxylic acids) to treatments by the individual oxone, ozone and H_2O_2. The best combination of oxone with H_2O_2 was 5wt%oxone+10wt%H_2O_2 and for ozone the best combination 5wt%ozone+10wt%H_2O_2 with the treatments applied at ambient temperature and pressure. The best reaction time for the oxone/H_2O_2 combination was 60 min while it was 90 min for the best ozone/H_2O_2

combination. However, both oxidation processes produced approximately the same AV due to the same degree of carboxylation. For this reason the oxone/H_2O_2 combination was chosen for further study due to ease of application.

In the second phase of the study, butyric acid anhydride pretreatment was tested to determine its efficacy in reducing RBO water content which also leads to catalyst deactivation during the HDO of RBO. The butyric acid anhydride pretreatment was added onto the oxidized product produced by the oxone/H_2O_2 treatment in both consecutive and simultaneous processes that produced pretreated products termed APOP and SOAPRBO, respectively. The application of butyric acid anhydride pretreatment directly to the RBO was also tested and compared with consecutive and simultaneous RBO oxidation and butyric acid anhydride pretreatments. The consecutive oxidation and butyric acid anhydride pretreatment to oxidized RBO produced APOP with lower water content compared to the DAPRBO and SOAPRBO products. The butyric acid anhydride pretreatment performed by addition of 25 wt% of butyric acid anhydride at a reaction temperature of 90 ^{o}C at the reaction time of 90 min was the optimal reaction. GC-MS results showed that butanoic acid alone produced 34.98 area% due to the conversion of butyric acid anhydride by reacting with the water present in the oxidized product. The water content of the produced product at the optimal treatment method had 18.7wt% compared to the 30.4 wt% for raw bio-oil. The AV produced by the optimal treatment method produced a product that had an AV 202.5% higher than that of the original bio-oil which had an AV of 90.2 mg KOH/g.

3.8 Disclaimer

3.9 References

1. Maggi, R.; Delmon, B. Comparison between ‘slow’ and ‘flash’ pyrolysis oils from biomass. 73, 5, 671-667, 1994.

2. Zanzi, R.; Sjostrom, K.; Bjornbom, E. Rapid high-temperature pyrolysis of biomass in a free-fall reactor. Fuel 75, 545–550, 1996.

3. Bridgwater, A.V. Production of high grade fuels and chemicals from catalytic pyrolysis of biomass. Catalysis Today 29, 285-295, 1996.

4. Wagenaar, B. M.; Prins, W.; VanSwaaij, W. P. M. Pyrolysis of biomass in the rotating cone reactor: modeling and experimental justification. Chemical Engineering Science. 1994, 49, 5109–5126.

5. Bridgwater, A.V.; Peacocke, G.V. C. Fast pyrolysis processes for biomass: *Renew Sustain Energy Rev*, 2000, *4*(1), 1-73.

6. Mohan D, Pittman Jr CU, Steele PH. Pyrolysis of wood-biomass for bio-oil: A critical review. Energy Fuels 2006, 20:848-889.

7. Czernik S, Bridgwater AV. Overview of applications of biomass fast pyrolysis oil. Energy Fuels 2004, 18:590-598.

8. Oasmaa, A.; Elliott, D.C.; Korhonen, J. Acidity of Biomass Fast Pyrolysis Bio-oils. Energy Fuels. 24, 6548-6554, 2010.

9. Huber, G. W.; Iborra, S.; Corma, A. synthesis of transportation fuels from biomass. *Chemistry, Catalysts and Engineering. Chem. Review*, 2006**,** *106*, 4044–4098.

10. Girard, P.; Blin, J.; Bridgwater A.V.; Boocock, D.G.G.; Meier, D. An assessment of bio-oil toxicity for safe handling and transportation: toxicological and ecotoxicological tests. In: proceedings Science in Thermal and Chemical Biomass Conversion. CPL Press, Newbury, UK, 2005.

11. Ingram, L., Mohan, D., Bricka, M., Steele, P.H., Strobel, D., Crocker, D., Mitchell, B., Mohammad, J., Cantrell, K., Pittman, Jr., C.U., 2008. Pyrolysis of wood and bark in an auger reactor: physical properties and chemical analysis of the produced bio-oils. Energy Fuels. 22, 614-625.

12. Bandi, A.; Baumgart, F.; Bridgwater, A. V. Stirling Engine with Flox Burner Fuelled with Fast Pyrolysis Liquid. In Progress in Thermochemical Biomass Conversion. Blackwell Science: Oxford, 1459-1467, 2001.

13. Gagnon, J.; Kaliaguine, S. Catalytic hydrotreatment of vacuum pyrolysis oil from wood, Industrial and Engineering Chemistry Research. 27, 1783-1788, 1988.

14. Diebold, J. P. A review of the chemical and physical mechanisms of the storage stability of the fast pyrolysis bio-oils. NREL/SR-570-27613. January, 2000.

15. Zhang, S. P.; Yan, Y. J.; Ren, Z.; Li, T. Study of hydrodeoxygenation of bio-oil from the fast pyrolysis of biomass. Energy Sources. 25, 1, 57-65, 2003.

16. Shanks, H. B.; Lohithrn, N. Upgrading of bio-oil: Effect of light aldehydes on acetic acid removal via esterification: *Catalysis Communications,* 2009, *11*, 96-99.

17. Hu, Xun.; Wang, D.M.; Gunawan, R.; Lievens, C.; Chaiwat, W.; Gholizadeh, M.; Wu, L.; Li, X.; Li, C.Z. Polymerization on heating up of bio-oil: A model compound study. AICHE Journal. 2012.

18. Xu, J.; Jiang, J.; Dai, W.; Zhang, T.; Xu, Y. Bio-oil upgrading by means of ozone oxidation and esterification to remove water and to improve fuel characteristics. Energy Fuels. 25, 1798-1801. 2011.

19. Lin, W. R.; Bartek, R. Removal of bound water from bio-oil. International patent. WO 2012/027428 A1. March, 1st, 2012.

20. Wang, S.; Gu, Y.; Liu, Q.; Yao, Y.; Guo, Z.; Luo, Z.; Cen, K. Separation of bio-oil by molecular distillation. Fuel Processing Technology. 90, 738-745, 2009 .

21. Guo, Z.; Wang, S.; Xu, G.; Cai, Q. Upgrading of bio-oil molecular distillation fraction with solid acid catalyst. Bioresources 6, 3, 2539-2550, 2011.

CHAPTER IV

PRETREATMENT OF BIO-OIL FOLLOWED BY UPGRADING VIA ESTERIFICATION TO BOILER FUEL

4.1 Abstract

Bio-oils produced from fast pyrolysis of renewable energy feedstocks are chemically complex organic liquids that contain over 200 different organic compounds. Many of these compounds are oxygenates which result in 40-45% oxygen content in the bio-oils. Due to this high oxygen content bio-oils have numerous negative properties that include low heating value, high acidity, high water content and variable viscosity. It is universally agreed that for production of a viable fuel pyrolysis bio-oils must be upgraded. Esterification is a viable means to produce a boiler fuel but maximum heating energies remain rather low and amount of alcohol usually added is uneconomic. In this study we tested oxidative pretreatment prior to esterification as a means to both increase heating energy and decrease the amount of alcohol required. The most effective oxidative pretreatment was with application of a combined ozone/H_2O_2 treatment. Following the pretreatment of bio-oil the esterification performed at a reaction temperature of 340 ^oC under pressurized hydrogen 300 psig for a reaction time 1.5 h using a mixture of Ru/γ-Al_2O_3 (4 wt%) and potassium carbonate (4 wt%) catalyst produced higher boiler fuel yield with improved characteristics The esterification of the ozone/H_2O_2 pretreated product produced a boiler fuel with improved yield and better physical/chemical properties compared to direct esterification of bio-oil. As compared to the product from direct esterification of bio-oil the esterified ozone/H_2O_2 pretreated bio-oil provided a 23% increased boiler fuel yield of 48 wt%; higher heating value was 5.7% higher at 35.3 MJ/kg.

Keywords: Bio-oil, oxidation pretreatment, oxidation, boiler fuel and esterification.

4.2 Introduction

Production of renewable fuels is of growing interest due to the ongoing concerns associated with the fossil fuels such as economic, socio-political and environmental. Biomass is an alternative renewable energy source [1,2] and can be converted into liquid fuels through both thermal and biological methods. One of the thermal decomposition methods is fast pyrolysis of lignocellulosic biomass to produce pyrolysis oil that is frequently referred to as bio-oil. Bio-oil conversion to fuels is a potential promising replacement for fossil fuels. Advantages of liquid bio-oil are the ease of transportation and storage. Fast pyrolysis includes heating the biomass at elevated temperatures in the range of 400 to 550 ^{o}C in the absence of oxygen [2-4].

Fast pyrolysis has the potential to convert any biomass type to a liquid fuel. As a fuel, biomass derived bio-oil has environmental advantages when compared to fossil fuels because, on combustion, bio-oil produces half of the NO_x, and negligible quantities of SO_x emissions and it is CO_2 neutral when compared to conventional fuels. Direct utilization of raw bio-oil is limited because of its negative physical and chemical properties such as high acidity, high moisture content, low energy density, immiscibility with petroleum products, and polymerization resulting in increased viscosity upon exposure to heat or during long-term storage. The chemically complex mixture of bio-oil contains over 200 different organic compounds [1,3,5]. Many of these are highly reactive oxygenated compounds that are responsible for most of the negative properties of bio-oil. The presence of oxygenated compounds results in typical bio-oil oxygen content of 40-50 wt%.

Aldehydes are oxygenates that can undergo homo-polymerization, acetalization and oligomerization by reacting with phenols which leads to polymerization that produces high molecular weight thermoplastic resins. The influences of aldehyde polymerization reactions mainly increase the viscosity of bio-oil during storage or from exposure to heat [6-8]. Aldehydes present in the raw bio-oil can be converted to carboxylic acids by subjecting them to oxidation. Scheme 4.1 symbolizes the conversion of all bio-oil aldehydes to carboxylic acids in the presence of an oxidizing agent reaction pathway [9,10]. Most of the research studies on present upgrading technologies such as hydrodeoxygenation (HDO), catalytic cracking and esterification report that these counter-productive aldehyde polymerization reactions that occur during the upgrading process are a major problem that results in coke formation and low product yields [6, 9-13].

$$\underset{\text{Aldehyde}}{\text{R-CHO}} \xrightarrow{\text{Oxidizing agent}} \underset{\text{Carboxylic acid}}{\text{R-COOH}}$$

Scheme 4.1 Oxidation pretreatment pathway of bio-oil aldehydes to carboxylic acids [9].

As previously described bio-oil is a complex mixture of different organic compounds containing numerous oxygenated functional groups, including carboxylic acids, aldehydes, ketones, furans, phenols and sugars. These functional groups are a key consideration in the upgrading of bio-oil. Esterification is a potential route to convert the carboxylic acids in bio-oils to esters by reacting them with alcohols to esters in the presence of an acid or base catalyst medium [12,14,15]. Esterification performed by reacting carboxylic acid and an alcohol in the presence of an acid catalyst (Fischer esterification reaction) is shown in Scheme 4.2.

$$\underset{\text{Acid}}{\text{R-COOH}} + \underset{\text{Alcohol}}{\text{R'-OH}} \xrightleftharpoons{\text{Catalyst}} \underset{\text{Ester}}{\text{R-COOR'}} + \underset{\text{Water}}{H_2O}$$

Scheme 4.2 Formation of ester by reacting acid and alcohol in presence of catalyst [14].

Furthermore, the conversion of acids also represents a simplification of the currently practiced upgrading processes applied to bio-oil such as hydroprocessing and catalytic pyrolysis. These routes to fuels require high reaction temperatures and hydrogen pressures that are expensive to apply [13,16]. The presence of high proportions of acids in bio-oil makes it highly corrosive. It has been demonstrated that esterification via methanol and ethanol will reduce the acidity of the bio-oil, thereby improving bio-oil quality and stability to some extent. To date researchers have used alkaline, resin acid, super critical fluid technology and solid acid catalyst for esterification of bio-oil.

Different parameters such as alcohols, catalysts and reaction conditions have been investigated by past researchers using bio-oil or model compounds [17-23].

Zhang et al. (2006) catalyzed the bio-oil esterification reaction with solid acid $40SiO_2/TiO_2\text{-}SO_4^{-2}$ and solid base $30K_2CO_3/Al_2O_3$- NaOH. This model esterification reaction was in a molar ratio of 2.5:1(ethanol:acetic acid). Catalyst was added at 5 wt% of the reaction solution. Researchers observed that the acid catalyst accelerated the esterification reaction to allow completion in 80 minutes to reach 88% of equilibrium conversion. The gross calorific value increased from 15.83 MJ/kg to 23.87 and 24.03 MJ/kg, respectively, for acid and base catalyst. The pH value of the upgraded bio-oil was lowered to 1.12 by the acid catalyst, while it was increased to 5.93 by the base catalyst [21].

Shanks et al. (2009) studied the impact of reactive oxygenated groups such as aldehydes on the esterification of organic acids using organic-inorganic mesoporous silica functionalized with propylsulfonic acid (SBA-15-SO_3H) catalyst. A bio-oil model compound was prepared by mixing acetaldehyde, propionaldehyde and acetic acid. To examine the effect of aldehydes (acetaldehyde and propionaldehyde) on esterification of acetic acid with ethanol using molar ratio of (ethanol/acetic acid) 2.7, researchers conducted the esterification of acetic acid with and without aldehydes at three different temperatures of 100 °C, 70 °C and 50 °C. The conversion of acetic acid to ethyl esters was not affected by the presence of aldehydes at 100 °C. However, at 70 °C and 50 °C, the acetic acid to esters conversion in the absence of aldehydes was higher than when aldehydes were present. They also found that the impact of aldehydes on esterification of acetic acid at 50 °C was even higher when compared at 70 °C. At 70 °C, the acetic acid conversion to esters in the presence of aldehydes was lowered by 6% when compared to the same reaction without aldehydes. At 50 ^{o}C, the acetic acid conversion in the presence of aldehydes was lowered by 28% when compared to the same reaction without aldehydes. It was also observed that excess of ethanol was consumed due to the formation of acetals by acetalization reactions in the presence of aldehydes. Researchers concluded that there is a significant effect of aldehydes and temperatures on the esterification of carboxylic acids [12].

Tang et al. (2009) upgraded bio-oil with the combination of the esterification, hydrotreatment, cracking under super critical ethanol conditions. Researchers prepared a crude oil by a combination of the raw bio-oil of 33 wt% and anhydrous ethanol of 67wt%; this prepared crude bio-oil was upgraded at a temperature of 280 ^{o}C under pressurized hydrogen of 2 MPa for a reaction time 3 h. The upgraded bio-oil produced had HHV of 14.7-20.1 MJ/kg with a water content of 16.2-17.3 wt%. Researchers reported that esters content was higher in the upgraded bio-oil compared to the raw bio-oil via esterification reaction and aldehydes and ketones were decreased due to the hydrotreating reaction. However, the HHV and water content of the upgraded bio-oil needs to improved and consumption of alcohol was very high [19].

Wang et al. (2010) studied catalytic esterification of both model compound and bio-oil with 732 and NKC-9 type ion exchange resins as esterification catalysts. The catalytic activity of resins was first investigated by model compound reaction of acetic acid and methanol at a temperature of 70 and 50 ^{o}C for 5 h with 10 wt% of catalyst. The acetic acid conversion at a temperature of 70 ^{o}C with 732 resin catalyst showed slightly higher activity compared to NKC-9 catalyst. The esterification of bio-oil with methanol for both 732 and NKC-9 resin catalysts was performed in a batch reactor with a bio-oil to methanol ratio of 1:2. Bio-oil esterification experiments were conducted at a temperature of 50 ^{o}C for 5 h with 10 wt% of catalyst. The esterified bio-oil acid values decreased by 88.5% and 86.0%, calorific values increased by 32.3% and 31.6%, water contents were lowered by 27.7% and 30.9%; densities were lowered by 21.8% and viscosities were reduced for both by approximately 97.0% after esterification by 732 and NKC-9 resin catalysts, respectively [15].

Weerachanchai et al. (2012) investigated the effects of esterification of palm shell bio-oil such as reaction temperature, reaction time, catalyst type, alcohol type and alcohol to carboxylic acid molar ratio on the reaction conversion. The effect of temperature and time was investigated by esterification of bio-oil with 3.25:1 mole ratio of methanol to the acids in bio-oil at temperatures in the range of 25-60 ^{o}C with 5 wt% of Amberlyst15 catalyst for 24 h. Results of the effect of temperature showed that as the temperature increased the acid conversion also increased. The reaction conversion sharply increased in the first 1 h of reaction time to about 40%, followed by a slow increase and started to attain equilibrium after about 12 h of reaction time. To study the effect of catalyst type, researchers performed the esterification reactions under the same conditions at a temperature of 60 ^{o}C without catalyst and with 5 wt% of Amberlyst15 or H_2SO_4 catalysts. Esterification conversion without catalyst gave only 13.13% but with Amberlyst15 it increased to 86.87% and with H_2SO_4 catalyst conversion increased dramatically to 93.75%. The effect of alcohol type was investigated using methanol and ethanol at the same reaction conditions. Bio-oil upgraded by using methanol exhibited a much higher conversion of 73.39% compared with the use of ethanol which gave only

54.80% conversion. Relatively high HHVs in the range of 23.10-23.78 MJ/kg were obtained with methanol, whereas the upgraded bio-oil using ethanol gave a slightly higher value of 25.40 MJ/kg. Respective physical properties for raw and upgraded bio-oils were densities of 0.79 and 0.80 g/cm^3, viscosities of 0.58 and 1.22 mm^2/s, flash points of 11 and 14 ^{o}C and pH values of 6.63 and 6.58 [14].

Xu et al. (2011) introduced an ozone oxidation method for bio-oil derived from rice husks. A laboratory scale ozone generator provided ozone at 5 g/h. The oxidation pretreatment reactions were performed by continuously introducing the ozone into a batch glass reactor at a temperature range of 20-22 ^{o}C for 10 h. This oxidized bio-oil was then esterified by addition of 100% butanol at 116 ^{o}C for 3-4 h. This oxidation of bio-oil followed by esterification changed the characteristics of the esterified product. The gross calorific value of raw bio-oil (9.5 KJ/g) increased to 27.4 KJ/g for esterified bio-oil without pretreatment; for esterified bio-oil with pretreatment the increase was to 25.0 KJ/g [9].

Considerable research has been performed on the esterification of raw bio-oils to produce upgraded biofuels. Based on previous studies esterification of raw bio-oil produces esters with maximum heating value of 24-28 MJ/kg and also the consumption of alcohols to raw bio-oil ratio has been relatively high. Zhang esterified bio-oil with a 2.5:1 (250%) alcohol addition. Mahfud esterified bio-oil with a 100% addition of butanol [16]. Moens noted that a typical bio-oil required 10-14 mol of alcohol per kilogram of bio-oil to completely esterify aldehydes, acids and ketones [16,17,21]. Reduction of alcohol required for esterification may be reduced if the aldehydes and ketones are converted to carboxylic acids prior to esterification. Our current study tests an oxidation pretreatment method applied to raw bio-oil to convert aldehydes and ketones to carboxylic acids followed by esterification to improve the raw bio-oil characteristics. The oxidative pretreatment followed by esterification increased HHV, decreased acidity and lowered water content and viscosity. This product is considered suitable for boiler fuel based on the high HHV value.

4.3 Objective

The objective of this study was to apply esterification on the oxidized bio-oil to produce a high energy boiler fuel. The sub-objective is to reduce consumption of the amount of alcohol used for the esterification process.

4.4 Materials and methods

4.4.1 Materials

Ru/γ-Al_2O_3 (0.5% Ru) catalyst was obtained from Acros organics. Hydrogen peroxide (H_2O_2) 50 wt% solution in water was obtained from Sigma-Aldrich. All chemicals were used with no further purification. Ozone used in this study to oxidize the raw bio-oil was produced by pumping the pure oxygen (obtained from nexAir) through an OZV-8 ozone generator with 8 g/h ozone flow directly into the pretreatment reaction vessel.

Bio-oil required for this research was produced from loblolly pine wood chips with a size of 1-3 mm and moisture content of 8-10% on dry-weight basis. Bio-oil was produced by the fast pyrolysis process performed at a temperature of 450 ^{o}C with nitrogen carrier gas at a biomass utilization rate of 7 kg/h with an auger-feed pyrolysis reactor located in the Department of Sustainable Bioproducts, Mississippi State

University (MSU). The MSU auger fast pyrolyzer produced 60-65 wt% of liquid product, 10-15% of non-condensable gases and 20-25% of char on a dry biomass weight basis.

4.4.2 Methods

4.4.2.1 Oxidation pretreatment of RBO

All pretreatments of raw bio-oil were performed in a 250 ml round bottom flask equipped with an electronic stirrer in a closed hood; oxidation reactions were performed at ambient temperature and pressure. The oxidation of raw bio-oil was tested with three oxidation reactants: H_2O_2 alone, ozone alone and a combination of ozone and H_2O_2 (ozone/H_2O_2). The best pretreatment oxidant was deemed to be that with the highest production of carboxylic acids as measured by magnitude of acid value (AV). The oxidation of raw bio-oil by H_2O_2 alone was performed by addition of 10 wt% of commercial 50 wt% H_2O_2 solution in water followed by stirring for 60 min at room temperature. The oxidation of raw bio-oil by ozone alone was performed by pumping 3-5 psig ozone into the pretreatment reaction vessel followed by stirring for 60 min at room temperature. The oxidation of raw bio-oil was conducted by a mixture of ozone/H_2O_2 by pumping 3-5 psig ozone into the pretreatment reaction vessel containing a mixture of raw bio-oil and 10 wt% of commercial 50 wt% H_2O_2 solution in water followed by stirring for 60 min at room temperature. It was observed that the dark colored raw bio-oil changed to a reddish brown color during ozone/H_2O_2 pretreatment. This color change was not noticed for ozone or H_2O_2 oxidation when each was applied separately. The pretreatment with the highest AV was selected as having the best performance because it indicated the highest production of carboxylic acids, which in turn represented an increased conversion of aldehydes and ketones. The raw bio-oil pretreated by ozone/H_2O_2

produced oxidized bio-oil which was referred to as the *oxidized product-II* for future reference in this study.

4.4.2.2 Esterification of oxidized product-II and RBO

Esterification was performed in a stainless steel, high-pressure batch autoclave reactor equipped with an overhead magnetic stirrer, a pressure indicator with a maximum capacity of 5000 psig and a thermocouple for temperature monitoring in the range of 0-500 °C. The autoclave was equipped with an electrical heating and cooling system to control the temperature inside the reactor. The effect of the reaction temperature on the esterification of the oxidized product-II was tested at 320, 340 and 360 °C reaction temperatures. The esterification was performed by addition of 20 wt% of butanol to the ozone/H_2O_2 pretreated bio-oil in the presence of a mixture of Ru/γ-Al_2O_3 (4 wt%) and potassium carbonate (4 wt%) catalyst at a temperature of 340 °C and under pressurized hydrogen at 2 MPa for 90 min. The esterified organic fraction produced from oxidized product-II referred as the *BF2* in this study. As a control raw bio-oil was also esterified without application of pretreatment by following the same esterification procedure as described above. The esterified organic fraction produced from direct raw bio-oil product referred as the *BF1* in this study.

In each experiment, once the reaction was complete, the liquid products were cooled to room temperature in the reactor. The mixture was collected in centrifuge test tubes which were centrifuged to separate the resulting aqueous and organic phases; the time for centrifuging to separation ranged from 2-4 h. Both phases were separated and weighed for mass balance computation. The organic fraction was comprised of the higher HHV product suitable for boiler fuel. Yields were calculated by Equation 4.1 [24].

Yield of boiler fuel (wt%) = (P (g) × 100)/bio-oil weight (g) Eq. 4.1

Where:

Yield of boiler fuel = Esterified organic fraction produced

P = organic fraction obtained (Total esterified products weight in grams – aqueous fraction weight in grams)

Bio-oil weight = Total raw bio-oil used weight in grams

4.5 Data analysis

The raw bio-oil, pretreated product and boiler fuel were characterized by following ASTM methods. The densities were determined by Anton Parr DMA 35n portable density meter by ASTM D4052 method. Viscosities were determined by Ubbelohde capillary viscometer at 40 ^{o}C water bath temperature by ASTM D445 method. Higher heating values (HHV) were determined by Ika-5000 bomb calorimeter by ASTM D240 method. The acid values (AV) were determined by dissolving 1 g of bio-oil in 50 ml of 35:65 ratio of isopropanol to water mixtures and titrating to a pH of 8.5 with 0.1N KOH solution by ASTM D664 method. The pH values were determined by addition of 1 g of bio-oil to 50 ml of 35% of isopropanol mixture. The pH values were determined by ASTM E70 method. Elemental carbon, hydrogen, and nitrogen were determined by EAI CE-440 elemental analyzer with oxygen content determined by difference according to ASTM D5291 method. Water content was determined by Karl-Fisher titration by ASTM E203. The GC-MS analysis of the fuels was performed with a Hewlett-Packard HP 5890-Series II GC equipped with a Hewlett-Packard HP 5971 series MS. FTIR spectra were obtained by Varian 3500 FTIR analyzer with standard potassium bromide disk technique and spectra were analyzed by Varian-Resolutions software.

4.6 Results and discussion

4.6.1 Raw bio-oil pretreated by ozone, H_2O_2 individually and combined ozone/H_2O_2.

Figure 4.1 compares acid values of the pretreated products obtained from 1-h pretreatments of raw bio-oil with ozone alone, H_2O_2 alone and the ozone/H_2O_2 combination. Figure 4.1 indicates that after pretreatment of raw bio-oil with ozone pretreatment the AV increased from 90.3 of raw bio-oil to 107.7 mg KOH/g; with H_2O_2 pretreatment the AV increased from 90.3 to 118.3 mg KOH/g. For the combined ozone/H_2O_2 pretreatment AV increased from 90.3 to 161.9 mg KOH/g. The 161.9 mg KOH/g AV for the ozone/H_2O_2 pretreatment represented respective 50.3% and 36.8% increases in AV above the values for the ozone and H_2O_2 alone pretreatments.

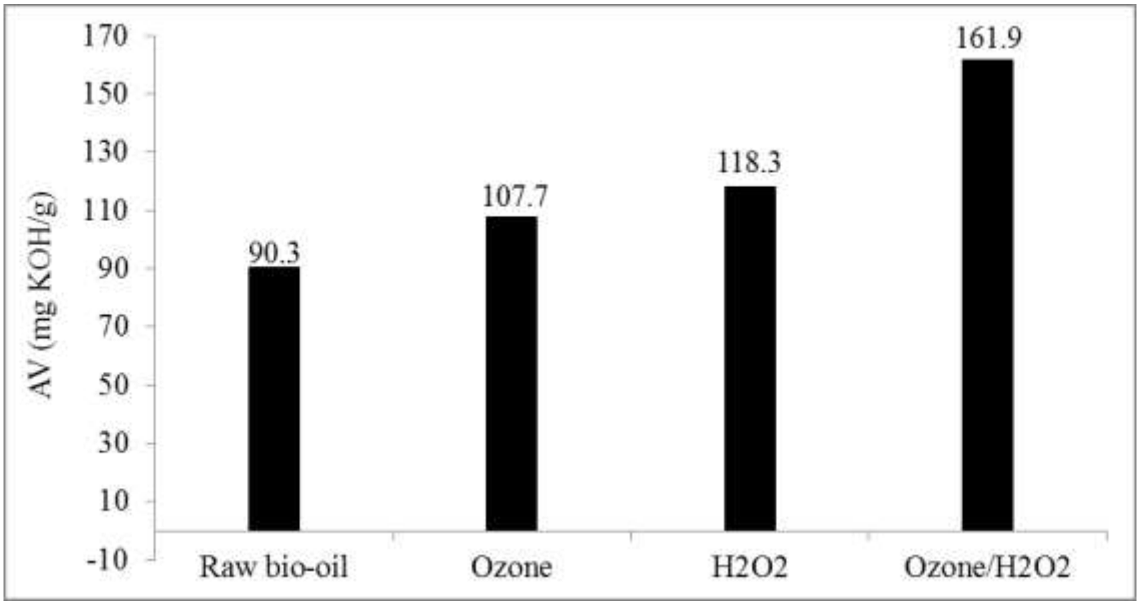


Figure 4.1 Effect on AVs of ozone, H_2O_2 and combined ozone/H_2O_2 oxidation pretreatments applied to raw bio-oil over a time period of 1 h.

The high AV of the ozone/H_2O_2 pretreatment indicated the conversion of carbonyl compounds (mainly aldehydes and ketones) and alcohols to carboxylic acids. Therefore, the best pretreatment for oxidation of raw bio-oil, based on highest AV obtained, was by far the ozone/H_2O_2 combined pretreatment. For that reason subsequent analyses were performed on the product from this most-promising pretreatment.

4.6.2 FTIR analysis of the raw bio-oil and oxidized product-II

Figure 4.2 compares the FTIR spectra of raw bio-oil and the ozone/H_2O_2 pretreated bio-oil (OPTBO). Characteristic vibrational modes are observed at 1650-1710 cm-1 (C=O stretching) and 3600-3000 cm-1 (HO stretching). It was observed that C=O stretching was decreased and OH stretching was intensified, indicating that carbonyl compounds (mainly aldehydes and ketones) were converted to carboxylic acids.

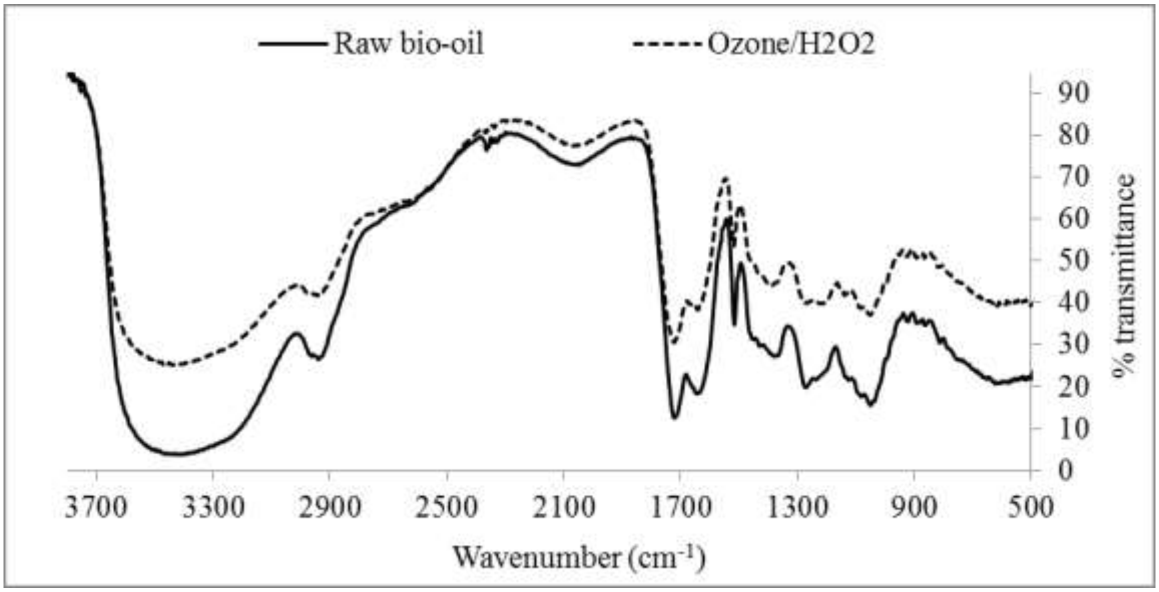


Figure 4.2 FTIR spectrum comparison of raw bio-oil and oxidized product-II (ozone/H_2O_2 pretreated product) showing.

4.6.3 Effect of reaction time on the ozone/H_2O_2 pretreatment to raw bio-oil

Figure 4.3 shows the effect of combined ozone/H_2O_2 pretreatment on raw bio-oil AV over time and tested at 15 min time intervals. The AV of the combined ozone/H_2O_2 bio-oil treatment at time zero was 110.4 mg KOH/g; the AV of raw bio-oil after 1 h of pretreatment was considerably increased to 161.2 mg KOH/g. However, the increase in AV was at a maximum at a time period of 1 h. After 1h the AV remained essentially constant as shown in Figure 4.3.

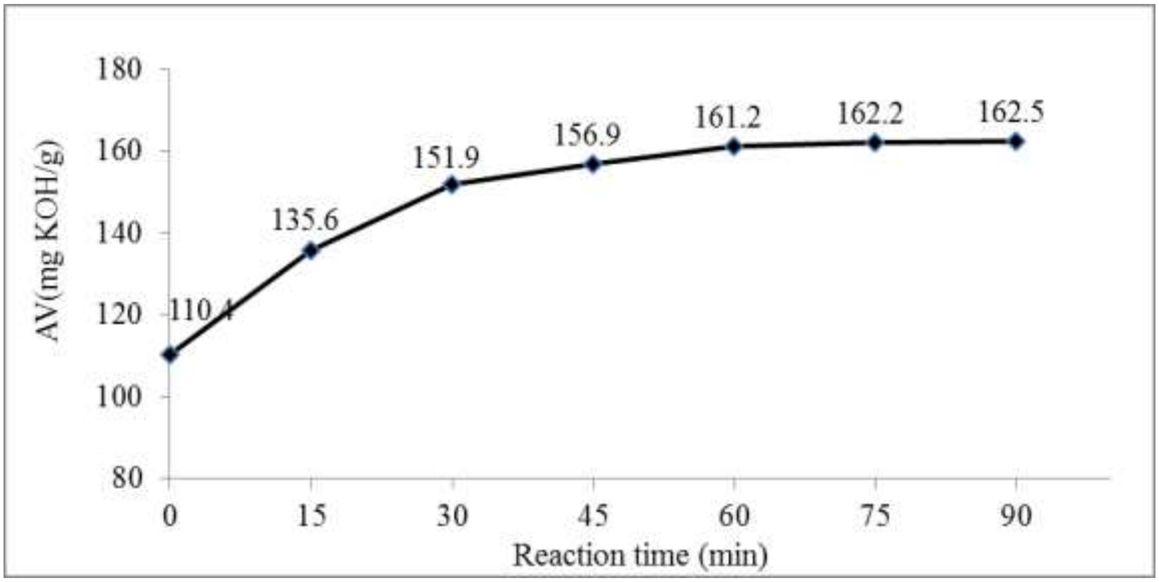


Figure 4.3 Effect of ozone/H_2O_2 pretreatment on AV of raw bio-oil over time as measured at 15-min intervals.

4.6.4 Esterification of the raw bio-oil and oxidized product-II

4.6.4.1 Effect of reaction temperature on the esterification of oxidized product-II

Figure 4.4 compares the HHVs, AVs and esterified bio-oil yields of the BF2s produced at reaction temperatures at 320, 340 and 360 °C by esterification. As shown in

Figure 4.4, the HHVs of the BF2s produced at the reaction temperatures of 320, 340 and 360 °C were 32.2, 35.3 and 35.9 MJ/kg, respectively. As shown in Figure 4.4, as the reaction temperature increased HHVs of the BF2s produced were increased. The HHV of the BF2 produced at a reaction temperature 340 °C was 9.6% higher than BF2s produced at 320 °C; when compared to the BF2 produced at 360 °C it had 1.7% lower HHV. Therefore, HHV of the BF2 considerably increased from 320 to 340 °C; then there is no substantial increase in the HHV at 360 °C. The respective AVs of the BF2s produced at 320, 340 and 360 °C were 37.7, 34.9 and 34.2 mg KOH/g. The AVs of the BF2s decreased from 320 to 340 °C and 340-360 °C were 7.4 and 2.0%. The esterification tested from 340 to 360 °C produced BF2 AV was not largely decreased. The esterified BF2 yields obtained were 54.6, 57.4 and 56.0 wt% for the respective treatment temperatures of 320, 340 and 360 °C. Among the esterification reactions performed at 320, 340 and 360 °C, BF2 produced was considered to be the best treatment.

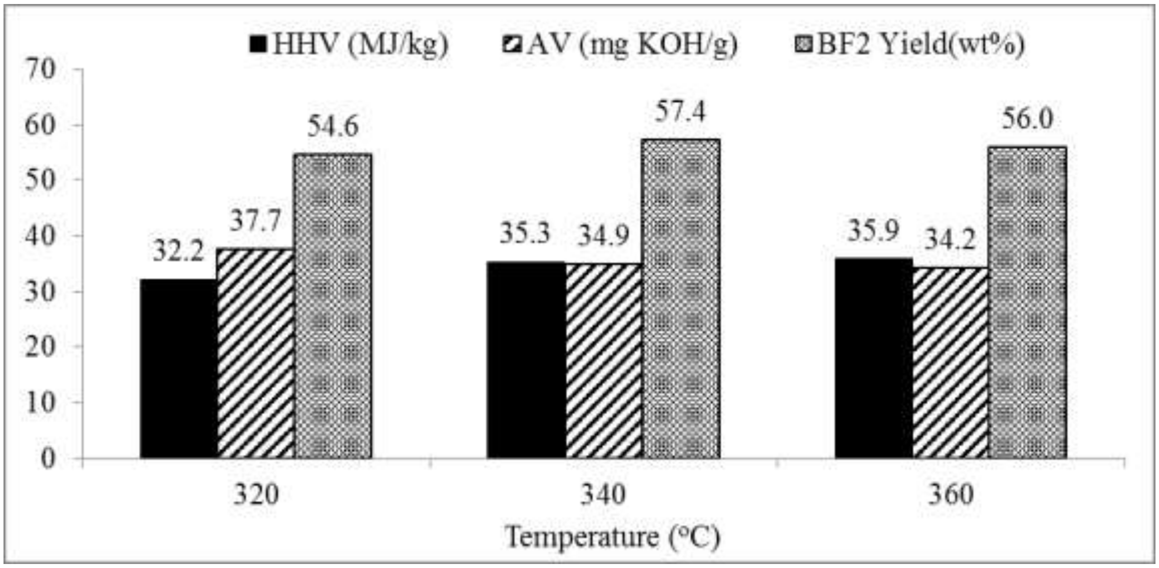


Figure 4.4 Compares HHVs, AVs and yield of BF2 produced at reaction temperatures at 320, 340 and 360 °C by esterification.

In this study we have applied oxidation pretreatment to raw bio-oil and followed by subsequent esterification to produce a product with high HHV suitable for boiler fuel and compared with direct esterification of the raw bio-oil resulted boiler fuel. Table 4.1 shows a comparison of physical and chemical properties of raw bio-oil, ozone/H_2O_2 pretreated bio-oil (OPTBO) and raw bio-oil without pretreatment after esterification produced boiler fuel type 1(BF1) and OPTBO after esterification produced boiler fuel type 2 (BF2) are compared. All the results shown in Table 4.1 were average values of three replica of the each treatment. As shown in Table 4.1, after pretreatment the AV of OPTBO increased to 165.4 mg KOH/g from 90.3 mg KOH/g, the value of raw bio-oil. The total AV increased by 83.16 %, which indicates the oxidation of aldehydes/ketones and alcohols to acids. The viscosity decreased from 12.0 to 9.2 cSt and water content increased from 30.4 to 33.5%. The HHV of the oxidized product increased from 16.0 to 16.4 MJ/kg. Density decreased from 1.2 to 1.0 g/ml and pH was reduced to 2.3 from 3.1. Oxygen content increased somewhat from 53.9 to 55.3 wt%. This oxygen content resulted from both increased acid and water content.

Table 4.1 Comparison of some physical and chemical properties of raw bio-oil, OPTBO, BF1 and BF2.

Properties	Raw bio-oil	OPTBO	BF1	BF2
HHV, MJ/Kg	16.0	16.4	33.4	35.3
AV (mg KOH/g)	90.3	165.4	25.8	34.3
Water content (%)	30.4	33.5	4.6	3.6
Density, g/ml	1.2	1.0	1.0	0.9
Kinematic viscosity,40 °C, cSt	12.0	9.2	25.9	10.1
pH	3.1	2.3	4.4	4.2
Elemental analysis (%)				
C	38.4	37.6	71.8	71.6
H	7.6	7.6	9.8	10.3
N	0.2	0.2	0.4	0.3
O	53.7	54.6	17.9	17.7
Yield (wt%)	-	-	39.0	48.0

The RBO and pretreated product (OPTBO) were then subjected to esterification to produce BF1 and BF2, respectively, as described in the esterification method section 4.4.2.2. The resulting liquid product was comprised of both an organic phase as a top layer and an aqueous phase at the bottom. The organic fraction was separated by centrifuging for 3-4 h followed by separation of the water fraction with a separatory funnel. For the organic fraction of the esterified boiler fuels some physical and chemical properties were determined by ASTM test methods.

Comparing the pretreated product (OPTBO) to the boiler fuel produced from it (BF2) we note that the HHV nearly doubled for the esterified BF2 product with an increase from 16.4 MJ/Kg to 35.3 MJ/Kg. The AV for the BF2 product was dramatically reduced from the OPTBO value of 165.4 mg KOH/g to 34.3 mg KOH/g, a decrease of 382.2 %. Water content of the BF2 product was reduced to nearly 10.7% of the value of 33.5% for OPTBO to 3.6. Density and viscosity were essentially unchanged when OPTBO was esterified to BF2. Carbon content of BF2 nearly doubled to 71.6 from 37.6 from that of OPTBO. Hydrogen content was 35.5% higher for BF2 at 71.6% compared to the 37.6% of OPTBO. Nitrogen increased from 0.22% for OPTBO to 0.31% for BF2, a 40.9% increase. BF2 oxygen content was reduced by the esterification of OPTBO with a decrease from 54.6 to 17.7%, a 208.5% decrease. Therefore, the esterification of OPTBO to produce BF2 substantially increased the quality of its most important characteristics (HHV, AV, water, hydrogen and oxygen content, and pH value); density and viscosity remain essentially the same. The only negative change was the small increase in nitrogen content.

The esterification of raw bio-oil produced BF1 resulting in more than a 100% increase in HHV. AV decreased from 90.3 for raw bio-oil to 25.8 for BF1, a 250% decrease. Water content of the BF1 product was reduced to approximately 15.2% of the value of 30.4 for raw bio-oil to 4.6. Density was decreased from 1.2 to 1.0, a decrease of 20%. Viscosity was increased from 12.0 to 25.9, an increase by 115.8%. Carbon content of BF1 increased to 71.8 from 38.4 for raw bio-oil. Hydrogen content was increased by

28.9%. Nitrogen was increased from 0.2 to 0.4. BF1 oxygen content was reduced from raw bio-oil, 53.7 to 17.9 wt%, a decrease of 200%.

A comparison of BF1 to BF2 will indicate whether the OPTBO treatment is sufficiently advantageous, or whether simple esterification of raw bio-oil is a better choice. For BF2 the HHV of 35.3 MJ/Kg was slightly higher (5.7%) than BF1 which had a value of 33.4 MJ/Kg. AV was higher for the BF2 product. Water content of BF2 was 28% less than the BF1. Density value of both BF1 and BF2 remained essentially unchanged. BF2 viscosity was reduced greatly to 10.1 compared to BF1 value of 25.9, a reduction of 156.4%. The esterification of OPTBO compared to esterification of direct raw bio-oil produced the BF2 fuel with improved characteristics in terms of reduced viscosity and water content and increased HHV. The BF2 obtained from OPTBO also produced 9% higher yield compared to BF1 obtained from direct raw bio-oil esterification. The viscosity value of BF1 is a particular problem as pumping such viscous material into a boiler may be problematic. Based on the increased characteristics in terms of yield, viscosity, HHV and water content it is clear that BF2 is the superior boiler fuel.

The esterification of OPTBO to produce BF2 utilized only 20% of alcohol to produce a boiler fuel with an HHV of 35.3 MJ/kg compared to past researchers who have utilized or recommended alcohol additions of 100 to 250% or more.

4.6.5 FTIR spectral analysis comparing spectra of raw bio-oil to pretreated and esterified products

In our study, FTIR spectral data was used to analyze the raw bio-oil, OPTBO and boiler fuels (BF1 and BF2). Characteristic vibrational modes are observed at 1100-1300 cm-1 (C-O stretching), 1710 cm-1 (C=O stretching), 2850-2980 cm-1 (CH stretching, aliphatic) and 3600-3000 cm-1 (OH stretching). From Figure 4.5, it was evident that after ozone/H_2O_2 pretreatment C=O stretching peak was decreased and OH stretching was intensified. The decreasing of C=O stretching peak and increasing of OH stretching indicate increase in carboxylic acids after ozone/H_2O_2 pretreatment. Furthermore, on esterification the intensity of CH stretching band dramatically increased and OH absorption band is considerably decreased due to conversion of carboxylic acids to esters and decrease in water content. As shown in Figure 4.5, it is clear that the decreasing of OH stretching peak of BF2 is higher than BF1 which implies that conversion of acids to esters and separation of water after esterification of OPTBO was improved compared to the esterification of raw bio-oil. The FTIR spectral data shown in Figure 4.5 was in good agreement with the properties shown in Table 4.1 and Figure 4.4.

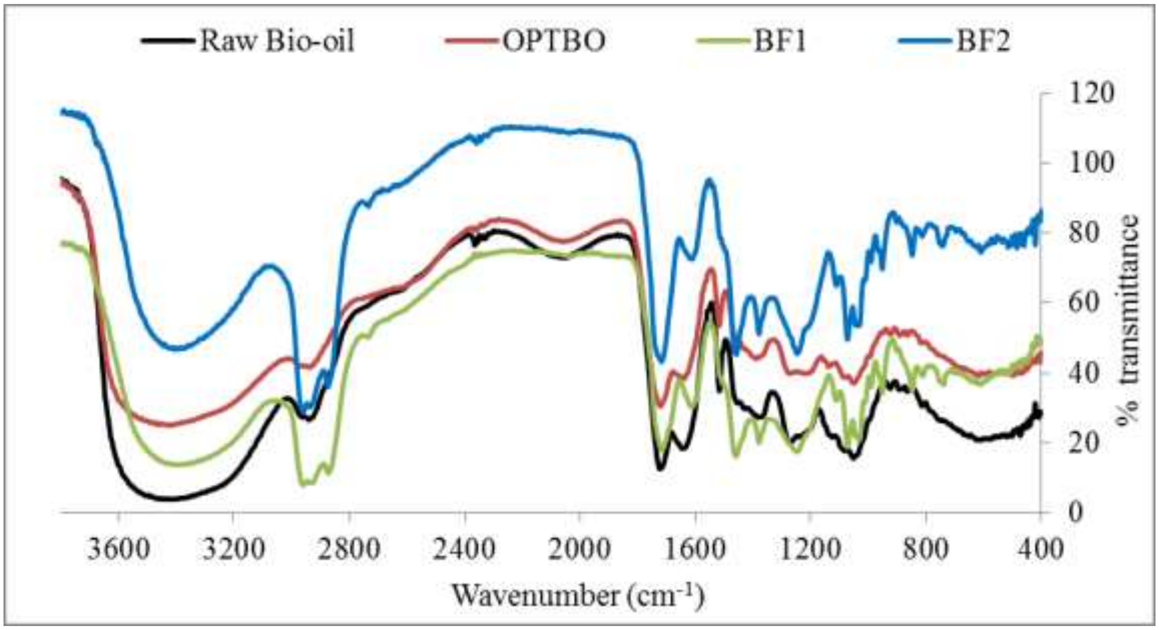


Figure 4.5 FTIR spectra comparison between raw bio-oil, OPTBO, BF1 and BF2.

4.6.6 GC-MS chemical compounds analysis of raw bio-oil and BF2.

Table 4.2 shows the chemical composition of raw bio-oil and BF2 analyzed by GC-MS. Approximately 50 chemical compounds were identified by GC-MS in both samples. The chemical compound name and their area percentages are given in Table 4.2. The total area percentages of the major fifty compounds present in raw bio-oil and BF2 were 98.12% and 78.93%, respectively. As shown in Table 4.2 it is very clear that BF2 chemical composition as measured by GC-MS area percentage was considerably changed compared to raw bio-oil. The carboxylic acids present in the raw bio-oil decreased from 9.8 area% to 1.2 area% for BF2, a reduction of 87.8%. Ester and ether compounds of BF2 increased to 22.63 area% from the 12.1 area% of raw bio-oil, an increase of 87.0%; this is due to the conversion of carboxylic acids to esters and ethers during the esterification reaction. The 11.59 area% aldehydes of the raw bio-oil were decreased to 1.99 area% for BF2. The ketones of raw bio-oil decreased from 24.23 area% to 13.78 area% for BF2. Phenols and other alcohols of raw bio-oil from 39.3 area% increased to 46.77 area% for BF2; this is due to the presence of 1-butanol solvent approximately 34.12 area% in the BF2. Phenol conversion decreased from the 34.74 area% of raw bio-oil to 11.58 area% for BF2, a decrease of 66.7%. Other miscellaneous compounds of raw bio-oil from 2.1 area% increased to 5.05 area% for BF2.

BF2 fuel is an esterified bio-oil meant to be a boiler fuel. As shown in this section the major chemical compounds present in the boiler fuel are esters, ethers, ketones, phenols and alcohols. When combusted the product emissions are expected to be water vapor, CO_2, CO, hydrogen, nitrogen and carbon soot.

Table 4.2 Raw bio-oil and BF2 chemical composition analysis by GC-MS with area percentages.

Raw bio-oil		**Boiler fuel (BF2)**	
Compound name	Area%	Compound name	Area%
Acids		**Acids**	
Acetic acid	5.1	Hexanoic acid	0.58
Heptanoic acid	1.42	5-Ethylcyclopent-1-ene-1-carboxylic acid	0.61
Benzoic acid, 4-hydroxy-3-methoxy-	0.75	**Esters & Ethers**	
Benzeneacetic acid, alpha-hydroxy-	1.96	Acetic acid, butyl ester	8.99
benzeneacetic acid, 4-hydroxy-3-methyl	0.54	Oxalic acid, isobutyl nonyl ester	1.36
Esters & Ethers		Propanoic acid, butyl ester	3.04
acetic acid, 1-methylethyl ester	1.82	Propanoic acid, 2-methyl-, butyl ester	0.77
pentanoic acid, ethyl ester	0.92	Butanoic acid, octyl ester	2.69
n-heptyl hexanoate	0.94	Butyl 2-methylbutanoate	0.68
Hexanoic acid, 1-methylhexyl ester	1.85	Pentanoic acid, butyl ester	1.82
1-propene, 1-methyoxy-2-methyl-	0.93	Valeric acid, 2-methyl- pentyl ester	0.49
Furan, 2-ethoxy-2,3-dihydro-4-methyl	0.58	Hexanoic acid, butyl ester	1.96
2,6-Dimethoxytoluene	0.9	4-(N-Dimethylamino) phenol, acetate	0.83
3-methoxy-4-methylaniline	1.25	**Aldehydes**	
4,4'-Dimethoxy-biphenyl-2-carboxyl-	0.98	Benzaldehyde, 3, 4-dihydroxy	1.99
Aldehydes		**Ketones**	
furfural	1.94	2-butanone, 3-methyl	0.56

Table 4.2 (Continued)

2-furancarboxaldehyde, 5-methyl-	0.63	Cyclopentanone, 2-methyl	2.51
Glutaraldehyde	1.16	3-methyl cyclopentanone	0.89
cyclopentanecarboxaldehyde	0.82	2-heptanone	0.88
2-Furancarboxaldehyde, 5-methyl-	1.78	Cyclohexanone, 3-dimethyl	0.87
5-methyl-2-thiophenecarboxaldehyde	0.55	Cyclohexanone, 2,3-dimethyl	0.83
vanillin	1.39	Ethanone, 1-cyclohexyl	0.58
9,12-octadecadienal	0.6	2-cyclopenten-1-one, 2,3-dimethyl	0.59
Benzaldehyde, 3-hydroxy-, oxime	0.74	2-cyclopenten-1-one, 3,4,4-trimethyl	0.71
4-hydroxy-2-mehoxycinnamaldehyde	0.71	3H-Pyrazol-3-one, 2,4-dihydro-5-methyl	0.65
4-hydroxy-2-methylacetophenone	1.27	Cyclohexanone, 2-butyl	1.08
Ketones		4-Hepten-3-one, 4-methyl	0.47
4H-Pyran-4-one, 3,5-dihydroxy-2-methyl-	0.58	2-propanone, 1-94-methoxyphenyl)-	3.16
2-propanone, 1-94-hydroxy-3-methoxy)-	0.84	**Alcohols**	
2-cyclopenten-1-one, 2-hydroxy-3-methyl	1.84	1-Butanol	34.12
2-cyclopenten-1-one, 2-hydroxyl-	1.42	Phenol	0.71
Ethanone, 1-(4-hydroxy-3-methoxyphenol)	19.55	Phenol, 3-methyl	0.54
Alcohols		Phenol, 4-methyl	2.59
2-Propanone, 1-hydroxy	3.63	Phenol, 2,4-dimethyl	1.42
phenol, 2-methyl-	1.14	Phenol, 4-propyl	0.84
phenol, 4-methyl-	0.72	Phenol, 2-ethyl-6-methyl	1.04

Table 4.2 (Continued)

phenol, 2-methoxy-	4.15	phenol, 4-butyl	0.53
4-mercaptophenol	0.59	phenol, 2-butyl	0.52
Phenol, 2-methoxy-4-methyl-	10.81	Phenol, 4-(1,1-dimethylpropyl)-	0.78
1,2-Benzenediol, 3-methyl-	0.93	Phenol, 2-methoxy-4-propy	0.55
phenol, 4-ethyl-2-methoxy-	2.61	Phenol, 5-methoxy-2,3-dimethyl	2.06
1,2-Benzenediol, 4-methyl-	1.31	Ethanol, 2-(4-(1,1-dimethylpropyl)	1.07
Eugenol	1.78	**Other**	
1-propene, 1-methyoxy-2-methyl-	0.93	3-Undecene, 6-methyl-	1.47
phenol, 2-methoxy-4-(1-propenyl)-	1.65	Cyclopropane, trimethylmethylene	0.86
Phenol, 2-methoxy-3-(2-propenyl)-	3.28	Cyclooctane	0.74
phenol, 2-methoxy-4-propyl-	3.16	Bicyclo[3.1.1] heptan-2-one, 6,6-dimethyl	0.61
homovanillyl alcohol	0.98	1-(cyclopropylmethyl)-4-(methyloxyl)	0.77
phenol, 2-methoxy-4-(methoxymethyl)-	0.65	Cyclopentane, 1,2,3,3,5-pentamethyl	0.86
Ethyl, 4-hydroxy-7-trifluoromethyl-quinoline	0.98	1-Tyrophanamide	0.51
Other		Total	78.93
3,4-anhydro-d-galactosan	2.1		
Total	98.12		

As shown in Table 4.2, GC-MS chemical composition analysis the hydrocarbons were increased to 3.7 area% for BF2 from 1.0 area% of RBO. This is due to the use of pressurized hydrogen during the esterification was lead to may be small percentage of hydrotreating side reaction. The effect of hydrotreating side reaction in the presents of hydrogen during the esterification reaction was tested without addition of alcohol solvent. It was observed that in absents of alcohol the esterification reaction was not taken place more over coke formation was observed. It was also observed that esterification of pretreated product under pressurized hydrogen produced better quality boiler fuel in terms of viscosity compared to the esterification performed without pressurized hydrogen conditions. This indicates that during the esterification reaction in-situ hydrotreating may be occurred to convert higher molecular weight compounds to lighter weight compounds. As shown in GC-MS results, increase in hydrocarbon content in the produced esterified boiler fuel is in good agreement with the decrease in the viscosity of the boiler fuel.

Table 4.3 compares viscosity and density within each aging period of BF2 aging at 80 ^{o}C for 6, 12, 18, 24 h. To estimate the stability of the boiler fuel produced in this method an accelerated aging test was performed at 80 ^{o}C over a 24 h period with viscosity tested at each 6 h intervals of aging time. All BF2 samples were stored in sealed vials and weighed before and after each aging period. Samples were heated in an aerated oven at 80 °C for 6, 12, 18, and 24 h. As shown in the Table 4.3 both untreated raw bio-oil and control BF2 specimens were tested without application of temperature. Viscosity of raw bio-oil was 12.0 cSt and density was 1.2 g/ml. The BF2 untreated control specimen comprised 9.9 cSt with density of 0.96 g/ml. The BF2 viscosity values replicates measured at 6, 12, 18, 24 h, respectively, heating at 80 ^{o}C were 8.82, 8.88, 8.62

and 9.10 cSt; density values for the same respective time periods were 0.95, 0.95, 0.94 and 0.95 g/ml. The observation of viscosity and density values indicates that esterified bio-oil produced has a lower viscosity and density compared to raw bio-oil. Further, this viscosity and density changes over time as unchanged by the accelerated aging test results.

Table 4.3 Comparison of viscosity and density within each aging period of BF2 at 80°C for 6, 12, 18, 24 h with control untreated raw bio-oil and BF2 at room temperature.

Sample	Temp (°C)	Viscosity (cSt)	Density (g/ml)
Untreated Raw bio-oil	Room temp ~25	12.0	1.2
Control BF2	Room temp ~25	9.9	0.96
BF2 @ 6 h	80	8.82	0.95
BF2 @ 12 h	80	8.88	0.95
BF2 @ 18 h	80	8.62	0.94
BF2 @ 24 h	80	9.10	0.95

4.7 Summary

The objective of this study's comparison of oxidation pretreatments was to determine the most effective pretreatment, of those tested, for production of maximum yield of carboxylic acids. The increased production of carboxylic acids provides an increased degree of esterification with a relatively low percentage of alcohol (20%). This led to production of a high HHV boiler fuel. Our approach of oxidation pretreatment of raw bio-oil with ozone/H_2O_2 pretreatment followed by esterification successfully produced boiler fuel (BF2) with improved fuel properties and yields. In addition to ozone/H_2O_2 pretreatment, ozone alone and H_2O_2 alone oxidation pretreatments were also investigated. Ozone/H_2O_2 pretreatment was shown to perform a higher degree of raw bio-oil oxidation as measured by magnitude of AV attained. The AV of raw bio-oil after ozone/H_2O_2 pretreatment was increased from 90.3 to 165.4 mg KOH/g. The boiler fuel (BF2) produced from the OPTBO product had an HHV of 35.3 MJ/Kg; the energy density of boiler fuel produced by this method was increased by 120.62% from raw bio-oil of 16.0 MJ/Kg. BF2 viscosity was reduced largely to 10.1 compared to BF1 value of 25.9, a reduction of 156.4%. The method of raw bio-oil pretreatment followed by esterification was reduced boiler fuel viscosity with a considerable amount. Oxygen content and acid value were reduced by 71.4% and 81.9%, respectively. The esterification of OPTBO compared to esterification of raw bio-oil produced boiler fuel with improved characteristics in terms of lower viscosity, density, water content and HHV. The boiler fuel (BF2) from OPTBO also resulted in production of 23% higher yield compared to boiler fuel (BF1) produced from direct raw bio-oil esterification.

4.8 Disclaimer

4.9 References

1. Yan, J.; Alvors, P.; Eidensten, L. A future for biomass: *Mechanical Engineering*, **1997,** *117*,94–98.

2. Huber, G. W.; Iborra, S.; Corma, A. synthesis of transportation fuels from biomass: *Chemistry, Catalysts and Engineering. Chem. Review*, **2006,** *106*, 4044–4098

3. 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.

4. Bridgwater, A.V.; Peacocke, G.V. C. Fast pyrolysis processes for biomass: *Renew Sustain Energy Rev*, **2000**, *4*(1), 1-73.

5. Czernik, S.; Bridgwater, A.V. Overview of applications of biomass fast pyrolysis oil: *Energy & Fuels*, **2004**, *18*, 590-598.

6. Diebold, J. P. A review of the chemical and physical mechanisms of the storage stability of the fast pyrolysis bio-oils: NREL/SR-570-27613, **2000**, January.

7. Hu, X.; Wang, D. M.; Gunawan, R.; Lievens, C.; Chaiwat, W.; Gholizadeh, M.; Wu, L.; Li, X.; Li, C. Z. Polymerization on heating up of bio-oil: A model compound study: *Reaction Engineering, Kinetics and Catalysis,* **2012**, *59*(3), 888-900.

8. Junming, X.; Jianchun, J.; Yunjuan, S.; Yanju, L. Bio-oil upgrading by means of ethyl ester production in reactive distillation to remove water and to improve storage and fuel characteristic: *Biomass and Bioenergy,* **2008**, *32*, 1056-1061.

9. Xu, J.; Jiang, J.; Dai, W.; Zhang, T.; Xu, Y. Bio-oil upgrading by means of ozone oxidation and esterification to remove water and to improve fuel characteristics: *Energy & Fuels,***2011,** *25*, 1798-1801.

10. Gagnon, J.; Kaliaguine, S. Catalytic hydrotreatment of vacuum pyrolysis oil from wood:*Industrial and Engineering Chemistry Research,* **1988,** *27*, 1783-1788.

11. Furimsky, E. Catalytic hydrodeoxygenation. Applied Catalysis A: **2000**, *199*, 147-190.

12. Shanks, H. B.; Lohithrn, N. Upgrading of bio-oil: Effect of light aldehydes on acetic acid removal via esterification: *Catalysis Communications,* **2009**, *11*, 96-99.

13. Elliot, D.C. Historical developments in hydroprocessing bio-oils. *Energy & Fuels*, **2007**,*21*, 1792-1815.

14. Weerachanchai, P.; Tangsathitkulchai, C.; Tangsathitkulchai, M. Effect of reaction conditions on the catalytic esterification of bio-oil: *Korean J. Chem. Eng,* **2012**, *29*(2), 182-189.

15. Wang, J.; Chang, J.; Fan, J. Catalytic esterification of bio-oil by ion exchange resins:*Jounal of fuel chemistry and technology*, **2010**, *38*, 5.

16. Mahfud, F.H., Melian-Cabrera, I., Manurung, R.; Heeres, J.J. Biomass to fuels upgrading of flash pyrolysis oil by reactive distillation using a high boiling alcohol and acid catalysts,*Process Safety and Environmental Protection*, **2007**, *85*, 466-472.

17. Moens, L., Black, S.K., Myers, M.D.; Czernik, S. Study of neutralisation and stabilization of a mixed hardwood oil, *Energy & Fuels*, **2009**, *23*, 2695-2699.

18. Xiong, W.M., Zhu, M.Z., Deng, L., Fu, Y.; Guo, Q.X. Esterification of organic acid in bio-oil using acidic ionic liquid catalyst, *Energy & Fuels*, **2009**, *23*, 2278-2283.

19. Tang, Y.; Yu, W.; Mo, L.; Lou, H.; Zheng, X. One-Step hydrogenation−esterification of aldehyde and acid to ester over bifunctional Pt catalysts: A model reaction as novel route for catalytic upgrading of fast pyrolysis bio-oil. *Energy & Fuels,* **2008,** *22*, 3484-3488.

20. Xu Ying, C. J., Zhang, Q.;, Wang Tiejun, Wang Chenguang. Upgrading of bio-oil by esterification over solid base catalyst. *Petrochemical Technology,* **2010,** *35*(7), 615-618.

21. Zhang, Q.; Chang, J., Wang, T-J.; Wu, C-Z.; Zhu, Xi-F. Study on upgrading of bio-oil catalyzed over solid acids. *Journal of Fuel Chemistry and Technology,* **2006,** *34*(6), 680-684.

22. Xiong, W-F.; Yao, F.; Lai, D-M.; Guo, Q-X. Upgrading of bio-oil via esterification catalysted with acidic ionexchange resin. *Chemical Journal of Chinese Universities,* **2009,** *30*(9), 1754-1758.

23. Tang, Z.; Lu, Q.; Zhang, Y.; Zhu, X.; Guo, Q. One step bio-oil upgrading through hydrotreatment, esterification, and cracking. *Industrial & Engineering Chemistry Research,***2009,** *48*(15), 6923- 6929.

24. Nkafamiya, I. I.; Maina, H. M.; Osemeahon, S. A.; Modibbo, U. U. Percentage oil yield and physiochemical properties of different groundnut species (Arachis hypogaea): *African journal of food science,* **2010**, *4*(7), 418-421.

CHAPTER V

PRETREATING BIO-OIL TO INCREASE YIELD AND REDUCE CHAR DURING HYDRODEOXYGENATION TO PRODUCE HYDROCARBONS

5.1 Abstract

Conversion of pyrolysis oil to hydrocarbons has been successfully performed under high hydrogen pressure in the presence of hydrodeoxygenation (HDO) catalysts at high heat. The high hydrogen pressures utilized are a more expensive application than for a lower hydrogen pressure. Development of a modified HDO method utilizing lower pressure hydrogen with the potential for reduction of hydrogen consumption would be economically beneficial to the process if equal or higher biofuel yields and quality are maintained. The method tested here is the oxidation pretreatment of raw bio-oil to increase carboxylic acids by conversion of aldehydes and ketones; phenols and other alcohols were also oxidized to some extent. This oxidation pretreatment of raw bio-oil allowed performance of the hydrotreating step with low hydrogen pressure and reduced hydrogen consumption. The hydrotreated oxidized bio-oil had a 30.5% higher organic fraction yield; char and water content were reduced by approximately 92.0% and 46.2%, respectively. The hydrotreated oxidized product was then hydrocracked at higher hydrogen pressure to produce mixed hydrocarbons found suitable for transportation fuels. The hydrocarbons produced had approximately a 181.9% HHV increase at 45.1 MJ/kg

compared to raw bio-oil (16.0 MJ/kg). The acid value, water and oxygen contents of the hydrocarbons were reduced to approximately zero.

Keywords: Pyrolysis oil, bio-oil, oxidation, hydrodeoxygenation, GC-MS, FTIR, simulated distillation.

5.2 Introduction

Bio-oil produced from fast pyrolysis of lignocellulosic biomass is a promising alternative fuel to replace fossil fuels. Fast pyrolysis includes heating the biomass at elevated temperatures in the range of 400 to 550 ^{o}C in the absence of oxygen. Bio-oil may also be produced by slow pyrolysis, liquefaction or other alternative methods [1-2]. Bio-oil has environmental advantages when compared to fossil fuels because, when combusted, bio-oil produces less air pollution than fossil fuels, specifically, half the NO_x, negligible quantities of SO_x emissions, and it is considered to be CO_2 neutral. Bio-oil chemical properties vary with material utilized for its production or the conditions under which it is produced. However, bio-oils demonstrate some common negative properties which include significant water content, high acidity, immiscibility with petroleum products, and viscosity increase over time when heated [3-7].

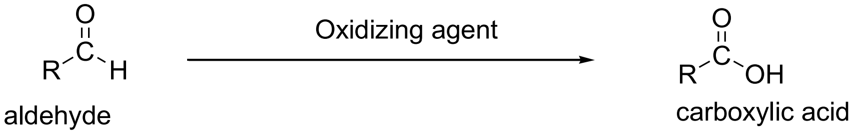
Presently, bio-oil upgrading techniques include hydrodeoxygenation (HDO), catalytic pyrolysis and decarboxylation to reduce the oxygen content present in the bio-oil [8-16]. HDO is an upgrading process for reducing heavy molecules into lighter hydrocarbons through the catalytic addition of hydrogen. HDO of bio-oil has been demonstrated to reduce the oxygen content of bio-oil and produces a liquid hydrocarbon mixture without the negative properties of raw bio-oil. This mixture can be distilled and its component hydrocarbons can be utilized as a transportation fuel. In general, HDO can be performed in either one or more steps. It has become traditional to hydroprocess liquid intermediates (particularly fast pyrolysis oil) by an initial 1st-stage hydrotreating step at a mild temperature [8,17] to prevent the polymerization caused by immediate application of hydrocracking which applies a more severe temperature. After hydrotreating the hydrocracking 2nd-stage can be applied at a higher temperature [8,13,14,18,19]. The general HDO reactions are shown in Scheme 5.1 below.

$$C_nCOOH \xrightarrow{\text{Catalyst}} C_{n+1} + 2H_2O$$

Scheme 5.1 HDO process reaction to form hydrocarbons from carboxylic acids [18].

Researchers have utilized various catalysts, temperature levels and hydrogen pressures to perform HDO on bio-oil. Pressures applied have been relatively high, ranging from 1510 to 3000 psig [8,10,13-16,18-23]. Creating this high-pressure hydrogen is more expensive than would be the case for lower pressure HDO. These high pressures are expensive to apply and a means to reduce the pressure required and to potentially reduce hydrogen consumed would be beneficial to the eventual economic commercialization of the conversion of bio-oil to hydrocarbons via HDO.

Bio-oil aldehydes play a vital role in bio-oil stability from thermal application or stability over time. Aldehydes readily react with phenols and sugars to form higher molecular weight resins and oligomers via polymerization and condensation; oligomerization reactions lead to coke formation [16,24-26]. Aldehydes present in the raw bio-oil can be converted to carboxylic acids by subjecting them to oxidation. Xu et al. (2011) developed a method to convert aldehydes present in the bio-oil to carboxylic acids by treating with ozone for about 10 h [27]. Scheme 5.2 is a schematic of the chemical reaction for the conversion of bio-oil aldehydes to carboxylic acids in the presence of an oxidizing agent reaction pathway. No researcher has hydroprocessed the high acid mixture resulting from the oxidation process.



Scheme 5.2 Oxidation pretreatment pathway of aldehydes to carboxylic acids [27-29].

5.3 Objective

The objective of this research is to produce hydrocarbons more effectively by oxidizing bio-oil prior to application of HDO. Efficacy will be measured by increased hydrotreated organic fraction yield and higher heating value (HHV) and reduced char and oxygen content in the hydrocarbons produced from hydrotreating of the oxidized bio-oil. It is also desired to test whether oxidized bio-oil can be hydrotreated at lower hydrogen pressure than typically applied to hydrotreat raw bio-oil; the potential for reducing hydrogen consumption for hydrotreating at this low pressure will be explored.

5.4 Materials and methods

5.4.1 Materials

Nickel on silica-alumina (66±5% Ni) catalyst powder was obtained from Alfa Aesar. Potassium carbonate, copper(II)oxide, hydrogen peroxide (H_2O_2) 50 wt% solution in water and oxone (potassium monopersulfate triple salt) were obtained from Sigma-Aldrich. All chemicals were used with no further purification.

Bio-oil required for this research was produced from loblolly pine wood chips with a size of 1-3 mm and moisture content of 8-10% on dry-basis. Bio-oil was produced by fast pyrolysis performed at a temperature of 450 ^{o}C with nitrogen carrier gas at a rate of 7-kg/h with the auger-feed pyrolysis reactor located in the Department of Sustainable Bioproducts, Mississippi State University (MSU). Several pyrolysis runs were required to produce the study bio-oils for experiments. The mass balance for these runs varied but yields of products ranged from 60-65% for bio-oil, 10-15% of non-condensable gases and 20-25% char on dry biomass basis. The mean bio-oil yield for all of these runs was 62.1%.

5.4.2 Methods

5.4.2.1 Pretreatment of RBO by oxidation

Oxidation pretreatment was performed in a stainless steel, high pressure batch autoclave reactor equipped with an overhead magnetic stirrer, a pressure indicator with a maximum capacity of 5000 psig and a thermocouple for temperature monitoring in the range of 0-500 ^{o}C. The autoclave was equipped with an electrical heating and cooling system to control the temperature inside the reactor. Oxidation pretreatment was applied to raw bio-oil by addition of a mixture of oxone/H_2O_2 (oxidizing agent) followed by stirring for 90 min at room temperature and without applied pressure. This oxone/H_2O_2 solution was prepared by dissolving 5 wt% of oxone in 10 wt% of commercial 50 wt% H_2O_2 solution in water. This pretreatment considerably changed the bio-oil chemical composition by converting aldehydes and ketones into carboxylic acids. It was also observed that phenols and some other alcohol compounds were also oxidized. This oxidized product was utilized as a precursor material to produce hydrocarbons by HDO (hydrotreating followed by hydrocracking).

A patent application has been filed to protect the intellectual property represented by the production of oxidized bio-oil followed by HDO to produce transportation fuel equivalent hydrocarbons [30].

5.4.2.2 Hydrodeoxygenation of pretreated bio-oil

HDO comprised of hydrotreating followed by hydrocracking was performed in the same Parr batch autoclave described above. The 1st-stage hydrotreating of the oxidized product was performed in the presence of a mixture of nickel on silica-alumina (5 wt%) and potassium carbonate (3 wt%) catalyst at a temperature of 340 ^{o}C and under pressurized hydrogen at 800 psig for about 90 min. In the 2nd-stage, the hydrotreated top oil fraction was separated and hydrocracked by a mixture of nickel on silica-alumina (5 wt%) and copper(II)oxide (2 wt%) catalyst at a temperature of 425 ^{o}C and under pressurized hydrogen at 1400 psig for about 150 min. Hydrotreating of raw bio-oil was also performed as a control reaction using the same 1st-stage hydrotreating conditions described above.

In each experiment, once the reaction was complete the liquid products were cooled in the reactor. The mixture was collected in centrifuge test tubes and centrifuged for 2-4 h to separate the resulting aqueous and organic phases. Both phases were separated and weighed for mass balance computation. Reactions yields were calculated by Equation 5.1 [31].

$$\text{Yield (wt\%)} = (\text{P (g)} \times 100)/\text{bio-oil weight (g)} \qquad \text{Eq. 5.1}$$

Where:

P = organic fraction obtained

Bio-oil weight = Total raw bio-oil used

5.5 Data analysis

The raw bio-oil, oxidized product, hydrotreated products and hydrocracked hydrocarbon mixture produced were characterized following ASTM methods. The densities were determined by Anton Parr DMA 35n portable density meter by the ASTM D4052 method. Viscosities were determined by Ubbelohde capillary viscometer at 40 ^{o}C water bath temperature according to the ASTM D445 method. HHVs were determined by Ika-5000 bomb calorimeter by applying the ASTM D240 method. The acid values were determined by dissolving 1 g of bio-oil in 50 ml of 35:65 ratio of isopropanol to water mixtures and titrating to a pH of 8.5 with 0.1N KOH solution following the method of ASTM D664. The pH values were determined by addition of 1 g of bio-oil to 50 ml of 35% of isopropanol mixture. The pH values were determined by the ASTM E70 method. Elemental carbon, hydrogen, and nitrogen were determined by EAI CE-440 elemental analyzer with oxygen content determined by difference according to ASTM D5291 method. Water content was determined by Karl-Fisher titration by the ASTM E203 method.

The GC-MS analysis of the fuels was performed with a Hewlett-Packard HP 5890-Series II GC equipped with a Hewlett-Packard HP 5971 series MS. FTIR spectra were obtained by Varian 3500 FTIR analyzer with standard potassium bromide disk technique and spectra were analyzed by Varian-Resolutions software. A Varian CP-4900

Micro GC was used to analyze the gas composition of the remaining gas stream after each batch experiment. A mass balance for the fuels from the best performing catalyst was calculated. Simulated distillation data analysis was performed by the ASTM D2887 method with gas chromatography. Thermogravimetric analysis (TGA) was analyzed on the best performing both fresh and spent catalysts.

5.6 Results and discussion

5.6.1 Oxidation pretreatment of the RBO

The oxidation pretreatment of raw bio-oil was performed by treating with an oxidizing agent (oxone/H_2O_2) at an ambient temperature and pressure. This pretreatment considerably changed the bio-oil chemical composition by converting aldehydes and ketones to carboxylic acids. We also observed that phenols and some other alcohol compounds were also oxidized. The GC-MS compounds analysis between the raw bio-oil and oxidized product showed that the oxidized product's carboxylic acids area% was increased by 285.0%, aldehydes area% was decreased by 86.9%, ketones area% was decreased by 60.24% and phenols were decreased from 33.76 area% to 24.13 area%, a decrease of 39.91%.

Following oxidation of raw bio-oil, as shown in Table 5.1, the acid number increased from 90.3 to 155.7 mg KOH/g. Viscosity decreased by 45.1%; water content increased by about 11.0%. The HHV of the oxidized product decreased from 16.0 to 15.4 MJ/kg, probably due to the water content increase. Density decreased from 1.2 to 1.1 g/ml and pH was reduced to 2.8 from 3.1. Oxygen content increased somewhat from 53.9 to 56.7 wt%. This oxygen content increase resulted from both increased acid and water content.

Table 5.1 Comparison of raw bio-oil and oxidized product physical and chemical properties.

Properties	**Raw bio-oil**	**Oxidized product**
Density, g/mL	1.2	1.1
HHV, MJ/kg	16.0	15.4
Oxygen, wt%	53.9	56.7
Total acid number, mg KOH/g	90.3	155.7
pH	3.1	2.8
Water content, vol%	30.4	33.7
Kinematic viscosity, 40°C, cSt	12.0	6.6

5.6.2 Hydrotreating of the oxidized product and hydrocracking of the hydrotreated product.

5.6.2.1 Effect of reaction temperature on the hydrotreating of the oxidized product.

Figure 5.1 compares HHVs, AVs, oxygen contents and hydrotreated oils (OP-HTPs) yields produced at reaction temperatures of 320, 340 and 360 °C by hydrotreating the oxidized product. As shown in Figure 5.1, the HHVs of the OP-HTPs produced at the reaction temperatures of 320, 340 and 360 °C were 31.6, 34.5 and 35.4 MJ/kg, respectively. As the reaction temperature increased HHVs of the OP-HTPs increased. The respective AVs of the OP-HTPs produced at 320, 340 and 360 °C were 54.8, 48.6 and 42.2 mg KOH/g. Oxygen content values of the OP-HTPs were 18.2, 15.1 and 14.2 wt% for the respective temperatures at 320, 340 and 360 °C. The hydrotreating of the oxidized product at 320, 340 and 360 °C produced OP-HTPs yields of 35.9, 39.3 and 34.8 wt% for the respective temperature treatment. Comparing the HHVs, AVs, oxygen contents and yields of the OP-HTPs produced at reaction temperatures of 320, 340 and 360 °C, hydrotreating of the oxidized tested at a reaction temperature of 340 °C was considered as the best treatment.

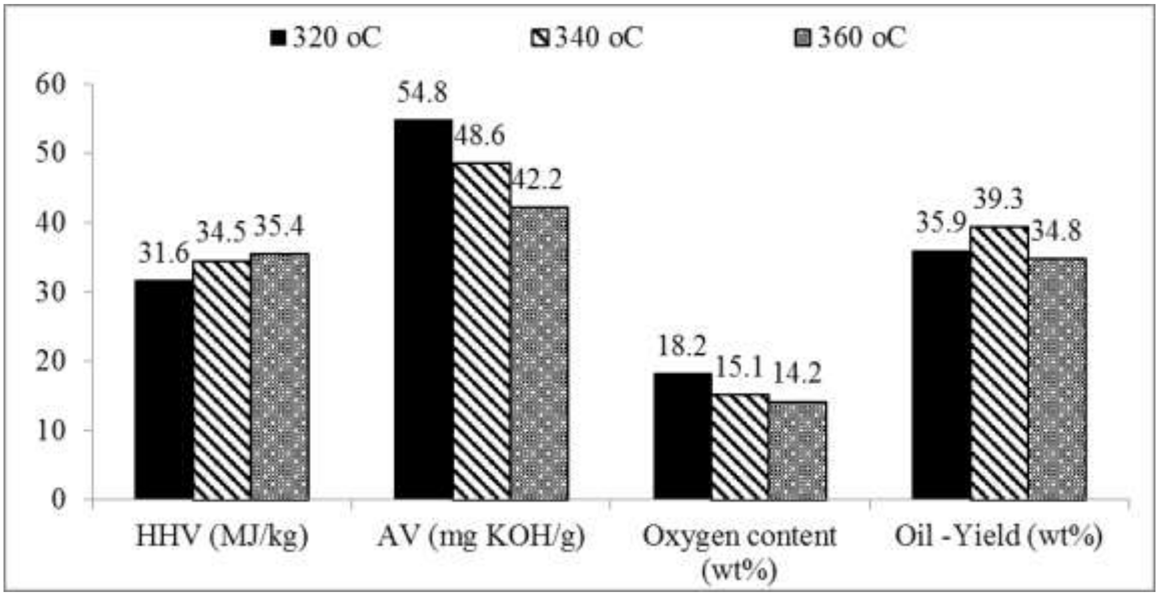


Figure 5.1 Comparison of the HHVs, AVs, oxygen contents and hydrotreated oil (OP-HTP) yields produced at reaction temperatures 320, 340 and 360 °C by hydrotreating of the oxidized product.

The oxidized product was then hydrotreated to produce partially deoxygenated bio-oil by using low hydrogen pressure of 800 psig as described in Section 5.4.2.2. After cooling, the partially deoxygenated product had an aqueous phase at the bottom of the vessel and an organic phase at the top. The aqueous fraction was separated from the organic fraction with a separatory funnel. A portion of the organic fraction was maintained for analysis of its properties. The organic fraction comprising the partially deoxygenated bio-oil was shown to have a relatively high HHV. This high HHV organic fraction could be utilized as an effective boiler fuel if it was not subjected to hydrocracking to produce a 100% hydrocarbon mixture. In this chapter the products produced from hydrotreating the oxidized product and following its separation as an organic fraction will be referred to as oxidized product-hydrotreated product (OP-HTP) and an organic fraction produced from direct hydrotreating of raw bio-oil will be referred to as raw bio-oil-hydrotreated product (RBO-HTP) to distinguish it from referenced conversion products. The OP-HTP resulting from separation of the organic fraction from the aqueous fraction was then subjected to hydrocracking as described in Section 5.4.2.2 to produce what will be referred to as the hydrocarbon mixture. The resulting hydrocarbon mixture contained both hydrocarbons as a top layer and a small percentage of an aqueous phase at the bottom. The hydrocarbon mix was separated by centrifuging for 2-4 h followed by separation of the water fraction with a separatory funnel. The physical and chemical properties of the oxidized product, OP-HTP, and hydrocarbon mixture were tested by following ASTM test methods as described in Section 5.5.

The properties of the oxidized product, the resultant OP-HTP following hydrotreating and the hydrocarbon mixture produced by hydrocracking, are given in Table 5.2. The HHV of the OP-HTP at 34.5 MJ/kg was more than double the 15.4 MJ/kg value of the oxidized product. OP-HTP oxygen content was dramatically reduced from 56.7 wt% to 15.1 wt%. Acid number was reduced from 155.7 mg KOH/g to 48.6 mg KOH/g and pH increased from 2.8 to 4.2. Water content of the OP-HTP was only 2.7 vol% compared to that of the oxidized product at 33.7 vol%. Density was reduced to 1.0

for OP-HTP compared to 1.1 for the oxidized product. Viscosity increased greatly from 6.6 to 28.2 cSt.

As a result of hydrocracking the properties of the hydrocarbon mixture were greatly improved above those of the OP-HTP. HHV increased to 45.1 MJ/kg, rivaling the value of most petroleum fuels. Oxygen content was 0.1 wt% and acid value was nearly zero. pH was on the basic side at 9.3. Water content was only 0.1 wt%. Density and viscosity were considerably lower at 0.9 g/ml and 1.7 cSt, respectively. The hydrocracking of the OP-HTP yielded a high energy hydrocarbon mixture (organic fraction) of 71.6%, aqueous fraction of 7.6%, gases of 20.8% and no char was observed.

Table 5.2 Comparison of the physical and chemical properties of oxidized product, OP-HTP and hydrocarbon mixture.

Properties	Oxidized product	OP-HTP	Hydrocarbon mixture
HHV, MJ/kg	15.4	34.5	45.1
Oxygen, wt%	56.7	15.1	0.1
Total acid number, mg KOH/g	155.7	48.6	0.05
pH	2.8	4.2	9.3
Water content, vol%	33.7	2.7	0.1
Density, g/ml	1.1	1.0	0.9
Kinematic viscosity, 40^{o}C, cSt	6.63	28.2	1.7

Figure 5.2 shows the elemental composition weight percentages of the raw bio-oil, hydrotreated product produced from raw bio-oil (RBO-HTP), oxidized product,

hydrotreated product produced from oxidized product (OP-HTP) and hydrocarbon mixture. The carbon content of the raw bio-oil was 37.6 wt%. The carbon content of the RBO-HTP was increased to 71.6 wt% from that of the raw bio-oil. The 75.5 wt% carbon content of the OP-HTP increased from that of the oxidized product 35.20 wt%. Carbon content of the hydrocarbon mixture was 86.6 wt%. The oxygen content of the raw bio-oil was 53.9 wt%. The oxygen content of the RBO-HTP was decreased to 18.2 wt% from that of the raw bio-oil. The oxygen content of the oxidized product decreased from 56.7 wt% to 15.1 wt% for OP-HTP to 0.1 wt% for the hydrocarbon mixture; therefore, the oxygen content of the OP-HTP was 3.1 percentage points lower than for the RBO-HTP. The hydrogen content of the raw bio-oil was 8.1 wt%. The RBO-HTP hydrogen content increased to 9.9 wt% from the 8.1 wt% value for the raw bio-oil. The OP-HTP hydrogen content increased to 9.0 wt% from 7.8 wt% for the oxidized product. Hydrogen content of the hydrocarbon mixture was 13.1 wt%. The raw bio-oil, RBO-HTP and oxidized product had approximately the same nitrogen content of 0.3 wt%. Nitrogen content of the hydrocarbon mixture was decreased to 0.2 wt% from 0.4 wt% for the oxidized product.

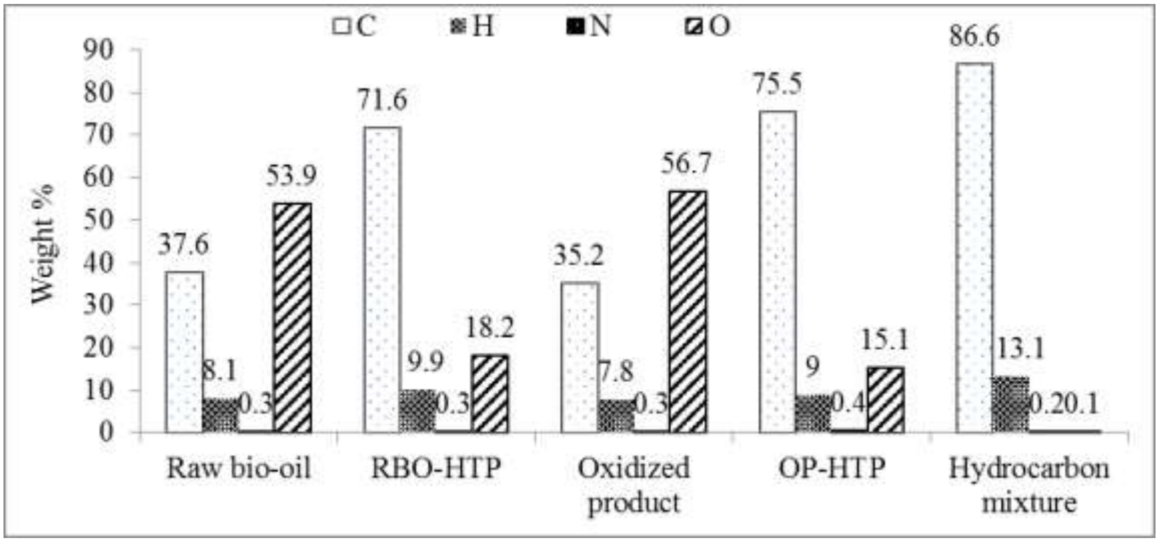


Figure 5.2 Comparison of elemental composition weight percentages for raw bio-oil, RBO-HTP, oxidized product, OP-HTP and hydrocarbon mixture.

5.6.3 FTIR analysis

Figure 5.3 shows the comparison of raw bio-oil, oxidized product, OP-HTP and hydrocarbon mixture FTIR spectra. These spectra identified the functional groups present in the product types. Characteristic vibrational modes were observed at 3200-3600 cm^{-1} (OH stretch), 2800-3100 cm^{-1} (CH aliphatic stretch), 1600-1750 cm^{-1} (C=O stretch), 1350-1470 cm^{-1} (CH bending) and 1000-1250 cm^{-1} (C-O stretch). The increase in C-O stretching and C=O stretching absorption bands of the oxidized product compared to raw bio-oil indicates the increase in carboxylic acid content in the oxidized product. It was also found that the oxidized product OH stretching, the C=O stretching (carbonyl functional group) and the C-O stretching (ether, alcohol functional group) were decreased. The CH (alkane functional group) aliphatic stretch and CH bending stretch absorption band were considerably increased. This change in absorption bands indicates that the carboxylic acids, aldehydes and other oxygenated chemical compounds were converted into hydrocarbons. The findings of the FTIR spectra were in good agreement with the physical and chemical properties described in Table 5.2 and GC-MS analysis as shown in Table 5.3.

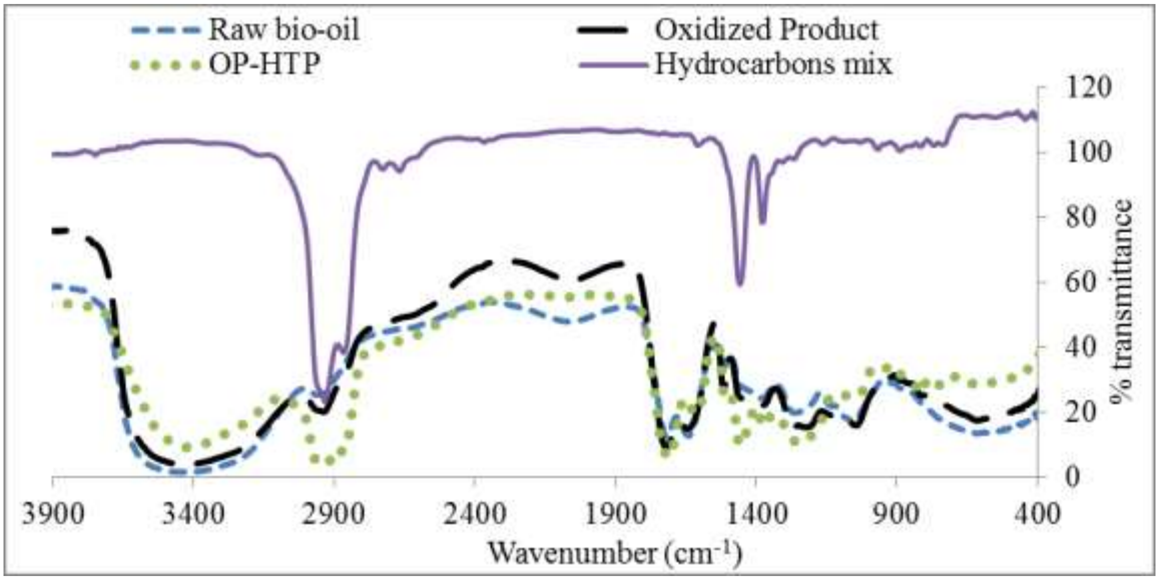


Figure 5.3 FTIR spectra comparing raw bio-oil, oxidized product, OP-HTP and hydrocarbon mixture.

(a) (b) (c)

Figure 5.4 Shows (a) raw bio-oil, (b) OP-HTP and (c) hydrocarbon mixture sample images.

Raw bio-oil, OP-HTP and hydrocarbon mixture sample images are shown in Figure 5.4. The raw bio-oil shown in Figure 5.4(a) is comprised of various chemical compounds and approximately 30 wt% water and is a single-phase dark-colored mixture. The OP-HTP is clearly separated from water as shown in Figure 5.4(b); the bottom layer is water and the top layer is OP-HTP floating on the water. The hydrocarbon mixture as shown in Figure 5.4(c) is a clear liquid fuel.

5.6.4 GC-MS analysis

Table 5.3 compares the chemical composition of hydrotreated product (OP-HTP) and the hydrocarbons mixture analyzed by GC-MS. Approximately 50 chemical compounds were identified by GC-MS in both samples. The chemical compound name and their area percentages are given in Table 5.3. The total area percentages of the major fifty compounds present in boiler fuel and hydrocarbon mixture were 98.81% and

99.99%, respectively. As shown in Table 5.3 there was a substantial change in the chemical composition and area% the of hydrocarbon mixture produced by hydrocracking of the OP-HTP. The OP-HTP produced by hydrotreating the oxidized product was comprised of hydrocarbons with 8.5 area%, acids with 23.0 area%, ketones with 21.3 area% (no aldehydes observed), esters and ethers had 14.6 area% and alcohols had 31.4 area%. The hydrocarbon mixture produced by hydrocracking of the 1st-stage OP-HTP was comprised of approximately 97.0 area% of hydrocarbon compounds. The hydrocarbon mixture was also comprised of small fractions of alcohols at 1.22 area%, esters and ethers at 0.99 area% and ketones at 0.79 area%.

Table 5.3 OP-HTP and hydrocarbon mixture chemical composition analysis by GC-MS with area percentages.

OP-HTP		**Hydrocarbon mixture**	
Compound	Area %	Compound	Area %
Hydrocarbons		**Hydrocarbons**	
2-Heptene	1.05	1-Butene	2.02
Cyclohexane, 1,2-dimethyl-, cis-	4.18	2,3-Dihydrofuran	0.94
Cyclooctene	0.9	Heptane	1.13
Cyclohexane, methyl-	1.07	Cyclohexane, methyl-	7.34
Bicyclo[4.2.0]oct-1-ene, 2-methyl-	1.32	Cyclohexane, 1,3-dimethyl-, cis-	1.67
Acids		Cyclopentane, 1-ethyl-3-methyl-	1.41
Propanoic acid, 2,2-dimethyl-	1.11	Cyclohexane, 1,2-dimethyl-, cis-	1.7
2-Furancarboxylic acid, 2-tetrahydro	1.49	Cyclohexane, 1,4-dimethyl-, cis-	0.86

Table 5.3 (Continued)

2-butyl-3-Hydroxy-4-methylbenzoic acid	1.46	Cyclohexane, ethyl-	4.69
n-Hexadecanoic acid	2.85	Cyclopentane, 1-methyl-2-propyl-	0.98
Octadecanoic acid	5.5	1-Ethyl-4-methylcyclohexane	1.56
1-Phenanthrenecarboxylic acid	3.79	Cyclohexane, 1-ethyl-4-methyl-, cis	0.82
Butanoic acid, 2-(cyano)(2,4,6-tri Ethyl 4-hydroxy-7-trifluoromethyl	5.23	Hexane, 2,4-dimethyl-	0.75
Carbamic acid, N-(1-naphthyl)-	1.57	1-Ethyl-3-methylcyclohexane	1.42
Aldehydes and ketones		3-Hexyne	0.83
2-Pentanone	0.86	Cyclohexane, propyl-	8.14
Cyclopentanone, 2-methyl-	3.21	1H-Indene, octahydro-, trans-	0.94
Cyclohexanone	2.84	Cyclohexane, 1-methyl-4-(1-methyl)	0.75
Cyclopentanone, 2-ethyl-	1.16	Cyclohexane, 1-methyl-2-propyl-	1.49
Cyclohexanone, 3-methyl-	1.54	Cyclohexane, butyl-	0.75
Cyclohexanone, 2-propyl-	1.16	1H-Indene, octahydro-, cis-	1.23
Ethanone, 1-phenyl-, oxime	1.03	Decane	0.76
2H-1,4-Benzoxazin-3(4H)-one	1.78	Cyclohexane, butyl-	1.24
2',5'-Dimethoxypropiophenone	0.82	Cyclohexene, 1-butyl-	1.04
1,2-Naphthoquinone	6.9	Naphthalene, decahydro-	0.88
Esters & ethers		Cyclohexane, 1-methyl-2-propyl-	1.06
Butanoic acid, methyl ester	1.73	1-Decene, 5-methyl-	1.31

Table 5.3 (Continued)

Pentanoic acid, methyl ester	1.17	Naphthalene, decahydro-2-methyl-	1.01
Hexanoic acid, methyl ester	1.07	Naphthalene, decahydro-2-methyl-	0.78
Hexadecanoic acid, methyl ester	1.75	Cycloundecene, 1-methyl-	0.71
Benzene, 1-methoxy-4-propyl-	1.25	Benzene, (3-methyl-2-butenyl)-	0.74
m-Methoxybenzamide	1.62	Benzene, (2-methyl-1-butenyl)-	1.26
Anthracene, 1,4-dimethoxy-	2.16	Cyclohexane, hexyl-	0.99
Octadecanoic acid, methyl ester	2.12	Hexylidencyclohexane	0.98
9-Oxabicyclo[6.1.0]nonane	1.7	Tridecane	1.3
Alcohols		Cyclopentene, 1-octyl-	0.7
Phenol	1.37	Cyclotetradecane	1.12
Dicyclopropyl carbinol	0.95	Phenanthrene, tetradecahydro-Bicyclo[4.1.0]heptane	1.4
Phenol, 3-methyl-	1.09	Phenanthrene, tetradecahydro-cis-3-Methyl-endo-tricyclo[5.2.1.0	0.86
Phenol, 4-methyl-	5.95	Pentadecane	2.97
Phenol, 2,4-dimethyl-	2.85	Cyclohexane, (3-cyclopentylpropyl)	0.89
Phenol, 4-ethyl-	2.29	Heptadecane	11.18
Phenol, 3-ethyl-	2.54	Anthracene, 1,2,3,4,5,6,7,8-octahydro	1.76
Bicyclo[3.3.0]octan-2-ol	1.07	4-(4-ethylcyclohexyl)Bicyclo[3.1.1]heptan-3-one	0.78

Table 5.3 (Continued)

Phenol, 2-methoxy-4-methyl-	0.84	Naphthalene, 6-ethyl-1,2,3,4-tetra Pyridine	1.58
Phenol, 2,4-dimethyl-	1.61	aphtho[1,2-b]furan-4,5-dione	2.57
Phenol, 2-(2-methylpropyl)-	1.39	Undecane	15.7
Phenol, 2-ethyl-4-methyl-	1.02	**Alcohol**	
Phenol, 3-(1-methylethyl)-	1.56	Cyclooctanemethanol	1.22
Phenol, 2-propyl-	5.09	**Esters & Ethers**	
Phenol, 4-ethyl-2-methoxy-	0.88	8-Oxabicyclo[5.1.0]octane	0.99
Phenol, 4-(1-methylpropyl)-	0.92	**Ketones**	
Total	98.81	Bicyclo[2.2.1]heptane-2,5-dione	0.79
		Total	99.99

5.6.5 ^{1}H-NMR spectroscopic analysis

Figure 5.5 shows the ^{1}H-NMR spectra of the oxidized product (a), hydrotreated product (OP-HTP) (b) and liquid hydrocarbon mixture (c). As shown in Figure 5.5(a), (b) and (c) it is evident that there is a considerable difference between ^{1}H-NMR spectra. The oxidized product spectrum shown in Figure 5.5(a) is very complex and consists of a large number of proton signals due to the presence of various chemical compounds. Following the hydrotreating of the oxidized product the number of proton signals reduced largely in the OP-HTP as shown in Figure 5.5(b). Comparison of Figures 5.5 (a) and 5.5(b) shows the methoxy group (-OCH_3) single proton signal with a downfield chemical shift of 5.2 ppm present in Figure 5.5(a) was absent in Figure 5.5(b); this indicates that the hydrotreating of oxidized product eliminated the methoxy group of guaiacol or substituted guaiacol compounds (one of the major components of the bio-oil).

Comparison of Figure 5.5(a) spectra of oxidized bio-oil to the OP-HTP spectra of Figure 5.5(b) shows the phenols, substituted phenols and other aromatic compounds' (derived from lignin and sugars) proton signals with a downfield chemical shift of 5.8-8.0 ppm. Likewise comparison of Figures 5.5(a) and 5.5(b) shows some oxygenated compounds' proton signals with a chemical shift of 2.0-2.8 ppm (acyl, benzylic and aliphatic hydroxyl functional groups) during hydrotreating. Again, for the same comparison of Figures 5.5 (a) and 5.5(b) spectra hydrotreating caused other oxygenated compounds' proton signals to chemically shift from 3.2-5.2 ppm (esters, ethers and lignin derived methoxy phenols). Therefore, phenols, substituted phenols and the described two groups of oxygenated compounds were all reduced in the OP-HTP spectra of Figure 5.5(b) as compared to the oxidized product (Figure 5.5(a)). By contrast to the reduction of oxygenated compounds, the aliphatic hydrocarbons proton signals with an upfield chemical shift of 0.8-1.8 ppm were increased in the OP-HTP. A similar increase was also observed in the aromatic hydrocarbons proton signals with a chemical shift of 6.4-7.6 ppm in Figure 5.5(b) as compared to Figure 5.5(a) due to the conversion of phenols and guaiacols to aromatic hydrocarbons during the hydrotreating.

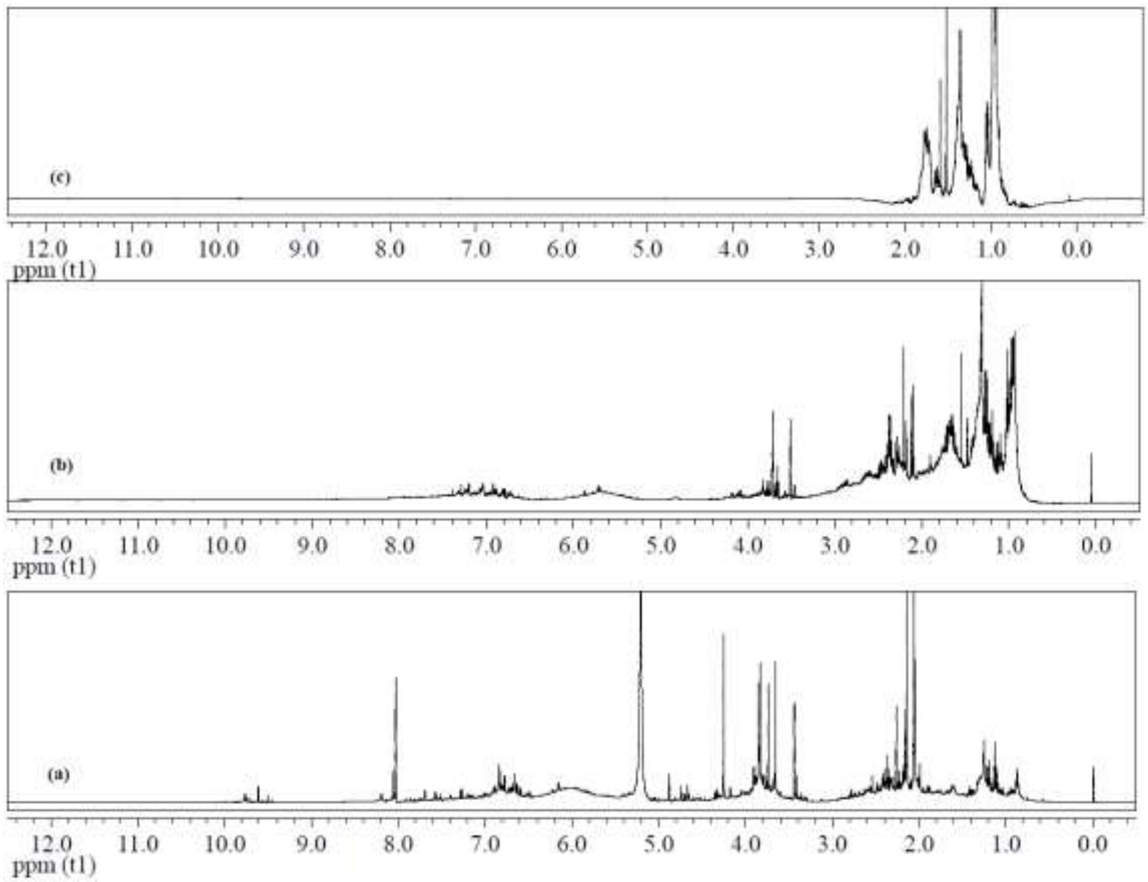


Figure 5.5 ^{1}H-NMR spectra analysis of oxidized product (a), OP-HTP (b) and hydrocarbon mixture (c)

As shown in Figure 5.5(c) of the hydrocracking applied to the OP-HTP produced liquid hydrocarbon mixture aliphatic alkanes' (hydrocarbons) proton signals with an upfield chemical shift of 0.8-1.8 ppm were increased compared to OP-HTP as shown in Figure 5.5(b). Some of the remaining aromatic compounds, phenols and substituted phenols were reduced with a downfield chemical shift of 5.0-7.5 ppm in hydrocarbon mixture (Figure 5.5(c)). Likewise, the esters, ethers, carbonyl compounds and hydroxyl groups' proton signals showed a downward chemical shift of 3.2-5.2 ppm. However, there was considerable reduction in the phenols, substituted phenols, esters, ethers carbonyl compounds and hydroxyl groups in Figure 5.5(c) spectra. Both the increase and decrease of proton signals discussed were due to the conversion of several oxygenated and aromatic compounds to aliphatic hydrocarbons during the hydrocracking.

5.6.6 Simulated distillation of hydrocarbon mixture

Figure 5.6 shows the petroleum fuel equivalent based on vaporization temperature. Simulated distillation of the hydrocarbon mixture was performed by ASTM D2887 method. The boiling temperature ranges are given below the named petroleum equivalents in Figure 5.6. These petroleum equivalents were of the molecular weights of gasoline (50-180 ºC, 41.0 wt%), jet fuel (180-250 ºC, 21.0 wt%), diesel (250-350 ºC, 34.0 wt%) and 4 wt% of heavy fuel produced at temperatures above 350 ºC.

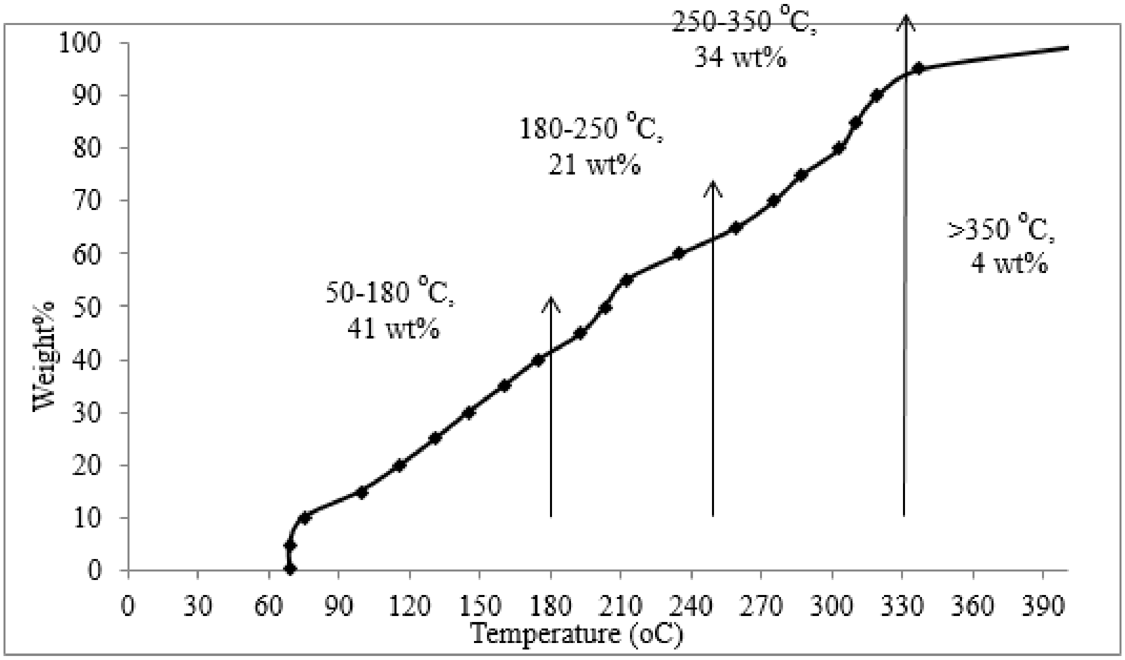


Figure 5.6 Petroleum equivalents of gasoline, jet fuel and diesel range molecular weight fuels based on vaporization temperature weight percentages present in hydrocarbon mixture results.

Hydrotreating of raw bio-oil was also performed as a control reaction to compare the yields to the hydrotreated oxidized product (pretreated bio-oil). Figure 5.7 shows that the hydrotreatment of the oxidized product produced approximately 30.5% higher yield of organic fraction compared to the yield from hydrotreating raw bio-oil. Figure 5.7 also shows the water (aqueous fraction), char and gas yields produced from the hydrotreated raw bio-oil and hydrotreated oxidized product. The water and char wt% yields also decreased as a result of hydrotreating the oxidized product as compared to raw bio-oil.

The gas stream produced during hydrotreating of the oxidized product increased in volume compared to the hydrotreated raw bio-oil. For the OP-HTP the gas volume comprised 29.8% while RBO-HTP comprised 21.6%. The gas volume (29.8%) produced during hydrotreating of the oxidized product comprised of 42.5% hydrogen gas and the gas volume (21.6%) produced during hydrotreating of the raw bio-oil comprised of 40.5% hydrogen gas. Meaningful comparison of the hydrogen values in the two gas streams required normalization of the volumes produced. Based on this normalization the hydrogen content produced in the gas stream produced by hydrotreating the oxidized product was 17.9 percentage points higher than that from hydrotreating the raw bio-oil. This result indicates that a lower amount of hydrogen was required to produce a hydrotreated product compared to simply hydrotreating raw bio-oil with H_2. A commercial hydroprocessing system would include a hydrogen recapture process such that the increased volume of hydrogen gas available from hydrotreating oxidized bio-oil could be captured and reutilized. This would prove an economic gain to offset increased costs required for the bio-oil oxidation process. It is outside the scope of this initial exploration of the results of oxidizing bio-oil to provide a techno economic analysis of the benefits versus the costs of the process.

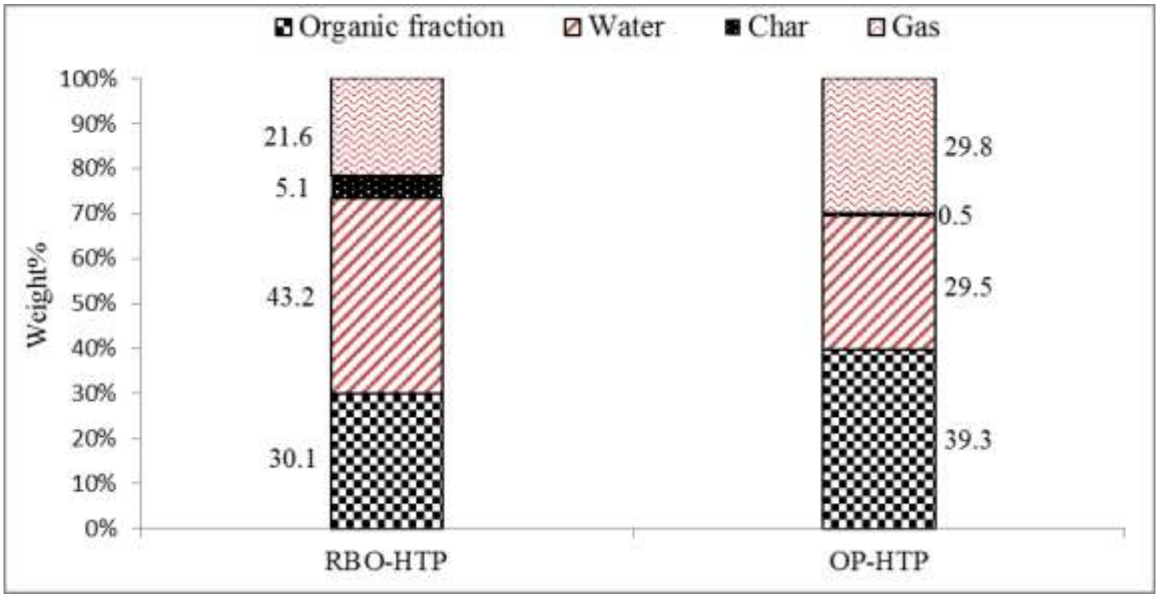


Figure 5.7 Shows the yields of organic fraction, water, char and gas produced from the hydrotreated (HT) raw bio-oil and oxidized product.

Table 5.4 shows the raw bio-oil hydrotreating (RBO-HTP), oxidized product hydrotreating (OP-HTP) and OP-HTP hydrocracking (HCM) exit gases percentage components analysis performed by micro GC analyzer. A comparison of the H_2% between RBO-HTP and OP-HTP exit gases shows that the OP-HTP contained a slightly high percentage of H_2. This indicates that the oxidized product did not consume high hydrogen required for hydrotreatment. Production of the lower molecular weight hydrocarbon gases such as CH_4 and C_2H_6 were about half for OP-HTP compared to RBO-HTP reaction. The CO_2% is slightly higher for OP-HTP compared to RBO-HTP. This small increase in CO_2 for the OP-HTP probably occurred because of the higher conversion of carboxylic acids to hydrocarbons for this oxidized product. The CO% values are nearly the same at 0.71% for RBO-HTP and OP-HTP at 0.60%. The O_2% value for OP-HTP at 0.96% compared to 0.48% for RBO-HTP. As shown in Table 5.4 2nd-stage hydrocracking reaction exit gas was comprised of 74.57% H_2; this result implies that consumption of H_2 during the reaction was approximately 25.43%. HCM exit gas was also comprised of 0.68% of O_2, 2.33% of N_2, 5.85% of CH_4, 13.58% of CO_2, 0.74% of C_2H_6 and no CO was obtained.

Table 5.4 Hydrotreating and hydrocracking reactions exit-gas percentages components analysis by micro GC analyzer**.**

Exit Gas	**H2 %**	**O2 %**	**N2 %**	**CH4 %**	**CO %**	**CO2 %**	**C2H6 %**
RBO-HTP	40.45	0.48	1.39	1.14	0.71	20.99	0.31
OP-HTP	42.59	0.96	4.65	0.56	0.60	22.03	0.13
HCM	74.57	0.68	2.33	5.85	0.0	13.58	0.74

The carbon balance of organic, aqueous and gas phases of both the RBO-HTP and OP-HTP were calculated. The organic phase of the RBO-HTP and OP-HTP contained 57.3% and 78.9%, respectively, of the carbon in the original raw bio-oil. Comparing RBO-HTP's to OP-HTP's organic fraction, the latter had 21.6 percentage points higher carbon content. The aqueous phase of the respective RBO-HTP and OP-HTP fractions contained 3.8% and 1.2% of the carbon in the original raw bio-oil. The gaseous phase of the respective RBO-HTP and OP-HTP fractions contained 23.6% and 18.5% of the carbon in the original raw bio-oil. The 2nd-stage hydrocracking organic, aqueous and gaseous phase products carbon balance were also calculated. Relative to the original raw bio-oil carbon content the hydrocracked product organic fraction (hydrocarbon mixture) contained 64.8%; the aqueous fraction contained 0.4% and the gaseous phase contained 34.8%.

The aqueous fraction oxygenates present in the OP-HTP could not be analyzed by GC-MS due to the high water content of this phase. However, the carbon balance for the aqueous phase was 1.2% of that present in the raw bio-oil. Low carbon content indicates a very low presence of organic molecules such as oxygenates or hydrocarbons. In addition, the pH of the aqueous phase was neutral at 6.8 indicating absence of acids; again, absence of acids equates to low oxygenate presence. Therefore, it can be concluded that oxygenates content of the aqueous fraction of the OP-HTP is very low.

5.6.7 Thermo gravimetric analysis (TGA)

TGA was performed on the fresh and used catalysts to determine the amount of residual carbon deposited on the catalyst surface. A SDT Q600 performed the TG analysis. A required amount of catalyst was placed in an alumina pan and a temperature program was ramped up at a rate of 10 °C/min starting at 20 °C and terminating at 1000 °C. The runs were performed under N_2 flow of 100 mL/min. The percentage weight loss of the fresh Ni/SiO_2-Al_2O_3+K_2CO_3 and its spent catalyst from the hydrotreating of the oxidized product reaction were compared in Figures 5.8 and 5.9.

Figures 5.8 and 5.9 show weight loss of the fresh Ni/SiO_2-Al_2O_3+K_2CO_3 and spent Ni/SiO_2-Al_2O_3+K_2CO_3 catalysts utilized to hydrotreat oxidized product to produce OP-HTP. As shown in Figure 5.8, there is a considerable weight loss during the initial heating period at the temperature range between 200-400 °C. Whereas in the case of spent Ni/SiO_2-Al_2O_3+K_2CO_3 (Figure 5.9) catalyst initial heating period at the same temperature range from 200-400 °C, a large percentage of weight loss was observed. This weight loss may be due to the removal of moisture content from the surface of the catalyst and it could be due to the oxidative process mass losses and removal of carbonaceous species formed during initial decomposition of lower molecular weight carbon compounds. This indicates that there was a carbon deposition on the spent Ni/SiO_2-Al_2O_3+K_2CO_3.

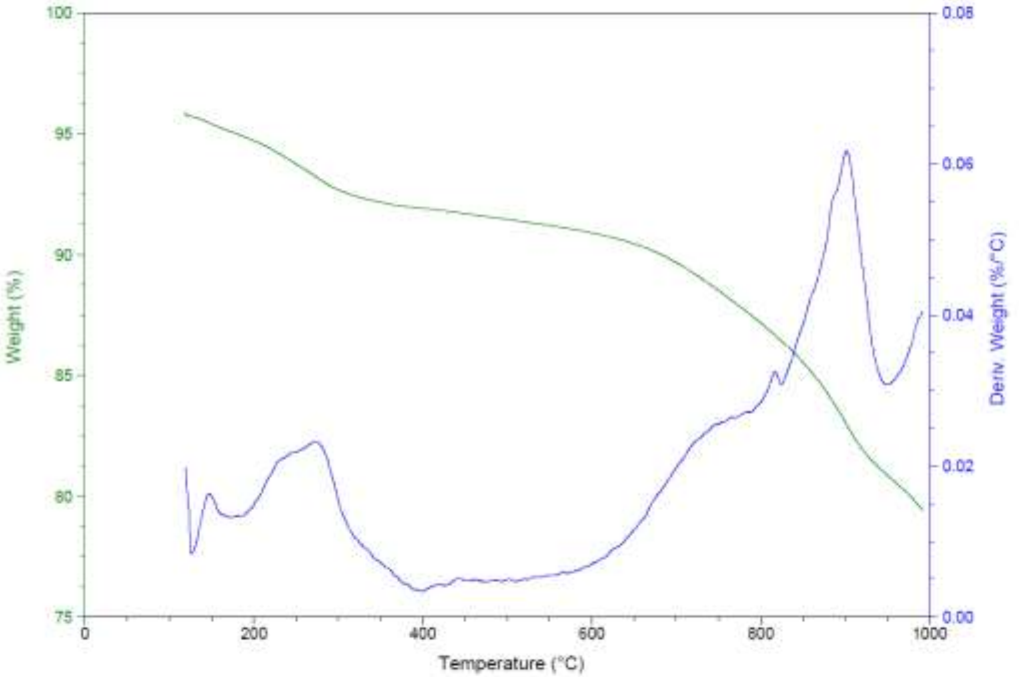


Figure 5.8 TGA of the fresh Ni/SiO2-Al2O3 plus K2CO3 catalyst.

As shown in Figures 5.8 and 5.9, it was also observed that both fresh Ni/SiO_2-Al_2O_3+K_2CO_3 and spent Ni/SiO_2-Al_2O_3+K_2CO_3 catalysts lost weight at the temperature range between 850-950 °C. In contrast, as compared to the spent catalyst, the fresh catalyst lost a high percentage of weight loss. This weight loss was probably due to catalyst K_2CO_3 present in the fresh catalyst decomposition. However, as expected in the case of spent Ni/SiO_2-Al_2O_3+K_2CO_3 a large weight loss was not observed and approximately 6 wt% was lost during the heating of the catalyst.

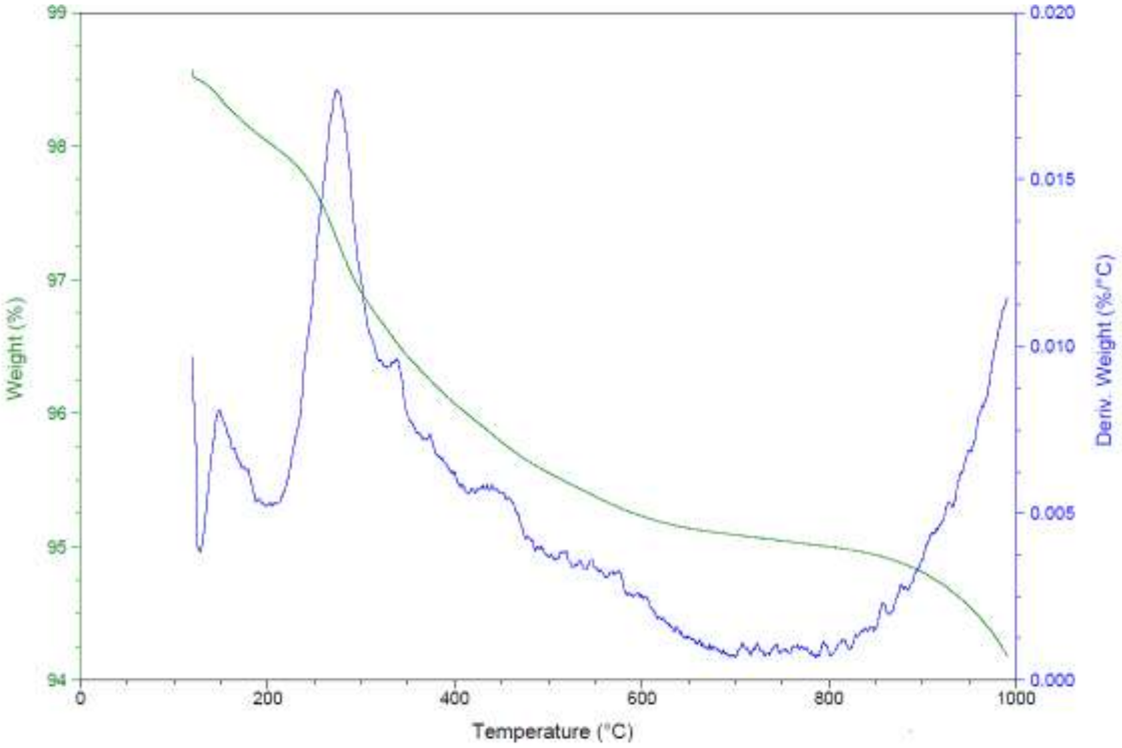


Figure 5.9 TGA of the spent Ni/SiO2-Al2O3 plus K2CO3 catalyst.

5.7 Conclusions

Our approach of pretreating raw bio-oil by oxidation followed by HDO successfully produced hydrocarbons of transportation fuel quality. The objective of this novel pretreatment was to convert aldehydes and ketones to carboxylic acids to reduce char and hydrogen pressure required to perform hydrotreating. The pretreatment of raw bio-oil by oxidation allowed us to hydrotreat oxidized bio-oil under lower hydrogen pressure (800 psig) compared to the current relatively high (1510 to 3000 psig) hydrogen pressures required for hydrotreating raw bio-oil. The oxidation process allowed the lower 800 psig pressure to be utilized to produce a superior partially deoxygenated product compared to that produced under the same pressure for raw bio-oil. During hydrotreating the nature of the oxidation product resulted in slightly lower utilization of hydrogen compared to that required for raw bio-oil. Quality improvement in the hydrotreated oxidized bio-oil included a 30.5% higher yield of hydrotreated organic product, 90.2% reduced char and 46.5% less water content. Hydrocracking of partially deoxygenated bio-oil from oxidized bio-oil hydrotreatment was performed. Results showed that 97.0 area% of the total GC-MS spectrum was produced as petroleum equivalents of gasoline, jet fuel and diesel range molecular weight hydrocarbons. The hydrocarbons produced from this process had an HHV of 45.1 MJ/kg. Oxygen content and acid value were 0.1 wt% and 0.05 mg KOH/g, respectively. pH was on the basic side at 9.3. Water content was only 0.1 wt%. Density and viscosity were considerably lower at 0.9 g/ml and 1.7 cSt, respectively. The energy density of hydrocarbons produced by this method was increased by 181.9 % from raw bio-oil. The hydrocarbon mixture was comprised of petroleum equivalent molecular weights of gasoline (41 wt%), jet fuel (21 wt%), diesel (34 wt%) and heavy fuel (4 wt%). Relative to the original raw bio-oil carbon content, the hydrocarbon mixture produced by this process contained 64.8% of the carbon.

5.8 Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

5.9 References

1. Bridgwater AV, Meier D, Radlein D. An overview of fast pyrolysis of biomass. Organic Geochemistry 1999;30:1479-1493.

2. Mohan D, Pittman Jr CU, Steele PH. Pyrolysis of wood-biomass for bio-oil: A critical review. Energy Fuels 2006;20:848-889.

3. Mckendry P. Energy production from biomass (Part 1): Overview of biomass. Bioresource Technol 2002;83(1):37–46.

4. Czernik S, Bridgwater AV. Overview of applications of biomass fast pyrolysis oil. Energy Fuels 2004; 18:590-598.

5. Huber GW, Iborra S, Corma A. Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. Chem Review 2006;106:4044–4098.

6. Mullen CA, Boateng AA. Chemical composition of bio-oils produced by fast pyrolysis of two energy crops. Energy Fuels 2008;22:2104-2109.

7. Das KC, Jena U. Comparative evaluation of thermochemical liquefaction and pyrolysis for bio-oil production from microalgae. Energy Fuels 2011;25:5472-5482.

8. Elliott DC. Historical developments in hydroprocessing bio-oils. Energy Fuels 2007;21:1792-1815.

9. Jones SB, Holladay JE, Elliot DC, Valkenburg C, Stevens DJ, Walton CW, Kinchin C, Czernik S. Production of gasoline and diesel from biomass via fast pyrolysis, hydrotreating and hydrocracking: A design case. Pacific Northwest National Laboratory 2009; PNNL-18284.

10. Wildschut J, Melian-Cabrera I, Heeres HJ. Catalyst studies on the hydrotreatment of fast pyrolysis oil. Applied catalysis B: Environmental 2010;99(1-2):298-306.

11. Subramaniam B, Jackson WF, Raghunath CV. Deoxygenation of bio-oils and other compounds to hydrocarbons in supercritical media. US Pat 2011/0028773 A1.

12. Choudhary TV, Phillips CB. Renewable fuels via catalytic hydrodeoxygenation. Applied Catalysis A: General 2011;397(1-2):1-12.

13. De Miguel Mercader FM, Groneveld MJ, Kersten SRA, Geanetet C, Toussaint G, Way NWJ, Schaverien CJ, Hogendoorn JA. Hydrodeoxygenation of pyrolysis oil fractions: Process understanding and quality assessment through co-processing in refinery units. Energy Environ Sci 2011;4:985-997.

14. Elliott DC, Hart TR, Neuenschwander GG, Rotness L, Olarte MV, Zacher AH, Solantausta Y. Catalytic hydroprocessing of fast pyrolysis bio-oil from pine sawdust. Energy Fuels 2012;26:3891-3896.

15. Wang H, Male J, Wang Y. Recent advances in hydrotreating of pyrolysis bio-oil and its oxygen-containing model compounds. ACS Catal 2013;3:1047-1070.

16. Li X, Gunawan R, Wang Y, Chaiwat W, Hu X, Gholizadeh M, Mourant D, Bromly J, Li C. Upgrading of bio-oil into advanced biofuels and chemical. Part III. Changes in aromatic structure and coke forming propensity during the catalytic hydrotreatment of a fast pyrolysis bio-oil with Pd/C catalyst. Fuel 2014;116:642-649.

17. Elliot DC and Baker EG. Process for upgrading biomass pyrolyzates. US Pat 1989/4,795,841.

18. Wildschut J, Mahfud FH, Venderbosch RH, Heeres HJ. Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. Industrial & engineering chemistry research 2009;48:10324-10334.

19. Wang Y, Tao H, Liu K, Wu J, Fang Y. From biomass to advanced bio-fuel by catalytic pyrolysis/hydro-processing: Hydrodeoxygenation of bio-oil derived from biomass catalytic pyrolysis. Bioresource Technology 2012;108:280-284.

20. Zhang SP, Yan YJ, Ren Z, Li T. Study of hydrodeoxygenation of bio-oil from the fast pyrolysis of biomass. Energy Sources 2003;25(1):57-65.

21. Venderbosch RH, Ardiyanti AR, Wildschut J, Oasmaa A, Heeres HJ. Stabilization of biomass-derived pyrolysis oils. J Chem Technol Biotechnol 2010;85:674-686.

22. McCall MJ, Brandvold TA, Elliott DC. Fuel and fuel blending components from biomass derived pyrolysis oil. US Pat 2012/8,329,969 B2.

23. Furimsky E. Hydroprocessing challenges in biofuels production. Catalysis Today 2013;217:13-56.

24. Gagnon J, Kaliaguine S. Catalytic hydrotreatment of vacuum pyrolysis oil from wood. Industrial and Engineering Chemistry Research 1988;27:1783-1788.

25. Shanks HB, Lohithrn N. Upgrading of bio-oil: Effect of light aldehydes on acetic acid removal via esterification. Catalysis Communications 2009;11(2):96-99.

26. Hu X, Wang DM, Gunawan R, Lievens C, Chaiwat W, Gholizadeh M, Wu L, Li X, Li CZ. Polymerization on heating up of bio-oil: A model compound study. AICHE Journal 2012;59(3):888-900.

27. Xu J, Jiang J, Dai W, Zhang T, Xu Y. Bio-oil upgrading by means of ozone oxidation and esterification to remove water and to improve fuel characteristics. Energy Fuels 2011;25:1798-1801.

28. Travis BR, Meenakshi S, Hollist GO, Borhan B. Facile oxidation of aldehydes to acids and esters with oxone. Org Lett 2003;7(5):1031-1034.

29. Gandhari R, Maddukuri PP, Vinod TK. Oxidation of aromatic aldehydes using oxone. Journal of chemical education 2007;84(5):852-854.

30. Steele PH, Tanneru SK, Gajjela SK. Composition and methods for improved fuel production. US Pat 2013/0291431 A1, November 7, 2013.

31. Nkafamiya II, Maina HM, Osemeahon SA, Modibbo UU. Percentage oil yield and physiochemical properties of different groundnut species (Arachis hypogaea). African journal of food science 2010;7(4):418-421.

CHAPTER VI

PRODUCTION OF LIQUID HYDROCARBONS FROM PRETREATED BIO-OIL VIA CATALYTIC DEOXYGENATION WITH SYNGAS

6.1 Abstract

Biomass-derived fast pyrolysis oil (bio-oil) is a potential alternative replacement for conventional transportation fuels. But negative properties such as lower energy density, higher water content and acidity prevent the direct use of pyrolysis oil as a fuel. Catalytic deoxygenation of pyrolysis oils to hydrocarbons has been studied widely with application of high heat and hydrogen pressure. However, consumption of a large amount of expensive hydrogen has remained a problem for this technology. Therefore, development of an efficient and reduced hydrogen deoxygenation method would be desirable. In this study, we have applied catalytic deoxygenation of pretreated bio-oil in the presence of pressurized syngas to produce liquid hydrocarbons. The pretreatment is an oxidation step that converts aldehydes to carboxylic acids that are more conducive to catalytic conversion to hydrocarbons than are raw bio-oils. The pretreated bio-oil allowed performance of a partial deoxygenation step with a low amount of hydrogen (syngas). This partially deoxygenated product was then fully deoxygenated with pure hydrogen to produce hydrocarbons. Properties of the resultant liquid hydrocarbons were analyzed by ASTM standards for transportation fuels. The hydrocarbon mixture obtained by our

process was analyzed by Fourier transform infrared spectroscopy, detailed hydrocarbon analysis, nuclear magnetic resonance spectroscopy and simulated distillation.

Keywords: Pyrolysis oil, oxidation, pretreatment, catalytic deoxygenation, liquid hydrocarbons.

6.2 Introduction

Fast pyrolysis is one thermochemical process for conversion of biomass to liquid products. Bio-oil produced from fast pyrolysis of biomass is a potential alternative fuel to replace conventional fuels. Fast pyrolysis includes heating the biomass at rapidly elevated temperatures in the range of 400 to 550 ^{o}C in the absence of oxygen. More specifically, bio-oil is a dark brown liquid with pungent phenolic odor. Bio-oil chemical properties vary with material utilized for its production or the conditions under which it is produced [1-4]. Bio-oil has environmental advantages when compared to conventional fuels, because when combusted, bio-oil produces less pollution than fossil fuels, it produces half the NO_x, negligible quantities of SO_x emissions and it is considered CO_2 neutral [5-6]. However, there are serious disadvantages when using raw bio-oils for other than heating fuels. For example, untreated bio-oil has a high water content, high acidity, immiscibility with petroleum products, its viscosity increases over time and when heated, and it has a distinctive odor.

Chemically, bio-oil is a complex mixture of water (15-30%), carboxylic acids (10-25%), aldehydes (10-15%), ketones (1-5%), alcohols (2-5%), sugars (5-15%), phenols (5-10%), furans and pyrans (1-5%) and 10% miscellaneous compounds [2,3,6-8]. When tested for use as an engine fuel, bio-oil has caused damage to all but Sterling engines. In light of the many disadvantages of using untreated bio-oil as a fuel, it has not been adopted for commercial use except as a heating fuel in some limited applications [9,10].

Advanced fuels are liquid transportation range fuels such as green gasoline, jet fuel and green diesel fuels that are derived from renewable sources. They are defined as fuels that can reduce greenhouse gas emissions by 50 percent compared to fossil fuels [11]. The Renewable Fuel Standard II (RFS2) mandates the increased production of advanced fuels to 5.5 billion gallons by 2015 [12]. Therefore, considerable research has been focused on the production of advanced fuels from renewable resources by various upgrading technologies.

Current bio-oil upgrading techniques to produce transportation fuels include deoxygenation [13,14], catalytic pyrolysis [15,16] and steam reforming [17] mainly to reduce the oxygen content present in the bio-oil. Deoxygenation is a method by which oxygen is removed from oxygenated compounds. Deoxygenation can be applied by hydrodeoxygenation (HDO) or decarboxylation [18-24]. The general HDO reaction is shown as Scheme 6.1 [19,25].

$$\text{-(CHO)-} + H_2 \xrightarrow{\text{Catalyst}} \text{-(CH)-} + H_2O$$

Scheme 6.1 General HDO reaction

HDO of bio-oil with pure pressurized hydrogen in the presence of suitable catalysts has been demonstrated to reduce the oxygen content of bio-oil and produces a liquid hydrocarbon mixture that can be utilized as a transportation fuel. In general, HDO can be performed in one, two, or more steps. It has become traditional to hydroprocess fast pyrolysis oil by an initial 1st-stage hydrotreating step at mild temperatures (200-400 °C) to prevent bio-oil polymerization; typical hydrogen pressure applied for this 1st stage ranges from 4 to 10 MPa in the presence of a heterogeneous hydrotreating catalyst. In the 2nd stage, a hydrocracking step is performed at more severe temperatures (300-500 °C) and also at high pressure ranges from 10 to 20 MPa in the presence of a heterogeneous hydrocracking catalyst [6,13-14,18-22,24-28]. However, conversion of bio-oil to hydrocarbons via application of pure hydrogen requires a large volume of expensive hydrogen to deoxygenate the bio-oil.

Bio-oil aldehydes play a vital role in bio-oil stability from thermal application or continued stability over time. Aldehydes readily react with phenols and sugars to form higher molecular weight resins and oligomers via polymerization and condensation; oligomerization reactions lead to coke formation [21,29,30]. Aldehydes present in the raw bio-oil can be converted to carboxylic acids by subjecting them to oxidation [31-34].

Steele et al. (2013), Parapati et al. (2014) and Tanneru and Steele (2014) demonstrated that pretreatment of raw bio-oil by oxidation increased the acid value of oxidized bio-oil from 90.3-92.5 to 161.0-165.7 mg KOH/g. Further, Tanneru and Steele (2014) showed that this high-acid value bio-oil allowed performance of the hydrotreating step, utilizing pure hydrogen, with low hydrogen pressure and reduced hydrogen consumption. Properties of the hydrotreated oxidized bio-oil were also improved with a 30% higher organic fraction yield and reduction of char and water content by approximately 92% and 46%, respectively.

There has been increased interest by researchers in recent years to produce hydrogen by various technologies to allow hydrogen to be utilized as a versatile fuel.

Much interest is in its use as a transportation fuel. This is due to the fact that hydrogen combustion produces only water as a byproduct. Hydrogen can be produced from the water gas shift (WGS) reaction shown in Scheme 6.2 [35,36]. Synthesis gas produced purposely by biomass gasification contains significant percentages of both hydrogen and CO in addition to other gases with nitrogen and CO_2 being the major additional gases. Despite the presence of other gases the WGS reaction will occur when the syngas is pressurized, the proper heat is applied and in the presence of an effective WGS catalyst and water [35,37,38]. Bio-oil water content typically ranges from 25 to 30 wt%. Therefore, the theoretical conditions (CO and H_2O) are present for utilization of the WGS reaction to produce increased hydrogen content in biomass syngas during bio-oil catalysis.

$$CO + H_2O \xleftrightarrow{\text{Catalyst}} H_2 + CO_2$$

Scheme 6.2 Water gas shift (WGS) reaction

6.3 Objective

The objective of this research was to extend the work of Tanneru and Steele (2014) to conserve hydrogen by utilization of syngas which contains a low percentage of hydrogen. We hypothesized that the WGS reaction will take place by reaction of the CO contained in the syngas with the water contained in the oxidized bio-oil during partial deoxygenation. This was hypothesized to produce sufficient additional hydrogen to allow the partial deoxygenation reaction to occur during the 1st stage of partial deoxygenation. The 2nd stage of full deoxygenation of the partially deoxygenated product was performed in the presence of pressurized pure hydrogen. We will term this combination of 1st-stage syngas partial deoxygenation followed by 2nd-stage full hydrogen deoxygenation as catalytic deoxygenation (CDO) in this study.

6.4 Materials and methods

6.4.1 Materials

Bio-oil required for this research was produced from loblolly pine wood chips with a particle size of 1-3 mm and moisture content of 8-10% on a dry weight basis. Bio-oil was produced by fast pyrolysis performed at a temperature of 450 °C with nitrogen carrier gas at a rate of 7-kg/h with an auger-feed pyrolysis reactor located in the Department of Sustainable Bioproducts, Mississippi State University (MSU). The MSU auger fast pyrolyzer produced 60-65 wt% of liquid product, 10-15% of non-condensable gases and 20-25% of char on a dry biomass weight basis.

Biosyngas utilized in this study was produced in a downdraft gasifier at Mississippi State University and compressed to 1500 psi in laboratory tanks for our experiments. Production of syngas was performed with a Bio Max 25 gasifier. This syngas was comprised of approximately 18-20% hydrogen, 19-22% carbon monoxide, 11% carbon dioxide, 2% methane and 47-49% nitrogen [35,39]. Hydrogen gas used in this research was obtained from nexAir.

Potassium carbonate, hydrogen peroxide (H_2O_2) 50 wt% solution in water, chloroform-d ($CDCl_3$) 99.96 atom % D which contains 0.03 % (v/v) TMS, oxone (potassium monopersulfate triple salt) and copper(II)oxide were obtained from Sigma-Aldrich. Nickel on silica-alumina (66±5% Ni) catalyst powder was obtained from Alfa Aesar. All chemicals were used with no further purification.

6.4.2 Methods

6.4.2.1 Pretreatment of RBO by oxidation

Oxidation pretreatment was performed in a stainless steel, high-pressure batch autoclave reactor equipped with an overhead magnetic stirrer, a pressure indicator with a maximum capacity of 5000 psig and a thermocouple for temperature monitoring in the range of 0-500 ^{o}C. The autoclave was equipped with an electrical heating and cooling system to control the reactor temperature. Oxidation pretreatment was applied to raw bio-oil by addition of a mixture of oxone/H_2O_2 (oxidizing agent) followed by stirring for 90 min at room temperature and without applied pressure. This oxone/H_2O_2 solution was prepared by dissolving 5 wt% of oxone in 10 wt% of commercial 50 wt% H_2O_2 solution in water. This oxidation pretreatment considerably increased the bio-oil acid value by converting aldehydes into carboxylic acids. This pretreated bio-oil (oxidized product) was utilized as a precursor material to produce hydrocarbons by CDO.

6.4.2.2 Catalytic deoxygenation of pretreated bio-oil

CDO comprised of partial deoxygenation followed by full deoxygenation was performed in the same Parr batch autoclave described above. The 1st-stage partial deoxygenation of the oxidized product was performed in the presence of a mixture of nickel on silica-alumina (5 wt%), potassium carbonate (3 wt%) and copper(II)oxide (2 wt%) catalyst at a temperature of 360 ^{o}C and under pressurized syngas at 5.5 MPa for about 90 min. In the 2nd-stage, the partially deoxygenated top oil fraction was separated and fully deoxygenated by a mixture of nickel on silica-alumina (5 wt%) and copper(II)oxide (2 wt%) catalyst at a temperature of 425 ^{o}C and under pressurized hydrogen at 9.6 MPa for about 150 min. As a control, partial deoxygenation of direct raw bio-oil with syngas was also performed at the same 1st-stage partial deoxygenation reaction conditions. However, no product was able to be produced due to heavy coke formation during the reaction. It appears that partial deoxygenation of raw bio-oil with pressurized syngas is not possible unless applied to oxidized bio-oil.

In each experiment, once the reaction was complete, the liquid products were cooled in the reactor. The mixture was collected in centrifuge test tubes and centrifuged for 2-4 h to separate the resulting aqueous and organic phases. Both phases were separated and weighed for mass balance computation. The byproducts produced in this process included water and off-gas. Yields were calculated by Eq. 6.1 [40].

$$\text{Yield (wt\%)} = (\text{P (g)} \times 100)/\ \text{bio-oil weight (g)} \qquad \text{Eq. 6.1}$$

Where:

P = Organic fraction products obtained

Bio-oil weight = Total raw bio-oil used

6.5 Data analysis

The raw bio-oil, oxidized product, partially deoxygenated product (boiler fuel) and fully deoxygenated product (hydrocarbon mixture) produced were characterized following ASTM methods. Higher heating values (HHV) were determined by Ika-5000 bomb calorimeter by applying the ASTM D240 method. Acid values were determined by dissolving 1 g of bio-oil in 50 ml of 35:65 ratio of isopropanol to water mixture and titrating to a pH of 8.5 with 0.1N KOH solution following the method of ASTM D664. pH values were determined by ASTM E70. Densities were determined by Anton Parr DMA 35n portable density meter by ASTM D4052. Viscosities were determined by

Ubbelohde capillary viscometer at 40 °C water bath temperature according to the ASTM D445. Elemental carbon, hydrogen, and nitrogen were determined by EAI CE-440 elemental analyzer with oxygen content determined by difference according to ASTM D5291. Water content was determined by Karl-Fisher titration by ASTM E203.

The Fourier Transform Infrared Spectroscopy (FTIR) spectra were obtained by a Varian 3500 FTIR analyzer with standard potassium bromide disk technique and spectra were analyzed by Varian-Resolutions software. A Varian CP-4900 Micro GC analyzed the gas composition of the remaining gas stream after each batch experiment. A mass balance for the fuels from the best performing catalyst was calculated. Simulated distillation data analysis was performed by ASTM D2887 with gas chromatography. A detailed hydrocarbon analysis (DHA) was performed by ASTM D6730-01. Nuclear magnetic resonance spectroscopy (NMR) spectra were collected using a Bruker 600 MHz spectrometer. Each sample was dissolved in chloroform-d ($CDCl_3$ as a solvent) and the proton (^1H) NMR spectra were obtained. The spectra of the oxidized product, the syngas partial deoxygenated product, the liquid hydrocarbon mixture produced by our CDO process and a hydrocarbon mixture comprised of equal parts of commercial petroleum gasoline, jet fuel and diesel were obtained.

6.6 Results and discussion

6.6.1 Oxidation of the RBO

Table 6.1 compares some raw bio-oil and oxidized product physical and chemical properties. As shown in Table 6.1 raw bio-oil acid value increased from 90.28 to 161.0 mg KOH/g following oxidation; viscosity decreased by 45.16% and water content increased by about 11%. The HHV of the oxidized product decreased from raw bio-oil's

16.01 to 15.40 MJ/kg probably due to water content increase in the oxidized product. Density decreased from 1.22 to 1.14 g/ml and pH was reduced to 2.87 from 3.16. Oxygen content of the bio-oil following oxidation increased somewhat from 53.58 to 58.96. This likely resulted from both increased acid and water content.

Table 6.1 Comparison of raw bio-oil and oxidized product physical and chemical properties.

Properties	Raw bio-oil	Oxidized product
Density, g/mL	1.22	1.14
HHV, MJ/kg	16.01	15.40
Oxygen, wt%	53.58	58.96
Total acid value, mg KOH/g	90.28	161.0
pH	3.16	2.87
Water content, vol%	30.45	33.75
Kinematic viscosity, 40°C, cSt	12.09	6.63

6.6.2 Partial deoxygenation of the oxidized product and full deoxygenation of the partially deoxygenated product

The oxidized product was then partially deoxygenated in the presence of pressurized syngas at 5.5 MPa at a reaction temperature of 360 °C as described in section 6.4.2.2. After cooling, the partially deoxygenated product had an aqueous phase at the bottom of the vessel and an oil phase at the top. The aqueous fraction was separated from the oil fraction. A portion of the organic fraction was maintained for testing as a boiler fuel product. The remainder of the organic fraction was subjected to full deoxygenation under hydrogen pressure at 9.6 MPa at a temperature 425 ºC for 150 min as described in section 6.4.2.2. The resulting liquid contained both hydrocarbons as a top layer and a small percentage of an aqueous phase at the bottom.

The properties of the oxidized product, the resultant boiler fuel following partial deoxygenation and the hydrocarbon mixture produced by full deoxygenation are given in Table 6.2. The HHV of the boiler fuel at 35.40 MJ/kg was more than double the 15.40 MJ/kg value of the oxidized product. Boiler fuel oxygen content was dramatically reduced from 58.96 to 14.0. Acid value was reduced from 161.0 to 51.6. pH was increased from 2.87 to 4.24. Water content of the boiler fuels was only 2.7 vol% compared to that of the oxidized product at 33.75 vol%. Density was reduced to 1.04 for boiler fuel compared to 1.14 for the oxidized product. Viscosity increased greatly from 6.63 to 28.25 cSt.

As a control, partial deoxygenation of raw bio-oil was also performed several times at the same 1st-stage partial deoxygenation reaction conditions but the reaction was hindered due to coke formation. The partial deoxygenation of raw bio-oil was not able to be performed with pressurized syngas. It appears that the bio-oil oxidation step is required to produce a product that can be partially deoxygenated with syngas.

The properties of the hydrocarbon mixture were greatly improved above those of the boiler fuel. HHV of hydrocarbon mixture was increased to 45.30 from the boiler fuel HHV of 35.40 MJ/kg, an increase by 27.97%. Oxygen content was reduced from 14 wt% to zero and acid value was also decreased to zero from 51.6 mg KOH/g. pH was on the basic side at 9.5. Water content was decreased from 2.7 vol% to 0.08 vol%, a decrease by 97.0%. Density was considerably lowered from 1.04 to 0.88 g/ml; viscosity was reduced greatly from 28.25 cSt to 2.38 cSt, a decrease of 91.57%.

Table 6.2 Comparison of oxidized product, boiler fuel and hydrocarbon mixture physical and chemical properties.

Properties	**Oxidized product**	**Boiler fuel**	**Hydrocarbon mixture**
HHV, MJ/kg	15.40	35.40	45.30
Oxygen, wt%	58.96	14.0	0
AV,mg KOH/g	161.0	51.6	0
pH	2.87	4.24	9.5
Water content, vol%	33.75	2.7	0.08
Density, g/ml	1.14	1.04	0.88
Kinematic viscosity, 40°C, cSt	6.63	28.25	2.38

Figure 6.1 Shows the elemental composition weight percentages of the oxidized product, boiler fuel and hydrocarbon mixture. The carbon content of the boiler fuel of 76.4 wt% increased from that of the oxidized product at 33.10 wt%. Carbon content of the hydrocarbon mixture was 87.06. The oxygen content of the oxidized product decreased from 58.96 wt% to 14.0 wt% for boiler fuel to zero for the hydrocarbon mixture. Nitrogen content was not altered by CDO.

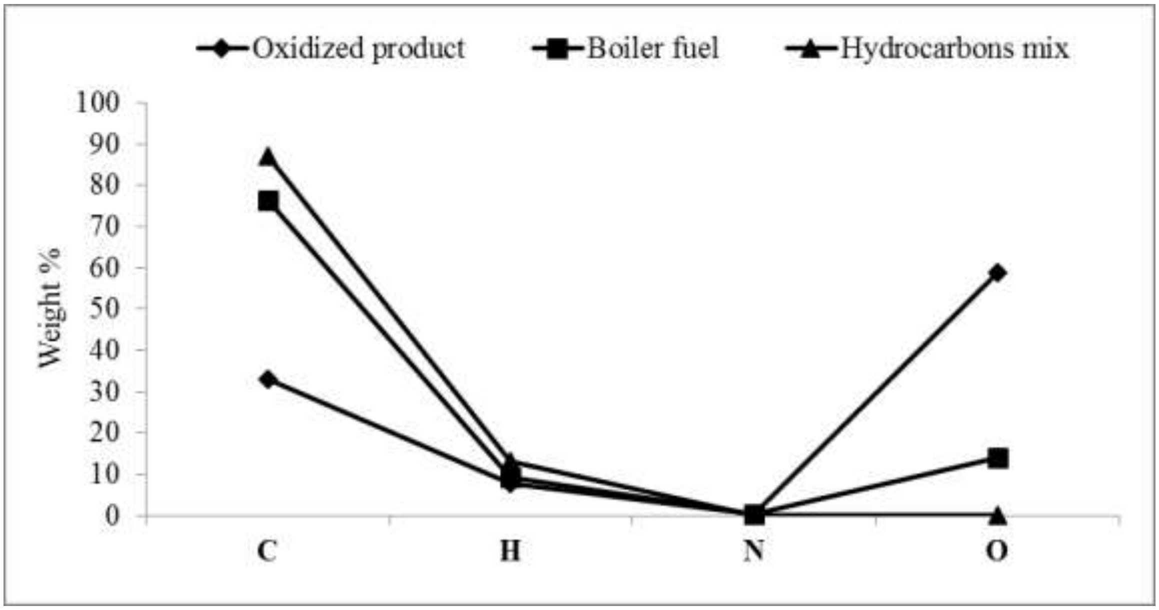


Figure 6.1 Oxidized product, boiler fuel and hydrocarbon mixture elemental analysis comparison.

6.6.3 GC-MS analysis of the RBO and hydrocarbon mixture

Table 6.3 compares the chemical composition of boiler fuel produced from partial deoxygenation of the oxidized product under pressurized syngas and the hydrocarbons mixture produced by full deoxygenation of the partially deoxygenated fuel that were analyzed by GC-MS. Approximately 50 chemical compounds were identified by GC-MS in both samples. The total area percentages of the major fifty compounds present in both boiler fuel and hydrocarbon mixture were 100%. Chemical compound names and area% were shown in Table 6.3. There was a considerable change in the chemical composition and area% of the hydrocarbon mixture compared to the boiler fuel. The boiler fuel hydrocarbons content from 11.8 area% greatly increased to 98.8 area% for the hydrocarbon mixture. This indicates that boiler fuel chemical components 8.2 area% of acids, 25.9 area% of ketones, 52.6 area% of alcohols including phenols and other components with 1.6 area% converted to hydrocarbons during the full deoxygenation. The hydrocarbon mixture was also comprised of small fractions of alcohols 1.2 area%.

Table 6.3 Boiler fuel and hydrocarbon mixture chemical composition analysis by GC-MS with area percentages.

Boiler fuel		**Hydrocarbon mixture**	
Compound Name	Area%	Compound Name	Area%
Hydrocarbons		**Hydrocarbons**	
3-Methyl-3-hexene	1.6	1-Butene	2.6
Cyclohexane,1-2-dimethyl-,cis	1.6	Cyclopropane, 1,1-dimethyl	2.0
2-Heptene	1.2	Heptane	1.0
3,4-Heptadiene	1.2	Cyclohexane, methyl	6.7
1-Phenyl-1-octyne	1.1	1-Hexene, 4-methyl	1.6
2-Methyl-2-bornene	1.8	Cyclohexane, 1,3-dimethyl, cis	1.9
Phosphine, dimethylphenyl	1.2	Cyclopentane, 1-ethyl-3-methyl	2.4
Benzo[h] quinoline, 2,4-dimethyl	2.2	Cyclohexane, 1,2-dimethyl, trans	1.6
Acids		Cyclohexane, 1,3-dimethyl, trans	1.0
Phenylphosphonous acid	1.8	Cyclohexane, 1,2-dimethyl, cis	1.7
Benzeneacetic acid, 3,4-dihydroxy-	3.1	Cyclohexane,ethyl	4.0
3-Quinolinecarboxylic acid, 4-hydroxyl	3.3	Cyclopentane,butyl	1.3
Ketones		Cyclohexane,1-ethyl-4-methyl, cis	4.2
Cycloheptanone	1.6	Cyclohexane,propyl	5.4
Cyclohexanone,3-methyl,®	1.6	2-Hexene,4-ethyl-2,3-dimethyl	0.9
Cyclohexanone	1.5	Bicyclo[3.3.1] nonane	1.2
Cyclopentanone,2-ethyl	1.7	Cyclohexane, 1-methyl-2-propyl	1.7
Cycloheptanone	2.4	Cyclohexane, 1,3-dimethyl,trans	1.0
Cycloheptanone,2-methyl	1.3	1,2-Dipropylcyclopropene	1.8

Table 6.3 (Continued)

2-Cyclopenten-1-one,2,3-dimethyl	1.8	Cyclohexane,butyl	1.2
2-Cyclopenten-1-one,2,3,4-trimethyl	1.6	Cyclohexene,1-butyl	1.7
Ethanone,1-(1-cyclohexen-1-yl)	1.1	Naphtalene,decahydro-,trans	0.9
Tricyclo [2.2.1.0 (1,4)] heptan-2-one	1.5	Cyclopentane,1,1'-ethylidenebis-	1.5
Bicyclo[3.1.1] hept-3-en-2-one 4,6	1.4	Cyclohexane,1-ethyl-2-propyl-	1.5
2,5-Dihydroxypropiophenone	1.3	1,4-Heptadiene,3-methyl-	1.5
3-Pentanone	2.6	Cyclohexene,1-butyl	0.8
Cyclopentanone,2-methyl	4.5	Naphtalene,decahydro-2-methyl	1.0
Alcohols		1-Phenyl-1-butene	0.9
1,3-Benzenediol, 4,5-dimethyl	1.6	Benzene, (1-methyl-1-butenyl)	1.0
Ethanol,2-(2-propynyloxy)	1.8	Benzene, (2-methyl-1-butenyl)	1.1
Phenol, 2-ethyl	1.6	Cyclohexene,1,6-dimethyl	0.9
Phenol,3,5-dimethyl	3.9	Naphthalene, decahydro-2,6-dimethyl	1.4
Phenol, 4-ethyl	1.7	Naphthalene, 1,2,3,4-tetrahydro-1 Benzene,1-ethenyl-4methyl	1.1
Phenol, 3-ethyl	2.1	Benzene, (2,2-dimethyl-1methylene)	1.0
Phenol,2,5-dimethyl	1.1	1,13-Tetradecadiene	1.4
Phenol,3-methoxy-2-methyl	3.8	1.11-Dodecadiene	1.0
Phenol, 2,4,6-trimethyl	1.3	Naphthalene,1,2,3,4-tetrahydro-1, 1H-Indene,2,3-dihydro-1,1,5-trimethyl	2.6
Phenol,2-methyl	1.8	Naphthalene,1,2,3,4-tetrahydro-1, 1H-Indene,2,3-dihydro-1,1,5,6-tetramethyl	3.6

Table 6.3 (Continued)

Phenol	2.2	Pentadecane	3.0
Phenol, 4-methyl	5.2	1-Phenylbicyclo(4.1.0)heptane	0.9
Phenol, 2-ethyl-4-methyl	1.2	Benzene,[(tetramethylcyclopropyl)	4.9
Phenol, 2,3,6-trimethyl	2.0	Benznene,1,3-bis (1-methylethenyl)	1.3
Phenol, 4-ethyl	3.6	Heptadecane	9.3
Benzene, 1,4-dimethoxy-2-methyl	1.8	9-Methyl-S-octahydroanthracene	4.0
Phenol, 2-methoxy-4-propyl	1.3	1H-Indene,2,3-dihydro-1,1-dimethyl	3.4
Phenol, 2-methoxy-3-methyl	2.4	Naphthalene,1,2,3,4-tetrahydro-1	1.6
O-Methoxy-.aplha.-methylbenzyl alcohol	2.0	Benz[a]anthracene,7-methyl	0.3
Phenol, 4-(3-methyl-2-butenyl)	1.5	**Alcohols**	
1-Naphthalenol,2-methyl	1.6	Cyclohexaneethanol	1.2
1-Naphthalenol,4-methyl	1.5	Total	100.0
1-Naphthol, 5,7-dimethyl	1.6		
1-Naphthol, 5,7-dimethyl	4.3		
other			
Benzene, 1,2-dimethyl-4-nitro	1.6		
Total	100.0		

6.6.4 DHA analysis of the hydrocarbon mixture

A DHA was performed by ASTM D6730-01. This test is often referred to the as PIANO method (paraffins, iso-paraffins, aromatics, naphthenes and olefins) to classify the hydrocarbons present in the hydrocarbon mixture. The results of the DHA are given in Figure 6.2. These results show that the hydrocarbon mixture contained n-paraffins of

6.84 mass%, iso-paraffins of 17.51 mass%, olefins of 26.90 mass%, naphthenes of 13.78 mass%, aromatics of 7.21 mass%, total C14+ of 15.02 mass% and unknown compounds of 10.04 mass%.

This DHA analysis also calculated the liquid hydrocarbon mixture octane number of 61.8. Octane number is one of the characteristics of spark-ignition engine fuels such as gasoline, diesel and jet fuel. The octane number indicates anti-knock characteristic of a fuel and strongly depends on the hydrocarbon type. There are two commonly used octane numbers are research octane number (RON) and motor octane number (MON). The RON is measured under low speed condition by ASTM D 908 while MON is measured under high speed condition by ASTM D 357.

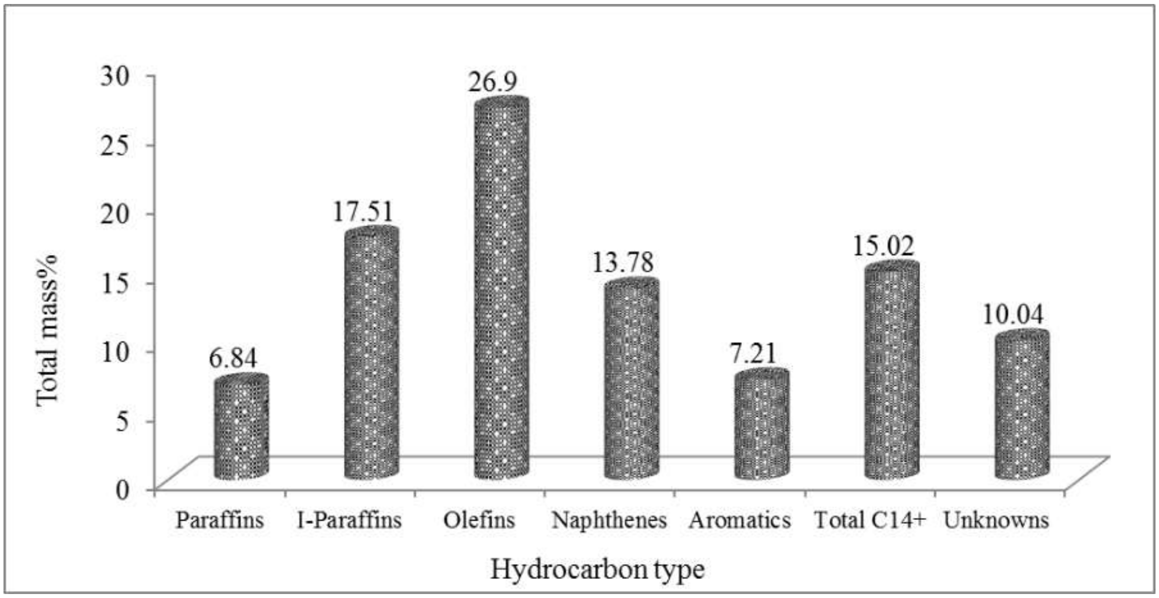


Figure 6.2 Hydrocarbon types and their mass percentages present in liquid hydrocarbon mixture results analyzed by DHA ASTM D6730-01.

6.6.5 Simulated distillation analysis of the hydrocarbon mixture

Simulated distillation of the hydrocarbon mixture was performed by ASTM D2887 for boiling range distribution of petroleum fractions by gas chromatography. Simulated distillations of the hydrocarbon mixture results are shown in Figure 6.3 as the petroleum fuel equivalent based on vaporization temperature. These boiling temperatures are given below the named petroleum equivalents. These petroleum equivalents were of the molecular weights of gasoline (45%), jet fuel (20%) and diesel (30%). Not shown in Figure 6.3 is the 5% of heavy fuel produced at temperatures above 350 °C.

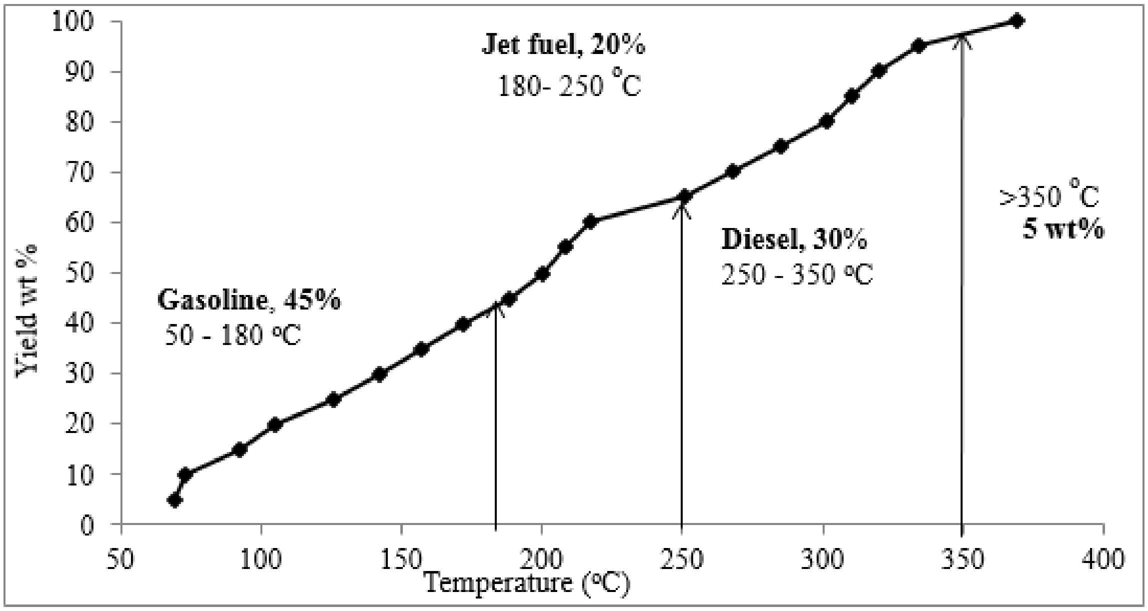


Figure 6.3 Gasoline, jet fuel and diesel fuels weight percentages present in hydrocarbon mixture results from simulated distillation analysis by the ASTM D2887.

6.6.6 FTIR analysis

Figure 6.4 shows the comparison of oxidized product, boiler fuel and hydrocarbon mixture FTIR spectra. These spectra identified the functional groups present in the product types. Characteristic vibrational modes were observed at 3200-3600 cm^{-1} (OH stretch), 2800-3100 cm^{-1} (CH aliphatic stretch), 1600-1750 cm^{-1} (C=O stretch), 1350-1470 cm^{-1} (CH bending) and 1000-1250 cm^{-1} (C-O stretch). The OH (carboxylic acids) stretching was decreased and CH (alkanes) aliphatic stretch and CH bending stretch absorption bands were considerably increased from oxidized product to boiler fuel and for the hydrocarbon mixture. The decrease in both OH and C=O stretch absorption bands and increase in CH aliphatic stretch absorption band indicates that the carboxylic acids and other oxygenated chemical compounds were converted into hydrocarbons. The findings of the FTIR spectra are in good agreement with the physical and chemical properties described in Table 2 and DHA results in Figure 6.2.

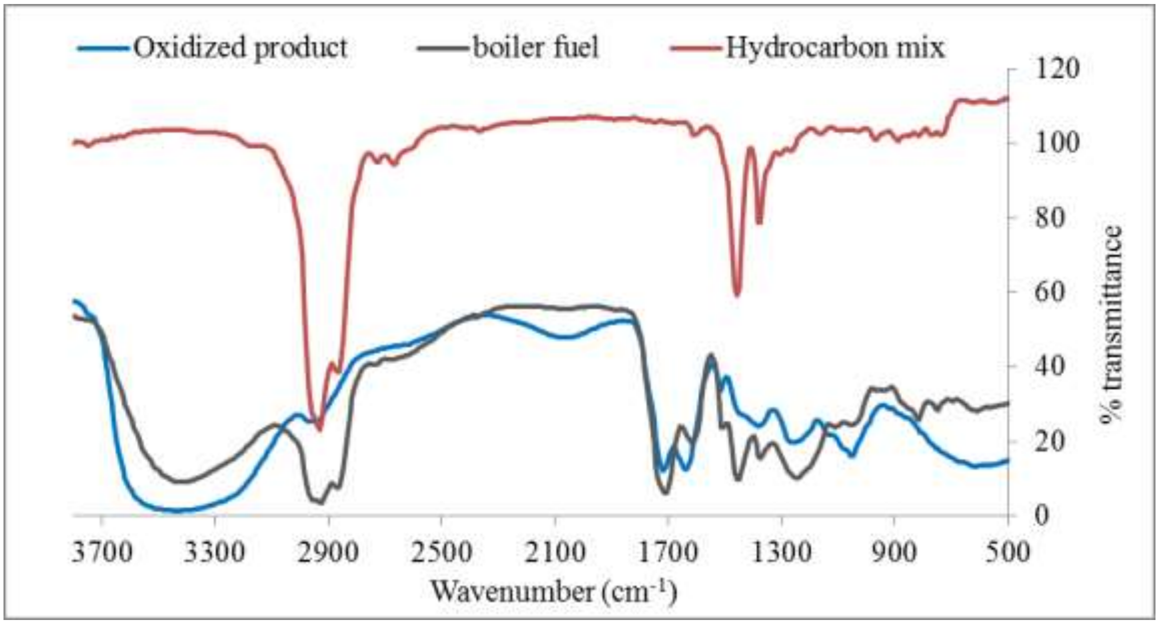


Figure 6.4 FTIR spectra comparing oxidized product, boiler fuel and hydrocarbon mixture.

6.6.7 Proton (^{1}H) NMR spectroscopic analysis

Proton NMR spectra of the oxidized product (a), syngas partial deoxygenated product (b), liquid hydrocarbon mixture (c) and commercial gasoline-jet fuel-diesel mixture (d) are shown in Figure 6.5. As shown in Figures 6.5 (a), (b) and (c) it is evident that there is a significant difference between ^{1}H-NMR spectrum of the oxidized product, syngas partial deoxygenated product and hydrocarbon mixture. The oxidized product spectrum in Figure 6.5(a) is very complex and consists of a large number of proton signals due to the presence of various compounds with differing functional groups. After the catalytic deoxygenation of the oxidized product the number of proton signals reduced considerably in the partially deoxygenated product spectrum (Figure 6.5(b)) and fully deoxygenated product spectrum (Figure 6.5(c)). This was due to the conversion of various oxygenated compounds to aliphatic and aromatic hydrocarbons.

Comparison of Figures 6.5 (a) and 6.5(b) show clearly that the partial deoxygenation of oxidized product eliminated the methoxy (-OCH_3) group of guaiacol or substituted guaiacol compounds (one of the major components of the bio-oil). The methoxy group single proton signal with a downfield chemical shift of 5.2 ppm present in Figure 6.5(a) was absent in Figure 6.5(b).

Comparison of the Figure 6.5(a) spectra of oxidized bio-oil to the partially deoxygenated spectra of Figure 6.5(b) shows that the phenols, substituted phenols and other aromatic compounds' (derived from lignin and sugars) proton signals had a downfield chemical shift of 5.8-8.0 ppm. Likewise comparison of Figure 6.5(a) and 6.5(b) show that some oxygenated compounds' proton signals demonstrated a chemical shift of 2.0-2.8 ppm (acyl, benzylic and aliphatic hydroxyl functional groups) during partial deoxygenation. Again, for the same comparison of Figures 6.5 (a) and 6.5(b) spectra partial deoxygenation caused other oxygenated compounds' proton signals to chemically shift from 3.2-5.2 ppm (esters, ethers and lignin derived methoxy phenols). Therefore, phenols, substituted phenols and the described two groups of oxygenated compounds were all reduced in the spectra of Figure 6.5(b) as compared to the oxidized product (Figure 6.5(a)) as a result of partial deoxygenation. By contrast to the reduction of oxygenated compounds contrast, the aliphatic hydrocarbons proton signals with an upfield chemical shift of 0.8-1.8 ppm were increased. A similar increase was also observed in the aromatic hydrocarbons proton signals with a chemical shift of 6.4-7.6

ppm in Figure 6.5(b) as compared to Figure 6.5(a) due to the conversion of phenols and guaiacols to aromatic hydrocarbons during the partial deoxygenation.

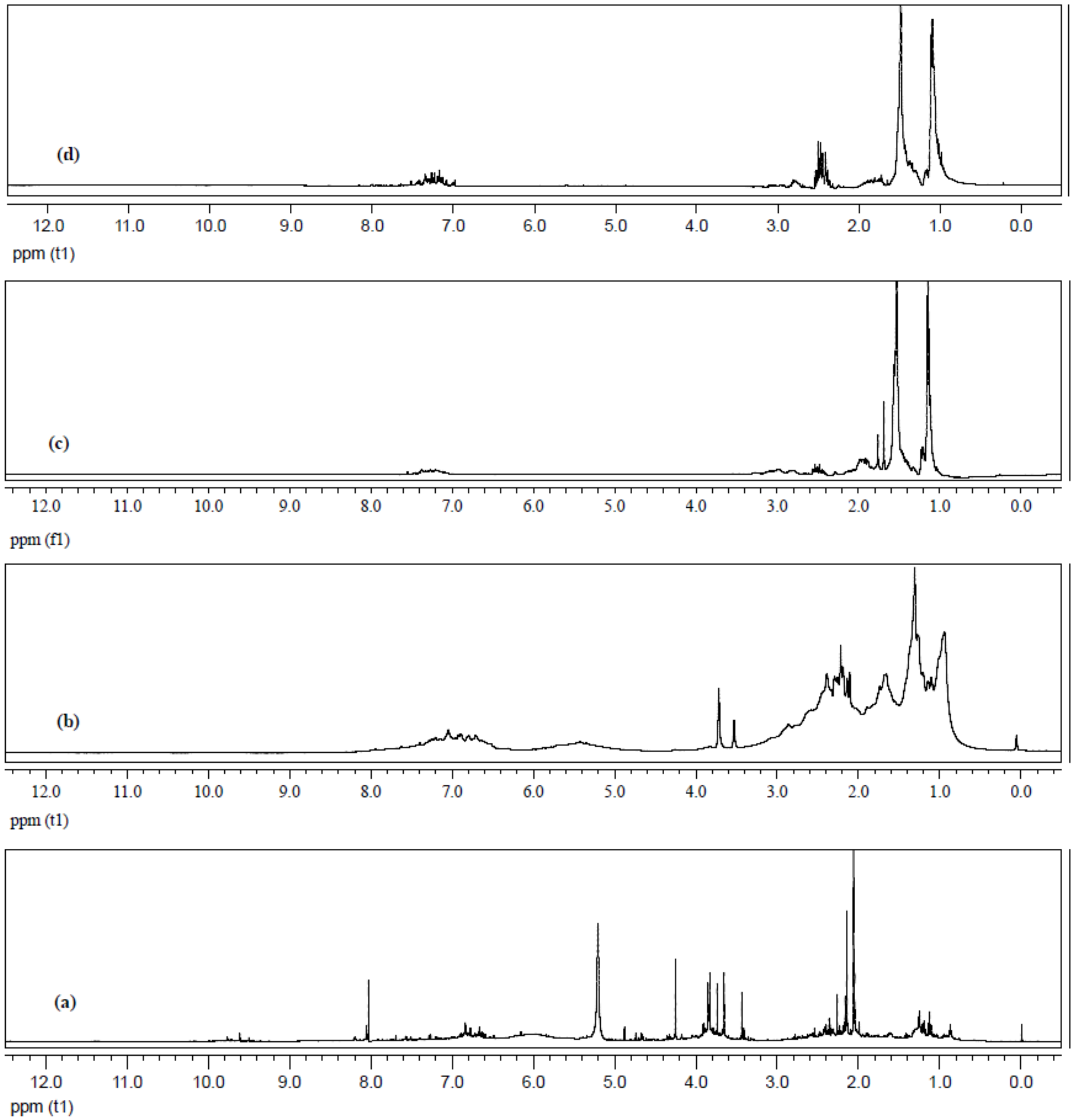


Figure 6.5 ^{1}H-NMR spectra analysis of oxidized product (a), partial deoxygenated product (b), hydrocarbon mixture (c) and commercial gasoline-jet fuel-diesel mixture (d).

As shown in Figure 6.5(c) the full hydrogen deoxygenation step applied to the syngas partially deoxygenated product of Figure 6.5(b) increased the aliphatic alkanes' (hydrocarbons) proton signals with an upfield chemical shift of 0.8-1.8 ppm. By contrast to the increase in aliphatic alkanes' upfield shift comparison of Figures 6.5 (b) to 6.5(c) shows that some remaining aromatic compounds, phenols and substituted phenols, were reduced with a downfield chemical shift of 5.0-7.5 ppm. Likewise, the esters, ethers, carbonyl compounds and hydroxyl groups' proton signals demonstrated a downward chemical shift of 3.2-5.2 ppm. Therefore, full deoxygenation spectra in Figure 6.5(c) showed an increase in aliphatic alkane groups. However, there was considerable reduction in the phenols, substituted phenols, esters, ethers carbonyl compounds and hydroxyl groups in Figure 6.5(c) spectra. Both the increase and decrease of proton signals discussed was due to the conversion of several oxygenated and aromatic compounds to aliphatic hydrocarbons during the full deoxygenation.

The liquid hydrocarbon mixture (comprised of gasoline, jet fuel and diesel weight compounds) produced by this study ^{1}H-NMR spectrum Figure 6.5(c) was also compared with the commercial gasoline-jet fuel-diesel mixture (prepared by physical mixing of equal parts of commercial gasoline, jet fuel and diesel) ^{1}H-NMR spectrum Figure 6.5(d). As shown in Figure 6.5(c) and 6.5(d), it is very clear that both spectra proton signals resemble each other. The fact of this resemblance is further strengthened by the results of the DHA analysis (Figure 6.2), simulated distillation analysis (Figure 6.3) and FTIR spectra analysis (Figure 6.4).

6.6.8 Micro GC gas analysis

Table 6.4 shows the micro GC analysis of the input pressurized syngas applied for partial deoxygenation and exit gas compositions resulting from the partial deoxygenation reactions of both input syngas and hydrogen. As shown in Table 6.4, input syngas was comprised of 18.0% of H_2, 22.0% of CO and 11% of CO_2; exit gas from the syngas partial deoxygenation reaction was comprised of 1.1% of H_2, 5% of CO and 38.8% of CO_2. The exit gas produced from the syngas partial deoxygenation reaction indicates consumption of 17 percentage points of CO; in addition, the reaction resulted in the production of an additional 28.8 percentage points of CO_2. This high consumption of CO and the high production of CO_2 during the syngas partial deoxygenation step indicate that the Scheme 2 WGS reaction occurred between the CO present in the syngas and H_2O present in the bio-oil to produce hydrogen and CO_2 as a byproduct.

Table 6.4 Partial deoxygenation reaction In-gas and Exit-gas components analysis by micro GC analyzer.

Sample Name	**H_2%**	**CO%**	**CO_2%**
Syngas [In gas]	18.0	22.0	11.0
Syngas partial deoxygenation [Exit gas]	1.1	5.0	38.8
Hydrogen [In gas]	100	0.0	0.0
Hydrogen partial deoxygenation [Exit gas]	51.0	0.6	15.9

Pure hydrogen was also applied to perform the partial deoxygenation of the oxidized product as a comparative control of exit gas composition. As shown in Table 6.4 the exit gas from the hydrogen partial deoxygenation reaction was comprised of 51.0% of H_2, 0.6% of CO and 15.9% of CO_2. This result indicated that 49% of the input 100% hydrogen was required (leaving 51% in the exit gas) to perform the partial deoxygenation under the conditions applied. The release of the small respective percentages of 0.6% CO and 15.9% CO_2 would be expected during the pure hydrogen partial deoxygenation reaction. Comparing the pure hydrogen and syngas partial deoxygenation exit gas left over hydrogen gas compositions; it is evident that approximately 32 percentage points of hydrogen consumption was reduced by our syngas partial deoxygenation process.

A remaining question is whether the H_2 contained in the input syngas combined with the H_2 produced by the WGS reaction performed satisfactory deoxygenation of the oxidized bio-oil. Table 6.5 repeats the description of the syngas partial deoxygenated product given in Table 6.2 above to allow a comparison to the study results of pure hydrogen partial deoxygenated product performed on oxidized bio-oil. A comparison of these Table 6.5 results shows that there was very little difference between the partially deoxygenated product produced by pure hydrogen and syngas partial deoxygenation product. HHV, acid value, pH, water content, density and viscosity have nearly equivalent values with the greatest difference in the oxygen content values. The oxygen value difference showed a lower oxygen content value (14.00 wt%) for the syngas partial deoxygenation product compared to the pure hydrogen partial deoxygenated product (15.10 wt%), a 7.2% decrease. Therefore, it can be concluded that the syngas partially deoxygenated and hydrogen partially deoxygenated products are nearly identical. This indicates that the H_2 contained in the raw syngas combined with that added by the WGS reaction provided sufficient H_2 to drive the partial deoxygenation reaction to the same degree as for pure hydrogen when performed on identical samples of oxidized bio-oil.

Table 6.5 Comparison of some physical and chemical properties of boiler fuels produced from both syngas and hydrogen partial deoxygenation reactions.

Properties	Boiler fuel [Syngas]	Boiler fuel [Hydrogen]
HHV, MJ/kg	35.40	34.50
Oxygen, wt%	14.00	15.10
Total acid value, mg KOH/g	51.60	48.60
pH	4.24	4.20
Water content, vol%	2.70	2.70
Density, g/ml	1.04	1.00
Kinematic viscosity, 40°C, cSt	28.25	28.00

6.7 Conclusions

The pretreatment of raw bio-oil followed by a partial deoxygenation in the presence of pressurized syngas and full deoxygenation with pure hydrogen successfully produced liquid hydrocarbons of transportation fuel quality. Upgrading with syngas appears to provide sufficient hydrogen required for CDO of oxidized bio-oil reactions. Simultaneously, the CDO large reduction in water content in the partially deoxygenated product that is produced by the WGS should render the final hydrogen deoxygenation step more efficient in hydrogen utilization. The liquid hydrocarbons produced from CDO had an HHV of 45.30 MJ/kg. The oxygen content of raw bio-oil was decreased from 53.58 wt% to 0.0 wt% of the syngas CDO hydrocarbon mixture. Acid value and water content were nearly zero. pH was on the basic side at 9.5. Density and viscosity were considerably lowered at 0.88 g/ml and 2.38 cSt, respectively. The energy density of hydrocarbons produced by this method was increased by approximately 182% from raw bio-oil. Our results indicated that the syngas partially deoxygenated and hydrogen partially deoxygenated products were nearly identical. DHA, ^{1}H-NMR, FTIR and simulated distillation analysis results showed that the liquid hydrocarbon mixture produced by this study (CDO) was comprised of petroleum equivalent molecular weights of gasoline (45%), jet fuel (20%) and diesel (30%).

6.8 Disclaimer

6.9 References

1. Maggi, R., B. Delmon. Comparison between 'slow' and 'flash' pyrolysis oils from biomass. Fuel. 73, 5, 671-667, 1994.

2. Bridgwater, A.V., D. Meier, D. Radlein. An overview of fast pyrolysis of biomass. Organic. Geochemistry. 30, 1479-1493, 1999.

3. Mohan, D., C. U. Pittman, Jr., P. Steele. Pyrolysis of wood-biomass for bio-oil: A Critical Review. Energy & Fuels. 20, 848-889, 2006.

4. Ingram, L., D. Mohan, M. Bricka, P. Steele, D. Strobel, D. Crocker, B. Mitchell, J. Mohammad, K. Cantrell, C. U. Pittman, Jr. Pyrolysis of wood and bark in an auger reactor: physical properties and chemical analysis of the produced bio-oils. Energy & Fuels. 22, 614-625, 2008.

5. Mckendry, P. Energy production from biomass (Part 1): Overview of biomass. Bioresource. Technology. 1, 83, 37–46, 2002.

6. Huber, G. W., S. Iborra, A. Corma. Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. Chemical. Review. 106, 4044–4098, 2006.

7. Oasmaa, A., D. C. Elliott, J. Korhonen. Acidity of biomass fast pyrolysis bio-oils. Energy Fuels. 24, 6548-6554, 2010.

8. Hu, X., C. Li, Y. Xu, Q. Wang, X. Zhu. On the thermal oxidation stability of pyrolysis biomass oil. Int. J. of Renewable Energy Technology. 2, 2, 155-168, 2011.

9. Bandi, A., F. Baumgart, A. V. Bridgwater. Stirling engine with flox burner fuelled with fast pyrolysis liquid. In: Progress in Thermochemical Biomass Conversion. Blackwell Science: Oxford, 1459-1467, 2001.

10. Czernik, S., A. V. Bridgwater. Overview of applications of biomass fast pyrolysis oil. Energy & Fuels. 18, 590-598, 2004.

11. Schnepf, R., B. D. Yacobucci. Renewable fuel standard (RFS): Overview and issues. CRS Report for Congress. March 14, page 4, 2013.

12. Solecki, M., A. Scodel, B. Epstein. Advanced biofuel market report. Environmental. Entrepreneurs. August 27, 2013.

13. Furimsky, E. Catalytic hydrodeoxygenation. Applied Catalysis A: 199, 147-190, 2000.

14. Elliott, D. C. Historical developments in hydroprocessing bio-oils. Energy & Fuels. 21, 1792-1815, 2007.

15. Corma, A., G. W. Huber, L. Sauvanaud, P. O. Connor. Processing biomass-derived oxygenates in the oil refinery: Catalytic cracking (FCC) reaction pathways and role of catalyst. Journal of Catalysis. 247, 307-327, 2007.

16. Tan, E. C.D., T. L. Marker, M. J. Roberts. Direct production of gasoline and diesel fuels from biomss via integrated hydropyrolysis and hydroconversion process - A techno-economic analysis. Environmental Progress & Sustainable Energy. May 31, 2013. DOI: 10.1002/ep.11791.

17. Czernik, S., R. Evans, R. French. Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil. Catalysis Today. 129, 3-4, 2007.

18. Elliott, D. C., T. R. Hart, G. G. Neuenschwander, L. Rotness, M. V. Olarte, A. H. Zacher, Y. Solantausta. Catalytic hydroprocessing of fast pyrolysis bio-oil from pine sawdust. Energy & Fuels. 26, 3891-3896, 2012.

19. Wildschut, J., F. H. Mahfud, R. H. Venderbosch, H. J. Heeres. Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. Industrial & Engineering Chemistry Research. 48, 10324-10334, 2009.

20. Ardiyanti, A.R., A. Gutierrez, M. L. Honkela, A. O. I. Krause, H. J. Heeres. Hydrotreatment of wood-based pyrolysis oil using zirconia-supported mono and bimetallic (Pt, Pd, Rh) catalysts. Applied Catalysis A: General. 407, 56-66, 2011.

21. Gagnon, J., S. Kaliaguine. Catalytic hydrotreatment of vacuum pyrolysis oil from wood. Industrial & Engineering Chemistry Research. 27, 1783-1788, 1988.

22. Subramaniam, B., W. F. Jackson, C. V. Raghunath. Deoxygenation of bio-oils and other compounds to hydrocarbons in supercritical media. Patent Pub. No. US2011/0028773 A1, 2011.

23. Dickerson, T., J. Soria. Catalytic fast pyrolysis: A Review Energies. 6, 514-538, 2013.

24. Wang, H., J. Male, Y. Wang. Recent advances in hydrotreating of pyrolysis bio-oil and its oxygen-containing model compounds. ACS Catal. 3, 1047-1070, 2013.

25. Jones, S. B., J. E. Holladay, D. C. Elliot, C. Valkenburg, D. J. Stevens, C. W. Walton, C. Kinchin, S. Czernik. Production of gasoline and diesel from biomass via fast pyrolysis, hydrotreating and hydrocracking: A design case. Pacific Northwest National Laboratory. 18284, 2009.

26. Elliott, D. C., E. G. Baker. Process for upgrading biomass pyrolyzates. US Patent 4,795,841, 1989.

27. Wildschut, J., C. I. Melian, H. J. Heeres. Catalyst studies on the hydrotreatment of fast pyrolysis oil. Applied Catalysis B: Environmental. 99, 1-2, 298-306, 2010.

28. Bulushev, D. A., J. R. H. Ross. Catalysis for conversion of biomass to fuels via pyrolysis and gasification: A review. Catalysis Today. 171, 1, 1-13, 2011.

29. Diebold, J. P. A review of the chemical and physical mechanisms of the storage stability of the fast pyrolysis bio-oils. NREL/SR-570-27613. January, 2000.

30. Hu, X., D. M. Wang, R. Gunawan, C. Lievens, W. Chaiwat, M. Gholizadeh, L. Wu, X. Li, C. Z. Li. Polymerization on heating up of bio-oil: A model compound study AICHE Journal. 59, 3, 888-900, 2013.

31. Xu, J., J. Jiang, W. Dai, T. Zhang, Y. Xu. Bio-oil upgrading by means of ozone oxidation and esterification to remove water and to improve fuel characteristics. Energy & Fuels. 25, 1798-1801. 2011.

32. Steele, P. H., S. K. Tanneru, S. K. Gajjela, SK. Composition and methods for improved fuel production. US Patent 2013/0291431 A1, 2013.

33. Parapati, D. R., V. K. Guda, V. K. Penmetsa, P. H. Steele, S. K. Tanneru. Single stage hydroprocessing of pyrolysis oil in a continuous packed bed reactor. Environmental Progress & Sustainable Energy. February 13, 2014, DOI: 10.1002/ep.11954.

34. Tanneru, S. K., P. H. Steele. Pretreating bio-oil to increase yield and reduce char during hydrodeoxygenation. Fuel. 133, 326-331, 2014

35. Street, J., F. Yu, J. Wooten, E. Columbus, M. G. White, J. Warnock. Gasoline-range hydrocarbon production using biomass derived synthesis gas over Mo/H^+ZSM-5. Fuel. 96, 239-249, 2012.

36. Smith, B. R. J., M. Loganathan, M. S. Shantha. A review of the water gas shift reaction kinetics. Int. J. of Chemical Reactor Engineering. Review R4, 8, 2010.

37. Nagai, M., M. A. Zahidul, Y. Kunisaki, Y. Aoki. Water-gas shift reactions on potassium- and zirconium-promoted cobalt molybdenum carbide catalysts. Applied Catalysis A:General. 383, 58-65, 2010.

38. Akgul, G., A. Kruse. Influence of salts on the subcritical water-gas shift reaction. The J. of Supercritical Fluids. 66, 207-214, 2012.

39. Yan, Q., F. Yu, Z. Cai, J. Zhang. Catalytic upgrading nitrogen-riched wood syngas to liquid hydrocarbon mixture over a Fe-Pd/ZSM-5 catalyst. Biomass and Bioenergy. 47, 469-473, 2012.

40. Nkafamiya, I. I., H. M. Maina, S. A. Osemeahon, U. U. Modibbo. Percentage oil yield and physiochemical properties of different groundnut species (Arachis hypogaea). African J. of Food Science. 4, 7, 418-421, 2010.

CHAPTER VII

DIRECT HYDROCRACKING OF OXIDIZED BIO-OIL TO LIQUID HYDROCARBON MIXTURE

7.1 Abstract

Hydrodeoxygenation is considered a promising technology to convert bio-oils to liquid transportation fuels. Recently we tested a hydrodeoxygenation method to convert oxidized bio-oil to increase liquid fuel yield, reduce char and reduce required hydrogen. In this current study we tested direct hydrocracking of the oxidized bio-oil to produce high-energy liquid hydrocarbons. We tested various reaction conditions (reaction temperature, hydrogen pressure, time and catalyst type) on the hydrocracking of the oxidized bio-oil. Direct hydrocracking of the oxidized bio-oil produced 36.6% higher hydrocarbons yield compared to direct hydrocracking of the raw bio-oil. The hydrocarbons mixture produced had a higher heating value (HHV) of 43.6 MJ/kg. The oxygen content and acid value were 0.5 wt% and 0.3 mg KOH/g, respectively. Density and viscosity were considerably low at 0.9 g/ml and 1.8 cSt, respectively. pH value was 8.4. The hydrocarbon mixture was also analyzed by GC-MS, FTIR, NMR and DHA.

Keywords: Bio-oil, oxidation, hydrodeoxygenation, hydrocracking, HHV.

7.2 Introduction

Increasing energy demand and the approach of peak production of petroleum supply have led the world to search for renewable, sustainable and environmentally benign alternative fuels. According to the Renewable Fuels Standard the present use of renewable fuels is 14 billion gallons per year (BGY) and is projected to use 36 BGY by 2022 [1]. Woody biomass is one of the most important renewable energy resources for the production of sustainable liquid fuels [2]. Biomass as a renewable energy source will reduce dependency on conventional fuels and provides significant environmental advantages over fossil fuels. It is greenhouse gas neutral because the CO_2 emitted from the bio-fuels from which it is produced is recycled by photosynthesis [3,4]. The availability of biomass in the world is 220 billion dry tons per year and is the world's largest and most sustainable energy resource. These advantages make biomass a potential alternative energy source for fossil fuels.

Fast pyrolysis is one of the most promising thermal decomposition methods to produce pyrolysis oil (bio-oil) from lignocellulosic biomass [5]. Bio-oil produced from fast pyrolysis is a dark brown liquid with a pungent phenolic odor; its chemical properties vary with feedstock type and applied pyrolysis conditions [6]. As a fuel raw bio-oil has environmental advantages when compared to fossil fuels but its complex chemical composition contains numerous oxygenates such as carboxylic acids, aldehydes, ketones, alcohols, phenols and phenolic derivatives and others [7-9]. The high percentage of oxygenated compounds present in raw bio-oils results in a 40 to 50% oxygen content which causes negative properties such as low energy density, high acidity, immiscibility with petroleum products and viscosity increase with heating or over time [5,10]. It is universally agreed that bio-oils need to be significantly upgraded to allow their use to fuel internal combustion engines [4, 11, 12].

Hydrodeoxygenation (HDO) is a widely practiced method to produce hydrocarbons from pyrolysis oil [12-18]. Elliot and Baker (1989) [19] in U.S. Patent No. 4,795,841 disclosed a method to prevent bio-oil from polymerizing by practicing what they termed “mild hydrotreating” which consisted of utilizing a mild temperature regime in the range of 250 to 300 °C in the presence of hydrogen and a hydrotreating catalyst. It has now become traditional to apply this method to partially upgrade bio-oil prior to application of hydrocracking as a second stage to produce pure hydrocarbons. The utilization of a mild hydrotreating prevents polymerization of the bio-oil that would occur if direct hydrocracking were applied without this step [12, 18, 20, 21].

Many researchers have practiced application of the hydrotreating step at mild temperatures (200-400 °C) to prevent bio-oil polymerization; typical hydrogen pressure applied for hydrotreating ranges from 4 to 10 MPa in the presence of a heterogeneous hydrotreating catalyst. The hydrocracking step is performed at more severe temperatures (300-500 °C) and also at higher pressures ranging from 10 to 20 MPa in the presence of a heterogeneous hydrocracking catalyst [15, 19, 22-24]. The general HDO reaction is shown as Scheme 7.1 [25].

$$-(CH_2O)- \quad + \quad H_2 \quad \xrightarrow{\text{Catalyst}} \quad -(CH_2)- \quad + \quad H_2O$$

Scheme 7.1 General HDO reaction

Zhang et al. (2003) studied the mechanism and reaction conditions of bio-oil deoxygenation in the presence of a sulfide cobalt molybdate catalyst and with addition of the hydrogen donor tetralin. The effects of reaction time, temperature, and hydrogen pressure on the single-stage deoxygenation were examined. Researchers performed several reactions by varying temperature and reaction times. They concluded that, as the temperature and reaction time increased, the deoxygenation of bio-oil also increased. However, higher temperature and longer reaction times also led to coke formation and catalyst deactivation. They also reported that hydrogen pressure had a significant effect on results by increasing the deoxygenation of the bio-oil [22].

Wildschut et al. (2009) performed a two-stage HDO by which a hydrotreating 1st-stage was followed by a hydrocracking 2nd-stage on bio-oil with noble metal catalysts. Ru/Al_2O_3, Ru/C, Ru/TiO_2, Pd/C, Pt/C, CoMo/Al2O3, and sulfide $NiMo/Al_2O_3$ were tested. The hydrotreating 1st-stage was applied to bio-oil at a temperature of 250 °C and 100 bar hydrogen pressure and was followed by 2nd-stage hydrocracking at a temperature of 350 °C and 200 bar hydrogen pressure for 4 h in an autoclave reactor. The 1st-stage mildly deoxygenated hydrocarbon yields ranged between 21 to 58 wt% and the oxygen content ranged between 18.5 to 26.5 wt%. Pd/C was found to be the best choice for the 1st-stage hydrotreating process. The 2nd-stage hydrocracking process liquid hydrocarbon oil yields ranged between 25 to 65 wt% and oxygen content ranged between 6 and 11 wt% [20].

Wildschut et al. (2010) performed a study to gain insight into catalyst stability of ruthenium on alumina (Ru/Al_2O_3), ruthenium on carbon (Ru/C) and platinum on carbon (Pt/C) catalysts for the direct HDO by single-stage treatment of fast pyrolysis oil at 350

°C and 200 bar hydrogen pressure for 4 h in a batch reactor set-up. Researchers concluded that ruthenium or platinum on carbon catalysts provided equally superior yield and deoxygenation compared to the Pt/C and Ru/Al_2O_3 catalysts. The highest upgraded oil yield obtained with Ru/C was 65 wt% with reduction of oxygen content from 40 to 6 wt%. They also concluded that prolonged reaction time led to decreased end-product yields and increased levels of oxygen content. Researchers hypothesized that these results may have been due to the gasification of the products and depolymerization of solids. Complete deoxygenation of bio-oil by the applied method and catalysts was not achieved due to the mild temperature conditions applied in the single state of direct HDO applied [15].

McCall et al. (2012) in U.S. Patent No. 8,329,969, B2 disclosed a method to produce fuel and fuel-blending components from biomass-derived pyrolysis oil. The process included the production of hydrocarbons by a two-stage deoxygenation of mixed-wood pyrolysis oil. In an example, researchers performed partial deoxygenation by pumping the pyrolysis oil through a fixed bed reactor loaded with a hydrotreating catalyst at a mild temperature between 250-340 °C and pressurized hydrogen at 1950-2010 psi. Once the hydrotreating was completed the oil fraction was isolated after separation and removal of water generated in the reaction. This partially deoxygenated oil was then fully deoxygenated by pumping through a full deoxygenation zone loaded with a hydrocracking catalyst and with the application of a more severe temperature between 405-407 °C in the presence of pressurized hydrogen between 1510-1525 psi [21].

Xu et al. (2013) investigated two-stage catalytic HDO of fast pyrolysis oil to produce hydrocarbon liquid fuels. Researchers employed a first mild hydrotreating step to bio-oil to overcome coke formation using Ru/C noble catalyst at a temperature of 300 °C and 1500 psig hydrogen pressure. The hydrocracking step employed a more severe temperature of 400 °C and 1950 psig pressurized hydrogen using traditional NiMo/Al_2O_3 catalyst. Researchers reported that coke formation was effectively eliminated. The oxygen content of the hydrocarbon fuel decreased from 48.0 wt% rigidly contained in the bio-oil to 0.5 wt%. The HHV increased from 17.0 to 46.0 MJ/kg [18].

Tanneru et al. (2014) developed a method to produce a fuel with increased yield, reduced coke formation and water content, and lower hydrogen pressure with lower hydrogen utilization following a two-stage hydrodeoxygenation (hydrotreating followed by hydrocracking) of oxidized bio-oil. Researchers applied a 1st-stage hydrotreating at a temperature of 360 °C and under 800 psig hydrogen pressure. The 2nd-stage hydrocracking of the hydrotreated product was performed at a higher temperature of 425 °C and under 1400 psig hydrogen pressure [17].

7.3 Objective

The objective of our current study was to produce liquid hydrocarbons by direct hydrocracking of oxidized bio-oil. The effect of the hydrocracking conditions of reaction time, temperature, hydrogen pressure and catalyst type were tested to determine the most effective reaction conditions.

7.4 Materials and methods

7.4.1 Materials

Nickel on silica-alumina (66±5% Ni) catalyst powder was obtained from Alfa Aesar. Ru/C (5%, Ru), Ru/Al_2O_3 (5%, Ru) and Cu(II)O catalyst powder were obtained from Sigma-Aldrich. Copper(II)oxide, hydrogen peroxide (H_2O_2) 50 wt% solution in water and oxone (potassium monopersulfate triple salt) were also obtained from Sigma-Aldrich. Bio-oil required for this research was produced from bark-free loblolly pine wood chips with a size of 1-3 mm and moisture content of 8-10% on dry-weight basis. Raw bio-oil (RBO) was produced by the fast pyrolysis process performed at a temperature of 450 ^{o}C with nitrogen carrier gas at a rate of 7-kg/h with the auger-feed pyrolysis reactor located in the Department of Sustainable Bioproducts, Mississippi State University (MSU). The MSU auger fast pyrolyzer produced 60-65 wt% of liquid product, 10-15% of non-condensable gases and 20-25% of char on a dry biomass weight basis.

7.4.2 Methods

7.4.2.1 Oxidation pretreatment to RBO

Bio-oil pretreatment by oxidation was performed in a stainless steel, high-pressure batch autoclave reactor equipped with an overhead magnetic stirrer, a pressure indicator with a maximum capacity of 5000 psig and a thermocouple for temperature monitoring in the range of 0-500 ^{o}C. The autoclave was equipped with an electrical heating and cooling system to control the temperature inside the reactor. The proprietary oxidative pretreatment applied considerably changed the RBO chemical composition. All pretreatment experiments were performed by adopting the procedure followed in Tanneru et al. (2014). Briefly, this procedure utilized both oxone and hydrogen peroxide to oxidize RBO at room temperature and without pressure. In the remainder of this paper, for clarity of understanding, the pretreated RBO by oxidation will be termed *oxidized product.*

7.4.2.2 Hydrocracking of oxidized product

All hydrocracking experiments were performed in the same Parr batch autoclave described in section 7.4.2.1. Following the oxidative pretreatment of bio-oil direct hydrocracking was performed at temperatures of 375, 400 and 425 ^{o}C. The hydrogen pressures applied were 1000, 1200 and 1400 psig. Reaction times tested were 2.0, 2.5 and 3.0 h. The catalyst types tested were Ni/SiO_2-Al_2O_3, Ni/SiO_2-Al_2O_3+CuO, Ru/C+CuO and Ru/Al_2O_3+CuO. The best reaction condition was chosen based on the quality of the physical properties and yield of the hydrocarbons produced by hydrocracking the oxidized bio-oil. For the best reaction condition the hydrocracking of RBO was also performed as a control to compare hydrocracked RBO hydrocarbon properties and yield to those of the hydrocracked product produced from the oxidized product.

In each experiment, once the reaction was complete, the liquid products were cooled in the reactor. The liquid product was collected in test tubes and centrifuged for 2-4 h to separate the resulting aqueous and organic phases. Both phases were separated and weighed for mass balance computation. In this chapter the products produced from hydrocracking the oxidized product and following its separation as an organic fraction will be referred to as the hydrocarbon mixture (HCM). The products produced from hydrocracking the RBO and following its separation as an organic fraction will be referred to as the hydrocarbon mixture from RBO (HCM-RBO). The byproducts produced in this process included water and off-gas. Yields were calculated by Equation 7.1 [18, 26].

$$\text{Yield (wt\%)} = (\text{P (g)} \times 100)/\ \text{bio-oil weight (g)} \qquad \text{Eq. 7.1}$$

Where: P= products obtained

7.5 Data analysis

The RBO, oxidized product, HCM and HCM-RBO were characterized with ASTM standard analysis methods. The HHVs were determined by Ika-5000 bomb calorimeter by ASTM D240. The acid values (AVs) were determined by dissolving 1 g of bio-oil in 50 ml of 35:65 ratio of isopropanol to water mixtures and titrating to a pH of 8.5 with 0.1N KOH solution according to ASTM D664. pH values were determined by addition of 1 g of bio-oil to 50 ml of 35% of isopropanol mixture by ASTM E70. Elemental carbon, hydrogen, and nitrogen were determined by EAI CE-440 elemental analyzer with oxygen content determined by difference according to ASTM D5291. Water content was determined by Karl-Fisher titration by ASTM E203. The densities were determined by Anton Parr DMA 35n portable density meter by ASTM D4052. Viscosities were determined by Ubbelohde capillary viscometer at 40 ^{o}C water bath temperature according to ASTM D445.

The GC-MS analysis of the RBO, HCM and HCM-RBO were performed with a Hewlett-Packard HP 5890-Series II GC equipped with a Hewlett-Packard HP 5971 series MS. FTIR spectra were obtained by Varian 3500 FTIR analyzer with standard potassium bromide disk technique and spectra were analyzed by Varian-Resolutions software. A mass balance for the mixed hydrocarbons produced by the best performing catalyst was calculated. A detailed hydrocarbon analysis (DHA) of HCM was performed by ASTM D6730-01. Nuclear magnetic resonance spectroscopy (NMR) spectra were collected using a Bruker 600 MHz spectrometer. Each sample was dissolved in chloroform-d ($CDCl_3$ as a solvent) and the proton (^1H) NMR spectra were obtained.

7.6 Results and discussion

7.6.1 Pretreatment of the RBO

The physical and chemical properties of the RBO and oxidized product are compared in Table 7.1. As shown in Table 7.1, following the oxidative pretreatment of RBO the oxidized product AV increased to 156.4 mg KOH/g from 90.2 mg KOH/g of RBO, an increase of 73.4%. The 15.8 MJ/kg HHV of RBO decreased to 15.4 MJ/kg for the oxidized product. The water content of the oxidized product increased to 33.3 wt% from the 30.6 wt% value of raw bio-oil. The pH of the oxidized product decreased to 2.6 from the 3.1 of RBO; the pH decrease was due to increase of acid value of the oxidized product. Oxidized product density decreased from 1.2 g/ml for RBO to 1.0 g/ml. The viscosity of the RBO at 12.2 cSt decreased to 9.4 cSt for the oxidized product.

Table 7.1 Comparison of the RBO and oxidized product physical and chemical properties.

Properties	RBO	Oxidized product
Acid value, mg KOH/g	90.2	156.4
HHV, MJ/kg	15.8	15.4
Water content, wt%	30.6	33.3
pH	3.1	2.6
Density, g/ml	1.2	1.0
Viscosity, cSt	12.2	9.4

7.6.2 Effect of the reaction temperature on hydrocracking of the oxidized product

Figure 7.1 compares the HHVs, AVs, water contents, oxygen contents and HCM yields of the three hydrocracked oxidized product test samples at three tested reaction temperatures. As shown in Figure 7.1, the HHVs of the HCMs produced at the reaction temperatures of 375, 400 and 425 °C were 39.5, 40.5 and 43.6 MJ/kg, respectively. The AVs of the HCMs produced at 375, 400 and 425 °C were 28.2, 12.8 and 0.3 mg KOH/g, respectively. The water contents of the HCMs produced were 1.4, 0.7 and 0.5 wt% for the respective treatment temperatures of 375, 400 and 425 °C. The oxygen content of the HCMs produced at 375, 400 and 425 °C were 11.4, 8.6, and 0.5 wt%, respectively. The HCM yields were 16.1, 30.4 and 23.5 wt% for the respective treatment temperatures of 375, 400 and 425 °C.

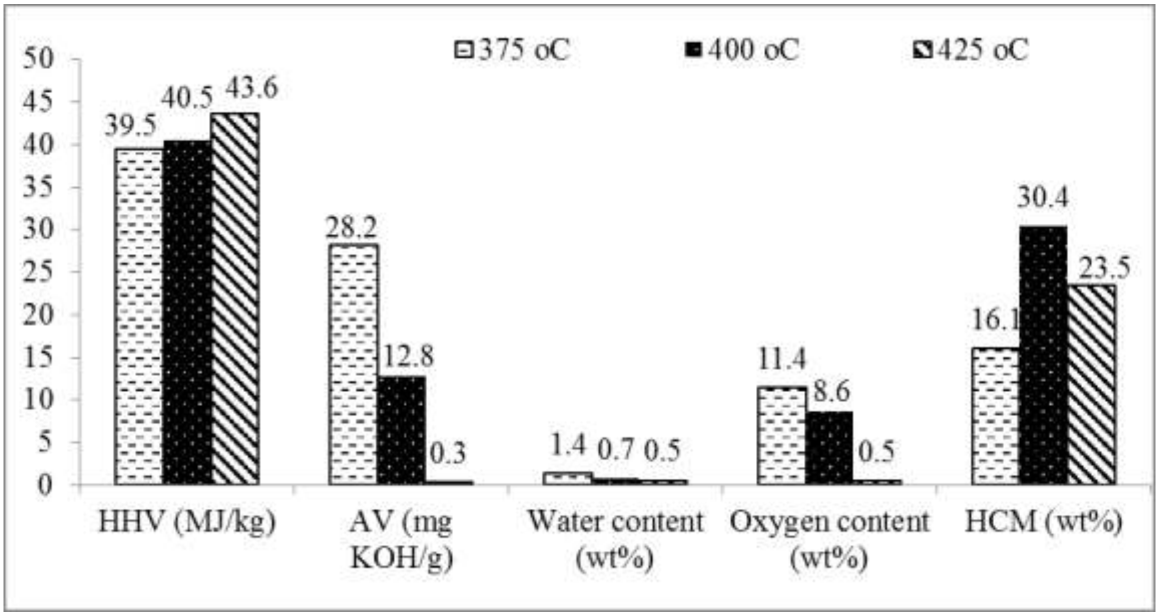


Figure 7.1 Comparison of HHVs, AVs, water content, oxygen content and HCM yields of the HCMs produced by the three hydrocracking runs at the reaction temperatures of 375, 400 and 425 °C.

The HCM produced at the 425 °C treatment had a 10.4% higher HHV, 98.9% lower AV, 64.3% lower water content, 95.6% less oxygen content and 45.9% higher yield when compared to the 375 °C treatment. The HCM produced at 425 °C had 7.7% higher HHV, 97.6% lower AV, 28.6% lower water content, 94.2% less oxygen content and 22.7% higher yield when compared to the 400 °C treatment. The direct hydrocracking was also tested at a reaction temperature of 350 °C under pressurized hydrogen 1400 psig (which was not shown in the Figure 7.1). It was observed that instead hydrocracking of the oxidized product hydrotreating was taken place by partial deoxygenation of oxygenated compounds to hydrocarbons.

Among these three temperatures tested, the hydrocracking reaction performed at 400 °C produced a higher HCM yield (30.4 wt%) compared to the 375 °C (16.1 wt%) and 425 °C (23.5 wt%) treatments. However, the HCM physical and chemical properties produced at 425 °C (Figure 7.1) were of considerably higher quality compared to those for the 375 °C and 400 °C treatments. Therefore, hydrocracking performed at the reaction temperature of 425 °C was considered to be the best treatment.

7.6.3 Effect of the reaction hydrogen pressure and time on hydrocracking of the oxidized product

As shown in Table 7.2, effects of reaction hydrogen pressure and time were investigated by performing the hydrocracking reactions under pressurized hydrogen at 1000, 1200 and 1400 psig. The effect of reaction times of 2.0, 2.5 and 3.0 h were also tested. The temperature applied was 425 °C and was found to produce the best HCM properties as discussed above.

Table 7.2 results show that the HHVs of the HCM produced at the reaction pressures of 1000, 1200 and 1400 psig were 39.3, 41.9 and 43.6 MJ/kg, respectively. Therefore the HCM produced at the 1400 psig pressurized reaction had 10.9% and 4.1% higher HHV compared to those for 1000 and 1200 psig, respectively. The AVs of the HCMs produced at 1000, 1200 and 1400 psig were 3.7, 2.1 and 0.3 mg KOH/g, respectively. The reduction of AV for the HCM produced at 1400 psig was 91.9% and 85.7% more compared to the 1000 and 1200 psig treatments. The water content values for the HCMs were 1.8, 0.9 and 0.5 wt% for the respective treatment pressures of 1000, 1200 and 1400 psig. The oxygen contents of the HCMs produced at 1000, 1200 and 1400 psig were 8.7, 3.8 and 0.5 wt%, respectively. The HCM yields for the 1000, 1200 and 1400 psig treatments were approximately the same at 23.5, 24.0 and 23.5 wt%.

Among the three hydrogen pressure conditions tested, the HCM produced at 1400 psig had higher HHV, lower AV, lower water content and lower oxygen content compared to the 1000 and 1200 psig HCM products. Therefore, hydrocracking performed at 1400 psig hydrogen pressure was considered the best treatment.

The effects of the reaction time on the hydrocracking of the oxidized product were tested at the previously ascertained most-effective reaction temperature of 425 oC and 1400 psig hydrogen pressure. The HHVs of the HCMs produced at reaction times 2.0, 2.5 and 3.0 h were 42.8, 43.6 and 44.3 MJ/kg, respectively. The respective AVs of the HCMs produced at 2.0, 2.5 and 3.0 h were 3.2, 0.3 and 0.3 mg KOH/g. The water content values of the HCMs were 0.7, 0.5 and 0.4 wt% for the respective treatment times of 2.0, 2.5 and 3.0 h. The oxygen content values of the HCMs produced at 2.0, 2.5 and

3.0 h were 3.4, 0.5 and 0.4 wt%, respectively. The HCM yields were 19.0, 23.5 and 20.0 wt% for the respective treatment times of 2.0, 2.5 and 3.0 h.

Among the three reaction times tested, the HCM produced at the 2.5 h reaction time (yield of 23.5 wt%) had yields 23.7% and 14.9% higher compared to those for 2.0 (19.0 wt%) and 3.0 h (20.0 wt%), respectively. The AV of the HCM produced at 2.5 h (AV of 0.3 mg KOH/g) had the same AV as for the 3.0 h reaction (AV of 0.3 mg KOH/g) and was 90.6% lower compared to that of the 2.0 h reaction (AV of 3.2 mg KOH/g). The oxygen content of the HCM produced at 2.5 h (oxygen content of 0.5 wt%) was 85.3% lower compared to the 2.0 h reaction (oxygen content of 3.4 wt%); the HCM produced at 3.0 h had approximately the same oxygen content. Therefore, hydrocracking performed at the 2.5 h reaction time produced an HCM with the highest yield and best property qualities and was considered as the best treatment.

Table 7.2 Comparison of the HCM HHVs, AVs, water content, oxygen content and yields at the reaction temperature of 425 °C for the three test hydrogen pressures.

TEST	HHV (MJ/kg)	AV (mgKOH/g)	Water content(wt%)	Oxygen content (wt%)	HCM (wt%)
Effect of pressure					
1000 Psig	39.3	3.7	1.8	8.7	23.5
1200 Psig	41.9	2.1	0.9	3.8	24.0
1400 Psig	43.6	0.3	0.5	0.5	23.5
Effect of time					
2.0 h	42.8	3.2	0.7	3.4	19.0
2.5 h	43.6	0.3	0.5	0.5	23.5
3.0 h	44.3	0.3	0.4	0.4	20.0

In summary, the hydrocracking of the oxidized product reaction performed at a reaction temperature of 425 °C under hydrogen pressurized of 1400 psig with a reaction time of 2.5 h was considered to be optimal. At these optimal reaction conditions the effects of the various commercial catalysts were tested by following the hydrocracking procedure described in section 7.4.2.2.

7.6.4 Effect of catalyst type on hydrocracking of the oxidized product

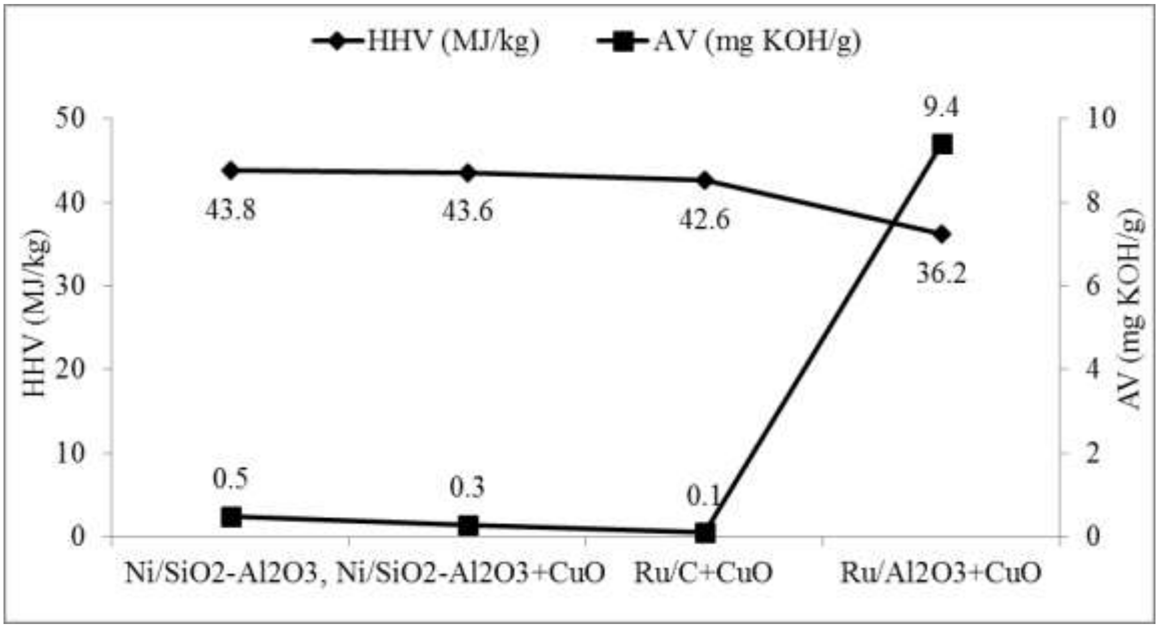


Figure 7.2 Comparison of the HHVs and AVs of the HCMs produced using Ni/SiO_2-Al_2O_3, Ni/SiO_2-Al_2O_3+CuO, Ru/C+CuO and Ru/Al_2O_3+CuO as catalysts via direct hydrocracking of the oxidized product reaction.

The efficacy of the hydrocracking of the oxidized product at our selected optimal reaction conditions was tested by performing the reaction in the presence of various commercially available catalysts. Figure 7.2 shows the comparison of the HHVs and AVs of the HCMs produced using Ni/SiO_2-Al_2O_3, Ni/SiO_2-Al_2O_3+CuO, Ru/C+CuO and Ru/Al_2O_3+CuO as catalysts via direct hydrocracking of the oxidized product. The HHVs of the HCMs produced using Ni/SiO_2-Al_2O_3, Ni/SiO_2-Al_2O_3+CuO, Ru/C+CuO and Ru/Al_2O_3+CuO were 43.8, 43.6, 42.6 and 36.2 MJ/kg, respectively. The AVs of the HCMs produced using Ni/SiO_2-Al_2O_3, Ni/SiO_2-Al_2O_3+CuO, Ru/C+CuO and Ru/Al_2O_3+CuO were 0.5, 0.3, 0.1 and 9.4 mg KOH/g, respectively.

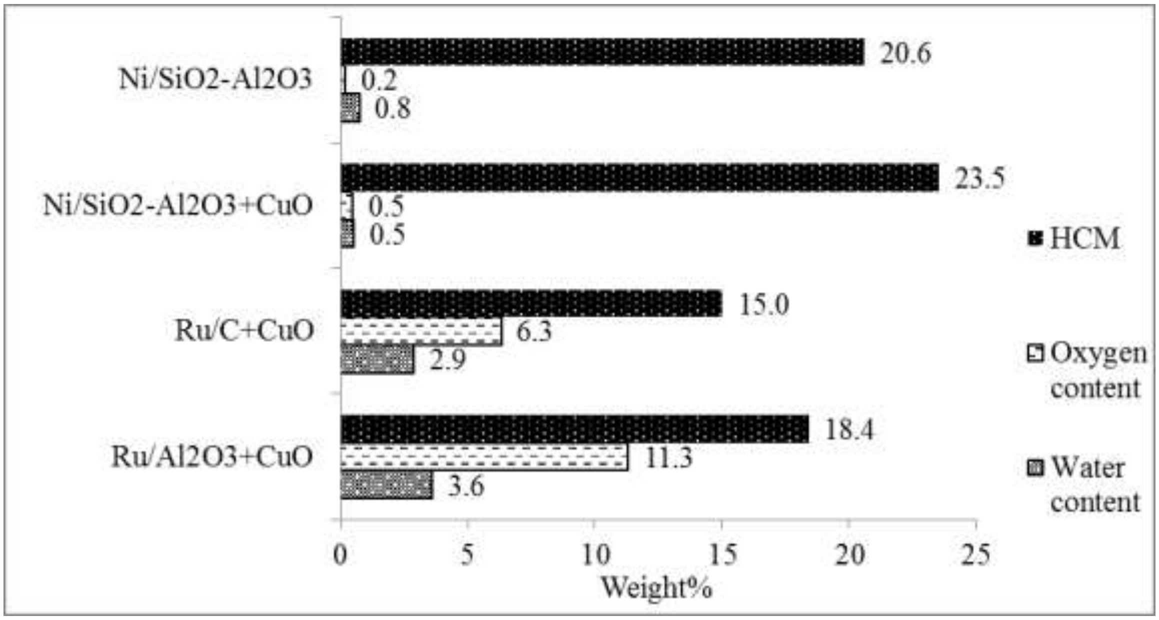


Figure 7.3 HCM yield, oxygen content and water content comparison for Ni/SiO_2-Al_2O_3, Ni/SiO_2-Al_2O_3+CuO, Ru/C+CuO and Ru/Al_2O_3+CuO catalysts.

Figure 7.3 compares the HCM yield, oxygen content and water content of the hydrocracking of the oxidized product reaction performed using Ni/SiO_2-Al_2O_3, Ni/SiO_2-Al_2O_3+CuO, Ru/C+CuO and Ru/Al_2O_3+CuO as catalysts. As shown in Figure 7.3, the HCM yields for the Ni/SiO_2-Al_2O_3, Ni/SiO_2-Al_2O_3+CuO, Ru/C+CuO and Ru/Al_2O_3+CuO as catalyst were 20.6, 23.5, 15.0 and 18.4 wt%, respectively. The oxygen contents were 0.2, 0.5, 6.3 and 11.3 wt% for the HCMs produced using the respective Ni/SiO_2-Al_2O_3, Ni/SiO_2-Al_2O_3+CuO, Ru/C+CuO and Ru/Al_2O_3+CuO catalysts. The water contents of the HCMs produced using Ni/SiO_2-Al_2O_3, Ni/SiO_2-Al_2O_3+CuO, Ru/C+CuO and Ru/Al_2O_3+CuO catalysts were 0.8, 0.5, 2.9 and 3.6 wt%, respectively. The HCM produced using Ni/SiO_2-Al_2O_3+CuO catalyst had 14.1%, 36.2% and 21.7% higher HCM yield compared to the Ni/SiO_2-Al_2O_3, Ru/C+CuO and Ru/Al_2O_3+CuO catalysts, respectively. Therefore, the HCM produced using Ni/SiO_2-Al_2O_3+CuO as catalyst produced with better quality HCM fuel compared to the Ni/SiO_2-Al_2O_3, Ru/C+CuO and Ru/Al_2O_3+CuO as catalysts.

7.6.5 FTIR analysis

Figure 7.4 shows the comparison of RBO and HCM products FTIR spectra. These spectra analyze the functional groups present in the product types. Characteristic vibrational modes were observed at 3200-3600 cm^{-1} (OH stretch), 2800-3050 cm^{-1} (CH aliphatic stretch), 1600-1750 cm^{-1} (C=O stretch), 1350-1470 cm^{-1} (CH bending) and 1000-1250 cm^{-1} (C-O stretch). As shown in Figure 4, it is clear that the very broad OH stretching absorption peak present in the RBO spectrum completely disappeared in the HCM spectrum. The CH aliphatic stretch absorption band at 2800-3050 cm^{-1} in the HCM spectrum dramatically increased compared to the RBO spectrum. The C=O absorption band of carbonyl functional group and the C-O absorption band of ether, alcohol functional groups were reduced in the HCM spectrum compared to the RBO spectrum. The change in the FTIR spectrum of HCM from RBO spectrum absorption bands indicated that the carboxylic acids, aldehydes and other oxygenated chemical compounds were converted into hydrocarbons.

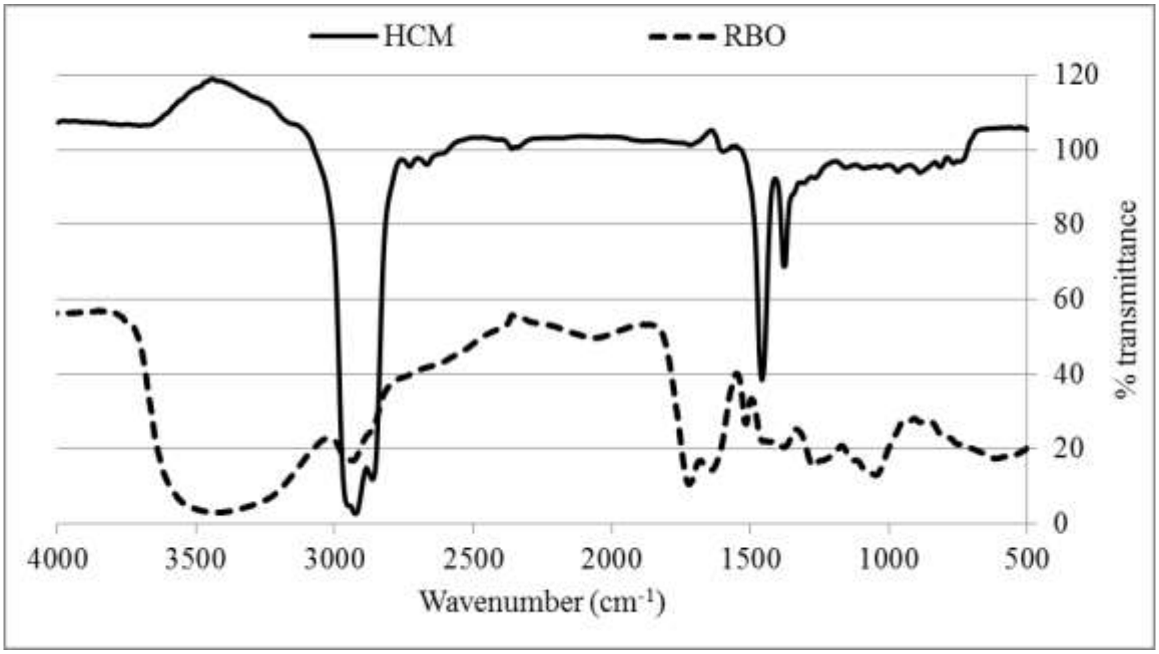


Figure 7.4 FTIR spectra comparing raw bio-oil, pretreated-hydrotreated product and hydrocarbon mixture.

7.6.6 GC-MS analysis

Table 7.3 shows the chemical composition of RBO and HCM identified by GC-MS. Approximately 50 major chemical compounds were analyzed by GC-MS in both samples. The chemical compound name and their area percentages are given in Table 7.3. The total area percentages of the major fifty compounds present in RBO and HCM were 98.12% and 99.9%, respectively. As shown in Table 7.3 there was a considerable change in the chemical composition and area% the of the RBO as compared to the HCM produced by direct hydrocracking of the oxidized product at the selected optimum reaction conditions (reaction temperature of 425 °C, hydrogen pressure of 1400 psig, reaction time of 2.5 h, Ni/SiO_2-Al_2O_3+CuO as the catalyst). The 9.8 area% of carboxylic acids, 12.1 area% of esters-ethers, 35.9 area% of aldehydes-ketones, 38.3 area% of alcohols-phenols and 2.1 area% of other RBO compounds were nearly 100% converted to hydrocarbon compounds via direct hydrocracking of the oxidized product. The HCM was comprised of approximately 99.2 area% of hydrocarbon compounds.

Table 7.3 RBO and HCM chemical composition analysis by GC-MS with area percentages.

Raw bio-oil		**HCM**	
Compound name	Area%	Compound	Area %
Acids		**Hydrocabons**	
Acetic acid	5.1	Cyclopentane, 1-methyl-	3.52
Heptanoic acid	1.42	Cyclohexane	5.32
Benzoic acid, 4-hydroxy-3-methoxy-	0.75	Cyclopantane, 1,3-dimethyl-, trans	2.13
Benzeneacetic acid, alpha-hydroxy-	1.96	Hexane, 3-dimethyl-	4.14
benzeneacetic acid, 4-hydroxy-3-methyl	0.54	Cyclohexane, 3-dimethyl-	11.02
Esters & Ethers		1-hexene, 3-methyl-	2.15
acetic acid, 1-methylethyl ester	1.82	Toluene	2.34
pentanoic acid, ehtyl ester	0.92	Cyclohexane, 1,3-dimethyl-, cis-	1.73
n-heptyl hexanoate	0.94	Cyclopentane, 1-ethyl-3-methyl-	2.1
Hexanoic acid, 1-methylhexyl ester	1.85	Octane	5.28
1-propene, 1-methyoxy-2-methyl-	0.93	Cyclohexane, 1,3-dimethyl-, trans-	1.13
Furan, 2-ethoxy-2,3-dihydro-4-methyl	0.58	Cyclopentane, propyl-	1.75
2,6-Dimethoxytoluene	0.9	Cyclohexane, ethyl-	6.9
3-methoxy-4-methylaniline	1.25	Ethylbenzene	0.87
4,4'-Dimethoxy-biphenyl-2-carboxyl-	0.98	o-Xylene	1.59

Table 7.3 (continued)

Aldehydes & Ketones		Cyclopentane, 1-methyl-2-propyl-	1.37
furfural	1.94	cis-1-Ethyl-3-methyl-cyclohexane	1.27
2-cyclopenten-1-one, 2-hydroxyl-	1.42	Cyclohexane, 1-ethyl-4-methyl-, cis	1.36
2-furancarboxaldehyde, 5-methyl-	0.63	Nonane	1.55
2-cyclopenten-1-one, 2-hydroxy-3-methyl	1.84	cis-1-Ethyl-3-methyl-cyclohexane	1.52
Glutaraldehyde	1.16	Cyclohexane, (1-methylethyl)-	1.2
4H-Pyran-4-one, 3,5-dihydroxy-2-methyl-	0.58	Cyclohexane, propyl-	7.04
cyclopentanecarboxaldehyde	0.82	Benzene, 1-ethyl-2-methyl-	1.5
2-Furancarboxaldehyde, 5-methyl-	1.78	Cyclohexane, 1-methyl-2-propyl-	1.15
5-methyl-2-thiophenecarboxaldehyde	0.55	Cyclohexane, (2-methylpropyl)-	0.81
Ethanone, 1-(4-hydroxy-3-methoxyphenol)	19.5	1H-Indene, octahydro-, cis-	1.55
4-hydroxy-2-methylacetophenone	1.27	Decane	1.0
Benzaldehyde, 3-hydroxy-, oxime	0.74	Benzene, 1-methyl-4-(1-methylethyl	1.04
4-hydroxy-2-mehoxycinnamaldehyde	0.71	Cyclohexane, butyl-	1.71
9,12-octadecadienal	0.6	Cyclohexene, 1-butyl-	1.41
2-propanone, 1-94-hydroxy-3-methoxy)-	0.84	Benzene, 1-ethyl-4-(1-methylethyl)	1.09
vanillin	1.09	trans-Decalin, 2-methyl-	0.86

Table 7.3 (continued)

Alcohols		Cyclohexane, pentyl-	0.87
2-Propanone, 1-hydroxy	3.63	1H-Indene, 2,3-dihydro-1,6-dimethy	1.49
phenol, 2-methyl-	1.14	Benzene, (2-methyl-1-butenyl)-	2.21
phenol, 4-methyl-	0.72	Cyclohexane, hexyl-	1.29
phenol, 2-methoxy-	4.15	Naphthalene, 1,2,3,4-tetrahydro-5-	2
4-mercaptophenol	0.59	Cyclohexane, (cyclopentylmethyl)-	0.93
Phenol, 2-methoxy-4-methyl-	10.81	Naphthalene, 5-ethyl-1,2,3,4-tetra	1.02
1,2-Benzenediol, 3-methyl-	0.93	Naphthalene, 1,2,3,4-tetrahydro-1,	1.51
phenol, 4-ethyl-2-methoxy-	2.61	Cyclohexane, (1-methylethyl)-	0.98
1,2-Benzenediol, 4-methyl-	1.31	Nonadecane	1.2
Eugenol	1.78	Naphthalene, 1,2,3,4-tetrahydro-1,	0.95
1-propene, 1-methyoxy-2-methyl-	0.93	1-Cyclohexylnonene	0.93
phenol, 2-methoxy-4-(1-propenyl)-	1.65	Hexadecane	1.95
Phenol, 2-methoxy-3-(2-propenyl)-	3.28	Benzene, 1,2-bis(1-buten-3-yl)-	0.79
phenol, 2-methoxy-4-propyl-	3.16	1H-Indene, 2,3-dihydro-1,1,5,6-tet	0.84
homovanillyl alcohol	0.98	2(1H)-Quinolinone, hydrazone	0.79
phenol, 2-methoxy-4-(methoxymethyl)-	0.65	Cyclopent[a]indene, 3,8-dihydro-1,	0.84
Ethyl, 4-hydroxy-7-trifluoromethyl-quinoline	0.98	Total	99.99

Table 7.3 (continued)

Other			
3,4-anhydro-d-galactosan	2.1		
Total	98.12		

7.6.7 DHA analysis

A DHA was performed by ASTM D6730-01 on the HCM produced at the optimum conditions. The DHA test is often referred to the as PIANO method (paraffins, iso-paraffins, aromatics, naphthenes and olefins) to classify the hydrocarbons present in the hydrocarbon mixture. The DHA results are given in Table 7.4. These results show that the hydrocarbon mixture contained n-paraffins of 0.6 mass%, iso-paraffins of 23.7 mass%, olefins of 26.1 mass%, naphthenes of 8.2 mass%, aromatics of 5.8 mass%, total C14+ of 6.2 mass% and unknown compounds of 17.9 mass%. This DHA analysis also calculated the liquid hydrocarbon mixture octane number as 58.6 and average molecular weight was computed to be 110.75.

Table 7.4 Hydrocarbon types and their mass% present in HCM results analyzed by DHA ASTM D6730-01.

Hydrocarbon type	**Total mass%**
Paraffins	0.6
Iso-paraffins	23.7
Olefins	26.1
Napthens	8.2
Aromatics	5.8
Total C14+	6.2
Unknowns	17.9
Octane number	58.6
Average molecular weight	110.7

7.6.8 Direct hydrocracking of RBO and oxidized product

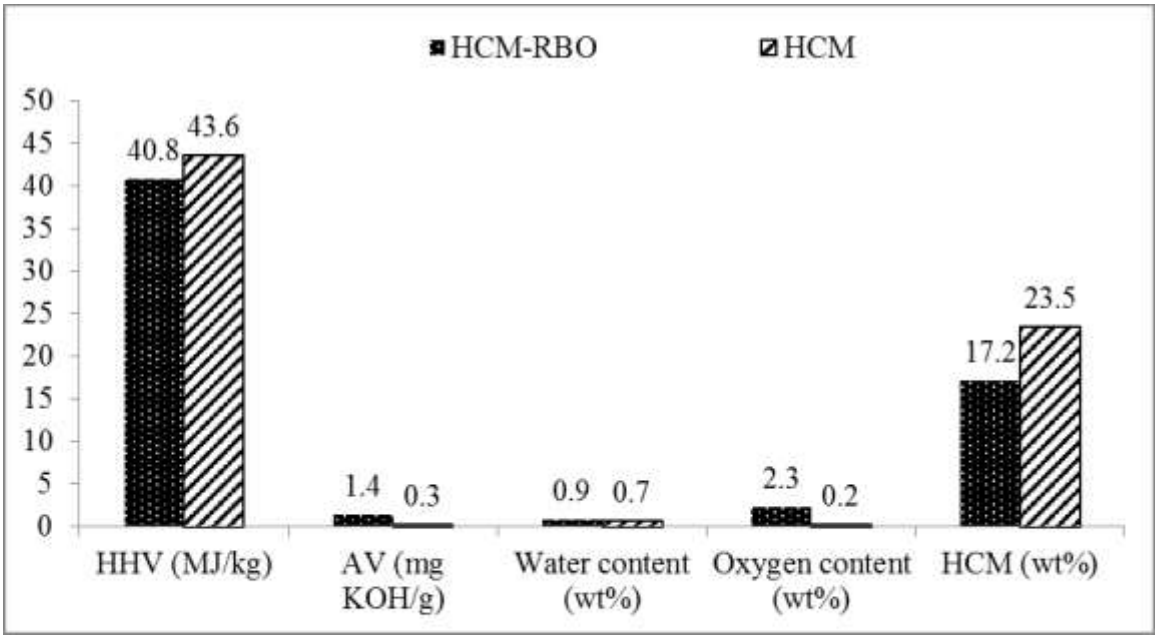


Figure 7.5 Comparison of HHVs, AVs, water content, oxygen content and HCM and HCM-RBO yields of the direct hydrocracking of both RBO and oxidized product at the optimal reaction conditions using Ni/SiO_2-Al_2O_3+CuO as catalyst.

As a control, the RBO was also tested by application of the direct hydrocracking treatment at the optimal reaction conditions using Ni/SiO_2-Al_2O_3+CuO as catalyst and its HCM-RBO was compared with the HCM produced from the oxidized product. Figure 7.5 compares the HHVs, AVs, water content, oxygen content and yields of both HCM and HCM-RBO. The HHVs of the HCM-RBO and HCM were 40.8 and 43.6 MJ/kg, respectively. The HCM had 6.9% higher HHV compared to the HCM-RBO. The AV of the HCM was 0.3 mg KOH/g compared to 1.4 mg KOH/g for the HCM-RBO, a reduction of 78.6%. The water content of the HCM-RBO and HCM were 0.9 and 0.7 wt%, respectively. The oxygen content of the HCM-RBO and HCM were 2.3 and 0.2 wt%, respectively. The HCM had 91.3% lower oxygen content compared to the HCM-RBO. The yield of HCM was 23.5 wt% compared to 17.2 wt% for the HCM-RBO. Hydrocracking of the oxidized product produced 36.6% higher HCM yield compared to the direct hydrocracking of the RBO. These results show that the oxidized product, when directly hydrocracked, produces both high quality and yields compared to RBO.

7.6.9 Proton (H^1)-NMR Spectroscopic analysis

Proton NMR spectra of the RBO (a), HCM-RBO (b) and HCM (c) are shown in Figure 7.6. As shown in Figure, 7.6 (a), (b) and (c) it is evident that there is a large difference between ^{1}H-NMR spectrum of the RBO, HCM-RBO and HCM. The RBO spectrum shown in Figure 7.6(a) is very complex and consists of a large number of proton signals due to the presence of various oxygenated compounds with differing functional groups.

Comparison of the Figure 7.6(a) spectra of RBO to the HCM-RBO in Figure 7.6(b) shows that the oxygenated compounds' proton signals at a chemical shift of 2.0-2.8 ppm (acyl, benzylic and aliphatic hydroxyl functional groups) and proton signals with chemical shift from 3.2-5.2 ppm (esters, ethers, lignin derived methoxy phenols) were not completely eliminated. This indicates that some of the oxygenated compounds present in the RBO were not deoxygenated or may not be fully converted to hydrocarbons during the hydrocracking of the RBO.

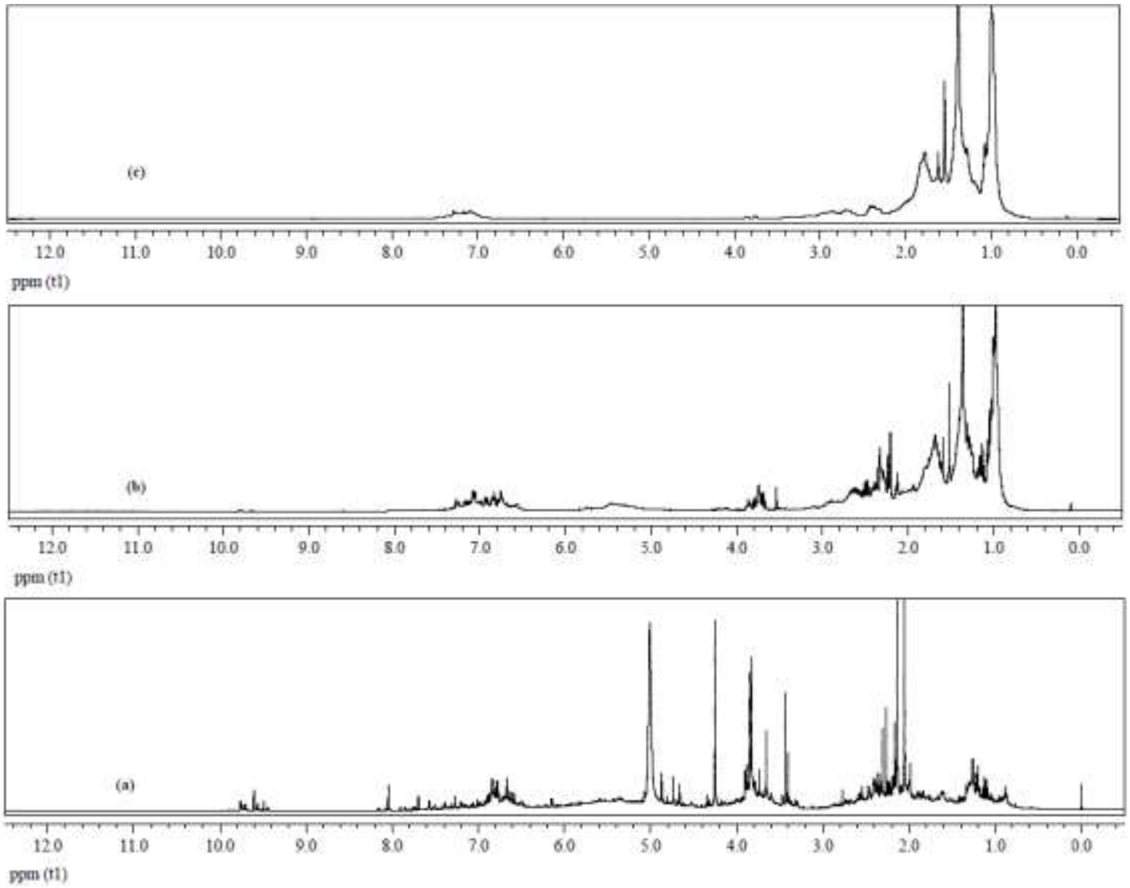


Figure 7.6 ^{1}H-NMR spectra analysis of RBO (a), HCM-RBO (b) and HCM (c)

Comparing the Figure 7.6(a) spectra of RBO and Figure 7.6(c) spectra of HCM shows that the proton signals at a chemical shift of 2.0-2.8 and 3.2-5.2 ppm were reduced considerably due to the higher conversion of oxygenated compounds present in the oxidized product. In the HCM product spectra the aliphatic hydrocarbons' proton signals, with an up-field chemical shift of 0.8-1.9 ppm were higher than HCM-RBO. The HCM spectrum's number of proton signals reduced considerably compared to the HCM-RBO spectrum. This indicates that oxidation pretreatment followed by direct hydrocracking of the oxidized product resulted in conversion of a high percentage of oxygenated compounds to hydrocarbons compared to the direct hydrocracking of the RBO.

7.7 Conclusions

The direct hydrocracking of oxidized bio-oil produced liquid hydrocarbons of transportation fuel quality. The optimum reaction conditions were found to be a reaction temperature of 425 °C under hydrogen pressure of 1400 psig for 2.5 h. Ni/SiO_2-Al_2O_3+CuO was the best catalyst. Hydrocracking of the oxidized product produced 36.6% higher HCM yield compared to hydrocracking of the RBO. The HCM had 6.9% higher HHV compared to the HCM-RBO. The HCM had 91.3% lower oxygen content compared to the HCM-RBO. The AV of the HCM was 0.3 mg KOH/g compared to 1.4 mg KOH/g for the HCM-RBO, a reduction of 78.6%.

7.8 Disclaimer

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7.9 References

1. Perlack RD, Stokes, BJ. U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry. ORNL/TM-2011/224. U.S. Department of Energy. Oak Ridge National Laboratory, Oak Ridge, TN. 2011, 227p.

2. Yan J, Alvors P, Eidensten L. A future for biomass: Mechanical Engineering 1997;117, 94–98.

3. Mckendry P. Energy production from biomass (Part 1): Overview of biomass. Bioresour. Technol 2002;1, 37–46.

4. Huber GW, Iborra S, Corma A. Synthesis of transportation fuels from biomass: Chem. Catal. Eng. Chem. Rev 2006;106, 4044–4098.

5. Ingram Jr L, Mohan D, Bricka M, Steele PH, Strobel D, Crocker D, Mitchell B, Mohammad J, Cantrell K, Pittman Jr CU. Pyrolysis of wood and bark in an auger reactor: physical properties and chemical analysis of the produced bio-oils. Energy Fuels 2008;22, 614-625.

6. Mohan D, Pittman Jr CU, Steele PH. Pyrolysis of wood-biomass for bio-oil: a critical review. Energy Fuels 2006;20, 848-889.

7. Bridgwater AV, Meier D, Radlein D. An overview of fast pyrolysis of biomass. Org. Geochem 1999;30, 1479-1493.

8. Czernik S, Bridgwater AV. Overview of applications of biomass fast pyrolysis oil. Energy Fuels 2004;18, 590-598.

9. Oasmaa A, Elliott DC, Korhonen, J. Acidity of biomass fast pyrolysis bio-oils. Energy Fuels 2010;24, 6548-6554.

10. Peng J, Chen P, Lou H, Zheng X. Catalytic upgrading of bio-oil by HZSM-5 in sub- and super-critical ethanol. Bioresour. Technol 2009;100, 3415-3418.

11. Choudhary TV, Phillips CB. Renewable fuels via catalytic hydrodeoxygenation. Appl. Catal. A: Gen 2011;397, 1-12.

12. Elliott DC. Historical developments in hydroprocessing bio-oils. Energy Fuels 2007;21, 1792-1815.

13. Senol OI, Viljava TR, Krause AOI. Hydrodeoxygenation of methyl esters on sulphided NiMo/[gamma]-Al2O3 and CoMo/[gamma]-Al2O3 catalysts. Catal. Today 2005;100, 331-335.

14. Bu Q, Lei H, Zacher AH, Wang L, Ren S, Liang J, Wei Y, Liu Y, Tang J, Zhang Q, Ruan R. A review of catalytic hydrodeoxygenation of lignin-derived phenols form biomass pyrolysis. Bioresour. Technol 2012;124, 470-477.

15. Wildschut J, Melian CI, Heeres HJ. Catalyst studies on the hydrotreatment of fast pyrolysis oil. Appl. Catal. B: Environ 2010;99, 298-306.

16. De Miguel Mercader F, Groeneveld MJ, Kersten SRA, Way NWJ, Schaverien CJ, Hogendoorn JA. Production of advanced biofuels: Co-processing of upgraded pyrolysis oil in standard refinery units. Appl. Catal. B: Environ 2010;96, 57-66.

17. Tanner KS, Steele PH. Pretreating bio-oil to increase yield and reduce char during hydrodeoxygenation to produce hydrocarbons. Fuel 2014;133, 326-331.

18. Xu X, Zhang YL, Zhai Y, Zhang R. Two-step catalytic hydrodeoxygenation of fast pyrolysis oil to hydrocarbon liquid fuels. Chemosphere 2013;93, 652-660.

19. Elliott DC, Baker EG. Process for upgrading biomass pyrolyzates. U.S. Pat. 4,795,841, 1989.

20. Wildschut J, Mahfud FH, Venderbosch RH, Heeres HJ. Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. Ind. Eng. Chem. Res 2009;48, 10324-10334.

21. McCall MJ, Brandvold TA, Elliott DC. Fuel and fuel blending components from biomass derived pyrolysis oil. U.S. Pat. 8,329,969 B2, 2012.

22. Zhang SP, Yan YJ, Ren Z, Li T. Study of hydrodeoxygenation of bio-oil from the fast pyrolysis of biomass. Energy Sources 2003;3, 57-65.

23. Elliott DC, Hart TR, Neuenschwander GG, Rotness L, Olarte MV, Zacher AH, Solantausta Y. Catalytic hydroprocessing of fast pyrolysis bio-oil from pine sawdust. Energy Fuels 2012;26, 3891-3896.

24. Steele PH, Tanneru SK, Gajjela SK. Composition and methods for improved fuel production. U.S. Pat. 0291431 A1, 2013.

25. Ahmad MM, Fitrir M, Nordin R, Azizan MT. Upgrading of bio-oil into high-value hydrocarbons via hydrodeoxygenation. Am. J. Appl. Sci 2010;7, 746-755.

26. Nkafamiya, I. I., H. M. Maina, S. A. Osemeahon, U. U. Modibbo. Percentage oil yield and physiochemical properties of different groundnut species (Arachis hypogaea). African J. of Food Science. 4, 7, 418-421, 2010.

CHAPTER VIII

SUMMARY AND FUTURE STUDY RECOMMENDATIONS

8.1 Summary

This dissertation research work was divided and performed in two parts:

In the first part of the study, the raw bio-oil was pretreated by novel oxidation and acid anhydride pretreatments prior to the upgrading to reduce coke formation and catalyst deactivation during upgrading. The first part of this research was described in Chapter III.

In the second part of the study, pretreated bio-oils produced by oxidation processes were utilized as a precursor material in Chapters IV to VII.

In chapter IV, boiler fuel was produced from pretreated bio-oil via esterification. In this study we have applied oxidation pretreatment to raw bio-oil followed by subsequent esterification to produce a product with high HHV suitable for boiler fuel.

In chapter V, pretreated bio-oil was converted to transportation fuels range hydrocarbon mixture by application of the hydrodeoxygenation (hydrotreating followed by hydrocracking) utilizing lower hydrogen pressures.

In chapter VI, catalytic deoxygenation of pretreated bio-oil was performed to produce high energy liquid hydrocarbon mixture in the presence of pressurized syngas during the partial deoxygenation stage followed by full deoxygenation utilizing the pure hydrogen.

In chapter VII, to conserve hydrogen, instead of traditional two-stage hydrotreating followed by hydrocracking of the bio-oil. Direct hydrocracking of pretreated bi-oil was tested to produce a liquid hydrocarbon mixture.

The end-products obtained from pretreatment methods and upgrading processes were analyzed by following the ASTM methods for HHV, water content, viscosity, density, acid value and elemental analysis. The best performing fuels based on high HHV and low acid value were analyzed by FTIR, GC-MS, DHA, H^1NMR and simulated distillation.

8.2 Future study recommendations

The objective of the chapters II and IV is to reduce the consumption of the alcohol consumption during the production of boiler fuels via olefination and esterification processes. Results of this study showed that there was a considerable conservation of the alcohol to upgrade the raw bio-oil and pretreated bio-oils to boiler fuels. However, it is recommended to develop a cheaper catalyst to apply these methods to reduce the cost of the processes as well.

The aim of the chapter III is to develop and apply pretreatment methods to raw bio-oil to improve the upgrading processes efficacy. It is very clear from the results of the chapter III, researcher was successfully developed novel pretreatment methods to reduce the negative aldehydes to carboxylic acids to reduce the coke formation during the heating or upgrading. As consecutive second pretreatment butyric acid anhydride also achieved a good success to reduce the water content present in the bio-oil by converting to corresponding carboxylic acids. However, it is recommended to develop a cheap oxidizing and more efficient methods will reduce the cost of the process and make it practical to industrialization.

The goal of the chapters V, VI and VII is to apply hydrodeoxygenation, catalytic deoxygenation and direct hydrocracking of the oxidized product, respectively, to produce transportation range equivalent hydrocarbons. The sub-objectives are to reduce consumption of the hydrogen and improve upgraded fuels yields from previous studies. The most of this study was concentrated on the production of high energy liquid hydrocarbon mixture from oxidized product and compared with the direct use of raw bio-oil. Results of chapters V, VI and VII were showed that hydrodeoxygenation, catalytic deoxygenation and direct hydrocracking of the oxidized product produced better fuel quality hydrocarbons with higher yields compared to the direct use of raw bio-oil. The conservation of hydrogen was successfully achieved in all above mentioned upgrading processes in the production of transportation range hydrocarbons. However, it is recommended to develop inexpensive and efficient heterogeneous hydrotreating, hydrocracking and water gas shift reactions catalyst to reduce the cost of the processes to make it industrialization.